

# A Framework for Chemical Plant Safety Assessment under Uncertainty

**Xiaoyan Zeng, Mihai Aniteşcu\***,

Mathematics and Computer Science Division, Argonne National Laboratory,  
9700 South Cass Avenue, Building 221,  
Argonne, IL 60439-4844, U.S.A  
Email: anitescu@mcs.anl.gov

**Candido Pereira and Monica Regalbuto**

Chemical Sciences and Engineering Division, Argonne National Laboratory,  
9700 South Cass Avenue, Building 205,  
Argonne, IL 60439-4837, U.S.A

**\*Mihai Aniteşcu dedicates his work on this article to the 60th birthday of Dr. Neculai Andrei. Neculai, thanks for your extraordinary work for the benefit of the numerical optimization community in Romania and everywhere.**

**Abstract:** We construct a framework for assessing the risk that the uncertainty in the plant feed and physical parameters may mask the loss of a reaction product. To model the plant, we use a nonlinear, quasi-steady-state model with stochastic input and parameters. We compute the probability that more than a certain product amount is diverted, given the statistics of the uncertainty in the plant feed, in the values of the chemical parameters, and in the output measurement. The uncertainty in the physical parameters is based on the one provided by the recently developed concept of thermochemical tables. We use Monte Carlo methods to compute the probabilities, based on a Cauchy-theorem-like approach to avoid making anything but the safest asymptotic assumptions, as well as to avoid the excessive noise in the region of low-probability events.

**Keywords:** Safety Assessment, Uncertainty, Chemical Process, Stream Methane Reforming, Active Thermochemical Tables, Monte Carlo Methods

**Xiaoyan Zeng** has received the Bachelor degree in Applied Mathematics in 2000 and the Master degree in Applied Mathematics in 2003 in Wuhan University. She obtained the PhD in Applied Mathematics of Illinois Institute of Technology in 2008. She is currently working as a postdoctoral fellow in Mathematics and Computer Science Division at Argonne National Laboratory. Her research interests are in the areas of Monte Carlo and quasi-Monte Carlo methods, stochastic optimization and spline methods.

**Mihai Aniteşcu** has obtained his Engineer (M.Sc.) Diploma in electrical engineering from the Polytechnic University of Bucharest in 1992 and his Ph.D. degree in applied mathematical and computational sciences from the University of Iowa in 1997. Between 1997 and 1999 he was the Wilkinson fellow in computational science in the Mathematics and Computer Science Division at Argonne National Laboratory. Between 1999 and 2002 he was an assistant professor of mathematics at the University of Pittsburgh, where he is currently an adjunct associate professor. Since 2002, he has been a computational mathematician in the Mathematics and Computer Science Division at Argonne National Laboratory. Dr. Aniteşcu is a Senior Editor for Optimization Methods and Software and a member of the editorial boards of Mathematical Programming series A, a series B. In 2009, Dr. Aniteşcu will be the member of the Organizing Committees of the SIAM Annual Meeting and of the International Symposium on Mathematical Programming.

**Candido Pereira** received his PhD in Chemical Engineering from the University of Pennsylvania. He is currently a Principal Engineer at Argonne National Laboratory where he leads the Process Simulation and Equipment Design Group, which develops computer codes and equipment designs for the treatment of spent nuclear fuel. He has been at Argonne since 1992, he has also worked on the Integral Fast Reactor program and on the development of hydrocarbon reforming systems for fuel cell applications.

**Monica Regalbuto** received her PhD in Chemical Engineering from Notre Dame University. She is currently Head of the Process Chemistry and Engineering Department, responsible for programmatic and financial management. She manages the activities of three research groups conducting research on spent fuel separations, process modeling and simulation, and repository waste form corrosion. Prior to joining Argonne she was a Senior Research Engineer at BP Amoco where she developed new technologies to reduce pollutants from gasoline combustion; she was also responsible for all separation needs at four refineries. In an earlier stint at Argonne, she developed material balance, solvent loading and speciation computer models for the TRUOX Program.

## 1. Introduction

Chemical plant safety is an issue that affects a large number of plants in the United States. Currently, more than 15,000 chemical plant sites in the United States are required to file a risk management plan with the U.S. Environmental Protection Agency [3]. Such plans consider both worst-case scenarios and alternative case scenarios. Such alternatives include the moderately abnormal release of controlled materials or illegal plant interference [17]. While sudden, massive release is likely detectable by safety measures in place, the same cannot be said of long-term, slow releases that can be confused with measurement noise or other uncertain information. In this paper, we present a novel framework that uses the plant model and prior statistical information about the uncertainty for estimating the risk posed by a diverting agent to a chemical plant. The diverting agent can be damage, an insufficient design, or an individual engaged in the illegal activity [3, 17].

For this initial application of our framework, we will assume that the chemistry is described by nonlinear equations, that is, that the reactions involved are in steady state [27]. This approximation is reasonable in the case where the chemical reactions have time constants that are much smaller than the typical frequencies in the input [9, 27]. However, to preserve a dynamical aspect of the inputs, which is essential for our work, we will employ a description of the chemical process whereby, due to our assumption of the chemical process having much smaller reaction times compared to the characteristic times over the input, the equilibration following the introduction of additional feed and extraction of the reaction products is instantaneous [9]. Therefore, our model will have discrete dynamics due to the progressive introduction of additional feed and extraction of the reaction products, but it will have no dynamics due to the chemistry. The equations of state are obtained by requiring that the reaction rates be zero and that the total mass of the individual components be conserved.

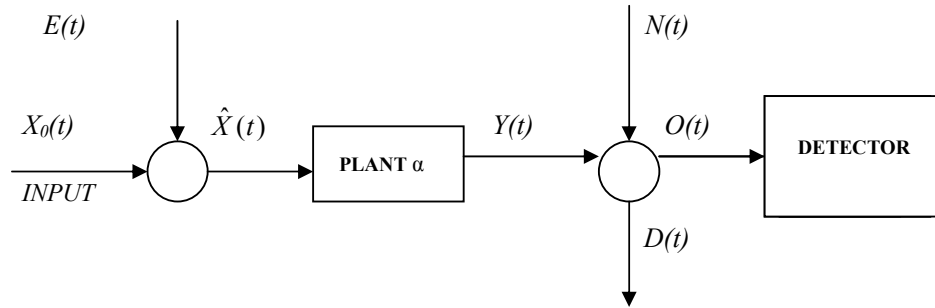
The key question that we are interested in answering is the following: Given the uncertainty in the input of a plant and in the physical parameters of the reaction, how confident can one be of the estimate of the amount of reaction product diverted from the plant?

