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 practise.

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,**
2. **P. A. Ramachandran and R. V. Chaudhari, *Three-Phase Catalytic Reactors*, Gordon & Breach, London (1983).**
3. **P. L. Mills, P. A. Ramachandran, and R. V. Chaudhari, *Reviews in Chemical Engineering*, 8, pp. 1-192 (1992).**
4. **P. L. Mills and R. V. Chaudhari, "Multiphase catalytic reactor engineering and design for pharmaceuticals and fine chemicals," *Catalysis Today*, 37(4), pp. 367-404 (1997).**

Multiphase Catalytic Reactions

$$\boxed{\text{Reactants}} \xrightarrow[\text{Catalyst}]{\Delta} \boxed{\text{Products}}$$

- Gases
- Liquids
- Solids
- Solvent

Homogeneous

Heterogeneous

Enzyme

Bacteria

Cells

Present ↓ Future

- Gases
- Liquids
- Solids
- Solvent

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/agrichemicals
- 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, ….

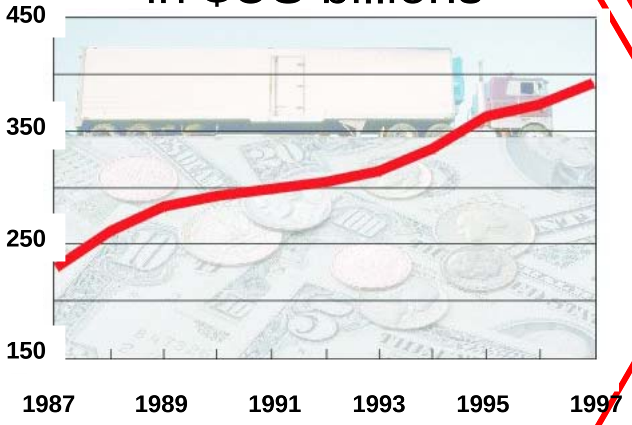
Petroleum Refining

HDS, HDN, HDM, Dewaxing, Fuels, Aromatics, Olefins, ...

Bulk Chemicals

Aldehydes, Alcohols, Amines, Acids, Esters, LAB’s, Inorg Acids, ...

Value of Shipments in $US billions



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

Polymer Manufacture

Polycarbonates, PPO, Polyolefins, Specialty plastics

Fine Chemicals & Pharmaceuticals

Ag Chem, Dyes, Fragrances, Flavors, Nutraceuticals,...

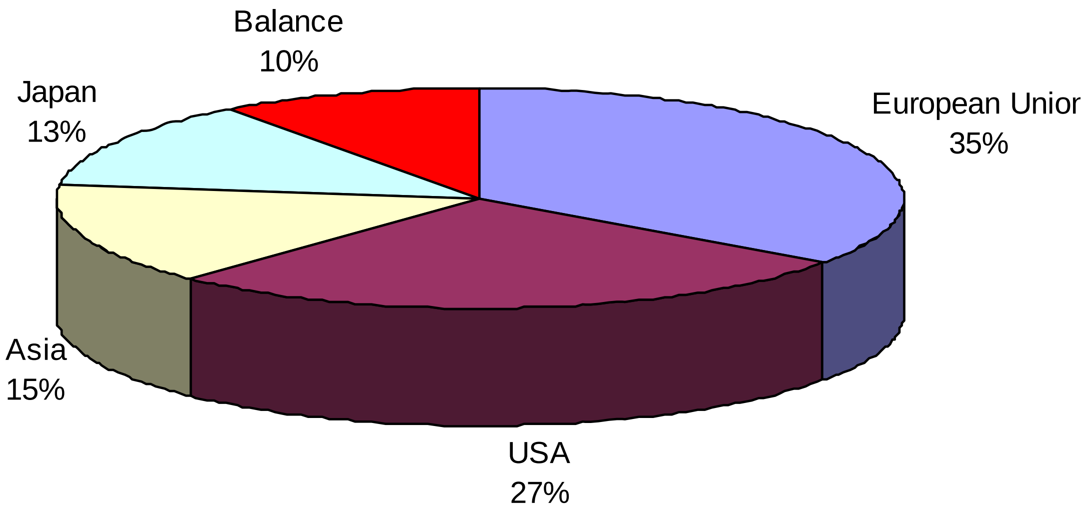
Environmental Remediation

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

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:



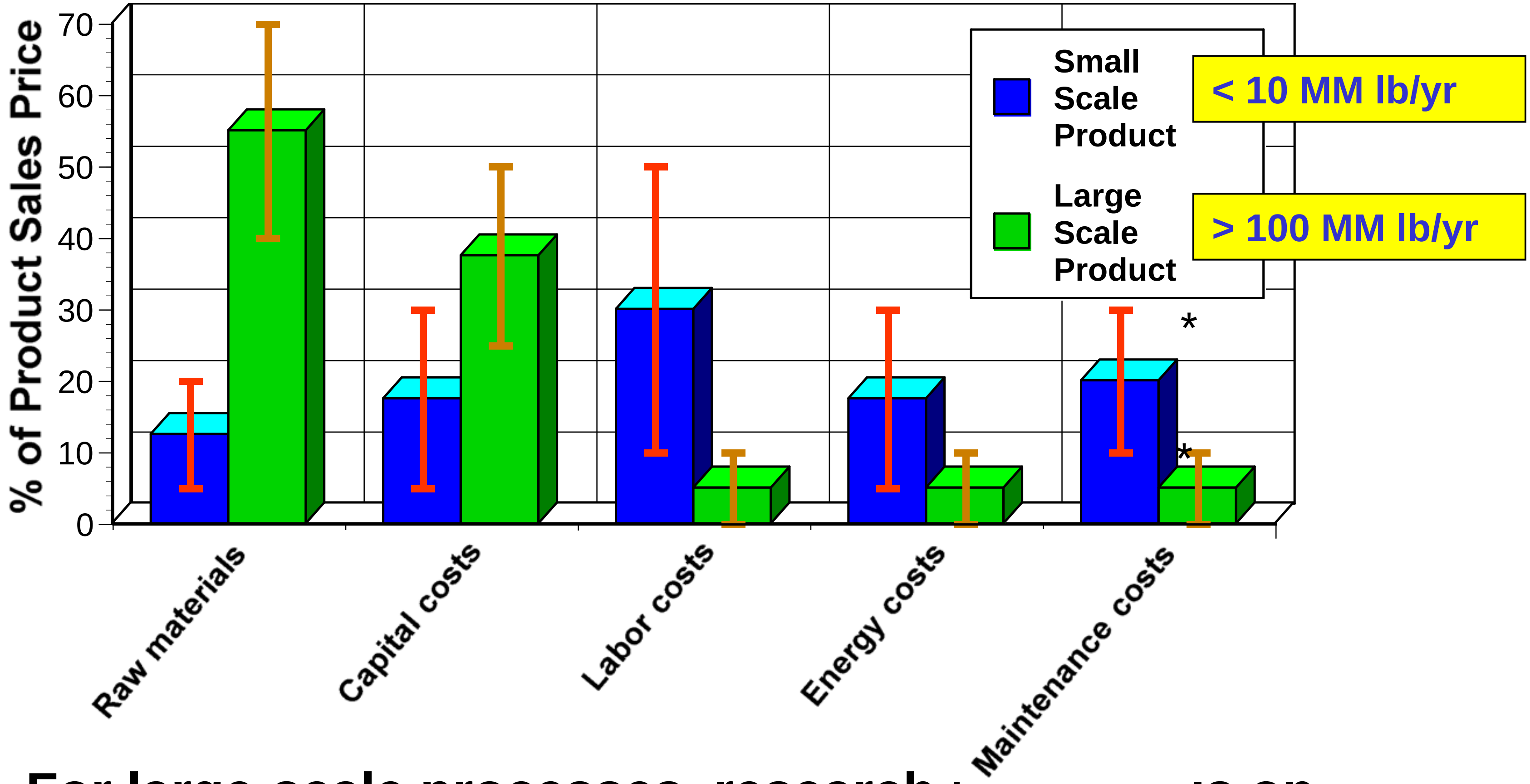
Multiphase Catalytic Reactions

- Business Drivers -

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

Technology Vision 2020, The US Chemical Industry, Dec. 1996
http://www.eere.energy.gov/industry/chemicals/pdfs/chem_vision.pdf

