Lecture#3: **Analytical Models of Chemico-Technological Processes**

Goal

This lecture introduces students to the development and application of analytical models in chemical engineering. It aims to demonstrate how fundamental conservation laws, thermodynamics, and reaction kinetics are combined to derive analytical relationships for predicting process performance, reactor design, and transport phenomena. Through examples in reactor modeling, heat transfer, and separation processes, students will learn how analytical modeling serves as a foundation for understanding and optimizing chemico-technological systems.

What is an Analytical Model?

An analytical model in chemical engineering represents a system or process using mathematical equations that can be solved directly. These models are derived from fundamental principles, including mass and energy balances, reaction kinetics, thermodynamics, and transport phenomena.

Analytical models offer insights into how systems behave by providing exact solutions (when possible), unlike numerical models that rely on approximations. These models are essential for understanding the key features of chemico-technological processes, such as chemical reactions, heat transfer, and mass transport.

Why Use Analytical Models?

- Predictive Power: Analytical models help predict system behavior without the need for large computational resources.

- Optimization: Analytical models are useful for optimizing operating conditions, such as temperature, pressure, and flow rates.

- Design: These models help design reactors, heat exchangers, distillation columns, and other chemical processing equipment.

Key Principles in Analytical Models for Chemico-Technological Processes

Conservation Laws

1. Mass Conservation:

- A fundamental principle stating that mass cannot be created or destroyed. It forms the basis of mass balance equations in chemical processes:

$$\frac{dM}{dt} = \text{Mass In - Mass Out + Generation}$$

- Mass balance is crucial in processes such as chemical reactors, separators, and distillation units.

2. Energy Conservation:

- Energy balance ensures that the total energy in a system remains constant unless there is an energy source or sink:

$$\frac{dE}{dt} = \text{Energy In - Energy Out + Heat Generation}$$

- This is particularly important in heat exchangers, reactors with heat release, and evaporators.

3. Momentum Conservation:

- Used to describe fluid flow, momentum conservation is vital for understanding fluid dynamics in pipes, reactors, and mixing vessels:

$$\rho \frac{d\mathrm{v}}{dt} = \mathbf{F}_{pressure} + \mathbf{F}_{viscous} + \mathbf{F}_{body}$$

- Momentum balance helps in determining pressure drops, fluid velocity profiles, and mixing efficiency.

Reaction Kinetics

In chemical reactors, reaction kinetics governs how fast chemical reactions occur. Analytical models use rate laws (e.g., first-order, second-order reactions) to predict product yields, conversion, and selectivity.

- First-Order Reactions:

$$\frac{dC_A}{dt} = -kC_A^1$$

Where $\boldsymbol{C_A}$ is the concentration of reactant A, and $\boldsymbol{k}$ is the rate constant. The solution to this equation gives the concentration of A as a function of time, allowing the prediction of how quickly reactants are consumed.

- Second-Order Reactions:

$$\frac{dC_A}{dt} = -kC_A^2$$

This model is applied when two molecules of reactant A are involved in the reaction.

Thermodynamics

Thermodynamics plays a vital role in determining equilibrium conditions and phase changes in processes like distillation and separation.

- Gibbs Free Energy Minimization is often used to predict equilibrium states.

- Raoult's Law and Henry's Law provide the basis for phase equilibrium models used in distillation, absorption, and other separation processes.

Applications of Analytical Models in Chemico-Technological Processes

Reactor Design

Analytical models are essential in the design of different types of reactors, such as:

- Batch Reactors: Used when reactions are carried out in closed systems.

- Continuous Stirred Tank Reactors (CSTRs): Models help predict the steady-state concentration of reactants and products.

- Plug Flow Reactors (PFRs): Analytical models based on mass balance and reaction kinetics describe how reactant concentrations change along the reactor length.

Example:

Plug Flow Reactor

The design equation for a PFR, considering a first-order reaction, is:

$$\frac{dC_A}{dz} = -\frac{kC_A}{\mathrm{v}}$$

Where: $\boldsymbol{C_A}$ is the concentration of reactant A; **z** is the reactor length; **v** is the volumetric flow rate.

By solving this equation analytically, we can determine the reactor size required to achieve a desired conversion.

Heat Exchangers

Heat exchangers are widely used in chemical processes to transfer heat between fluids. Analytical models predict the heat transfer rate and temperature profiles.

