ChE 512
Transport Effects in Chemical Reactors
PART 2
Module 1
Introduction to Heterogeneous Reactors and Application Areas

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Topical Outline

• Introduction
• Kinetic models
• Transport effects
• Gas-solid reactions
• Gas-liquid reactions
• Three Phase Reactors
• Biochemical reactors
• Electrochemical reactors
Course Objectives

• Review basic multiphase reaction engineering reactor types and applications in petroleum processing, fine chemicals, and specialty chemicals.

• Develop basic relationships that describe the coupling between transport effects and kinetics for multiphase systems on a local level.

• Derive the basic performance equations for integral reactor performance using ideal flow patterns for the various phases.

• Present case studies or examples where the theory is put into practice.
Module 1 Outline

• Industrial Applications and Examples
• Review of Common Reactor Types
• Guidelines for Reactor Selection
Starting References

1. Doraiswamy L.K. and Sharma. M. M. Heterogenous Reactions,


Multiphase Catalytic Reactions

Reactants

- Gases
- Liquids
- Solids
- Solvent

Catalyst

Δ

Homogeneous
Heterogeneous
Enzyme
Bacteria
Cells

Products

- Gases
- Liquids
- Solids
- Solvent

Present

Future
Classification Based on Number of Phases

- Gas-Solid Catalytic
- Gas-Solid Non-Catalytic
- Gas-Liquid
- Gas-Liquid Solid Catalytic
- Gas-Liquid with Solid Reacting
- Liquid-Liquid
- Gas-Liquid-Liquid-Solid
Some Examples of Multiphase Catalytic Processes

- Hydrogenation of specialty chemicals
- Oxidation of glucose to gluconic acid
- Oxidation of n-paraffins to alcohols
- Methanol synthesis
- Fischer-Tropsch (FT) synthesis
- Hydrodesulfurization (HDS) of heavy residuals
- Adiponitrile synthesis
- Production of animal cells
- Fermentation processes
Other Emerging Multiphase Catalytic Technologies

- Catalysis by water soluble metal complexes in biphasic and nonionic liquid media
- Reactions in supercritical fluid media
- Asymmetric catalysis for chiral drugs/agricheamicals
- Polymerization with precipitating products (e.g., Polyketones)
- Phase transfer catalysis
- Catalysis by adhesion of metal particles to liquid-liquid interfaces
- Catalysis by nano-particles and encapsulation of metal complexes
Multiphase Reactor Technology Areas

**Syngas & Natural Gas Conversion**
- MeOH, DME, MTBE, Paraffins, Olefins, Higher alcohols, ...

**Petroleum Refining**
- HDS, HDN, HDM, Dewaxing, Fuels, Aromatics, Olefins, ...

**Bulk Chemicals**
- Aldehydes, Alcohols, Amines, Acids, Esters, LAB’s, Inorg Acids, ...

**Polymer Manufacture**
- Polycarbonates, PPO, Polyolefins, Specialty plastics

**Fine Chemicals & Pharmaceuticals**
- Ag Chem, Dyes, Fragrances, Flavors, Nutraceuticals, ...

**Environmental Remediation**
- De-NOx, De-SOx, HCFC’s, DPA, “Green” Processes ...

Value of Shipments in $US billions

http://www.eia.doe.gov/

P. L. Mills
NASCRE 1,
Houston, Jan 2001
The Global Chemical Industry

- Generates > $2 trillion gross income
  - 70,000 products
  - 1000 corporations (many small ones)

- Largest contributor to GDP

- Distribution:
Multiphase Catalytic Reactions
- Business Drivers -

- Increased globalization of markets
- Societal demands for higher environmental performance
- Financial market demands for increased profitability and capital productivity
- Higher customer expectations
- Changing work force requirements

http://www.eere.energy.gov/industry/chemicals/pdfs/chem_vision.pdf
Cost Breakdown for Chemical Production