## 2. Description of the Setup

Our scheme is depicted as in Figure 1, with the notations therein. The input  $X(t)$  represents the amount of feed (number of mols, for example) at time  $t$ . The amount cannot be exactly determined, and this is modeled by the influence of noise,  $E(t)$  which is combined (“modulated”) with the input, to obtain the stochastic feed signal  $\hat{X}$ . In all our simulations, we will consider additive noise, but other types of modulation can be accounted for in similar fashion. In Section 4, we colored noise to model uncertainty in the input. This reflects the fact that the reactant feeds have large amounts of temporal correlation. This is indeed a valid assumption, for example, in a reprocessing plant where successive amounts of feed originate in the same area of a nuclear reactor and are therefore significantly correlated.

$\hat{X}(t)$  constitutes the plant input. After  $\hat{X}(t)$  is processed in plant,  $Y(t)$  is produced. In this paper, we assume a steady-state operation, and the modeling of this is done by a multivariate nonlinear function, in a manner that we describe in Section 2.1.

However, we now assume that there is an interference in the system. This can occur either because some output is diverted unbeknownst to the plant operator. We will call the mechanism by which this is done a “divertor”, whether human (illegal interference) or technological (such as unaccounted-for technological losses). The amount that is so diverted we call  $D(t)$ .



**Figure 1.** Block Description of the Chemical Plant

In addition, we assume that the output cannot be faithfully measured, that is, that the measuring instruments have some amount of error. To achieve that, we will assume that the output has an additive noise in it,  $N(t)$ . Similarly, for the input noise we assume that we have sufficient data to determine its correlation and average faithfully. We thus have the relationship

$$D(t) = Y(t) - O(t) + N(t).$$

In this work, we assume that the noise models  $N(t)$  and  $E(t)$  have a simple quasi-stationary behavior, originating in stationary filtered and perhaps non-stationarily scaled white noise. Nonetheless, our approach can be easily modified to account for non-stationary noise both in the input and in the output. On the other hand, subsequent study is needed to determine appropriate models for such a noise, since the numbers of degrees of freedom in the representation of the noise increases tremendously for non-stationary processes, making it difficult to find enough data for calibration. In this work we do not address the parameter identification of the noise models; this is a well-covered topic in previous research [6, 11, 16], and only a marginal topic of this work.

## 2.1 Plant Model

The steady-state plant model we will use is obtained from a multivariate nonlinear function that has two components. One originates in the condition of the reaction

rates being 0, the steady state; the other originates in the condition that we preserve mass balance in the plant.

We introduce the effective reactant input in the plant, which we call  $X^{IN}(t)$ , and we split the output vector  $Y$  into two parts: the part that denotes the reaction product  $Y^{OUT}$  and the part that denotes what is left of the reactants after equilibration,  $Y^X$ . First, we assume that the reaction product is always obtained under equilibrium conditions. Therefore, we write the equation

$$F_1(Y^{OUT}, Y^X; \alpha) = 0,$$

where the left-hand side of the equation represents the algebraic expression of the reaction rate. The parameters  $\alpha$  represent the physical parameters on which the reaction rates or equilibrium equations depend. An important example of such parameters is the equilibrium parameters [22, 20]. The second equation models the mass balance. That is, we write

$$F_2(X^{IN}, Y^X, Y^{OUT}) = 0.$$

The effective input vector,  $X^{IN}$ , models the total reactant quantity that exists in the reactor. It therefore has two parts: the amount of that is put into it,  $\hat{X}$ , and the amount that remains after equilibration,  $Y^X$ . Our rationale is as follows. We model the reactor as a burst and equilibrate device. In the case of a pulsed distillation column, this is achieved if we average the equations over the length of the column. That is, we feed  $\hat{X}$

into the reactor, which already has about  $Y^X$  reactant in it after the prior equilibration, and we let the reactor equilibrate, producing  $Y^{OUT}$  as the reaction product.

If we consider continuous time, the relations above can be written as a function of the feed in the following manner:

$$0 = F(\hat{X}(t), Y(t); \alpha) = \begin{pmatrix} F_1(Y^{OUT}(t); Y^X(t); \alpha) \\ F_2(\hat{X}(t) + Y^X(t); Y^X(t); Y^{OUT}(t)) \end{pmatrix} \quad (1)$$

If we consider discrete time, we have two options. Either we use the relationship above to write

$$0 = F(\hat{X}(t_i), Y(t_i); \alpha) = \begin{pmatrix} F_1(Y^{OUT}(t_i); Y^X(t_i); \alpha) \\ F_2(\hat{X}(t_i) + Y^X(t_i); Y^X(t_i); Y^{OUT}(t_i)) \end{pmatrix} \quad (2)$$

or, as an alternative, we consider that the effective input in the plant at time  $t_i$  is  $X^{IN}(t_i) = \hat{X}(t_i) + Y^X(t_{i-1})$ , that is, that the net input in the reactor includes the product of the last equilibration, which results in the model

$$0 = \hat{F}(\hat{X}(t_i), Y(t_i), Y(t_{i-1}); \alpha) = \begin{pmatrix} F_1(Y^{OUT}(t_i); Y^X(t_i); \alpha) \\ F_2(\hat{X}(t_i) + Y^X(t_{i-1}); Y^X(t_i), Y^{OUT}(t_i)) \end{pmatrix} \quad (3)$$

Of course, in the limit of small time steps and short bursts, the two models will give the same behavior. For relatively large time steps, however, it may be more beneficial to use the latter, since it is a more accurate description of the dynamical process.

In case (2), we have that  $F(X, Y; \alpha) = 0$  uniquely determines  $Y$  for a given  $X$ . In case (3), we have that  $\hat{F}(X, Y^1, Y^2; \alpha)$  uniquely determines  $Y^1$  as a function of  $X, Y^2$ . Here,  $Y^1, Y^2$  stand for  $Y(t_i), Y(t_{i-1})$  respectively as in (3). To simplify notation, however, we will use only the notation  $F(X, Y; \alpha) = 0$ , even if we mean an operation brought about by  $\hat{F}$ .

The case where we have intermediate reaction products is modeled in our framework by considering a part of the input  $X$  with 0 feed.

## 2.2 The Problem to Be Solved

The task before us is to estimate the probability that the diverted amount exceeds a certain value. This has to be done accounting for the uncertainty in the input and for measurement noise. The data used in the determination of the uncertainty model of the input feed can originate in quality control data sheets or, in the case of waste processing plants, can be obtained from simulation packages on waste state.

On the other hand, the availability of well-defined and properly quantified uncertainties for principal thermochemical properties, such as enthalpies of formation, that properly convey the inherent degree of confidence that may be placed in these values is an often-neglected (and hence generally underutilized) but equally important aspect that significantly contributes to the overall reliability and consistency of thermochemical knowledge. Active Thermochemical Tables (ATcT, described in more detail in [19], [20], [21] and [22]) provide the information about the uncertainties. For example, ATcT provides a full covariance matrix between the enthalpies of formation of all species described in reaction (5) and (6), but it also provides entirely correlated Monte Carlo manifolds (normal distribution) that explore the uncertainty in the equilibrium constants  $k_{eq1}$  and  $k_{eq2}$ , which in our framework (3) are components of the parameter set  $\alpha$ . We use ATcT to provide the distribution information for  $\alpha$ .

