Chapter 2: Theoretical Models of Chemical Processes

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Chapter Overview

This chapter consists of the following topics:

1. Process Model:
   - Definition
   - General Modeling Principles
   - Why Dynamic Process Models?
2. Modeling Approaches
   - Theoretical Models
   - Empirical Models
   - Semi-Empirical Models
3. Conservation Laws

Chapter Overview

This chapter consists of the following topics:

4. Development of Dynamic Models
    - Example 1: Blending Process
    - Example 2: Stirred Tank Heating Process
    - Example 3: Liquid Storage Systems
5. Summary

Learning Objectives

At the end of this chapter, you will be able to:

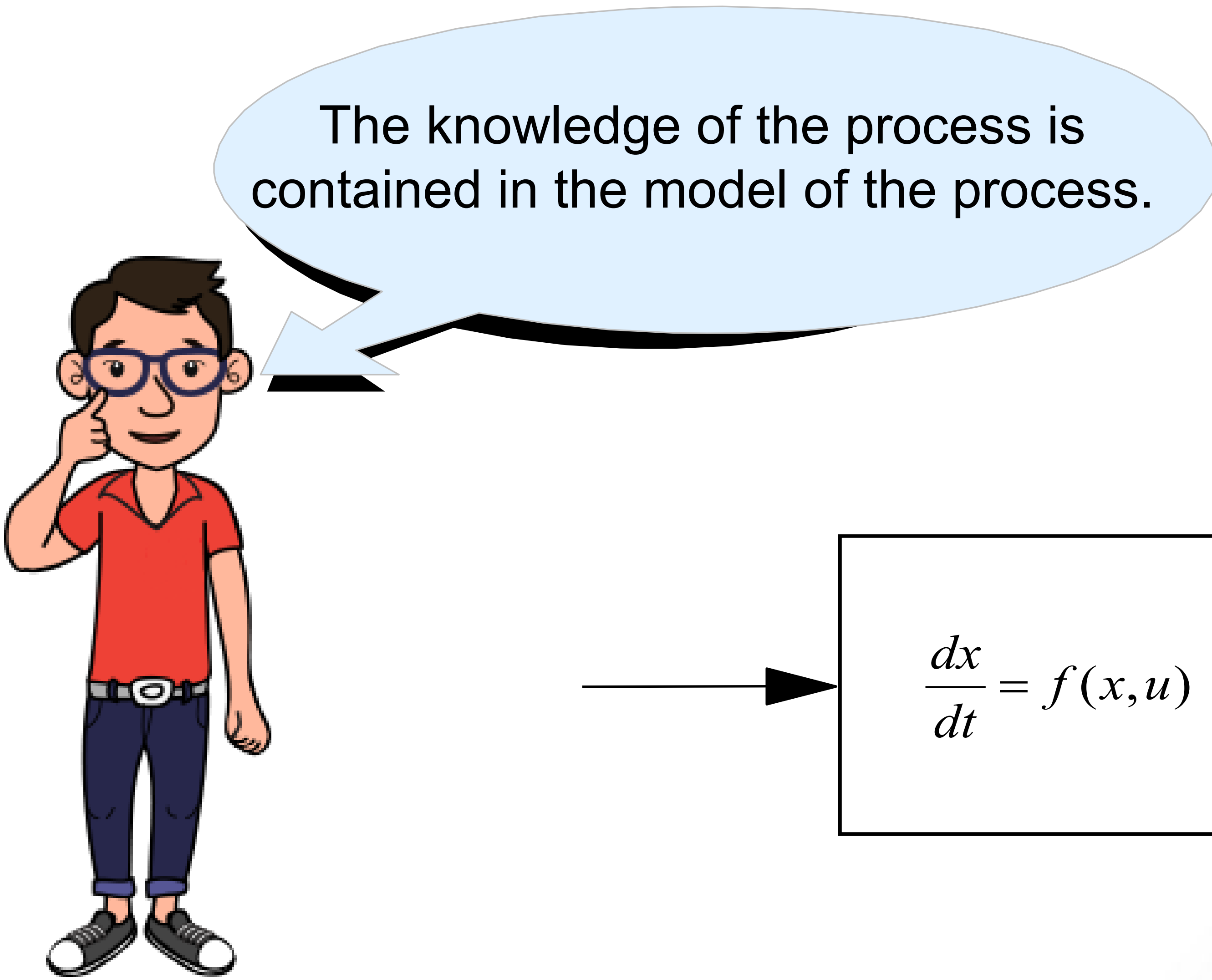
- Explain the concept of process model and modeling principles
- List the three modeling approaches
- Develop dynamic models represented as ordinary differential equations (ODE) using conservation laws

Learning Objectives

At the end of this chapter, you will be able to:

- Analyse dynamic models of representative processes as follows:
  - ✓ Blending process
  - ✓ Stirred tank heating process
  - ✓ Liquid storage systems
- Explain the use of assumptions to simplify models

What Is a Process Model?



$$\frac{dx}{dt} = f(x,u)$$

What is a Process Model?

