Chapter 2

Theoretical Models of Chemical Processes
Rationale for Dynamic Models

1. Improve understanding of the process
2. Train Plant operating personnel
3. Develop control strategy for new plant
4. Optimize process operating conditions
Type of Models

1. Theoretical model
- developed using the principles of chemistry, physics, and biology
- applicable over wide ranges of conditions
- expensive and time consuming
- some model parameters such as reaction rate coefficients, physical properties, or heat transfer coefficients are unknown

2. Empirical models
- obtained fitting experimental data
- range of the data is typically quite small compared to the whole range of process operating conditions
- do not extrapolate well

3. Semi-empirical models
- combination of 1 and 2
- overcome the previously mentioned limitations to many extents
- widely used in industry
General Modeling Principles

• The model equations are at best an approximation to the real process.

• *Adage*: “All models are wrong, but some are useful.”

• Modeling inherently involves a compromise between model accuracy and complexity on one hand, and the cost and effort required to develop the model, on the other hand.

• Process modeling is both an art and a science. Creativity is required to make simplifying assumptions that result in an appropriate model.

• Dynamic models of chemical processes consist of ordinary differential equations (ODE) and/or partial differential equations (PDE), plus related algebraic equations.
Table 2.1. A Systematic Approach for Developing Dynamic Models

1. State the modeling objectives and the end use of the model. They determine the required levels of model detail and model accuracy.

2. Draw a schematic diagram of the process and label all process variables.

3. List all of the assumptions that are involved in developing the model. Try for parsimony; the model should be no more complicated than necessary to meet the modeling objectives.

4. Determine whether spatial variations of process variables are important. If so, a partial differential equation model will be required.

5. Write appropriate conservation equations (mass, component, energy, and so forth).

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6. Introduce equilibrium relations and other algebraic equations (from thermodynamics, transport phenomena, chemical kinetics, equipment geometry, etc.).

7. Perform a degrees of freedom analysis (Section 2.3) to ensure that the model equations can be solved.

8. Simplify the model. It is often possible to arrange the equations so that the dependent variables (outputs) appear on the left side and the independent variables (inputs) appear on the right side. This model form is convenient for computer simulation and subsequent analysis.

9. Classify inputs as disturbance variables or as manipulated variables.
Table 2.2. Degrees of Freedom Analysis

1. List all quantities in the model that are known constants (or parameters that can be specified) on the basis of equipment dimensions, known physical properties, etc.

2. Determine the number of equations $N_E$ and the number of process variables, $N_V$. Note that time $t$ is not considered to be a process variable because it is neither a process input nor a process output.

3. Calculate the number of degrees of freedom, $N_F = N_V - N_E$.

4. Identify the $N_E$ output variables that will be obtained by solving the process model.

5. Identify the $N_F$ input variables that must be specified as either disturbance variables or manipulated variables, in order to utilize the $N_F$ degrees of freedom.
Conservation Laws

Theoretical models of chemical processes are based on conservation laws.

**Conservation of Mass**

\[
\begin{align*}
\left\{ \text{rate of mass accumulation} \right\} &= \left\{ \text{rate of mass in} \right\} - \left\{ \text{rate of mass out} \right\} \\
(2-6)
\end{align*}
\]

**Conservation of Component i**

\[
\begin{align*}
\left\{ \text{rate of component i accumulation} \right\} &= \left\{ \text{rate of component i in} \right\} \\
- \left\{ \text{rate of component i out} \right\} + \left\{ \text{rate of component i produced} \right\} \\
(2-7)
\end{align*}
\]

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Conservation of Energy

The general law of energy conservation is also called the First Law of Thermodynamics. It can be expressed as:

\[
\left\{ \text{rate of energy accumulation} \right\} = \left\{ \text{rate of energy in by convection} \right\} - \left\{ \text{rate of energy out by convection} \right\}
\]

\[
\left\{ \begin{align*}
\text{net rate of heat addition} & \quad + \quad \text{net rate of work} \\
\text{to the system from the surroundings} & \quad + \quad \text{performed on the system by the surroundings}
\end{align*} \right\} \quad (2-8)
\]

The total energy of a thermodynamic system, \( U_{tot} \), is the sum of its internal energy, kinetic energy, and potential energy:

\[
U_{tot} = U_{int} + U_{KE} + U_{PE} \quad (2-9)
\]
For the processes and examples considered in this book, it is appropriate to make two assumptions:

1. Changes in potential energy and kinetic energy can be neglected because they are small in comparison with changes in internal energy.

