LECTURE 03

Analytical Models of Chemico-Technological Processes

Department of Analytical, Colloidal Chemistry and Technology of Rare Elements

Modeling of chemico-technological processes | 6B07102 Chemical Engineering

Khaisa Avchukir, PhD, Acting Associate Professor

Avchukir Khaisa © 2024

Purpose and expected learning outcomes

Purpose: develop physically grounded models that connect measurable chemical-engineering behavior to governing equations and reliable predictions.

EXPLAIN

Identify governing phenomena and state assumptions.

CALCULATE

Apply equations using consistent physical units.

COMPARE

Evaluate alternative model formulations.

INTERPRET

Read simulated curves and measured responses.

EVALUATE

Test limitations, uncertainty and validity.

APPLY

Propose a reproducible modeling workflow.

Avchukir Khaisa © 2024

From physical system to engineering decisions

01 Define system

Boundaries, outputs

02 Formulate physics

Balances and kinetics

03 Specify parameters

Units and assumptions

04 Solve equations

Analytical or numerical

05 Validate outputs

Experiment and errors

06 Optimize process

Design and control

Industrial relevance: reactors • separations • electrolysis • energy storage • environmental treatment

Avchukir Khaisa © 2024

Material Balance Models

The material balance is one of the fundamental tools used in chemical engineering.

General material balance:

Accumulation = Input − Output + Generation − Consumption

For a continuous stirred-tank reactor (CSTR) operating at steady state:

$$F_{ao} - F_a + r_a V = 0$$

where:

- F_{ao} — inlet molar flow rate.
- F_a — outlet molar flow rate.
- r_a — net rate of formation of component A.
- V — reactor volume.

For a first-order reaction: $A \rightarrow B$

$$-r_a = kC_a$$

The conversion in an ideal CSTR is: $X = k\tau/(1 + k\tau)$

where $\tau = V/q$ is the space time.

Energy Balance and Heat Transfer Models

Energy balance equations describe temperature changes during chemical and technological processes.

General energy balance:

Accumulation = Energy input − Energy output + Heat generated − Heat consumed

For a simplified heat transfer process:

$$Q = UA\Delta T$$

where:

- Q — heat transfer rate.
- U — overall heat transfer coefficient.
- A — heat transfer area.
- ΔT — temperature difference (appropriate mean temperature difference for the system).

For transient heating of a well-mixed liquid:

$$mCp(dT/dt) = UA(T_a - T)$$

This model can be used to predict the temperature response of a reactor or heating vessel.

When analytical solutions exist

Closed-form models expose parameter dependencies under simplifying assumptions.

$$dC/dt = -kC \rightarrow C(t) = C_0 e^{-kt}$$

MODEL CONDITIONS First-order, well-mixed, isothermal batch reaction; k in s^{-1}.

ENGINEERING INTERPRETATION Estimate k from the slope of $\ln(C/C_0)$ versus t.

Further reading: Fogler, Elements of Chemical Reaction Engineering; Bard, Faulkner & White, Electrochemical Methods (where applicable).

Avchukir Khaisa © 2024

Batch versus continuous stirred reactors

Flow changes the relationship between residence time and conversion.

CSTR: $C/C_{in} = 1/(1+k\tau)$

MODEL CONDITIONS Steady, constant-volume, ideal-mixing, first-order reaction; $\tau = V/q$.

ENGINEERING INTERPRETATION For $k\tau = 2$, CSTR conversion is 66.7%.

Further reading: Fogler, Elements of Chemical Reaction Engineering; Bard, Faulkner & White, Electrochemical Methods (where applicable).

Avchukir Khaisa © 2024

Analytical Models of Mass Transfer and Reaction Kinetics

Mass transfer describes the movement of substances between different phases or within a single phase.

For molecular diffusion, Fick's First Law is:

$$J_a = -D_a(dC_a/dx)$$

For a first-order reaction:

$$-r_a = kC_a$$

The reaction rate constant depends on temperature according to the Arrhenius equation:

$$k = A \exp(-E_a/RT)$$

where:

- A — pre-exponential factor.
- E_a — activation energy.
- R — universal gas constant.
- T — absolute temperature.

These equations are used to analyze the combined effects of temperature, reaction kinetics, and mass transfer on process efficiency.

Plug-flow reactor design

An ideal PFR retains spatial variation along the flow direction.

PFR: $C/C_{in} = \exp(-k\tau)$

MODEL CONDITIONS Steady plug flow, constant volumetric flow and temperature.

ENGINEERING INTERPRETATION For $k\tau = 2$, PFR conversion is 86.5%.