- Mathematical Model
  - ✓ "a representation of the essential aspects of an existing system (or a system to be constructed) which represents knowledge of that system in a usable form" (Eykhoff, 1974).
  - ✓ Everything should be made as simple as possible, but no simpler.

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
  - ✓ Cost and effort required to develop the model
- Process modeling is both an art and a science.

General Modeling Principles

- Creativity is required to:
  - ✓ Simplify assumptions
  - ✓ Incorporate all important dynamics

- Dynamic models of chemical processes consist of:
  - ✓ ODE (Ordinary Differential Equation)
  - ✓ PDE (Partial Differential Equation)
  - ✓ Related algebraic equations

Why Dynamic Process Models?

- Improve understanding of the process
  - ✓ Transient process behaviour to be investigated
  - ✓ Valuable information about process before the plant is constructed

- Optimise process design/ operating conditions
  - ✓ Recalculate the optimum operating conditions periodically
  - ✓ Most profitable operating conditions

Why Dynamic Process Models?

- Design a control strategy for a new process
  - ✓ Allow alternative control strategies to be evaluated
    - ➢ Identify CVs (Controlled Variable), MVs (Manipulated Variable), etc.

- Train plant operating personnel

Source: Workers of Tobolsk-Polimer Chemical Plant. (2013, October 15). Retrieved March 4, 2016, from https://commons.wikimedia.org/wiki/File:Workers_of_Tobolsk-Polimer_chemical_plant.jpeg

Modelling Approaches

The key modelling approaches are: Theoretical Models, Empirical Models and Semi-Empirical Models.

- **Theoretical Model**
- Empirical Models
- Semi-Empirical Models

Theoretical Models

- ✓ Developed using principles of chemistry, physics or biology
  - ➢ Material/ energy balances
  - ➢ Heat, mass and momentum transfer
  - ➢ Thermodynamics, chemical kinetics
  - ➢ Physical property relationships
- ✓ Provides physical insight into process behaviour
- ✓ Good for extrapolation, scale-up
- ✓ Expensive and time consuming to develop
- ✓ Does not require experimental data to obtain (data required for validation and fitting)
- ✓ Model parameters not readily available

Modelling Approaches

The key modelling approaches are: Theoretical Models, Empirical Models and Semi-Empirical Models

- Theoretical Models
- **Empirical Models**
- Semi-Empirical Models

Empirical Models (black box model)

- ✓ Obtained by fitting experimental data
- ✓ Easier to develop than theoretical models
  - ➢ Linear regression
- ✓ **Do not extrapolate well**

Modelling Approaches

The key modelling approaches are: Theoretical Models, Empirical Models and Semi-Empirical Models

- Theoretical Models
- Empirical Models
- **Semi-Empirical Models**

Semi-Empirical Models

- ✓ Combination of the above models
- ✓ The numerical values of one/many parameters in the theoretical model are calculated from experimental data
- ✓ Incorporate theoretical knowledge
- ✓ Can be extrapolated over wider range as compared to empirical models
- ✓ Less development effort than theoretical models

Modelling Approach Examples

Conservation Laws

- Conservation of Mass

$$\left\{\begin{matrix}\text{Rate of mass}\\ \text{accumulation}\end{matrix}\right\} = \left\{\begin{matrix}\text{Rate of mass}\\ \text{in}\end{matrix}\right\} - \left\{\begin{matrix}\text{Rate of mass}\\ \text{out}\end{matrix}\right\} \quad (2-6)$$

- Conservation of Component i

$$\left\{\begin{matrix}\text{Rate of component i}\\ \text{accumulation}\end{matrix}\right\} = \left\{\begin{matrix}\text{Rate of component i}\\ \text{in}\end{matrix}\right\}$$

$$- \left\{\begin{matrix}\text{Rate of component i}\\ \text{out}\end{matrix}\right\} + \left\{\begin{matrix}\text{Rate of component i}\\ \text{produced}\end{matrix}\right\} \quad (2-7)$$