• For large-scale processes, research must focus on reducing cost of raw materials and/or capital
• Small-scale processes can benefit from almost any improvement

Adapted from Keller & Bryan, CEP, January (2000)
Oxidation of p-Xylene to Terephthalic Acid

- G-L (homogeneous) catalytic oxidation with precipitating solid product.
- Oxygen mass transfer limitation, starvation of oxygen (due to safety limits) and exothermicity are key issues in reactor performance.
- Undesired impurity 4-CBA in ppm level requires a separate hydrogenation step (g-l-s reaction) to purify TPA.
- Involves dissolution of impurities, hydrogenation and re-crystallization to achieve purified TPA.
- Selection of suitable multiphase reactors has been a major challenge.

**Oxidation:**

- Cat I: Co-Mn-Br
- Temp.: 190-205°C
- $P_{O_2}: 1.5-3.0$ MPa

**Hydrogenation:**

- Cat II: Pd/support
- Temp.: 225-275°C
# Key Multiphase Reactor Types

<table>
<thead>
<tr>
<th>Mechanically agitated tanks</th>
<th>Soluble catalysts &amp; Powdered catalysts</th>
</tr>
</thead>
<tbody>
<tr>
<td>Multistage agitated columns</td>
<td></td>
</tr>
<tr>
<td>Bubble columns</td>
<td></td>
</tr>
<tr>
<td>Draft-tube reactors</td>
<td></td>
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<tr>
<td>Loop reactors</td>
<td></td>
</tr>
<tr>
<td>Packed columns</td>
<td>Soluble catalysts &amp; Tableted catalysts</td>
</tr>
<tr>
<td>Trickle-beds</td>
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<tr>
<td>Packed bubble columns</td>
<td></td>
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<tr>
<td>Bullated-bed reactors</td>
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</tbody>
</table>
Classification of Multiphase Gas-Liquid-Solid Catalyzed Reactors

1. Slurry Reactors

Catalyst powder is suspended in the liquid phase to form a *slurry*.

2. Fixed-Bed Reactors

Catalyst pellets are maintained in place as a *fixed-bed* or *packed-bed*.

Modification of the Classification for Gas-Liquid Soluble Catalyst Reactors

1. Catalyst complex is dissolved in the liquid phase to form a *homogeneous phase*.

2. Random inert or structured packing, if used, provides *interfacial area* for gas-liquid contacting.
Common types of gas-solid reactors

- Packed bed
- Fluid bed
- Monolith
- Riser and Downer
Multiphase Reactor Types at a Glance

Middleton (1992)
Mechanically Agitated Reactors

-Batch or Semi-Batch Operation-

(a) Batch
"Dead-Headed"

(b) Semi-Batch
Mechanically Agitated Reactors
- Continuous Operation -

Multistage Agitated Column for the Synthesis of Vitamin “carbol”
(Wiedeskehr, 1988)
# Mechanically Agitated Reactors - Pros and Cons -

<table>
<thead>
<tr>
<th>Pros</th>
<th>Cons</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Small catalyst particles</td>
<td>• Catalyst handling</td>
</tr>
<tr>
<td>• High effectiveness factor</td>
<td>• Catalyst fines carryover</td>
</tr>
<tr>
<td>• Highly active catalysts</td>
<td>• Catalyst loading limitations</td>
</tr>
<tr>
<td>• Well-mixed liquid</td>
<td>• Homogeneous reactions</td>
</tr>
<tr>
<td>• Catalyst addition</td>
<td>• Pressure limitations</td>
</tr>
<tr>
<td>• Nearly isothermal</td>
<td>• Temp. control (hot catalysts)</td>
</tr>
<tr>
<td>• Straightforward scale-up</td>
<td>• Greater power consumption</td>
</tr>
<tr>
<td>• Process flexibility</td>
<td>• Large vapor space</td>
</tr>
</tbody>
</table>

