

Catalyst deactivation notes

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1 The PDE model

TODO from meeting:

1. It is also possible to use a grid in spatial space.
2. Plan for Caesar + Francesco meeting?
3. Does the aromatic and sulfur measurement corresponds directly to the a and s , or does it need some scalling?

[[Simo is trying to recall the equations by the notes]] I guess that the model was something like this: [[Muhammad: I have modified this, according to the original form from Price and Butt paper]]

$$\begin{aligned}\frac{\partial s}{\partial t} &= D_s \frac{\partial^2 s}{\partial z^2} - C_s \frac{\partial a}{\partial z} - K_1 r_s(s, T), c \\ \frac{\partial a}{\partial t} &= D_a \frac{\partial^2 a}{\partial z^2} - C_a \frac{\partial a}{\partial z} - K_2 r_a(a, c, T), c \\ \frac{\partial T}{\partial t} &= D_T \frac{\partial^2 T}{\partial z^2} - C_T \frac{\partial T}{\partial z} + K_3 r_a(a, c, T), c \\ \frac{\partial c}{\partial t} &= K_5 r_s(s, T) c,\end{aligned}\tag{1}$$

where $s = s(t, z)$, $a = a(t, z)$, $T = T(t, z)$, and $c = c(t, z)$. Also, note that $C_s = C_a$ and $C_T = \text{constant} * C_s$, K_1 , K_2 and K_3 are correlated. The boundary and initial conditions for the partial differential equations above are:

$$T(z = 0) = T_0, \quad \left. \frac{\partial T}{\partial z} \right|_{z=L} = 0. \tag{2a}$$

$$a(z = 0) = a_0, \quad \left. \frac{\partial a}{\partial z} \right|_{z=L} = 0, \tag{2b}$$

$$s(z = 0) = s_0, \quad \left. \frac{\partial s}{\partial z} \right|_{z=L} = 0, \tag{2c}$$

$$c(t = 0) = 1. \tag{2d}$$

Further we have

$$r_a(a, c, T) = -d_1 \exp(-d_2/T) a c \quad (3)$$

or something. We now measure $y_i = T(z_i) + \text{noise}$ at some points z_i .

Let us now denote $u(t, z) = K_3 r_a(a, c, T)c$, where the time dependence is implicitly defined by a, b, T . Then we have a model of the form

$$\frac{\partial T}{\partial t} = D_T \frac{\partial^2 T}{\partial z^2} - C_T \frac{\partial T}{\partial z} + K_3 u, \quad (4)$$

where we get measurements of $T(z_i)$ and we aim to "forget" that u actually depends on other variables and just replace that with a Gaussian process. We can now, e.g., use a basis function expansion on $T(z)$ or just simply interpolate the values of T so that we can estimate or represent the derivatives at the measurement points. We can also put a GP prior on $u(t, z)$ which then allows us to estimate $D_T, C_T, u(\cdot)$ with normal Gaussian process regression. We also then essentially know $T(z)$. Note that this can be more rigorously formulated as a "latent force model" this type of models were considered in paper Särkkä, Alvarez, Lawrence (2019) on them.

We now have a relation of the form

$$u(t, z) = W(t, z) a(t, z) c(t, z)^2, \quad (5)$$

where $W(t, z)$ and $u(t, z)$ are known. Let us put $\xi(t, z) = K_5 r_s(s, T)$ and again "forget" that it depends on s, T so that we can replace it with a GP, which allows us to write

$$\frac{\partial c}{\partial t} = \xi(t, z) c, \quad (6)$$

and solve

$$c(t, z) = c(0, z) \exp \left(\int_0^t \xi(t, z) dt \right) \quad (7)$$

where we can probably assume some kind of estimate of $c(0, z)$ [[it doesn't seem to be needed though]]. Let us also put $a(t, z) = \exp(\alpha(t, z))$, then we have

$$u(t, z) = W(t, z) \exp(\alpha(t, z)) c(0, z)^2 \exp \left(2 \int_0^t \xi(t, z) dt \right), \quad (8)$$

Taking logarithms gives

$$\log u(t, z) = \log W(t, z) + 2 \log c(0, z) + \alpha(t, z) + 2 \int_0^t \xi(t, z) dt, \quad (9)$$

where we can model $\alpha(t, z)$ and $\xi(t, z)$ as Gaussian processes. Then we can either just compute the correspond covariance function of $\Xi(t) = \int_0^t \xi(t, z) dt$

or use an ODE representation trick like $d\Xi/dt = \xi(t, z)$ to make a latent force model out of this. Furthermore, by using the original PDEs for s and a , we can probably determine or guess suitable covariance functions for processes α and ξ . This allows us to separate ξ from (28) and hence we can finally estimate $c(t, z)$ by using (26) or (27).

