LECTURE 04

Empirical Models in Chemical-Technological Processes

Department of Analytical, Colloidal Chemistry and Technology of Rare Elements

Modeling of chemico-technological processes | 6B07102 Chemical Engineering

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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.

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Types of Empirical Models

Empirical models can be classified according to their mathematical structure.

1. Linear Regression Model

$Y = \beta_0 + \beta_1 X$

Describes a linear relationship between an independent variable X and a response Y.

2. Multiple Linear Regression Model

$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \ldots + \beta_n X_n$

Describes the influence of several independent variables on a process response.

3. Polynomial Regression Model

$Y = \beta_0 + \beta_1 X + \beta_2 X^2$

Used to describe nonlinear trends using polynomial functions.

4. Nonlinear Empirical Models

$Y = aX^b$

Used when the relationship between variables cannot be adequately represented by a linear or polynomial model.

Experimental Data and Model Development

The quality of an empirical model depends strongly on the quality and quantity of experimental data.

Main stages of empirical model development:

1. Select independent variables and measurable responses.
2. Design and perform experiments.
3. Collect and organize experimental data.
4. Identify the mathematical form of the model.
5. Estimate model coefficients.
6. Evaluate statistical significance and model adequacy.
7. Validate the model using independent experimental data.

Example of a chemical process:

Investigation of the effect of temperature and reactant concentration on reaction yield.

Independent variables:

- X_1 — reaction temperature.
- X_2 — initial reactant concentration.

Dependent variable:

- Y — product yield.

Regression Analysis and Model Evaluation

Regression analysis is a statistical method used to estimate the relationship between experimental variables and process responses.

The coefficients of a linear regression model are commonly determined using the least squares method.

The objective is to minimize the sum of squared residuals:

$$SSE = \Sigma(Y_i - \hat{Y}_i)^2$$

where:

- Y_i — experimental value.
- $\hat{Y}_i$ — predicted value.
- SSE — sum of squared errors.

Important statistical indicators:

Coefficient of determination (R^2): Describes the proportion of response variability explained by the regression model.

Root Mean Square Error (RMSE): Measures the typical magnitude of prediction errors.

p-value: Helps evaluate the statistical significance of model coefficients under the specified statistical assumptions.

Residual analysis: Helps identify systematic deviations, non-constant variance, and possible problems with the model structure.

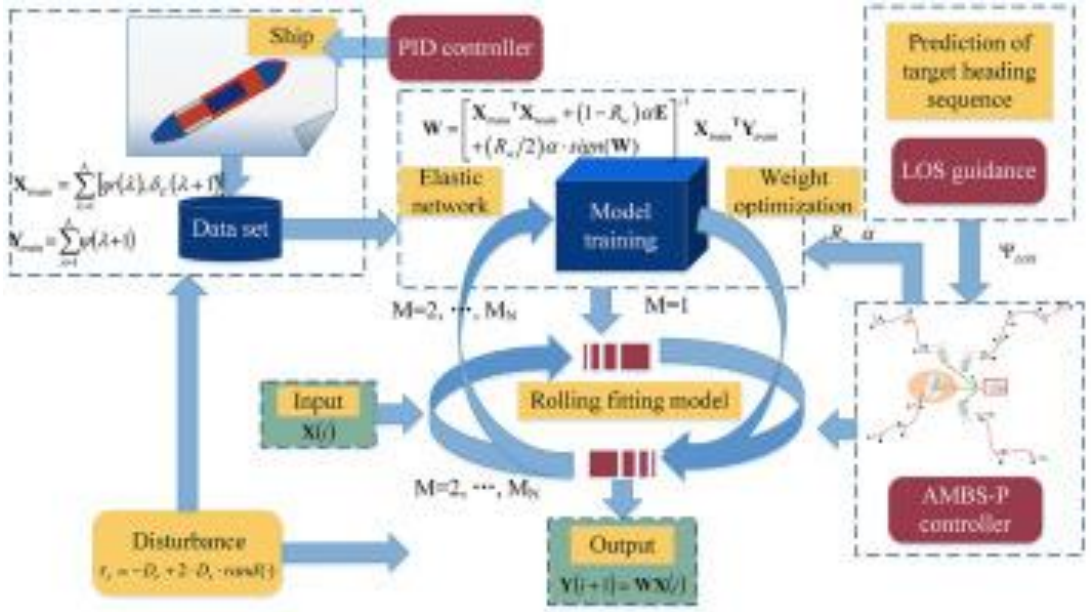
A high R^2 alone does not guarantee that a model is scientifically adequate or capable of accurate prediction.

Data-driven input–output relationships

Empirical models summarize measured relationships without proving mechanism.

$$\hat{y} = \beta_0 + \beta_1 x$$

MODEL CONDITIONS β parameters estimated from calibration observations; x must have defined units.



https://doi.org/10.1016/j.ijnaoe.2022.100445

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Least-squares parameter estimation

Regression minimizes squared residuals under a specified error model.

$$\hat{\beta} = (X^T X)^{-1} X^T y$$

MODEL CONDITIONS Requires full-column-rank X; weighted least squares if measurement variance differs.