Further reading: Fogler, Elements of Chemical Reaction Engineering; Bard, Faulkner & White, Electrochemical Methods (where applicable).

Avchukir Khaisa © 2024

Diffusion through a planar layer

Linear steady profiles arise without reaction or convection.

$$J = D(C_1 - C_2)/L$$

MODEL CONDITIONS Fick's law for constant D and 1D steady transport; J mol m^{-2} s^{-1}.

ENGINEERING INTERPRETATION Membrane thickness directly affects transport resistance.

Further reading: Fogler, Elements of Chemical Reaction Engineering; Bard, Faulkner & White, Electrochemical Methods (where applicable).

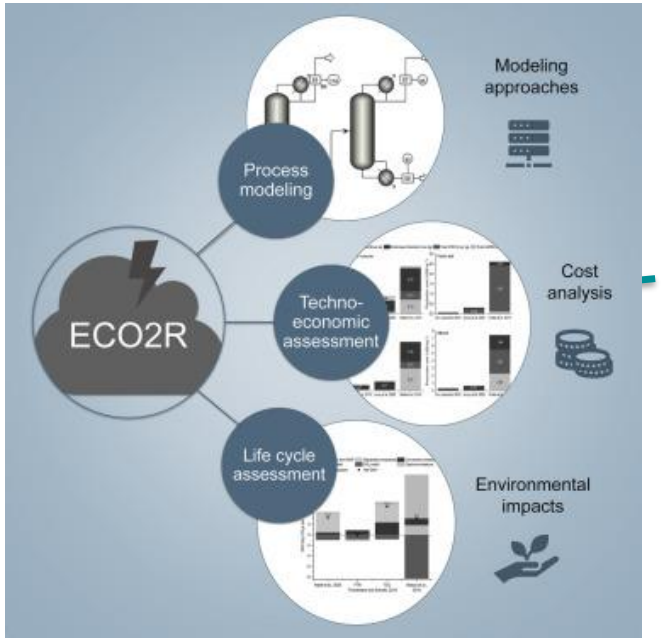
Avchukir Khaisa © 2024

Where analytical models break down

Nonlinear coupled PDEs may require numerical solution.

$$\partial C/\partial t = D\nabla^2 C - kC^2$$

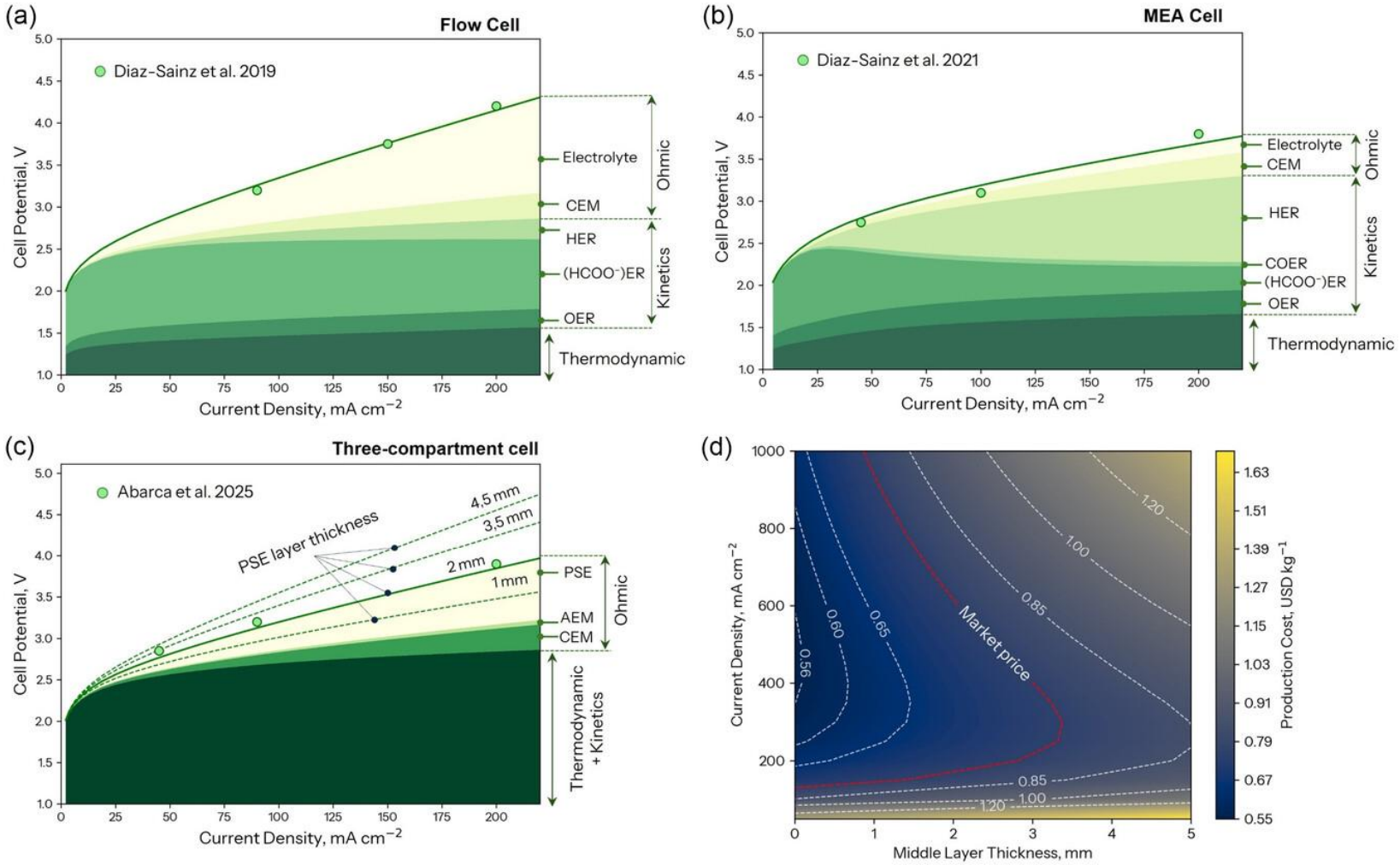
MODEL CONDITIONS Second-order reaction and diffusion can create spatially varying reaction zones.