There will be traps in this approach which are traps also in any approach that we attempt to use. In particular, if we don't have any measurements of a and c , then the separation of α and ξ will be solely based on how good covariance model we have for them. It is not going to be good and hence there will be trouble. However, any measurements that we can get from these variables can be incorporated into the model and they will improve the model – offline measurements can be used to improve the covariance models which helps a bit, but if we only could actually measure something on them in real time, then we could actually infer things in real time. This is a nice point for discussion.

From my understanding to the problem, there will be *no* measurement at all for s and a that happen inside the reactor. The only measurements related to s and a are taken in the stream before the reactor. As for the c , there will be no measurement at all.

2 Technical notes

- Estimate U
- Find correlation between U and c (deactivation rate); U and a (aromatic)
- coefficient of c is unknown.

2.1 About the boundary condition and the eigen-function

The solution of the PDE, i.e, for the temperature, can be given as $T(t, z) = T_0(t) + T'(t, z)$. Doing this similarly for the a and s , we end up having the following set of homogeneous boundary conditions for the new T', a' and s' , while c remains the same:

$$T'(z = 0) = 0, \quad \left. \frac{\partial T'}{\partial z} \right|_{z=L} = 0. \quad (10a)$$

$$a'(z = 0) = 0, \quad \left. \frac{\partial a'}{\partial z} \right|_{z=L} = 0, \quad (10b)$$

$$s'(z = 0) = 0, \quad \left. \frac{\partial s'}{\partial z} \right|_{z=L} = 0, \quad (10c)$$

$$c(t = 0) = 1. \quad (10d)$$

We then select the basis function ϕ to be the eigen function corresponding to the standard heat equation satisfying boundary condition (10). By the

Sturm–Liouville theorem, we know that the basis $\{\phi_j\}$ will be a complete orthonormal set. The basis ϕ_j $j = 1, \dots$, is given as follow

$$\phi_j(z) = \sqrt{\frac{2}{L}} \sin\left(\frac{(2j-1)\pi z}{2L}\right). \quad (11)$$

The corresponding eigen value is given by

$$\lambda_j = -\left(\frac{(2j-1)\pi}{2L}\right)^2. \quad (12)$$

For simplicity, from now on we will use the non primed variable for the primed one; i.e., T for T' .

2.2 Recursive Approach

Now, suppose we explicitly expand $T(t, z)$ in basis function in spatial variable only. This way, we could use Kalman filter/smoothen for the recursive calculation. Let say $T(t, z) = \Phi(z)\hat{T}(t, \omega_z)$. Here $\Phi(z) = [\phi_1(z), \dots, \phi_N(z)]$, where ϕ_j is an eigen-function of the Laplacian operator suitable to the boundary condition, and $\hat{T}(t, \omega_z)$ contains the spatial Fourier coefficient of T , with respect to some spatial frequency from $\omega_{z,1}$ to $\omega_{z,N}$. Then the partial differential equations on T translates to

$$\Phi(z) \frac{\partial \hat{T}(t, \omega_z)}{\partial t} = D_T \frac{\partial^2 \Phi(z)}{\partial z^2} \hat{T}(t, \omega_z) - C_T \frac{\partial \Phi(z)}{\partial z} \hat{T}(t, \omega_z) + K_3 \Phi(z) \hat{u}(t, \omega_z), \quad (13)$$

Taking the inner product, we have

$$\frac{\partial \hat{T}(t, \omega_z)}{\partial t} = D_T M_{z2} \hat{T}(t, \omega_z) - C_T M_z \hat{T}(t, \omega_z) + K_3 \hat{u}(t, \omega_z), \quad (14)$$