2. The net rate of work can be neglected because it is small compared to the rates of heat transfer and convection.

For these reasonable assumptions, the energy balance in Eq. 2-8 can be written as

\[
\frac{dU_{\text{int}}}{dt} = -\Delta \left( w\hat{H} \right) + Q \quad (2-10)
\]

\( U_{\text{int}} = \) the internal energy of the system
\( \hat{H} = \) enthalpy per unit mass
\( w = \) mass flow rate
\( Q = \) rate of heat transfer to the system

\( \Delta = \) denotes the difference between outlet and inlet conditions of the flowing streams; therefore

\(-\Delta \left( w\hat{H} \right) = \) rate of enthalpy of the inlet stream(s) - the enthalpy of the outlet stream(s)
The analogous equation for molar quantities is,

$$\frac{dU_{\text{int}}}{dt} = -\Delta(\tilde{w}\tilde{H}) + Q \quad (2-11)$$

where $\tilde{H}$ is the enthalpy per mole and $\tilde{w}$ is the molar flow rate.

In order to derive dynamic models of processes from the general energy balances in Eqs. 2-10 and 2-11, expressions for $U_{\text{int}}$ and $\tilde{H}$ or $\hat{H}$ are required, which can be derived from thermodynamics.
Development of Dynamic Models

Illustrative Example: A Blending Process

An unsteady-state mass balance for the blending system:

\[
\begin{align*}
\text{rate of accumulation of mass in the tank} & = \text{rate of mass in} - \text{rate of mass out} \\
\end{align*}
\]

Figure 2.1. Stirred-tank blending process.

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The unsteady-state component balance is:

\[ \rho \frac{d}{dt} (V \rho) = w_1 + w_2 - w \] 

where \( w_1, w_2, \) and \( w \) are mass flow rates.

For constant density, the corresponding model can be summarized as:

\[ \rho \frac{dV}{dt} = w_1 + w_2 - w \] 

(2-12)

\[ \rho \frac{d(Vx)}{dt} = w_1 x_1 + w_2 x_2 - wx \] 

(2-13)
Equation 2-13 can be simplified by expanding the accumulation term using the “chain rule” for differentiation of a product:

\[
\rho \frac{d(Vx)}{dt} = \rho V \frac{dx}{dt} + \rho x \frac{dV}{dt}
\]  

(2-14)

Substitution of (2-14) into (2-13) gives:

\[
\rho V \frac{dx}{dt} + \rho x \frac{dV}{dt} = w_1 x_1 + w_2 x_2 - wx
\]  

(2-15)

Substitution of the mass balance in (2-12) for \( \rho dV/dt \) in (2-15) gives:

\[
\rho V \frac{dx}{dt} + x(w_1 + w_2 - w) = w_1 x_1 + w_2 x_2 - wx
\]  

(2-16)

After canceling common terms and rearranging (2-12) and (2-16), a more convenient model form is obtained:

\[
\frac{dV}{dt} = \frac{1}{\rho} (w_1 + w_2 - w)
\]  

(2-17)

\[
\frac{dx}{dt} = \frac{w_1}{V \rho} (x_1 - x) + \frac{w_2}{V \rho} (x_2 - x)
\]  

(2-18)
Figure 2.3 Stirred-tank heating process with constant holdup, $V$. 