The formal problem is stated as follows: evaluate the probability

$$P\left(\int_0^T D(t) \geq D_0 dt \mid O(t), t \in [0, T]\right) \quad (4)$$

for a given value of  $D_0$ , given the statistics of  $\alpha$  and of the noise signals  $N(t)$  and  $E(t)$ .

### 3. Example Chemical Problem: Steam Methane Reforming

As an example of the application of our technique, we have used the steam methane reforming (SMR) process. This process is important in the petrochemical industry for the production of hydrogen used in oil refining. Our framework is applicable for virtually any chemical process that satisfies the assumptions in Section 2. We have nonetheless chosen SMR as an example because it is one of the few that are important, yet simple enough to describe, and for which the data are publicly available.

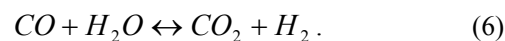
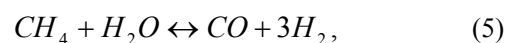
In this case, we have considered as the variable of interest that may be diverted the amount of hydrogen. Several hazards are associated with hydrogen, ranging from respiratory ailment to component failure, ignition, and burning. The primary hazard with hydrogen is the production of a flammable mixture, which can lead to a fire or explosion. Because its minimum ignition energy in air at atmospheric pressure is about 0.2 mJ, hydrogen is easily ignited. In addition, hydrogen gas is colorless, odorless, and not detectable by human senses. It is lighter than air and hence difficult to detect where accumulations cannot occur. Nor is it detectable by infrared gas-sensing technology.

Therefore the tracking of hydrogen in SMR is a good example of an application for model-based assessment of diversion. We now present in detail the way the chemistry is inserted in our framework, which can serve as an example for any other chemical process.

#### 3.1 The Description of the Steam Methane Reforming Reaction

The study of kinetics for SMR process can be traced back to early 20th century [12, 23]. Many kinetic models for SMR have been proposed afterwards [1, 2, 4, 14, 30].

The reaction equations chosen here for SMR are



We need to derive the rate equations to derive the kinetics for chemical reactions. The rate equation is used to link the rate of a reaction to the concentration of the various chemical reactants [13]. According to [25], the rate equations of (5) and (6) can be computed as

$$r_1 = a_1 \exp(-Ea_1 / RT) \sqrt{P} \left( z_{CH_4} - \frac{z_{CO} z_{H_2}^3 P^2}{k_{eq1} z_{H_2O}} \right), \quad (7)$$

$$r_2 = a_2 \exp(-Ea_2 / RT) \sqrt{P} \left( z_{CO} - \frac{z_{CO_2} z_{H_2}}{k_{eq2} z_{H_2O}} \right), \quad (8)$$

where  $R=0.73024 \text{ ft}^3 \text{ atm}^\circ \text{ R}^{-1} \text{ lb-mol}^{-1}$ ,  $T=1800^\circ \text{R}=1000 \text{ K}$ ,  $a_1=127 \text{ lb-mol/h lb of catalyst atm}$ ,  $a_2 = \exp(8.02) \text{ lb-mol/h lb of catalyst atm}$ ,  $Ea_1=15800 \text{ Btu/lb-mol}$ ,  $Ea_2=25000 \text{ Btu/lb-mol}$ ,  $P$  is the total pressure and  $z_i, i \in \{CH_4, CO, H_2, H_2O, CO_2\}$  is the mole fraction for gas  $i$ , in other words,

$$z_i = \frac{y_i}{\sum_i y_i}.$$

Here  $y_i, i \in \{CH_4, CO, H_2, H_2O, CO_2\}$  are moles for the gases. According to the ideal gas law [24], we have

$$PV = RT \sum_i y_i.$$

Note that the equilibrium constants  $k_{eq1}$  and  $k_{eq2}$  at  $1800^\circ \text{R}$  (1000 K) for reaction (5) and (6) are  $25.6961 \pm 0.22 \text{ atm}^2$  and  $1.4263 \pm 0.0064$  by considering the variations due to the uncertainties in the equilibrium constants (where the uncertainties are given as 95% confidence intervals, as is the norm in thermochemistry. The uncertainties in the two equilibrium constants are not entirely independent; their correlation coefficient is 0.221.).

Assume volume  $V=1$ , and replace  $P$  with  $RT \sum_i y_i$ . Then, we have

$$r_1 = a_1 \exp(-Ea_1 / RT) \sqrt{RT} \left( \frac{y_{CH_4}}{\sqrt{\sum_i y_i}} - \frac{y_{CO} y_{H_2}^3 (RT)^2}{k_{eq1} y_{H_2O} \sqrt{\sum_i y_i}} \right), \quad (9)$$

$$r_2 = a_2 \exp(-Ea_2 / RT) \sqrt{RT} \left( \frac{y_{CO}}{\sqrt{\sum_i y_i}} - \frac{y_{CO_2} y_{H_2}}{k_{eq2} y_{H_2O} \sqrt{\sum_i y_i}} \right). \quad (10)$$

If the input feed at time  $t$  of  $H_2O$  and  $CH_4$  are  $\hat{x}_{H_2O}(t)$  and  $\hat{x}_{CH_4}(t)$ , respectively, the dynamic equations then are

$$\frac{dy_{CO}}{dt} = r_1 - r_2, \quad (11)$$

$$\frac{dy_{H_2}}{dt} = 3r_1 + r_2, \quad (12)$$

$$\frac{dy_{CO_2}}{dt} = r_2, \quad (13)$$

$$\frac{dy_{H_2O}}{dt} = -r_1 - r_2 + \hat{x}_{H_2O}(t), \quad (14)$$

$$\frac{dy_{CH_4}}{dt} = -r_1 + \hat{x}_{CH_4}(t). \quad (15)$$

The initial value for this dynamics system is the initial input. The solution of the above system should be positive. If any of the chemicals goes to zero, then the RHS of equation representing the chemicals variation will be positive; that is, the mole of it would be increasing and away from zero. This dynamics system preserves the law of conservation of mass when it comes to the moles of C, H, and O. Denote the moles of C, H, and O by  $\bar{x}_C$ ,  $\bar{x}_H$  and  $\bar{x}_{O_2}$  respectively.