The same can also be said for the aromatics PDE, which is given by

$$\frac{\partial \hat{a}(t, \omega_z)}{\partial t} = D_a M_{z2} \hat{a}(t, \omega_z) - C_a M_z \hat{T}(t, \omega_z) - K_2 \hat{u}(t, \omega_z), \quad (15)$$

The input to the temperature PDE, u , can be selected from a class of Gaussian process that match the characteristics from the original PDE (1) of s , a , and c . At the moment, for simplicity assume that u is the output of the following PDE,

$$\begin{aligned} \frac{\partial v}{\partial t} &= D_v \frac{\partial^2 v}{\partial z^2} - C_v \frac{\partial v}{\partial z} + E_v w(t, z) \\ u &= H_v v, \end{aligned}$$

where H_v is a known linear operator acting on v . Therefore, we have

$$\begin{aligned} \frac{\partial \hat{v}(t, \omega_z)}{\partial t} &= D_v M_{z2} \hat{v}(t, \omega_z) - C_v M_z \hat{v}(t, \omega_z) + E_v \hat{w}(t, \omega_z) \\ \hat{u}(t, \omega_z) &= \hat{H}_v \hat{v}(t, \omega_z) \end{aligned}$$

Augmenting the temperatures, aromatics, and v , we have

$$\begin{aligned}\frac{\partial \hat{T}(t, \omega_z)}{\partial t} &= [D_T M_{z2} - C_T M_z] \hat{T}(t, \omega_z) + K_3 \hat{H}_v \hat{v}(t, \omega_z), \\ \frac{\partial \hat{a}(t, \omega_z)}{\partial t} &= [D_a M_{z2} - C_a M_z] \hat{a}(t, \omega_z) - K_2 \hat{H}_v \hat{v}(t, \omega_z), \\ \frac{\partial \hat{v}(t, \omega_z)}{\partial t} &= [D_v M_{z2} - C_v M_z] \hat{v}(t, \omega_z) + E_v \hat{w}(t, \omega_z), \\ y &= \hat{H} \hat{T}(t, \omega_z) + e\end{aligned}$$

In this form, if the measurement y consists of the temperature measurements at time t_k and height z_k , then the measurement equation is given as follows:

$$y(t_k, z_k) = T(t_k, z_k) + e(t_k) = \Phi(z_k) \hat{T}(t_k, \omega_z) + e(t_k),$$

that is $\hat{H} = \Phi(z_k)$. Using the augmented state as $\hat{x} = (\hat{T}, \hat{a}, \hat{v})$, we have the following augmented dynamics,

$$\frac{d\hat{x}(t, \omega_z)}{dt} = \begin{bmatrix} D_T M_{z2} - C_T M_z & 0 & K_3 \hat{H}_v \\ 0 & D_a M_{z2} - C_a M_z & -K_2 \hat{H}_v \\ 0 & 0 & D_v M_{z2} - C_v M_z \end{bmatrix} \hat{x}(t, \omega_z) + \begin{bmatrix} 0 \\ 0 \\ E_v \end{bmatrix} \hat{w}(t, \omega_z), \quad (16a)$$

$$y(t_k) = [\hat{H} \quad 0] \hat{x}(t_k, \omega_z) + e(t_k). \quad (16b)$$

These equations is discrete-continuous type of dynamics. We could use the Kalman filter/smoothen to get the posterior distribution of \hat{x} , which then can be recovered back to get the posterior distribution of T, a and u . One thing to note is that, it seems that we require D_a, C_a, K_2 to be known in order to make this scenario works.

The M_z is the Fourier representation of the derivative operator, which is quite dense, where for a spatial length of the domain as L , it is given by

$$\begin{aligned}(M_z)_{m,n} &= -\frac{L(-(2m-1) + (2n-1)(-1)^{m+n})}{2\pi(m-n)(m+n-1)} \\ &= \begin{cases} \frac{L}{\pi(m-n)} & , m+n \text{ odd}, \\ \frac{L}{\pi(m+n-1)} & , m+n \text{ even} \end{cases} \end{aligned} \quad (17)$$

The M_{z2} is a diagonal operator with diagonal entries being $-\omega_z^2$.