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Assumptions:

1. Perfect mixing; thus, the exit temperature $T$ is also the temperature of the tank contents.
2. The liquid holdup $V$ is constant because the inlet and outlet flow rates are equal, $w_i = w$.
3. The density $\rho$ and heat capacity $C$ of the liquid are assumed to be constant. Thus, their temperature dependence is neglected.
4. Heat losses are negligible.
For a pure liquid at low or moderate pressures, the internal energy is approximately equal to the enthalpy, \( U_{\text{int}} \approx H \), and \( H \) depends only on temperature. Consequently, in the subsequent development, we assume that \( U_{\text{int}} = H \) and \( \dot{U}_{\text{int}} = \dot{H} \) where the caret (\(^\wedge\)) means per unit mass. As shown in Appendix B, a differential change in temperature, \( dT \), produces a corresponding change in the internal energy per unit mass, \( d\dot{U}_{\text{int}} \),

\[
d\dot{U}_{\text{int}} = d\dot{H} = CdT \quad (2-29)
\]

where \( C \) is the constant pressure heat capacity (assumed to be constant). The total internal energy of the liquid in the tank is:

\[
U_{\text{int}} = \rho V \dot{U}_{\text{int}} \quad (2-30)
\]
An expression for the rate of internal energy accumulation can be derived from Eqs. (2-29) and (2-30):

\[
\frac{dU_{\text{int}}}{dt} = \rho VC \frac{dT}{dt}
\]  

(2-31)

Note that this term appears in the general energy balance of Eq. 2-10.

Suppose that the liquid in the tank is at a temperature \( T \) and has an enthalpy, \( \hat{H} \). Integrating Eq. 2-29 from a reference temperature \( T_{\text{ref}} \) to \( T \) gives,

\[
\hat{H} - \hat{H}_{\text{ref}} = C\left( T - T_{\text{ref}} \right)
\]  

(2-32)

where \( \hat{H}_{\text{ref}} \) is the value of \( \hat{H} \) at \( T_{\text{ref}} \). Without loss of generality, we assume that \( \hat{H}_{\text{ref}} = 0 \) (see Appendix B). Thus, (2-32) can be written as:

\[
\hat{H} = C\left( T - T_{\text{ref}} \right)
\]  

(2-33)
Chapter 2

Model Development - III

For the inlet stream

$$\hat{H}_i = C \left(T_i - T_{\text{ref}}\right) \quad (2-34)$$

Substituting (2-33) and (2-34) into the convection term of (2-10) gives:

$$-\Delta \left(w\hat{H}\right) = w \left[C \left(T_i - T_{\text{ref}}\right)\right] - w \left[C \left(T - T_{\text{ref}}\right)\right] \quad (2-35)$$

Finally, substitution of (2-31) and (2-35) into (2-10)

$$V \rho C \frac{dT}{dt} = wC \left(T_i - T\right) + Q \quad (2-36)$$
Degrees of Freedom Analysis for the Stirred-Tank Model:

3 parameters: \( V, \rho, C \)

4 variables: \( T, T_i, w, Q \)

1 equation: Eq. 2-36

Thus the degrees of freedom are \( N_F = 4 - 1 = 3 \). The process variables are classified as:

1 output variable: \( T \)

3 input variables: \( T_i, w, Q \)

For temperature control purposes, it is reasonable to classify the three inputs as:

2 disturbance variables: \( T_i, w \)

1 manipulated variable: \( Q \)
Continuous Stirred Tank Reactor (CSTR)

Fig. 2.6. Schematic diagram of a CSTR.
CSTR: Model Development

Assumptions:
1. Single, irreversible reaction, A → B.
2. Perfect mixing.
3. The liquid volume $V$ is kept constant by an overflow line.
4. The mass densities of the feed and product streams are equal and constant. They are denoted by $\rho$.
5. Heat losses are negligible.
6. The reaction rate for the disappearance of A, $r$, is given by,
   \[ r = k c_A \]  \hspace{1cm} (2-62)
   where $r$ moles of A reacted per unit time, per unit volume, $c_A$ is the concentration of A (moles per unit volume), and $k$ is the rate constant (units of reciprocal time).
7. The rate constant has an Arrhenius temperature dependence:
   \[ k = k_0 \exp(-E/RT) \]  \hspace{1cm} (2-63)
   where $k_0$ is the frequency factor, $E$ is the activation energy, and $R$ is the gas constant.
CSTR: Model Development (continued)

- **Unsteady-state mass balance**

\[
\frac{d(\rho V)}{dt} = \rho q_i - \rho q
\]

Because \( \rho \) and \( V \) are constant, \( q = q_i \). Thus, the mass balance is not required.