We then get

$$\frac{d\bar{x}_C}{dt} = \hat{x}_{CH_4}(t), \quad (16)$$

$$\frac{d\bar{x}_H}{dt} = 4\hat{x}_{CH_4}(t) + 2\hat{x}_{H_2O}(t), \quad (17)$$

$$\frac{d\bar{x}_{O_2}}{dt} = \hat{x}_{H_2O}(t). \quad (18)$$

Now we consider the steady-state process. That is, we are requiring that  $r_1$  and  $r_2$  both be zero. We therefore obtain that

$$y_{CH_4}[l] = (RT)^2 \frac{y_{CO}[l] \cdot y_{H_2}[l]^3}{k_{eq1} y_{H_2O}[l]}, \quad (19)$$

$$y_{CO}[l] = \frac{y_{CO_2}[l] \cdot y_{H_2}[l]}{k_{eq2} y_{H_2O}[l]}. \quad (20)$$

Suppose  $\hat{x}_{CH_4}[l]$  and  $\hat{x}_{H_2O}[l]$  to be the feed of  $CH_4$  and  $H_2O$  at the time  $t_l$ , respectively.

We will explain the mass balance equations in the case of discrete time and lagging of the equilibration reaction product, as in the second discrete time case in Section 2. We also assume that the product  $H_2$  and byproduct  $CO_2$  are taken out at each time  $t_l$ , leaving only  $CH_4$  and  $H_2O$ , and with newly added  $CH_4$  and  $H_2O$  participating in reaction at next step. Define

$$\bar{x}^C[l] = \hat{x}_{CH_4}[l] + y_{CH_4}[l-1] + y_{CO}[l-1], \quad (21)$$

$$\begin{aligned} \bar{x}^H[l] &= 4\hat{x}_{CH_4}[l] + 4y_{CH_4}[l-1] \\ &+ 2\hat{x}_{H_2O}[l] + 2y_{H_2O}[l-1], \end{aligned} \quad (22)$$

$$\bar{x}^O[l] = \hat{x}_{H_2O}[l] + y_{H_2O}[l-1] + y_{CO}[l-1]. \quad (23)$$

We have another three equations from decomposing and reaction products in their fundamental components and doing the mass balance:

$$y_{CH_4}[l] + y_{CO}[l] + y_{CO_2}[l] = \bar{x}^C[l], \quad (24)$$

$$4y_{CH_4}[l] + 2y_{H_2O}[l] + 2y_{H_2}[l] = \bar{x}^H[l], \quad (25)$$

$$y_{CO}[l] + 2y_{CO_2}[l] + y_{H_2O}[l] = \bar{x}^O[l]. \quad (26)$$

Combining (19) – (26) together with the condition that  $y$  is always positive gives the nonlinear system.

### 3.2 Description of the Problem in Our Modelling Framework

We now describe the problem in the language of Section 2. The input or feed vectors are the moles of  $CH_4$ ,  $CO$ , and  $H_2O$  (the feed of carbon monoxide, which is an intermediate product, will be taken to be zero, but the input would be whatever is in the plant at that moment). The plant output vector,  $Y$ , contains the plant output components  $CO_2$  and  $H_2$ , in addition to the feed components,  $CH_4$ ,  $CO$ , and  $H_2O$ . That is,

$$X = \begin{pmatrix} x_{CH_4} \\ x_{H_2O} \\ x_{CO} \end{pmatrix} \quad \text{and} \quad Y = \begin{pmatrix} y_{CH_4} \\ y_{H_2O} \\ y_{CO} \\ y_{CO_2} \\ y_{H_2} \end{pmatrix},$$

with the vector  $Y^X$  having the same type of components as  $X$ . The only part that is left is to define the functions  $F_1$  and  $F_2$  from which any of the formulations from Section 2 can be found. We have

$$F_1(X, Y; \alpha) = \begin{pmatrix} y_{CH_4} - (RT)^2 \frac{y_{CO} y_{H_2}^3}{k_{eq1} y_{H_2O}} \\ y_{CO} - \frac{y_{CO_2} y_{H_2}}{k_{eq2} y_{H_2O}} \end{pmatrix}.$$

Here the vector of reaction parameters is  $\alpha = (k_{eq1}, k_{eq2})$ . Suppose the effective input is

$$X^{IN} = \begin{pmatrix} x_{CH_4}^{IN} \\ x_{H_2O}^{IN} \\ x_{CO}^{IN} \end{pmatrix}.$$

From the mass balance equations, we have (recall,  $CO$  feed is 0, i.e.,  $\hat{X}_{CO} = 0$ )

$$F_2(X^{IN}, Y) = \begin{pmatrix} x_{CH_4}^{IN} + x_{CO}^{IN} - y_{CH_4} - y_{CO} - y_{CO_2} \\ 4x_{CH_4}^{IN} + 2x_{H_2O}^{IN} - 4y_{CH_4} - 2y_{H_2O} - 2y_{H_2} \\ x_{H_2O}^{IN} + x_{CO}^{IN} - y_{CO} - 2y_{CO_2} - y_{H_2O} \end{pmatrix}.$$

It can be seen that equations (21) and (26) are immediately obtained by applying the second discrete time approach in Section 2. From here on, we will use the abstract format with the definition of  $X$ ,  $Y$ ,  $F_1$ ,  $F_2$  above and the definition of the functions  $F$  and  $\hat{F}$  from Section 2.

### 4. Discrete Time Model

We denote by  $l=0,1,2,\dots,L-1$  the output time indices and by  $t_l$ , for the same indices, the output times (generally equally spaced).

The output noise  $N(t)$  and the input noise  $E(t)$  are modeled as quasi-stationary, colored noise processes or, equivalently, as filtered white noise processes (see [5,28]). In most applications of interest, there is correlation between successive input and output samples, which is responsible for the coloring.

To obtain them, we use the white noise signals (random numbers vectors)  $\xi = [\xi_0, \dots, \xi_{L-1}]$  and  $\eta = [\eta_0, \dots, \eta_{L-1}]$ . Components in  $\xi$  and  $\eta$  are uncorrelated. Suppose  $g = [g_0, \dots, g_M]$ , and  $h = [h_0, \dots, h_M]$  are filtering parameters and  $w_0(t_l)$ , and  $w_N(t_l)$ ,  $l=-M, \dots, L-1$ , are intensity parameters. Furthermore, let  $w_0(t_l) = w_N(t_l) = 0$  if  $l < 0$ . With these notations, we have that the noise vectors  $E(t_l)$  and  $N(t_l)$  are defined as

$$E(t_l) = \sum_{j=l-M}^l h_{l-j} w_0(t_j) \xi_j, \quad 0 \leq l < L, \quad (27)$$

$$N(t_l) = \sum_{j=l-M}^l g_{l-j} w_N(t_j) \eta_j, \quad 0 \leq l < L. \quad (28)$$

Note that, if  $w_0$  and  $w_N$  do not depend on  $t$ , then the noise signals  $E(t)$  and  $N(t)$  are properly stationary.