The parameters θ could be obtained from maximising the likelihood function. Suppose that is discretised in time into

$$\hat{x}(t+1, \omega_z) = F(\theta) \hat{x}(t, \omega_z) + G(\theta) \hat{w}(t, \omega_z), \quad (18a)$$

$$y(t) = H \hat{x}(t, \omega_z) + e(t). \quad (18b)$$

Now $y(t) \sim \mathcal{N}(H\hat{x}(t, \omega_z), R(\theta))$. The measurement statistical model y given parameters θ and $\hat{x}(t, \omega_z)$, is

$$p(y(t)|\hat{x}(t, \omega_z), \theta) = \frac{1}{\sqrt{(2\pi)^m |R(\theta)|}} \exp\left(-\frac{1}{2} \|y(t) - H\hat{x}(t, \omega_z)\|_{R(\theta)}^2\right). \quad (19)$$

Let us write $y(0 : N_t - 1) = (y(0), \dots, y(N_t - 1))$. The likelihood function can be stated in the following factorization

$$p(y(0 : N_t - 1)|\theta) = \prod_{t=0}^{N_t-1} p(y(t)|y(0 : t - 1), \theta), \quad (20)$$

where we write $p(y(0)|y(0 : -1), \theta) := p(y(0)|\theta)$. Using (20) and (19), we could calculate $p(y(0 : N_t - 1)|\theta)$ by marginalisation, [Särkkä, 2013]

$$p(y(t)|y(0 : t - 1), \theta) = \int_X p(y(t)|\hat{x}(t, \omega_z), \theta) p(\hat{x}(t, \omega_z)|y(0 : t - 1), \theta) d\hat{x}(t, \omega_z). \quad (21)$$

Let us define the negative log function as Ψ , and given by

$$\begin{aligned} \Psi &= -\log p(y(0 : N_t - 1)|\theta) - \log p(\theta), \\ &= -\log p(\theta) - \sum_{t=0}^{N_t-1} \log p(y(t)|y(0 : t - 1), \theta) \end{aligned} \quad (22)$$

This equation can be evaluated using Kalman filter [Särkkä, 2013], and given by

$$\begin{aligned} \Psi &= -\log p(y(0 : N_t - 1)|\theta) - \log p(\theta), \\ &= -\log p(\theta) + \frac{1}{2} \sum_{t=0}^{N_t-1} \log |2\pi S(t, \theta)| + \tilde{y}(t)^\top S(t, \theta)^{-1} \tilde{y}(t). \end{aligned} \quad (23)$$

In the above notation, we use the Kalman filter as follow

$$\hat{m}^-(t, \omega_z) = F(\theta) \hat{m}(t - 1, \omega_z), \quad (24a)$$

$$P^-(t, \theta) = F(\theta) P(t, \theta) F(\theta)^\top + G(\theta) G(\theta)^\top, \quad (24b)$$

$$\tilde{y}(t) = y(t) - H \hat{m}^-(t, \omega_z), \quad (24c)$$

$$S(t, \theta) = H P^-(t, \theta) H^\top + R(\theta), \quad (24d)$$

$$K = P^-(t, \theta) H^\top S(t, \theta)^{-1}, \quad (24e)$$

$$\hat{m}(t, \omega_z) = \hat{m}^-(t, \omega_z) + \tilde{y}(t), \quad (24f)$$

$$P(t, \theta) = P^-(t, \theta) - P^-(t, \theta) S(t, \theta)^{-1} P^-(t, \theta). \quad (24g)$$

Equation (23) can be minimised with respect to θ . This will give us the estimated temperature, and u as well as a . Then we can proceed.

The first term can be written as follows: $\text{tr}(\mathbb{E}[\tilde{y}(t_k) \tilde{y}(t_k)^\top]) = F_\theta \mathbb{E}[\hat{x}(t, \omega_z) \hat{x}(t, \omega_z)^\top] F_\theta + e(t_k)$