Source: P. L. Mills, R. V. Chaudhari, and P. A. Ramachandran
The BIAZZI Hydrogenation Reactor

- Inefficient heat and mass transfer
- Catalyst deposition in low turbulence area
- Poor mixing and non-homogeneous conditions in low turbulence area
- Ifficient cooling
- Sealing problems

Conventional Reactor

- Powerful gas dispersion and recirculation: high mass transfer
- No heat transfer limitations (up to 20 m²/m³)
- Easy catalyst recycling
- Negligible fouling
- Safer than the conventional reactors

BIAZZI Reactor
Multistage Agitated Column for Synthesis
“Carbol”-Pharmaceutical Intermediate

- Continuous reactor system with a cascade column and multistage agitator ensures good mixing, long mean residence time and narrow residence time distribution
- Gas phase voidage is minimum, hence safer for acetylene handling
- High productivity/smaller volume

\[ \text{R}_\alpha\beta\text{-unsaturated ketone} + \xrightarrow{\text{(i) aq. KOH}} \xrightarrow{\text{(ii) NH}_3, -5^\circ\text{C}} \xrightarrow{\text{(iii) H}_2\text{SO}_4} \text{Carbol} \]

Bubble Column Reactors at a Glance

Tarhan (1983)
Key Types of Bubble Columns

(a) Empty
*Semibatch or Continuous*

(b) Plate
*Continuous*

(c) Packed
*Semibatch or Continuous*
# Bubble Column Reactors - Pros and Cons -

<table>
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<tr>
<td>• Well-mixed liquid</td>
<td>• Homogeneous reactions</td>
</tr>
<tr>
<td>• Nearly isothermal</td>
<td>• Selectivity Control</td>
</tr>
<tr>
<td>• Lower power consumption</td>
<td>• No guidelines for internals</td>
</tr>
<tr>
<td>• High pressure operation</td>
<td>• More complex scaleup</td>
</tr>
</tbody>
</table>

Draft Tube and Loop Reactors

Internal Circulation

Concentric Draft Tube Loop

Concentric Draft Tube with Baffles

Concentric Draft Tube with Static Mixers

External Circulation

Tubular Loop

Split Cylinder Loop (Deep-shaft (ICI))

Channel Loop
Venturi Loop Reactors

Cramers et al. (1994)
Example: DuPont Butane to THF Process

\[
\begin{align*}
\text{n-C}_4 & \quad \text{O}_2 \quad \xrightarrow{\text{O}_2} \quad \text{Maleic anhydride} \\
& \quad \xrightarrow{\text{H}_2\text{O}} \quad \text{Maleic acid} \\
& \quad \xrightarrow{\text{H}_2} \quad \text{Tetrahydrofuran}
\end{align*}
\]

Pilot Plant Reactor
Ponca City, OK

n-C\textsubscript{4} Oxidation Reactor

Maleic acid Hydrogenation Reactor

Purification Train

Commercial Plant
Asturias, Spain
Other Types of Loop Reactors

- Internal Recirculation
- External Recirculation
- Jet Loop with External Recirculation
Jet Loop Recycle Reactors

Batch Operation

- Excellent mass & heat transfer performance
- Uniform catalyst distribution and mixing
- Commercially used in hydrogenation, alkylation, oxidation, amination, carbonylation and bio-catalytic reactions

Continuous Operation

- Higher Productivity/Throughput
- Lower Catalyst Consumption
- Safer Operation
- Higher Yields & Selectivity
- Lower Power Consumption