We assume that this can be carried out by the linear filter with intensity parameters  $w_1(t_l), l = -M, \dots, L-1$  with  $w_1(t_l) = 0$  if  $l < 0$ , and filtering parameters  $e = [e_0, \dots, e_M]$ , which result in the following input-intermediate rule:

$$X(t_l) = X_0(t_l) + E(t_l), \quad 0 \leq l < L, \quad (29)$$

$$\hat{X}(t_l) = \sum_{j=-M}^l e_{l-j} w_1(t_j) X(t_j), \quad 0 \leq l < L. \quad (30)$$

Here,  $X_0(t_l), l = 0, 1, 2, \dots, L-1$ , is the deterministic part of input data.

The plant is modeled by (2) or (3). For the purpose of discussion we use (3), which results in

$$\hat{F}(\hat{X}(t_l), Y(t_l), Y(t_{l-1}); \alpha) = 0.$$

We measure the output datum:  $O(t_l), l = 0, 1, 2, \dots, L-1$ , subject to the output noise  $N(t)$  described above.

The problem (4) in the discrete time framework is as follows: Compute

$$P\left(1/L \sum_{l=0}^{L-1} (Y(t_l) + N(t_l) - O(t_l)) \geq D_0\right) \quad (31)$$

for any  $D_0$ .

If we know the density functions of  $\xi_i$  and  $\eta_i$ , we can get the density functions of  $E(t_l)$  and  $N(t_l)$  after applying [10, Theorem 12.7, Theorem 15.3] repeatedly. We can therefore obtain the density function for  $\hat{X}(t_l)$ . Suppose that we have an explicit expression of the solution of the nonlinear system in (3). If we know the density functions of the elements of  $\hat{X}(t_l)$  and  $Y(t_{l-1})$ , we then can get the density function of  $D(t_l)$ . We therefore can compute the probability required in (31). Usually, however, the probability cannot be calculated this way. because it is always very difficult to find the density functions and get the explicit

expression of the solution even when  $L$  is moderately large.

Thus, we need to use Monte Carlo sampling (see [7, 18]) of the noise  $E(t)$  and  $N(t)$  and of the physical parameters  $\alpha$  in order to numerically estimate the probability in (4).

#### 4.1 Computation of the Upper Bound of the Probability by Using Chebyshev Inequality

To shorten the length of the formula, define

$$\bar{D} = 1/L \sum_{l=0}^{L-1} D(t_l), \quad \bar{Y} = 1/L \sum_{l=0}^{L-1} Y(t_l),$$

$$\bar{N} = 1/L \sum_{l=0}^{L-1} N(t_l) \quad \text{and} \quad \bar{O} = 1/L \sum_{l=0}^{L-1} O(t_l).$$

To compute the estimation of the probability, we need to know estimation of variance  $\sigma$  and mean  $\mu$  of  $\bar{Y}_i + \bar{N}_i$ , that is, the sample variance  $S^2$  and sample mean  $\bar{\mu}$ . Here  $i$  is the index of the component of the output,  $O_i$ , that is targeted for the diversion assessment. In this subsection we describe an approach for computing the probability form (4) and (31). Of course, one can try to compute the probability by doing simulations and counting the number of times the diverted output exceeds the value  $D_0$ , and dividing by the total number of scenarios. The difficulty is that the approach is well known to be slow to converge if the entire distribution, for all  $D_0$  values, is required. This situation may be acceptable if one has a reliable functional error estimate: an error estimate for the entire distribution. The problem is that the error estimates usually available assume either that one is close to the asymptotic regime of the normality, which would be unrealistic if one stops well before convergence, or that a good prior distribution is available, which would introduce extra nonquantifiable risk in the assessment.

In addition, for multiple output stream diversion, the density of the samples drops with the inverse power of the number of the streams, which is known as *the curse of dimensionality* [8]. This may result in real



power estimates for some  $D_0$  values. We defer assessment of multidimensional output stream diversion to future research. Nonetheless, we want to consider only approaches that are known to scale well. We thus decided on the following compromise approach. The average and standard deviation of the diverted output is computed by sampling and estimation using an asymptotic normality assumption. As described by Fact 1 and the sufficient conditions before Lemma 2, these are known to converge for moderate  $K$ . Therefore fast and good ways to accelerate them exist. When estimating the probability, however, we will use a Chebyshev-theorem approach, which makes no assumption about the normality of the convergence of the estimate of the probability in (4), but only about the mean and standard deviation.

To estimate the required probability, we use the following lemma.

**Lemma 1.** *Assume that  $f(x)$  is a monotonic and increasing function,  $P(D \geq f(x)) \leq \alpha$  and  $P(x \geq \hat{x}) \leq \beta$ . Then  $P(D \geq f(\hat{x})) \leq \alpha + \beta$ .*

**Proof:** Obviously, it follows that

$$P(D \geq f(\hat{x})) = P([D \geq f(\hat{x})] \cap [x \geq \hat{x}] + P([D \geq f(\hat{x})] \cap [x < \hat{x}]).$$

For the first term on the left of the equal sign, it can be easily verified that

$$P([D \geq f(\hat{x})] \cap [x \geq \hat{x}]) \leq P(x \geq \hat{x}) = \beta.$$

If  $x < \hat{x}$ , then  $f(x) \leq f(\hat{x})$  because  $f(x)$  is a monotonic and increasing function. Thus

$$P([D \geq f(\hat{x})] \cap [x < \hat{x}]) \leq P(D \geq f(x)) = \alpha,$$

which proves the claim.  $\square$

To provide the actual probability estimates, we need to identify statistics  $g_\mu(\bar{N}_i^k + \bar{Y}_i^k, \beta)$  and  $g_{\sigma^2}(\bar{N}_i^k + \bar{Y}_i^k, \beta)$  such that  $P(\mu \leq g_\mu(\bar{N}_i^k + \bar{Y}_i^k, \beta))$  and  $P(\sigma^2 \leq g_{\sigma^2}(\bar{N}_i^k + \bar{Y}_i^k, \beta))$  are bounded above with a high level of confidence.

To have a high level of confidence in the probability levels of such statistics, we need to use a minimum of assumptions in deriving them. In our derivation of  $g_\mu$  and  $g_{\sigma^2}$ , we use the following fact (see [10, 31]).

**Fact 1** (central limit theorem) *If the data,  $X^1, \dots, X^K$  are i.i.d. with mean  $\mu$  and finite variance  $\sigma^2$ , then  $Z_n = (\sum_{k=1}^K X^k - K\mu) / (\sqrt{K}\sigma)$  converges in distribution to  $Z$ , which is a random variable with standard normal distribution.*

Assume that observable data  $X^1, X^2, \dots, X^K$  satisfy following conditions:

- $X^1, X^2, \dots, X^K$  are i.i.d,
- $X^1, X^2, \dots, X^K$  are nonnegative.

The first condition on the data is required by the central limit theory. The second condition on the data implies  $\bar{\mu} > 0$ ; hence, by increasing  $K$ , we can make  $\bar{\mu} - z_\beta \frac{S}{\sqrt{K}} > 0$ ,

which will be used in derivation of  $g_{\sigma^2}$ .