2.3 Recovering the catalyst activity c

In the previous subsection, we have described how to make state estimation and parameter estimation via Kalman filter. The results are the Fourier coefficients corresponds to the temperatures and aromatics, and the “Fake” input. We also get the most-likely parameters θ that describes the data well. Now to recover the catalyst activity from these results we do the following. First we recover the non-primed variable by doing shifting; i.e., $T = T_0(t) + T'(t, z)$. Examine that we have the following relation of the form

$$u(t, z) = W(t, z) a(t, z) c(t, z)^2, \quad (25)$$

where $W(t, z)$ can be written in terms of the estimated temperature and $u(t, z)$ is given from the estimation result. Denote $\xi(t, z) = K_5 r_s(s, T)$ and again “forget” that it depends on s, T which allows us to write

$$\frac{\partial c}{\partial t} = \xi(t, z) c, \quad (26)$$

and solve

$$c(t, z) = c(0, z) \exp \left(\int_0^t \xi(t, z) dt \right) \quad (27)$$

where $c(0, z) = 1$ by initial condition. Since a is always greater than or equal to zero, let $a(t, z) = \exp(\alpha(t, z))$. This let us write

$$u(t, z) = W(t, z) \exp(\alpha(t, z)) \exp \left(2 \int_0^t \xi(t, z) dt \right), \quad (28)$$

Taking logarithms gives

$$\log u(t, z) = \log W(t, z) + \alpha(t, z) + 2 \int_0^t \xi(t, z) dt, \quad (29)$$

Now we could calculate $W(t, z)$ and α based on the estimated temperatures and aromatics. This will recover the integration term $\int_0^t \xi(t, z) dt$, which recovers the catalyst activity c via (27).

2.4 OLD:Batch approach in Fourier domain

Suppose we would write in the Fourier form: $T(t, z) = \Phi(t, z) \hat{T}(\omega)$. Then we have

$$(M_t - D_T M_{z2} + C_T M_z) \hat{T}(\omega) = -\hat{u}(\omega). \quad (30)$$

In this equation, M_t is the Fourier representation of partial derivative with respect to time, and M_z, M_{z2} are the Fourier representation of partial differentiation and Laplacian operator with respect to z .

For given measurement $y = \hat{H}\hat{T}(\omega) + e$, where e is assumed to follow some distribution, and now \hat{H} is the measurement operator in Fourier representation. Let us assume that u has a prior, which can be represented in Fourier domain as $\hat{u}(\omega) = A_u \hat{w}(\omega)$, where \hat{w} white Noise, then, we could write

$$A_u^{-1} (M_t - D_T M_{z2} + C_T M_z) \hat{T}(\omega) = \hat{w}(\omega), \quad (31)$$

$$H\hat{T}(\omega) = y - e. \quad (32)$$

If we limit the frequencies, then if D_T, C_T is given, we could solve \hat{T} using least square method.

This approach requires C_T, D_T to be known. However, since we also want to estimate c , we could use (29). Let us define $\log u = v, \log W = \eta, \log c(0, z) = \gamma_0$, then in the Fourier representation we have:

$$\hat{v} = \hat{\eta} + 2\hat{\gamma} + \hat{\alpha} + 2\hat{\Xi}. \quad (33)$$

Notice that at the beginning $c(0, z) = 1$, hence $\gamma_0 = 0$. If we assume that both α and Ξ are zero mean Gaussian processes with some covariance, we could write $\hat{\alpha} = A_\alpha \hat{w}, \hat{\Xi} = A_I \hat{w}'$. Hence

$$\hat{v} = \hat{\eta} + A_\alpha \hat{w} + 2A_I \hat{w}'. \quad (34)$$

Now, $W(t, z)$ is expected to be in the form $C \exp(-d_2/T)$, then $\log W = C + -d_2/T$, therefore,

$$\hat{\eta} = C\delta - d_2 f(\hat{T}). \quad (35)$$

Hence it is clear that $\hat{\eta}$ can be obtained once \hat{T} is known. This is the "batch" way to solve this problem.

3 Findings of System Identification from Non-linear modeling (matlab implementation)

We identify nonlinear black-box models from multiple-input / single-output (MISO) using system identification toolbox in MATLAB.

The input and output data is first encapsulated in an object using **iddata()**. We use default sampling time in this case. The input data u_i contains 608 samples with dimension 8. Each dimension refers to a particular concentration feed. The output (ΔT_i) contains 608 samples with dimension 21. In order to find a suitable model order and a nonlinear indication for each output (ΔT_i), we use the built-in function **advice()**.

Using this function we are interested in ΔT_i with $i = \{4, 5, 7, 10, 11, 12, 18, 20, 21\}$. There is a clear indication of nonlinear relationship between input and output data. The function also suggests a nonlinear ARX model of order [4, 4*ones(1, 8) 4*ones(1, 8)] and a treepartition nonlinearity estimator. Note that the value of i is heavily dependent on the number of data.