Source: Davy Process Technology
## Gas-lift and Loop Reactors - Pros and Cons -

<table>
<thead>
<tr>
<th>Pros</th>
<th>Cons</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Small catalyst particles</td>
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<td>• Well-mixed liquid</td>
<td>• Homogeneous reactions</td>
</tr>
<tr>
<td>• Nearly isothermal</td>
<td>• Selectivity control</td>
</tr>
<tr>
<td>• High pressure operation</td>
<td>• Possible pressure limitations</td>
</tr>
<tr>
<td>(Gas-lift reactor)</td>
<td>(Loop reactor)</td>
</tr>
<tr>
<td>• Process flexibility</td>
<td>• Greater power consumption</td>
</tr>
<tr>
<td></td>
<td>(Loop reactor)</td>
</tr>
<tr>
<td></td>
<td>• Catalyst attrition</td>
</tr>
</tbody>
</table>

Source: P. L. Mills, R. V. Chaudhari, and P. A. Ramachandran

Fixed-Bed Multiphase Reactors

(a) Trickle-Bed Cocurrent downflow
(b) Trickle-Bed Countercurrent flow
(c) Packed-Bubble Cocurrent upflow

Semi-Batch or Continuous Operation; Inert or Catalytic Solid Packing
Trickle Bed Reactors - Advantages -

- Plug flow of gas and liquid
- High catalyst / liquid ratio
- Stationary catalyst
- Minimal catalyst handling problems
- Operating mode flexibility
- High pressure operation
- Heat of reaction used to volatize liquid
- Large turndown ratio
- Low dissipated power
- Lower capital and operating costs
Trickle Bed Reactors
- Disadvantages -

- Larger particles, low catalyst effectiveness
- Possible poor liquid - solid contacting
- High crushing strength required for small particles
- Potential for reactor runaway
- Long catalyst life required
- Inability to handle dirty feeds
- Potential for liquid maldistribution
- More difficult to scale-up
Packed Bubble Flow Reactors
- Advantages -

- Complete liquid - solid contacting
- Higher liquid holdup
- Better temperature control
- Less problems with liquid maldisribution
- Higher heat and mass transfer rates
Packed Bubble Flow Reactors
- Disadvantages -

- Higher dissipated power than in TBR
- Throughput limited by bed fluidization velocity
- Increased potential for runaway
- Promotion of undesired homogeneous reactions
- Greater pressure drop
Bioreactor Types
(After Bailey and Ollis, 1986)

Mechanical agitation  External pumping  Gas agitation
## Commercial or Planned Bioprocesses

### High Volume Products

<table>
<thead>
<tr>
<th>Product</th>
<th>Carbon source</th>
<th>Production, t/year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lactic acid</td>
<td>corn syrup, whey permeate, agric. waste</td>
<td>300,000</td>
</tr>
<tr>
<td>Citric acid</td>
<td>molasses, glucose</td>
<td>550,000</td>
</tr>
<tr>
<td>Amino acids</td>
<td>molasses, glucose, corn syrup</td>
<td>250,000</td>
</tr>
<tr>
<td>Lysine, glutamic acid</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethanol</td>
<td>molasses, corn syrup, cellulose, agric. waste</td>
<td>28,000,000&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Single cell protein</td>
<td>methane</td>
<td>50,000&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>1,3 Propane diol</td>
<td>corn syrup</td>
<td>NA</td>
</tr>
<tr>
<td>Penicillin</td>
<td>glucose, corn steep liquor</td>
<td>25,000</td>
</tr>
<tr>
<td>Detergent enzymes&lt;sup&gt;c&lt;/sup&gt;</td>
<td>glucose, maltose, starch</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> for fuels only (US production 14.5x10<sup>6</sup> t/year in 1996)

<sup>b</sup> a target of 500,000 t/year is projected for Europe for 2010

<sup>c</sup> yearly product value in excess of 10<sup>9</sup> US$

Leib, Pereira & Villadsden, NASCRE 1, Houston 2001
Biological vs Chemical Systems

- Tighter control on operating conditions is essential (e.g., pH, temperature, substrate and product concentrations, dissolved O₂ concentration)

- Pathways can be turned on/off by the microorganism through expression of certain enzymes depending on the substrate and operating conditions, leading to a richness of behavior unparalleled in chemical systems.