Obviously, the data  $Y_i^k + N_i^k$  we obtained in the pseudo-code in Section 4.2 through the Monte Carlo method satisfy the first property. Because the example models the chemical process,  $Y_i^k$  must be positive and  $N_i^k$  is at noise level; hence, the second property will also be satisfied by our sampling method.

Because  $X^1, X^2, \dots, X^K$  are i.i.d, if the sample size  $K$  is large enough, then  $(\bar{\mu} - \mu) / (S / \sqrt{K})$  is approximately a  $N(0, 1)$  random variable based on central limit theory. Hence, practically, if  $K \geq 30$ , we can estimate the one-sided confidence interval of mean  $\mu$  at  $\beta$  confidence level as below (see [31])

$$P(\mu \leq \bar{\mu} + z_\beta S / \sqrt{K}) \approx 1 - \beta, \quad (32)$$

where  $z_\beta$  can be found in the standard normal table [31]. Equation (32) also implies

$$P(\mu \geq \bar{\mu} + z_{\beta} S / \sqrt{K}) \approx \beta. \quad (33)$$

Therefore,

$$g_{\mu}(X^k, \beta) = \bar{\mu} + z_{\beta} S / \sqrt{K}. \quad (34)$$

Let  $\bar{m}'_2$  be equal to  $\sum_{k=1}^K (X^k)^2 / K$ ; let the expectation of  $(X^k)^2$  be  $m'_2$ , which is also called the second raw moment; and let the sample variance of it be  $S'_2$ . According to central limit theory, we have

$$P(m'_2 \geq \bar{m}'_2 + z_{\beta/2} S'_2 / \sqrt{K}) \approx \beta/2, \quad (35)$$

For the variance  $\sigma^2$  we have

$$P(\sigma^2 \geq \bar{m}'_2 - \mu^2 + z_{\beta/2} S'_2 / \sqrt{K}) \approx \beta/2. \quad (36)$$

Because  $X^k$ 's are all nonnegative, we also can obtain for large enough  $K$  that

$$P(-\mu^2 \geq -(\bar{\mu} - z_{\beta/2} S / \sqrt{K})^2) < \beta/2. \quad (37)$$

Applying Lemma 1, we have

$$P(\sigma^2 \geq \bar{m}'_2 - (\bar{\mu} - z_{\beta/2} S / \sqrt{K})^2 + z_{\beta/2} S'_2 / \sqrt{K}) < \beta. \quad (38)$$

Hence, for the second statistic, we can use

$$g_{\sigma^2}(X^k, \beta) = \bar{m}'_2 - (\bar{\mu} - z_{\beta/2} S / \sqrt{K})^2 + z_{\beta/2} S'_2 / \sqrt{K}. \quad (39)$$

To make the use of the central limit theorem valid,  $K$  needs to be large enough. Sufficient conditions for  $K$  being large enough for the asymptotic regime to hold are:

- $K \geq 30$ ,
- $\bar{\mu} - z_{\beta/2} \frac{S}{\sqrt{K}} > 0$ ,
- $g_{\sigma^2}(X^k, \beta) > 0$ .

We are now ready to state the second result we will use.

**Lemma 2** Given a positive number  $P_0$ , if

$$P(\mu \geq g_{\mu}(\bar{N}^k + \bar{Y}^k, P_0/4)) < P_0/4$$

and

$$P(\sigma^2 \geq g_{\sigma^2}(\bar{N}^k + \bar{Y}^k, P_0/4)) < P_0/4,$$

then the probability defined in (31) is

$$P(\bar{D} \geq \Gamma | O(t_0), O(t_1), \dots, O(t_{L-1})) \leq \min(P_0/2 + \psi(\Gamma, \bar{O})/2, 1), \quad (40)$$

where

$$\psi(\Gamma, \bar{O}) = \begin{cases} 2, & \text{if } \Gamma \leq g_{\mu}(\bar{N}^k + \bar{Y}^k, P_0/4) - \bar{O}, \\ 2 \left( 1 + \frac{(\Gamma - g_{\mu}(\bar{N}^k + \bar{Y}^k, P_0/4) + \bar{O})^2}{g_{\sigma^2}(\bar{N}^k + \bar{Y}^k, P_0/4)} \right)^{-1}, & \text{o.w.} \end{cases}$$

**Proof:** Let  $0 < P_1 \leq 2$ . According to the one-sided Chebyshev's inequality (see [29]), it follows that

$$P\left(\frac{\bar{D} - \mu + \bar{O}}{\sigma} \geq \sqrt{(2 - P_1)/P_1}\right) \leq P_1/2.$$

Applying Lemma 1 twice, we have

$$P(\bar{D} \geq \sqrt{g_{\sigma^2}(\bar{N}^k + \bar{Y}^k, P_0/4)(2 - P_1)/P_1} + g_{\mu}(\bar{N}^k + \bar{Y}^k, P_0/4) - \bar{O}) \leq P_0/2 + P_1/2$$

Define

$$\Gamma = \sqrt{g_{\sigma^2}(\bar{N}^k + \bar{Y}^k, P_0/4)(2 - P_1)/P_1} + g_{\mu}(\bar{N}^k + \bar{Y}^k, P_0/4) - \bar{O}.$$

We then can solve if

$$\Gamma > g_{\mu}(\bar{N}^k + \bar{Y}^k, P_0/4) - \bar{O},$$

$$P_1 = 2 \left( 1 + \frac{(\Gamma - g_{\mu}(\bar{N}^k + \bar{Y}^k, P_0/4) + \bar{O})^2}{g_{\sigma^2}(\bar{N}^k + \bar{Y}^k, P_0/4)} \right)^{-1}.$$

If  $\Gamma \leq g_{\mu}(\bar{N}^k + \bar{Y}^k, P_0/4) - \bar{O}$ , let  $P_1 = 2$ .

Replacing  $P_1$  with  $\psi(\Gamma, \bar{O})$  completes the proof.  $\square$

## 4.2 Assessment Algorithm

We use Monte Carlo sampling to compute the sample mean  $\mu$  and sample variance  $S^2$  together with the estimation of second raw moment  $\bar{m}'_2$  and its sample variance,  $(S_2')^2$ . In our SMR example, we are concerned about how much of the hydrogen stream,  $H_2$ , is diverted. A pseudo-code is provided below.