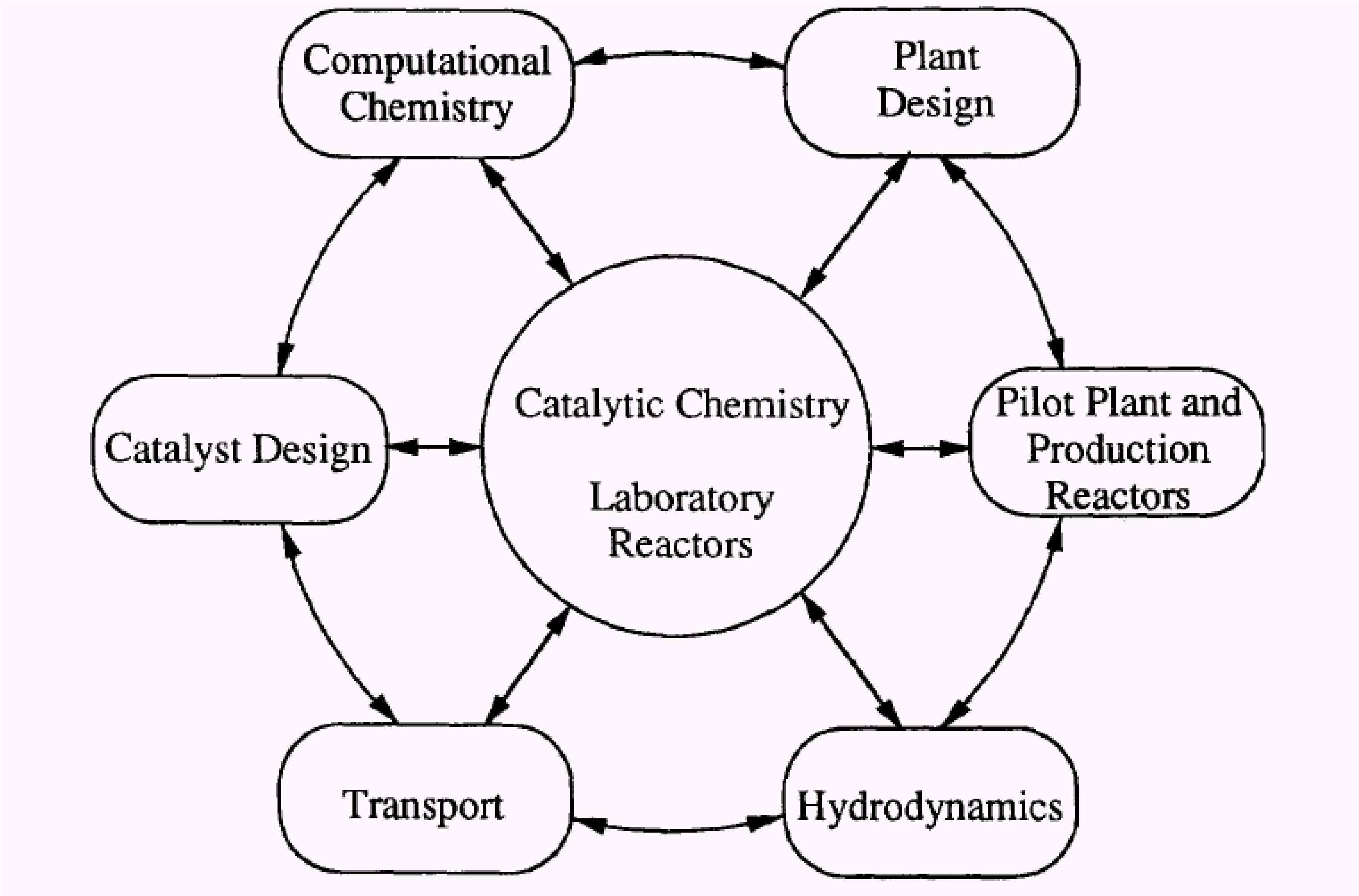
Cost Breakdown for Chemical Production



- **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**

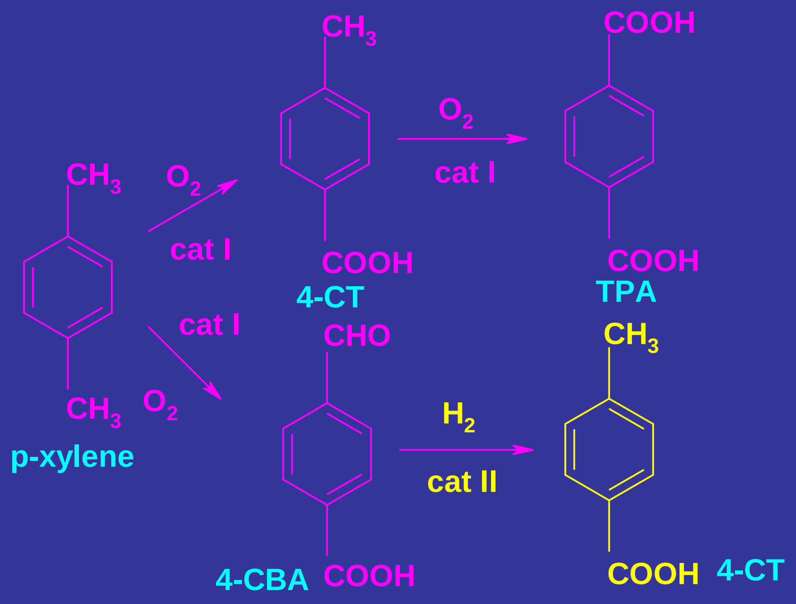
Adapted from Keller & Bryan, CEP, January (2000)

Process Development Methodology



Lerou & Ng, CES, 51(10) (1996)

Oxidation of p-Xylene to Terephthalic Acid



Oxidation:

Cat I: Co-Mn-Br
Temp.: 190-205°C
P_{O2}: 1.5-3.0 MPa

Hydrogenation:

Cat II: Pd/support
Temp.: 225-275°C

- 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

Key Multiphase Reactor Types

- Mechanically agitated tanks
- Multistage agitated columns
- Bubble columns
- Draft-tube reactors
- Loop reactors

Soluble catalysts
&
Powdered catalysts

- Packed columns
- Trickle-beds
- Packed bubble columns
- Ebullated-bed reactors

Soluble catalysts
&
Tableted catalysts

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*.