ENGINEERING INTERPRETATION Use analytical limits to verify numerical implementations.

Further reading: Fogler, Elements of Chemical Reaction Engineering; Bard, Faulkner & White, Electrochemical Methods (where applicable).

Avchukir Khaisa © 2024



Voltage breakdown of (a) flow cell, (b) MEA cell, (c) three-compartment cell configuration showing thermodynamic, kinetic, and ohmic contributions. Effect of middle-layer thickness and current density on HCOOH production cost in three-compartment cells (d).

Camilo E. Peralta, Jose Antonio Abarca, Guillermo Díaz-Sainz, Esther Santos, Angel Irabien, *ChemSusChem* 2026, 19, e202502269. https://doi.org/10.1002/cssc.202502269

Conclusions: a verified model is a useful model

PHYSICS

Identify dominant conservation and transport laws.

EQUATIONS

State variables, signs, units and assumptions.

PARAMETERS

Determine measurable coefficients and uncertainty.

NUMERICS

Check stability, convergence and physical balances.

EXPERIMENT

Validate predictions with independent observations.

APPLICATION

Use models for design, control and optimization.

Avchukir Khaisa © 2024

Homework: calculations, interpretation and research

1. THEORY Explain the assumptions behind "$dC/dt = -kC \rightarrow C(t) = C_0 e^{-kt}$" and identify when they fail.

2. CALCULATION For $C_0 = 2.0$ mol m^{-3}, $k = 0.020$ s^{-1} and $t = 60$ s, calculate $C = C_0 \exp(-kt)$ and conversion.

3. DATA Simulated normalized outputs at $t = 0, 20, 40, 60$ s are 1.00, 0.67, 0.45, 0.30. Estimate a first-order rate constant.

4. CRITIQUE Explain how transport limitations or nonideal mixing could invalidate a simple rate model.

5. RESEARCH Design a two-condition validation experiment for analytical models of chemico-technological processes; report measured variables, units and uncertainty.

Constants when needed: $F = 96485$ C mol^{-1}; $R = 8.314$ J mol^{-1} K^{-1}; $T = 298.15$ K.

Avchukir Khaisa © 2024

Recommended Literature

1. Fogler, H. S. *Elements of Chemical Reaction Engineering*. 5th ed., Pearson, 2016.
2. Himmelblau, D. M., Riggs, J. B. *Basic Principles and Calculations in Chemical Engineering*. 8th ed., Pearson, 2012.
3. Bird, R. B., Stewart, W. E., Lightfoot, E. N. *Transport Phenomena*. 2nd ed., John Wiley & Sons, 2002.
4. Levenspiel, O. *Chemical Reaction Engineering*. 3rd ed., John Wiley & Sons, 1999.
5. Bequette, B. W. *Process Control: Modeling, Design, and Simulation*. Prentice Hall, 2003.