- Overall Heat Transfer Equation:

$$Q=UA\Delta T_m$$

Where: Q is the heat transfer rate;U is the overall heat transfer coefficient; A is the surface area for heat exchange; ΔT_m is the mean temperature difference.

For heat exchangers like shell-and-tube or plate heat exchangers, analytical solutions help design the heat transfer area and optimize the fluid flow rates.

Distillation and Separation Processes

In distillation, the goal is to separate components in a mixture based on their boiling points. Analytical models for distillation use mass and energy balances, combined with thermodynamic phase equilibrium relations, to predict the number of stages required for separation.

- McCabe-Thiele Method: A graphical, analytical approach used for binary distillation, helping in the design of the number of theoretical stages.

- Fenske Equation: Used to estimate the minimum number of stages for a distillation column at total reflux:

$$N_{min} = \frac{ln\left(\frac{x_D/(1-x_D)}{x_B/(1-x_B)}\right)}{\ln(\alpha)}$$

Where $\boldsymbol{x_D}$ and $\boldsymbol{x_B}$ are the mole fractions of the more volatile component in the distillate and bottoms, respectively, and $\boldsymbol{\alpha}$ is the relative volatility.

Mass Transfer Operations

In operations like absorption, extraction, and adsorption, analytical models help predict the rate of mass transfer and design equipment such as packed columns and adsorption beds.

<u>- Fick’s Law of Diffusion:</u> Governs mass transfer driven by concentration gradients:

$$J = -D\frac{dC}{dx}$$

Where: J is the molar flux; D is the diffusion coefficient; $\frac{dC}{dx}$ is the concentration gradient.

For gas absorption, models based on mass transfer coefficients and equilibrium relations predict the performance of packed columns, enabling the design of absorber height and packing material.

Challenges in Analytical Modeling

Complexity and Non-Linearity

Many chemico-technological processes involve complex systems where the governing equations become non-linear. While analytical models are powerful, they often require simplifying assumptions (e.g., steady-state conditions, ideal behavior) that may not accurately reflect real-world behavior.

Multiphase and Multicomponent Systems

In multiphase systems (e.g., gas-liquid reactions), mass and energy transfer between phases adds complexity. Analytical solutions may be difficult or impossible to derive for such systems, requiring hybrid models or numerical approaches.

Reaction Coupling

In cases where multiple reactions occur simultaneously, such as in catalytic reactors, deriving analytical models becomes challenging due to the need to account for coupled reaction kinetics and mass transfer limitations.

Conclusion

Analytical models provide a powerful framework for understanding and designing chemico-technological processes, offering insights into reaction kinetics, heat transfer, mass transport, and thermodynamics. They enable engineers to predict the behavior of chemical reactors, heat exchangers, separation processes, and more. However, while analytical models are essential tools for process design and optimization, real-world complexity often necessitates the use of hybrid or numerical models when systems deviate from ideal conditions.

Learning Outcomes

By the end of this lecture, students will be able to:

1. Explain the concept of an analytical model and its role in understanding chemico-technological processes (related to LO 3, ID 3.1).

2. Derive and apply analytical equations based on mass, energy, and momentum conservation principles (related to LO 3, ID 3.2).

3. Apply rate laws and reaction-kinetic models to predict conversion and yield in batch, CSTR, and PFR reactors (related to LO 3, ID 3.2).

Questions and Self-study Assignments

1. Define an analytical model. How does it differ from numerical and empirical models?

2. Derive a mass-balance equation for a steady-state continuous stirred-tank reactor (CSTR) operating with a first-order reaction.

3. For a plug-flow reactor (PFR) performing a first-order reaction, derive the analytical relationship between conversion and reactor length.

4. Using Fick's law, derive the expression for molar flux in one-dimensional steady-state diffusion.

5. Discuss limitations of analytical modeling when applied to:

-multiphase systems,

-coupled reactions,

-non-ideal thermodynamics.

6.Read one recent journal article (published within the last 3 years) that applies analytical or semi-analytical modeling to a chemical process (reactor, separation, or electrochemical system). Summarize:

-the governing equations used;

-main assumptions and simplifications;

-how the model predictions compared with experimental data.

References

1. Finlayson B.A. Introduction to Chemical Engineering Computing. Second Edition. - John Wiley & Sons, 2012. ISBN 9781118309599, DOI: 10.1002/9781118309599

2. Ghasem N. Modeling and Simulation of Chemical Process Systems. - CRC Press, 2015. – 518 p. ISBN 1138568511