Conservation Laws

- Conservation of Energy

$$\begin{Bmatrix}\text{Rate of energy}\\ \text{accumulation}\end{Bmatrix} = \begin{Bmatrix}\text{Rate of energy in}\\ \text{by convection}\end{Bmatrix} - \begin{Bmatrix}\text{Rate of energy in}\\ \text{by convection}\end{Bmatrix}$$

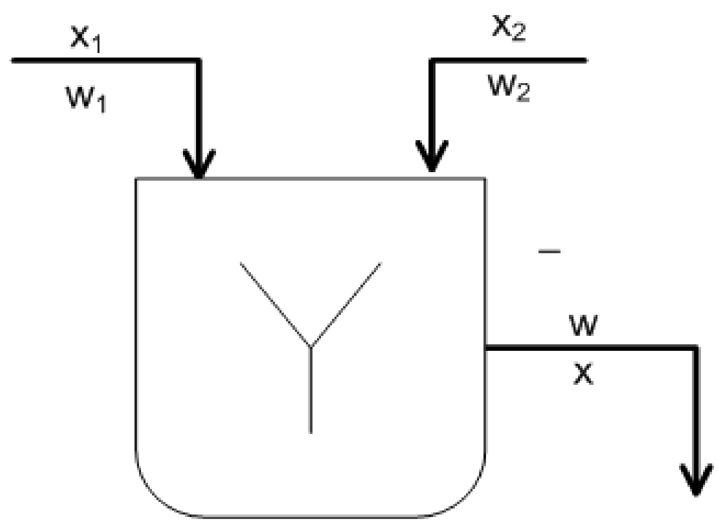
$$+ \begin{Bmatrix}\text{Net rate of heat}\\ \text{addition to the system}\\ \text{from the surroundings}\end{Bmatrix} + \begin{Bmatrix}\text{Net rate of work}\\ \text{performed on the system}\\ \text{by the surroundings}\end{Bmatrix} \qquad (2-8)$$

- The total energy of a thermodynamic system, U_{tot}

$$U_{tot} = U_{int} + U_{KE} + U_{PE} \; (2-9)$$

Development of Dynamic Models

- An illustrative example: A blending process



An unsteady-state mass balance for the blending system:

$$\begin{Bmatrix}\text{Rate of accumulation}\\ \text{of mass in the tank}\end{Bmatrix} = \begin{Bmatrix}\text{Rate of}\\ \text{mass in}\end{Bmatrix} - \begin{Bmatrix}\text{Rate of}\\ \text{mass out}\end{Bmatrix} \quad (2-1)$$

An Illustrative Example 1: A Blending Process

or $$\frac{d(V\rho)}{dt} = w_1 + w_2 - w \qquad (2-2)$$

where w_1, w_2, and w are mass flow rates.

- **The unsteady-state component balance is:**

$$\frac{d(V\rho x)}{dt} = w_1 x_1 + w_2 x_2 - wx \qquad (2-3)$$

The corresponding steady-state model was derived in Chapter 1 (cf. Eqs. 1-1 and 1-2). (Bar indicates nominal steady state).

$$0 = \bar{w}_1 + \bar{w}_2 - w \qquad (2-4)$$

$$0 = \bar{w}_1 \bar{x}_1 + \bar{w}_2 \bar{x}_2 - \bar{w}\bar{x} \qquad (2-5)$$

A Blending Process

- For constant ρ, Eqs. 2-2 and 2-3 become

$$\frac{d(V\rho)}{dt} = w_1 + w_2 - w \qquad (2-12)$$

$$\frac{\rho d(Vx)}{dt} = w_1 x_1 + w_2 x_2 - wx \qquad (2-13)$$

- Simplifying Eq. 2-13 using the "chain rule"

$$\rho \frac{d(Vx)}{dt} = \rho V \frac{dx}{dt} + \rho x \frac{dV}{dt} \qquad (2-14)$$

- Substitution of 2-14 into 2-13 gives

$$\rho V \frac{dx}{dt} + \rho x \frac{dV}{dt} = w_1 x_1 + w_2 x_2 - wx \qquad (2-15)$$

A Blending Process (Cont'd)

- Substitution of the mass balance in (2-12) for in (2-15) gives:

$$\rho V \frac{dx}{dt} + x(w_1 + w_2 - w) = w_1 x_1 + w_2 x_2 - wx \qquad (2-16)$$