K. Ostergaard, Adv. Chem. Engng., Vol. 7 (1968)

Modification of the Classification for Gas-Liquid Soluble Catalyst Reactors

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

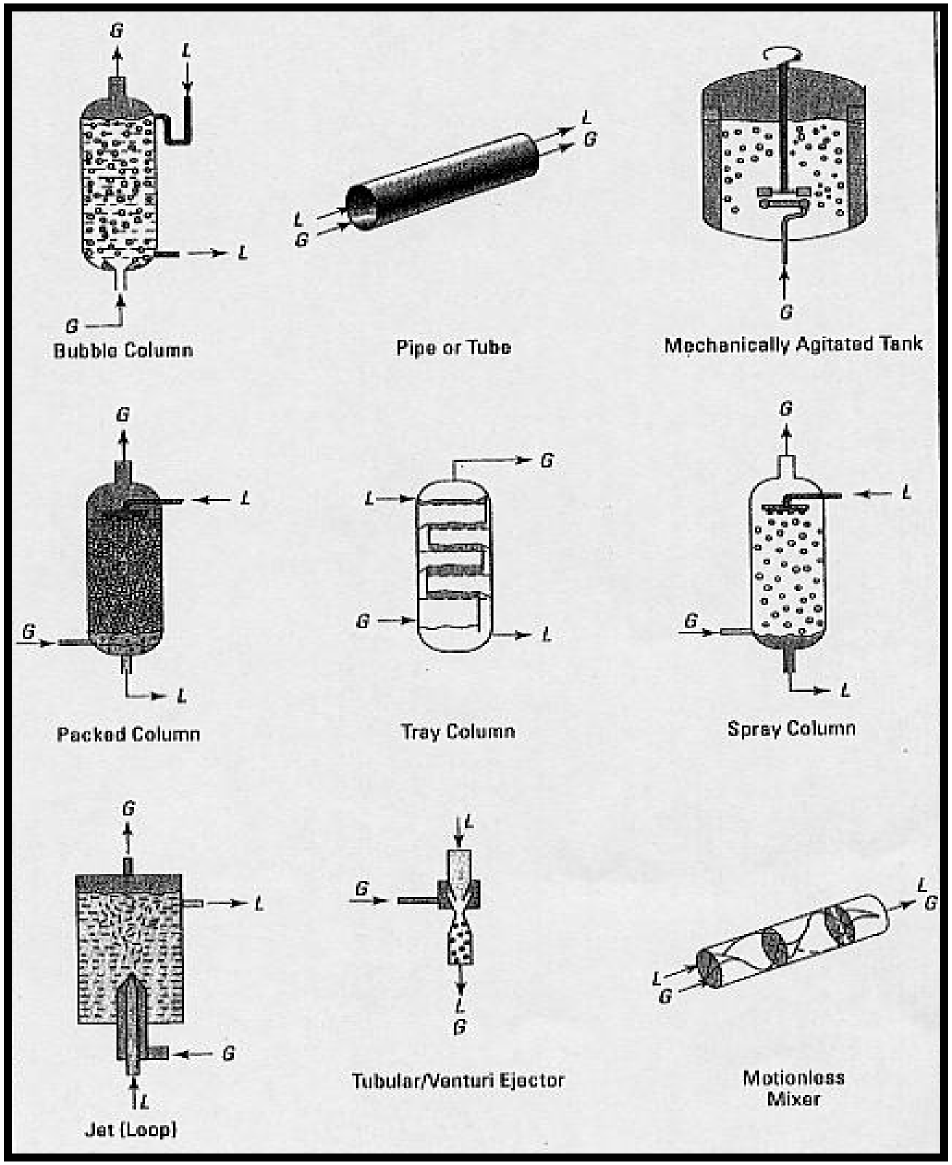
2. **Random inert or structured packing, if used, provides *interfacial area* for gas-liquid contacting.**

Common types of gas-solid reactors

- Packed bed
- Fluid bed
- Monolith
- Riser and Downer

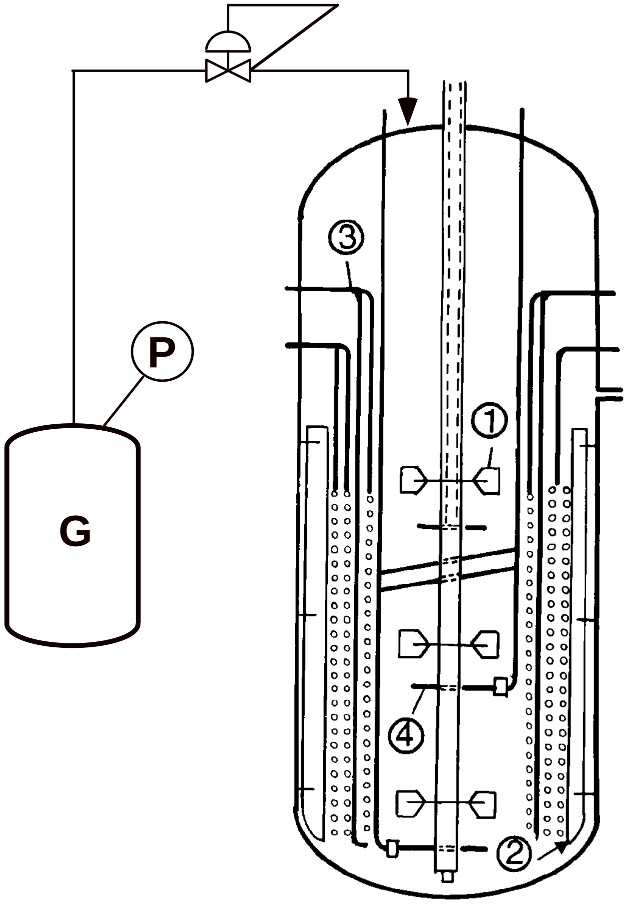
Multiphase Reactor Types at a Glance

Middleton (1992)