$g_m = 0$ , for  $m \neq 0$ , and 1 otherwise. We look for the diverted amount of hydrogen,  $i = H_2$ . We sampled  $k_{eq1}^j$  and  $k_{eq2}^j$ ,  $j = 1, \dots, 200$  by choosing from normal distributions. We then run Monte Carlo simulation described in the above pseudo-code for each  $k_{eq1}^j$  and  $k_{eq2}^j$  and get  $\bar{u}_{H_2}^j$ ,  $S_{H_2}^j$ ,  $\bar{m}_{2,H_2}^j$  and  $S_{2,H_2}^j$ .

```

Sample uniformly  $\xi_i^k$  and  $\eta_i^k$ ,  $k = 1, \dots, K$  by Monte Carlo methods.
Sample  $\alpha^j$ ,  $j = 1, \dots, J$  from Monte Carlo manifolds by ATcT.
for  $k = 1 : K$ 
  for  $l = 0 : L - 1$ 
    Compute  $X^k(t_l)$ ,  $\hat{X}^k(t_l)$  and  $N^k(t_l)$ .
    for  $j = 1 : J$ 
      Solve nonlinear system (3) with parameter  $\alpha^j$  at  $t_l$ 
    end
  end
  Compute  $\bar{Y}^{k,j} = 1/L \sum_{l=0}^{L-1} Y^{k,j}(t_l)$ 
  Compute  $\bar{N}^k = 1/L \sum_{l=0}^{L-1} N^k(t_l)$ 
end
Compute  $\bar{u}^j = 1/K \sum_{k=1}^K (\bar{Y}^{k,j} + \bar{N}^k)$ 
Compute  $(S^j)^2 = 1/(K-1) \sum_{k=1}^K (\bar{Y}^{k,j} + \bar{N}^k - \bar{u}^j)^2$ 
Compute  $\bar{m}_2^j = 1/K \sum_{k=1}^K (\bar{Y}^{k,j} + \bar{N}^k)^2$ 
Compute  $(S_j'^2)^2 = 1/(K-1) \sum_{k=1}^K ((\bar{Y}^{k,j} + \bar{N}^k)^2 - \bar{m}_2^j)^2$ 
Compute  $1/J \sum_{j=1}^J \min(\psi^j(\Gamma, \bar{O})/2 + P_0/2, 1)$  and plot it.

```

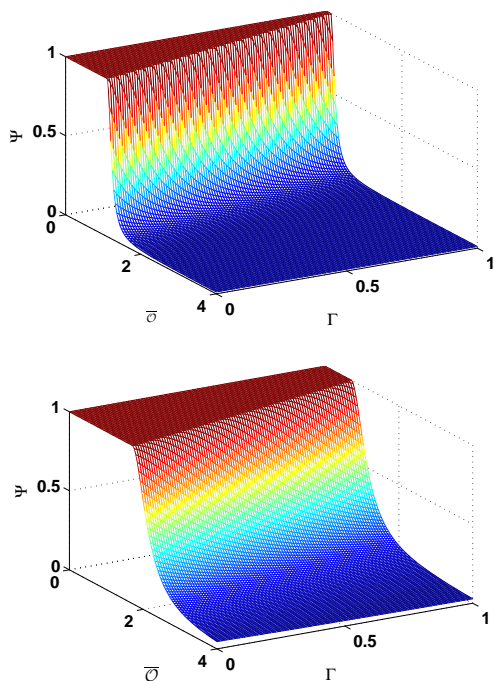
## 4.3 Numerical Results for Monte Carlo Methods for SMR

We simulate the SMR reaction described in Section 3. When simulating  $\alpha^j$ , we use the active table software ATcT. In addition, in the case of SMR,  $\alpha^j = (k_{eq1}^j, k_{eq2}^j)$ .

In terms of parameters described in the beginning of Section 4, we use  $w_0 = 0.1$  and  $w_0 = 1$ , where  $w_1(t_l)$  and  $w_N(t_l)$  are also constants, for  $l=0, 2, \dots, L-1$  (the stationary noise case). The filters used correspond to white noise, that is,  $h_m = 0$ ,  $e_m = 0$ , and

By averaging the RHS of (40), we then have the results shown in Figure 2 for the average surface of  $P_0/2 + \psi(\Gamma_{H_2}, \bar{O}_{H_2})/2$ , for two input noise variance level (1, and 10). We read the results as follows: Given the measured output of  $H_2$ , the probability that the diverted quantity of  $H_2$  exceeds the value  $\Gamma$  is no larger than the value of the surface at the coordinates  $\bar{O}$  and  $\Gamma$ . We see that for certain values of  $\Gamma$  the result is noninformative (i.e., the probability is 1). But the value of the probability surface drops quickly, and the probability drops sharply, a sign that we can guarantee the estimate very sharply, even for large variance in the input

(almost 10% relative uncertainty!). As expected, larger input variance results in a smoother and less sharp probability estimate surface.



**Figure 2.** Average probability surface  $\min(P_0/2 + \psi(\Gamma_{H_2}, \bar{O}_{H_2})/2, 1)$  of our experiment for  $H_2$ , where  $P_0 = 0.02$ ,  $w_0 = 0.1$  (top) and  $w_0 = 1$  (bottom)

The experiment well verified that when  $K$  is moderately large, the average and standard deviation of the diverted quantity are in the Fact 1 asymptotic regime, that is, they are close to be standard normal. In this model we do not include the possible control loops in a plant. We point out, nonetheless, that this is not essential for employing the proposed assessment framework. The equations in Section 2 could be easily modified to include feedback, and they already do to the extent where unconsumed reactant is refilled, as described in (3). In addition, we point out that for waste reprocessing plants, where the reactants are difficult to measure on a continuous basis, online control is not implemented in many circumstances in any case.

## 5. Conclusions and Future Research

We have presented a model-based framework for assessing the risk of diversion of a given

reaction product in a chemical plant in the presence of uncertainty. We have accounted for both feed and model parameter uncertainties. We have shown how the framework can be applied to chemical reaction models by tracking of hydrogen in the steam methane reforming reaction.

In future research, we will address the issue of obtaining superior estimates where we consider the entire covariance matrix that is obtained by our simulation. Therefore, in the language of this application, correlations between outputs would provide asymptotically sharper estimates than the one we have already obtained. In addition, we will be interested in formulating and solving the problem for the case with dynamics and a more faithful description of the input/output mechanism in the chemical plant (rather than all in - equilibration - all out, as we do at the moment). We will also apply quasi-Monte Carlo methods [15, 26] to sample the parameter  $\alpha$  to speed up the algorithm.

## Acknowledgments

We are grateful to Dr. Branko Ruscic for providing access to and expertise in ATcT software. We are grateful to Dr. Manuela Serban for help with the SMR reaction setup. We are grateful to Prof. Dan Negrut for comments on our manuscript. This work was supported by the Department of Energy through contract DE-AC02-06CH11357.