- Rearranging (2-12) and (2-16), a more convenient model form is obtained:

$$\frac{dV}{dt} = \frac{1}{\rho}(w_1 + w_2 - w) \qquad (2-17)$$

$$\frac{dx}{dt} = \frac{w_1}{V\rho}(x_1 - x) + \frac{w_2}{V\rho}(x_2 - x) \qquad (2-18)$$

Example 2: Stirred Tank Heating Process

- Assumptions:
  - ✓ Perfect mixing
  - ✓ Constant density and heat capacity of the liquid
  - ✓ Heat losses are negligible

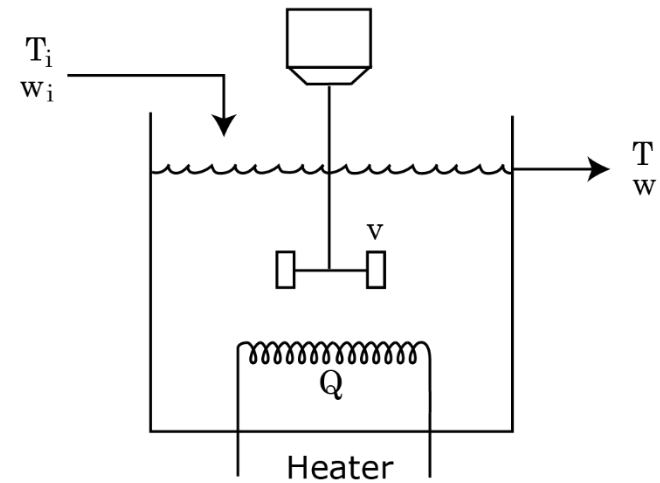


Figure 2.3 Stirred-tank heating process with constant holdup, V.

Source: Seborg, D. E., Edgar, T. F., Mellichamp, D. A., & Doyle, F. J., (2011). *Process dynamics and control* (3rd ed.)(pp.27). Hoboken, NJ: Wiley.

Stirred Tank Heating Process

- Case1: Constant holdup
  - ✓ Conservation of energy
  - ✓ Mass balance is not required

$$\frac{dU_{int}}{dt} = -\Delta\left(w\hat{H}\right) + Q \qquad (2-10)$$

Where U_{int} is the internal energy of the system, $\hat{H}$ is the enthalpy per unit mass, w is the mass flow rate, and Q is the rate of heat transfer to the system ($Q > 0$ when the system receives heat).

Converting equation (2-10) gives:

$$V\rho C\frac{dT}{dt} = wC(T_i - T) + Q \qquad (2-36)$$

Stirred Tank Heating Process (Cont’d)

- Case 2: Variable holdup
  - ✓ Material balance

$$\frac{d(Vp)}{dt} = w_i - w \qquad (2-37)$$

  - ✓ Energy balance

$$\frac{d(Vp\hat{H})}{dt} = w_i C\left(T_i - T_{ref}\right) - wC\left(T - T_{ref}\right) + Q \qquad (2-40)$$

  - ✓ Chain rule and rearranging give:

$$\frac{dV}{dt} = \frac{1}{p}(w_i - w) \qquad (2-45)$$

$$\frac{dT}{dt} = \frac{w_i}{Vp}(T_i - T) + \frac{Q}{pCV} \qquad (2-46)$$

Stirred Tank Heating Process (Cont'd)

- Case3: Constant holdup and energy transfer not instantaneous

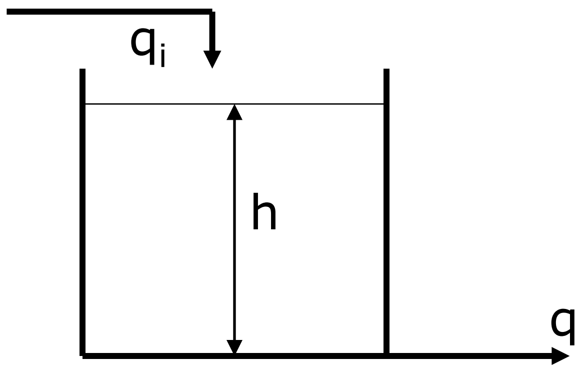
- Unsteady state balance for tank & heating element

Tank: $$mC\frac{dT}{dt} = wC(T_i - T) + h_eA_e(T_e - T) \qquad (2-47)$$

Element: $$m_eC_e\frac{dT_e}{dt} = Q - h_eA_e(T_e - T) \qquad (2-48)$$

- $m = \rho V$,
- m_eC_e = product of the mass of metal in the heating element and its specific heat
- h_eA_e = product of the heat transfer coefficient and area available for heat transfer