First, we use nonlinear ARX model (idnlarx) of order [5, 5*ones(1, 8), 5*ones(1, 8)] with tree partition estimator with 50 units. Then we use Hammerstein-Wiener (nhw) models. These models represent a series connection of static non-linear elements with a linear model. We may think of them as extensions of a linear output error models wherein we subject the input and output signals of the linear model to static nonlinearities such as saturation or dead zones. Here, we use two different variations of Hammerstein-Wiener model. Former one uses saturation and piecewise linear function for input and output, respectively while the later one uses sigmoid network for both input and output. Here, we use Levenberg-Marquardt least squares search with 4 iterations. The comparison of all of these models is shown in Figure 1.

4 Article review: Estimation of Catalyst Deactivation Parameters from Operating Reactor Data

If we know the catalyst activity model/profile, then we can estimate the parameters. From[Gavalas et al., 1972b]

4.1 Abstract

- Techniques for estimating the parameters of catalyst deactivation models from the operating data of industrial reactors are discussed.
- First order deactivation model, partial differential equations describe the main reaction and deactivation. The PDE is transformed to ODE.
- General model is treated approximately.
- Bi-functional catalyst is treated by special methods.

4.2 Introduction

Here, the authors focus on dynamic state optimization and the kinetic model is described by concentration depend power law as follows:

$$\frac{\partial s}{\partial t} = k(T)s^m \quad (36a)$$

$$k(T) = k_0 \exp\left(-\frac{E_d}{R_g T}\right) \quad (36b)$$

The aim is to estimate k_0 and E_d . This estimation must be carried out under non-isothermal conditions and often in the presence of transport limitations. Transport limitation is discussed in [Gavalas et al., 1972a].

For fixed bed catalytic process, the plug flow reactor equations can be written as

$$G \frac{\partial c}{\partial z} = f(s, c, T) \quad (37a)$$

$$G \frac{\partial T}{\partial z} = g(s, c, T) \quad (37b)$$

$$G \frac{\partial c}{\partial z} = sf(c, T) \quad (37c)$$

$$G \frac{\partial T}{\partial z} = sg(c, T) \quad (37d)$$

Studies exists for parameter estimation in PDE. However, with more than one parameter, the amount of computation involved in estimation algorithms is prohibitively large.

*Dynamic behavior in (adiabatic) Fixed bed reactors are based on some assumptions. (see page 37 of [Hsu, 1972])

4.3 First-order deactivation

Estimation of deactivation parameters for monofunctional catalysts. The partial differential equations for a single or one dimensional system are:

$$\frac{\partial s}{\partial t} = -sk_0 \exp\left(-\frac{E_d}{R_g T}\right) \quad (38a)$$

$$G \frac{\partial T}{\partial z} = sg(c, T) \quad (38b)$$

There are two approaches:

- combine Equation 38a and 38b.
- estimate decay params one by one. Involves an approximation by parametrization. Less accurate than the above.

4.4 Numerical example

4.4.1 Oxidative dehydrogenation of butene

Due to changes in density we must introduce the latent variables $x_i = c_i/\rho$ and express the concentrations as

$$c_i = \frac{\rho}{R_g T} \frac{x_i}{\sum x_i} \quad (39a)$$

The catalyst activity is defined as Equation 51 and 52 (rate equations) as

$$\frac{\partial s}{\partial t} = k(T)sc_1 \quad (40a)$$

$$k(T) = k_0 \exp\left(-\frac{E_d}{R_g T}\right) \quad (40b)$$

And the reactor equations are equation 53 (material balance eq.), 54 (energy balance eq.)