## REFERENCES

1. AKERS, W. and D. CAMP, **Kinetics of the methane-steam reaction**, *AIChE Journal*, 1 (1955), pp. 471–475.
2. ALLEN, D., E. GERHARD, and M. LIKINS JR, **Kinetics of the methane-steam reaction**, *Industrial & Engineering Chemistry Process Design and Development*, 14 (1975), pp. 256–259.
3. BELKE, J., **Chemical Accident Risks in US Industry a Preliminary Analysis of Accident Risk Data from US Hazardous Chemical Facilities**, United States Environmental Protection Agency, Chemical Emergency

- Preparedness and Prevention Office, Washington, D.C., 2000.
4. BODROV, N., L. APEL'BAUM, and M. TEMPKIN, **Kinetics of the reaction of methane with water vapour catalysed by nickel on a porous carrier**, Kinetika L Kataliz, 8 (1967), pp. 821–828.
  5. R. DUBES, **The theory of applied probability**, Prentice-Hall, 1968.
  6. FOGEL, E. and Y. HUANG, **Value of Information in System Identification-Bounded Noise Case.**, Automatica, 18 (1982), pp. 229–238.
  7. HAMMERSLEY, J., D. HANDSCOMB, **Monte Carlo methods**, Methuen, 1964.
  8. HASTIE, T., R. TIBSHIRANI, and J. FRIEDMAN, **The Elements of Statistical Learning: Data Mining, Inference, and Prediction**, Springer, Berlin, 2001.
  9. HELFFERICH, F., **Kinetics of Homogeneous Multistep Reactions**, Elsevier Science, 2001.
  10. JACOD, J. and P. PROTTER, **Probability Essentials**, Springer, Berlin, 2003.
  11. JUANG, J. and R. PAPPA, **Eigensystem realization algorithm for modal parameter identification and model reduction.**, Journal of Guidance, Control, and Dynamics, 8 (1985), pp. 620–627.
  12. MAREK, L. F. and D.A. HAHN, **Catalytic Oxidation of Organic Compounds in the Vapor Phase**, A. C. S. Monograph 61, Chemical Catalog Co., New York, 1932.
  13. MCQUARRIE, D.A. and J.D. SIMON, **Physical Chemistry: A Molecular Approach**, University Science Books, 1997.
  14. MOE, J. and E. GERHARD, **Chemical reaction and heat transfer rates in the steam methane reaction**, in AIChE Symposium, 56th National Meeting, San Francisco, Calif., May, 1965.
  15. NIEDERREITER, H., **Random number generation and quasi-Monte Carlo methods**, Society for Industrial and Applied Mathematics, Philadelphia, 1992.
  16. NORTON, J., **Identification of parameter bounds for ARMAX models from records with bounded noise**, International Journal of Control, 45 (1987), pp. 375–390.
  17. RAGAN, P., M. KILBURN, S. ROBERTS, and N. KIMMERLE, **Chemical plant safety- applying the tools of the trade to a new risk**, Chemical Engineering Progress, 98 (2002), pp. 62–68.
  18. RUBINSTEIN, R., **Simulation and the Monte Carlo Method**, John Wiley & Sons, Inc., New York, NY, USA, 1981.
  19. RUSCIC, B., **Active Thermochemical Tables**, Yearbook of Science and Technology (annual update volume to: McGraw-Hill Encyclopedia of Science and Technology), McGraw-Hill, New York City, 2004.
  20. RUSCIC, B., R.E. PINZON, M.L. MORTON, N.K. SRINIVASAN, M.-C. SU, J.W. SUTHERLAND, and J.V. MICHAEL, **Active thermochemical tables: Accurate enthalpy of formation of hydroperoxyl radical, HO<sub>2</sub>**, J. Phys. Chem. A, 110 (2006), pp. 6592–6601.
  21. RUSCIC, B., R.E. PINZON, M.L. MORTON, G.VON LASZEWSKI, S. BITTNER, S.G. NIJSURE, K.A. AMIN, M.MINKOFF, and A.F. WAGNER, **Introduction to active thermochemical tables: Several "key" enthalpies of formation revisited**, J. Phys. Chem. A, 108 (2004), pp. 9979–9997.
  22. RUSCIC, B., R.E. PINZON, G.VON LASZEWSKI, D. KODEBOYINA, A. BURCAT, D. LEAHY, D. MONTOYA, A. WAGNER, **Active thermochemical tables: Thermochemistry for the 21st century**, J. Phys. Conf. Ser., 16 (2005), pp. 561–570.
  23. SABATIER, P., **Catalysis in organic chemistry**, Van Nostrand, New York, 1922.
  24. SILBERBERG, M., R. DURAN, C. HAAS, and A. NORMAN, **Chemistry:**

**The Molecular Nature of Matter and Change**, McGraw-Hill, 2006.

25. SINGH, C., and D. SARAF, **Simulation of side-fired steam-hydrocarbon reformers**, Ind. Eng. Chem. Process Des. Dev., 18 (1979), pp. 1–7.
26. SLOAN, I.H., and S. JOE, **Lattice methods for multiple integration**, The Clarendon Press Oxford University Press, New York, 1994.
27. SMITH, J., H. VAN NESS, and M. ABBOTT, **Introduction to Chemical Engineering Thermodynamics**, McGraw-Hill Science / Engineering/ Math, 2004.
28. SPROTT, J., **Chaos and Time-Series Analysis**, Oxford University Press, 2003.
29. THERRIEN, C., and M. TUMMALA, **Probability for Electrical and Computer Engineers**, CRC Press, 2004.
30. VAN HOOK, J., **Methane-steam reforming**, Catalysis Reviews of Science Engineering, 21 (1980).
31. WACKERLY, D., W. MENDENHALL, and R. SCHEAFFER, **Mathematical statistics with applications**, Duxbury Pacific Grove, CA, 2002.

**List of Notations**

- $L$ : Number of knots in time space
- $M$ : Length of filter
- $K$ : Number of trials
- $J$ : Number of samples for physical parameters  $\alpha$
- $w_0$ : Intensity parameter
- $w_1$ : Intensity parameter
- $w_N$ : Intensity parameter
- $h, g, e$ : Filters
- $\xi, \eta$ : Random variables
- $X_0$ : Determinant part of input
- $\hat{X}$ : Real input
- $Y$ : Calculated output
- $N$ : Measurement Noise
- $D(t)$ : Diverted part at time  $t$
- $D_0$ : Threshold parameter of the probability as shown in (4)
- $O$ : Observed output
- $\bar{D} := 1/L \sum_{l=0}^{L-1} D(t_l)$ ,
- $\bar{Y} := 1/L \sum_{l=0}^{L-1} Y(t_l)$ ,
- $\bar{N} := 1/L \sum_{l=0}^{L-1} N(t_l)$
- $\bar{O} := 1/L \sum_{l=0}^{L-1} O(t_l)$ .
- $\mu_{H_2} := E(\bar{Y}_{H_2} + \bar{N}_{H_2})$
- $\sigma_{H_2}^2 := Var(\bar{Y}_{H_2} + \bar{N}_{H_2})$
- $\bar{\mu}$ : Sample mean
- $S^2$ : Sample variance
- $\bar{m}_2$ : Second raw moment
- $(S^2)^2$ : Sample variance of i.i.d  $X_i^2$
- $P_0, P_1$ : temporary notations to derive the upper bound of the probability as in (4)