- The global stoichiometry changes with operating conditions and feed composition; Kinetics and stoichiometry obtained from steady-state (chemostat) data cannot be used reliably over a wide range of conditions unless fundamental models are employed.

- Long term adaptations (mutations) may occur in response to environment changes, that can alter completely the product distribution

Leib, Pereira & Villadsden, NASCRE 1, Houston 2001
**Complex Reactor example: para-Amino Phenol by 4-Phase Hydrogenation**

An intermediate used in the manufacture of several analgesic and antipyretic drugs, e.g., paracetamol, acetanilide, & phenacetin

\[
\text{PhNO}_2 + 
\text{Pt/C} 
\rightarrow 
\text{PhNH}_2 \text{OH} 
\]

- Single step process
- Intermediate phenylhydroxylamine rearranged by interfacial reaction to para-aminophenol
- Selectivity determined by competing hydrogenation in organic phase and \& interfacial rearrangement with aqueous acid catalyst

R.V. Chaudhari et al., CES, 56, 1299, 2001

P. L. Mills, CAMURE-5, June 2005
Complex Reactor: Example 2
Phenyl Acetic Acid by 3-Phase Hydroformylation

Benzyl chloride

Reactant

CO/H₂

Pd-Catalyst

Products

Phenyl acetic acid

Gas-Liquid-Liquid w/Soluble Catalyst

Gas Phase

Organic Phase

Aqueous Phase

Soluble catalyst

Wan & Davis, 1993
Electrochemical Reactors

• Electrolytic production of chlorine and NaOH; Chloralkali industry.
• Aluminum production (Halls process)
• Fuel cells
• Monsanto adiponitrile process
• Paired electrosynthesis
• Pollution prevention; Metal recovery
Strategies for Multiphase Reactor Selection

- Maximize yield
- Ease of scale-up
- High throughput
- Low pressure drop
- Lowest Capital cost
- Other requirements

Desired Products
Undesired Products
Unconverted Reactants
Environmental and Safety

Intrinsically safe
“Green” processing
Zero emissions
Sustainable

“Wish List”

Reactants

Process Requirements

- Intrinsically safe
- “Green” processing
- Zero emissions
- Sustainable
Summary: Distinguishing Features of Multiphase Reactors

• *Efficient contacting* of reactive phases and separation of product phases *is key* to safety, operability and performance

• *Various flow regimes* exist, depending on phase flow rates, phase properties, operating conditions, and geometry

• Reaction and interphase *transport time-scales*, and phase flow patterns dictate reactor type, geometry and scale

• *Gradual scale-up* over several scales may be required for reliable commercialization
Three-Level Strategy for Reactor Selection

- Analyze process on three levels
- Make decisions on each level

Use fundamentals, data, & basic models for screening of various reactor alternatives
Multiphase Transport–Kinetic Interactions

Time & Length Scales

Reactor

Eddy or Particle

Molecular

Phase I, $Q_{in}^I$

$T_0^I, C_0^I, P_0^I$

L$(C_b^I) = \eta^I R^I(C_b^I, T_b^I)$

$L_h(T_b^I) = \sum_j (-\Delta H_{R_j}) \eta^I_j R^I_j(C_b^I, T_b^I)$

$\eta^I_j = f(\text{kinetics & transport in Phase I})$

Phase II, $Q_{in}^{II}$

$T_0^{II}, C_0^{II}, P_0^{II}$

L$(C_b^{II}) = \eta^{II} R^{II}(C_b^{II}, T_b^{II})$

$L_h(T_b^{II}) = \sum_j (-\Delta H_{R_j}) \eta^{II}_j R^{II}_j(C_b^{II}, T_b^{II})$

$\eta^{II}_j = g(\text{kinetics & transport in Phase II})$

Reactor Performance Determines Raw Material Utilization, Separations, Recycle Streams, Remediation, and Hence Process Economics & Profitability