$$G \frac{\partial x}{\partial z} = f(s, c, T) \quad (41a)$$

$$G \frac{\partial T}{\partial z} = g(s, c, T) \quad (41b)$$

$$f(s, c, T) = -\frac{\partial s}{\partial t} \quad (41c)$$

$$g(s, c, T) = \frac{-\Delta H}{c_p} \frac{\partial s}{\partial t} \quad (41d)$$

Then one can obtain dimensionless form Equation 56 and 61 from [Gavalas et al., 1972b]. This leads to the following ODE (Equation 64 and Equation 65):

$$\frac{d\theta}{d\tau} = -\frac{\beta[a - \lambda(\theta - 1)]}{\theta[b + \frac{1}{2}\lambda(\theta - 1)]} \exp[-\gamma(\frac{1}{\theta} - 1)] \int_1^\theta \frac{x[b + \frac{1}{2}\lambda(x - 1)]}{a - \lambda(x - 1)} \exp(\frac{-q}{x}) dx \quad (42a)$$

$$\frac{d\beta}{d\tau} = 0 \quad (42b)$$

$$\frac{dq}{d\tau} = 0 \quad (42c)$$

Three different examples are given in [Hsu, 1972] Page 120. s^2 can be linearized as follows:

$$s^2 \cong s^*(2s - s^*) \quad (43a)$$

4.5 General power model

Consider the PDE

$$\frac{\partial s}{\partial t} = -s^m k_0 \exp(-\frac{E_d}{R_g T}) \quad (44a)$$

$$G \frac{\partial T}{\partial z} = sg(c, T) \quad (44b)$$

For $m \neq 1$ it is not possible to obtain an ODE from Equation 44. We can approximate and obtain the following equations:

$$G \int_{T_0}^{T_{z_j}} \frac{dT'}{g(T', y_0, T_0)} = \sum_{i=1}^n M_{ji} s(z_i, t) \quad (45a)$$

$$s(z_j, t) = \left(\frac{1}{s(z_j, t_0)} + (m-1)k_d \int_{t_0}^t \exp(-E_d/RT(z_j, t')) dt' \right)^{-\frac{1}{m-1}}, m \neq 1 \quad (45b)$$

apply nonlinear regression.

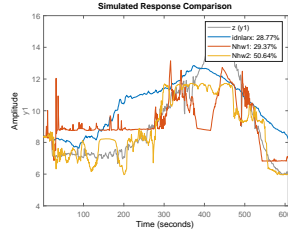
4.6 Bifunctional catalysts

does not tell clearly the step.

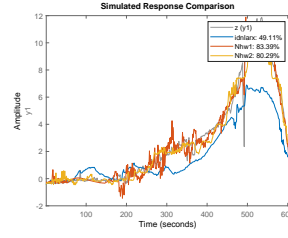
5 Estimation of catalyst activity profiles in fixed bed reactors

References

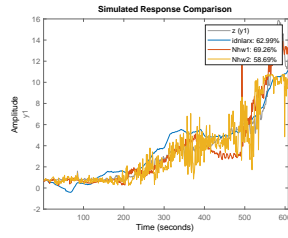
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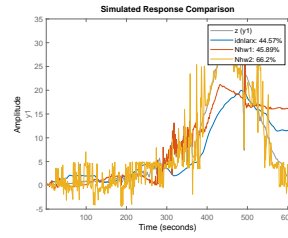
(a)



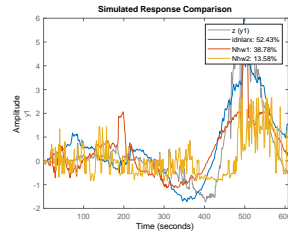
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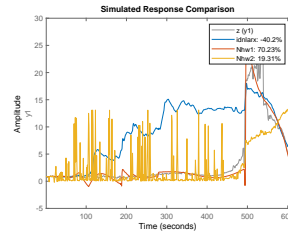
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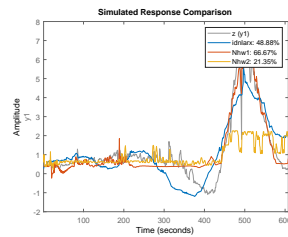
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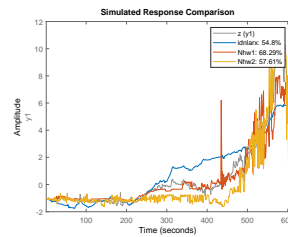
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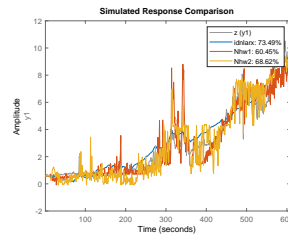
(f)



(g)



(h)



(i)

Figure 1: Nonlinear modeling