- **Unsteady-state component balance**

\[
V \frac{dc_A}{dt} = q(c_{Ai} - c_A) - V k c_A
\]
Assumptions for the Unsteady-state Energy Balance:

8. The thermal capacitances of the coolant and the cooling coil wall are negligible compared to the thermal capacitance of the liquid in the tank.
9. All of the coolant is at a uniform temperature, $T_c$. (That is, the increase in coolant temperature as the coolant passes through the coil is neglected.)
10. The rate of heat transfer from the reactor contents to the coolant is given by:

   $$Q = UA(T_c - T)$$

   where $U$ is the overall heat transfer coefficient and $A$ is the heat transfer area. Both of these model parameters are assumed to be constant.
11. The enthalpy change associated with the mixing of the feed and the liquid in the tank is negligible compared with the enthalpy change for the chemical reaction. In other words, the heat of mixing is negligible compared to the heat of reaction.
12. Shaft work and heat losses to the ambient can be neglected.

The following form of the CSTR energy balance is convenient for analysis and can be derived from Eqs. 2-62 and 2-63 and Assumptions 1 through 8 (Fogler, 1999; Russell and Denn, 1972),

$$V_pC \frac{dT}{dt} = wC(T_i - T) + (-\Delta H_R)Vkc_A + UA(T_c - T)$$

(2-68)
CSTR Model: Some Extensions

• How would the dynamic model change for:

1. Multiple reactions (e.g., $A \rightarrow B \rightarrow C$)?
2. Different kinetics, e.g., 2nd order reaction?
3. Significant thermal capacity of the coolant liquid?
4. Liquid volume $V$ is not constant (e.g., no overflow line)?
5. Heat losses are not negligible?
6. Perfect mixing cannot be assumed (e.g., for a very viscous liquid)?
Simulation Softwares

Matlab  www.mathworks.com
Mathematica  www.wolfram.com
HYSYS  www.aspentech.com
Modelica  www.modelica.org
gPROMS  www.psenterprise.com
Aspen Custom Modeller  www.aspentech.com
Global Cape Open  www.global-cape-open.org
Simulation Softwares

Matlab  www.mathworks.com
Mathematica  www.wolfram.com
HYSYS  www.aspentech.com
Modelica  www.modelica.org
gPROMS  www.psenterprise.com
Aspen Custom Modeller  www.aspentech.com
Global Cape Open  www.global-cape-open.org
Dynamics Are Important for the Analysis of Process Safety

I suppose that I should have paid attention in Process Control!
Chapter 2

The cooling water pumps have failed. How long do we have until the exothermic reactor runs away?

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We must keep %C4 close to but below the combustion limit.

We want to control this critical variable, which valve should we use?
Dynamics Are Important for the Analysis of Process Safety

Causal yes & fast
How about v3?

Safety-critical variable

Causal yes, & fast!
How about v4?

Causal yes, but rather slow
How about v2?
Feed material is delivered periodically, but the process requires a continuous feed flow. How large should the tank volume be?

Dynamics Are Important for the Analysis of Process Inventories (Feed, Products, Intermediates)
The tank must be at least this large.
Dynamics Are Important for Product Quality

We’ve studied distillation. I suppose that we should know what to manipulate to control the distillate composition!
Dynamics Are Important for Product Quality

Adjusting the reflux has a strong and fast response on the top composition.
For all of these practical applications, we need to understand and use dynamic analysis.

- Formulate models based on fundamental principles
- Determine how the key model parameters depend on the process conditions and equipment design
  - Steady-state gain ($K_p$)
  - Time constants ($\tau$)
  - Dead time (discussed soon)
- Determine the transient behavior for specific input function (e.g., step, impulse, ramp)
  - Solve Linear equations analytically
  - Solve Non-linear equations using numerical methods
  - Solve linearized approximations analytically
  - Use qualitative analysis (e.g., step response)

Very important to know how the process affects the dynamics!