Example 3: Liquid Storage Systems



- Mass balance

$$\frac{d(pV)}{dt} = pq_i - pq \qquad (2-53)$$

- q_i & q: Volumetric flow rate
- Assumption
  - ✓ Constant density
  - ✓ Tank is cylindrical with cross-sectional area A & $V = AH$

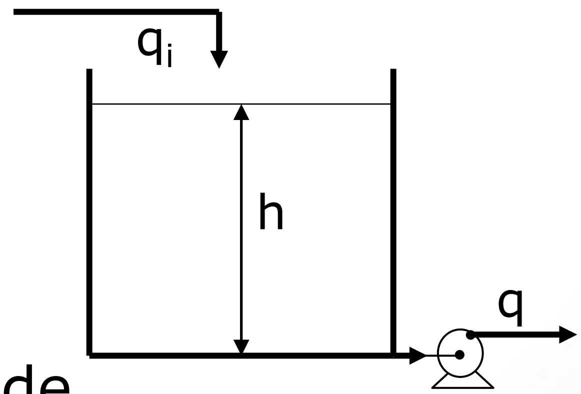
$$A\frac{dh}{dt} = q_i - q \qquad (2-54)$$

- Volume is not conserved for fluids, due to constant density assumption.

Liquid Storage Systems

Three important variations:

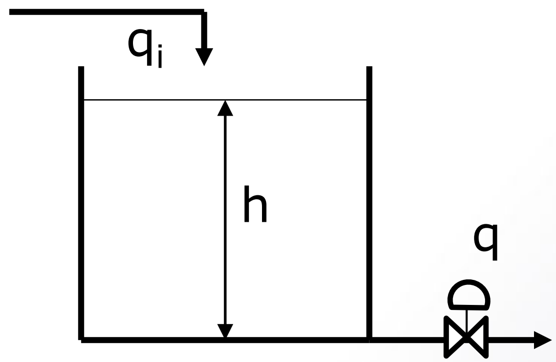
- Case 1: Inlet or outlet flow rates is constant
  - ✓ Exit flow rate is constant
  - ✓ Constant speed pump
  - ✓ Exit flow rate is completely independent of liquid level over wide range of conditions
  - ✓ Tank operates as a flow integrator



Liquid Storage Systems

- Case 2: Tank exit line may function as a resistance to flow along the line
  - ✓ It may contain valve that provides significant resistance at a point
  - ✓ Flow may be linearly related to the driving force, i.e., liquid level (Ohm's law)

$$h = qR_v \quad \text{or} \quad q = \frac{1}{R_v}h \qquad (2\text{-}55)$$



  - ✓ R_v = Resistance of the line or valve
  - ✓ Substituting (2-55) into (2-54) gives

$$A\frac{dh}{dt} = q_i - \frac{1}{R_v}h \qquad (2\text{-}57)$$

Liquid Storage Systems

- Case 3: A fixed valve has been placed on the exit line and turbulent flow can be assumed
- Driving force for flow through the valve is the pressure drop ΔP

$$\Delta P = P - P_a \qquad (2-58)$$

  - ✓ P: Pressure at the bottom of tank
  - ✓ P_a: Ambient Pressure

- Flow is assumed to be nonlinear related to the driving force such that it is proportional to the square root of the pressure drop

$$q = C_v^* \sqrt{P - P_a} \qquad (2-59)$$

Liquid Storage Systems

- Pressure P at the bottom of the tank

$$P = P_a + \frac{\rho g h}{g_c} \qquad (2-60)$$

- Substituting (2-59) & (2-60) into (2-54) gives

$$A\frac{dh}{dt} = q_i - C_v^* \sqrt{\frac{\rho g h}{g_c}} = q_i - C_v\sqrt{h} \qquad (2-61)$$

Summary

In this chapter, we have covered:

- Modeling principles
- Motivation for dynamic process models
- Dynamic models of representative processes
  - ✓ Blending process
  - ✓ Stirred tank heating process
  - ✓ Liquid storage systems

Suggested Reading: Chapter 2 of SEMD (Seborg, Edgar, Mellichamp and Doyle *Third Edition*)

Review Questions

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Event code
CH3101CHAPTER2

Chapter 2: Theoretical Models of Chemical Processes

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