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Nonlinear empirical kinetics

Power laws and exponentials can capture curved responses.

$$r = k\, C_A^{m}\, C_B^{n}$$

MODEL CONDITIONS Orders m and n are empirical; they need not match stoichiometric coefficients.

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Multiple factors and interactions

Response surfaces quantify interactions between controllable variables.

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_{12} x_1 x_2 + \beta_{11} x_1^2$$

MODEL CONDITIONS Coded x values simplify experimental design and coefficient comparison.

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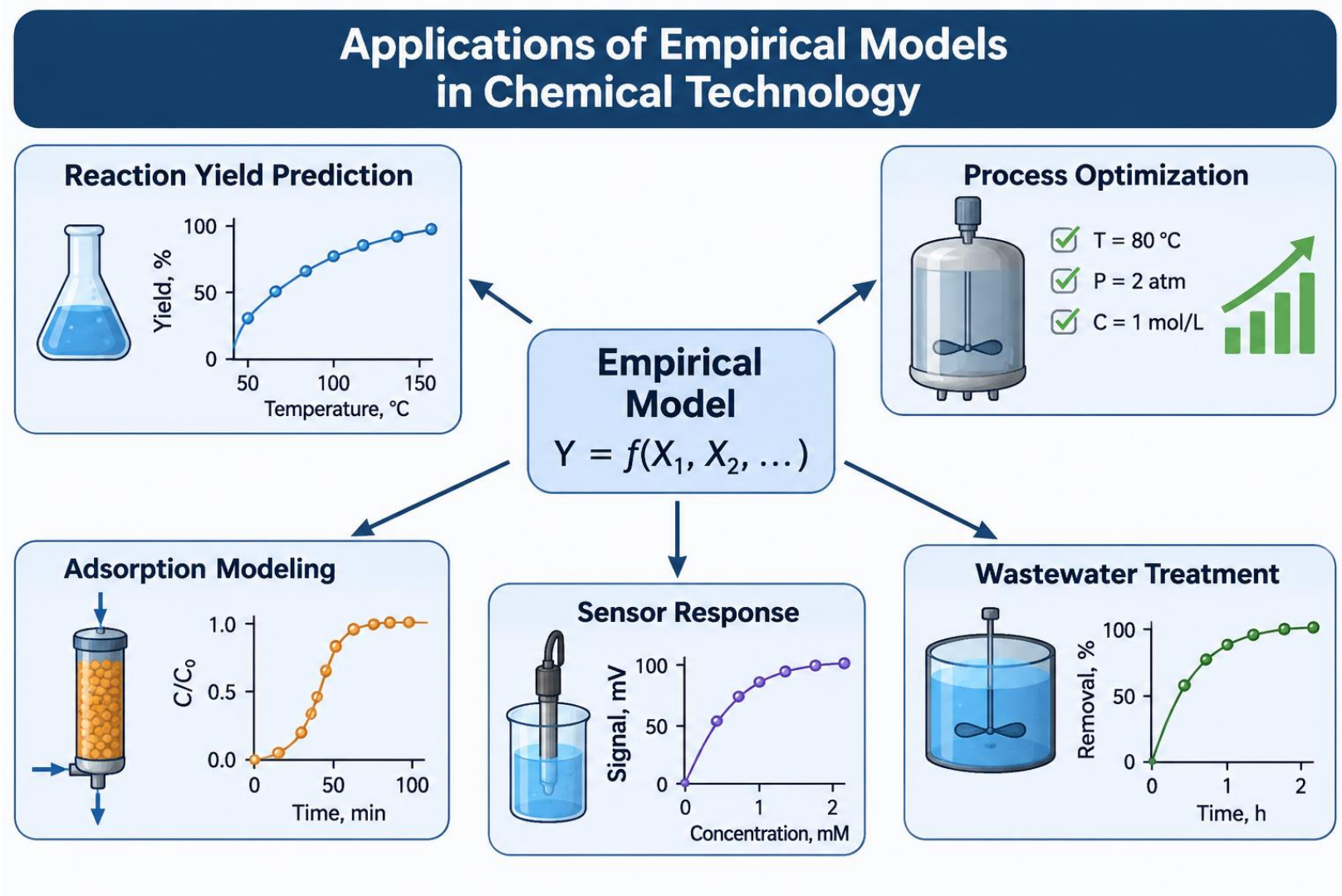
Applications, Advantages, and Limitations

Applications in chemical technology:

- Prediction of reaction yield.
- Optimization of temperature and pressure.
- Modeling adsorption and extraction processes.
- Prediction of electrochemical sensor responses.
- Optimization of wastewater treatment.
- Evaluation of analytical measurement conditions.

Advantages:

- Relatively simple to develop.
- Based on actual experimental observations.
- Useful for process optimization.
- Can describe complex relationships without a complete mechanistic understanding.



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.

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Homework: calculations, interpretation and research

1. THEORY Explain the assumptions behind "$\hat{y} = \beta_0 + \beta_1 x$" 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 empirical models in chemical-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.

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Recommended Literature

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