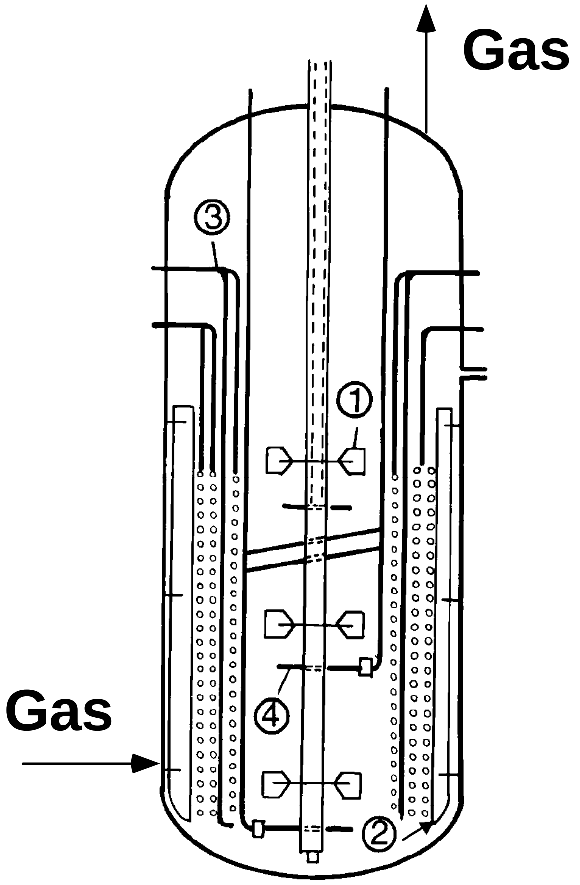


Mechanically Agitated Reactors

-Batch or Semi-Batch Operation-



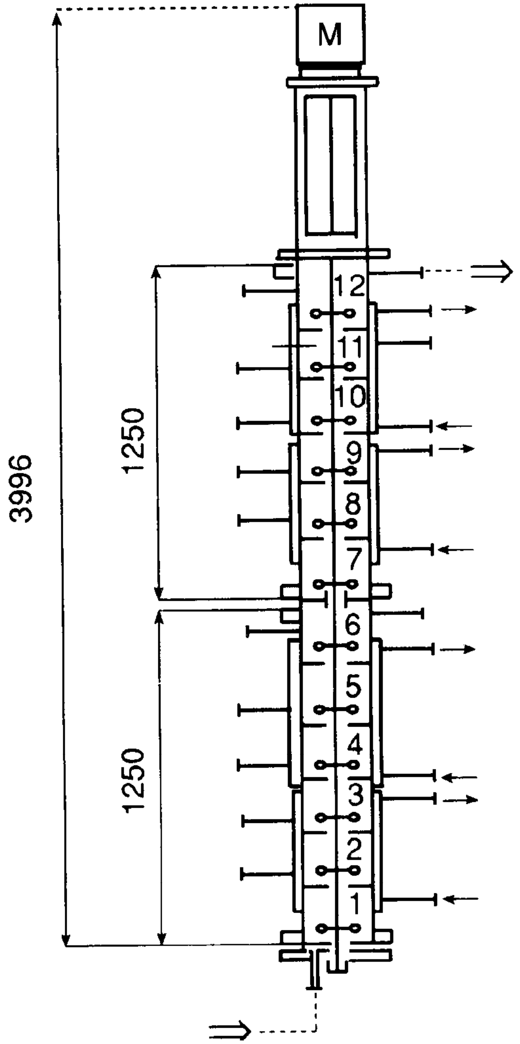
(a) Batch
“ Dead - Headed “



(b) Semi - Batch

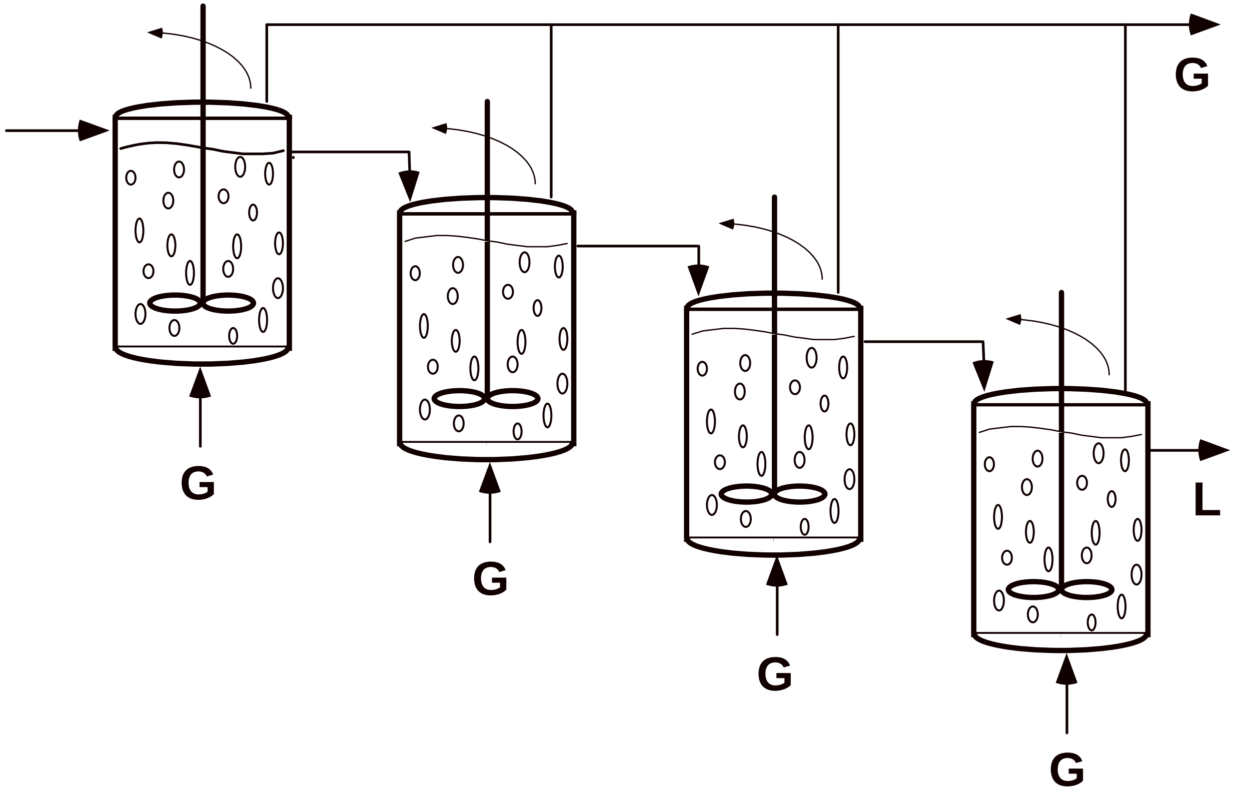
Mechanically Agitated Reactors

- Continuous Operation -



Volume = 120 Liters

Stirred Chambers = 12



Multistage Agitated Column for the Synthesis of Vitamin "carbol" (Wiedeskehr, 1988)

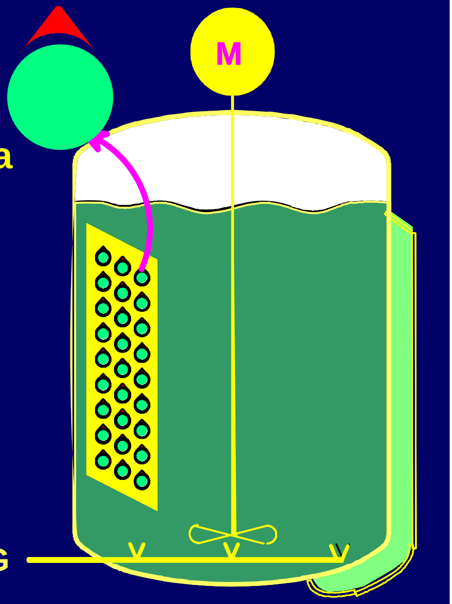
Mechanically Agitated Reactors
- Pros and Cons -

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

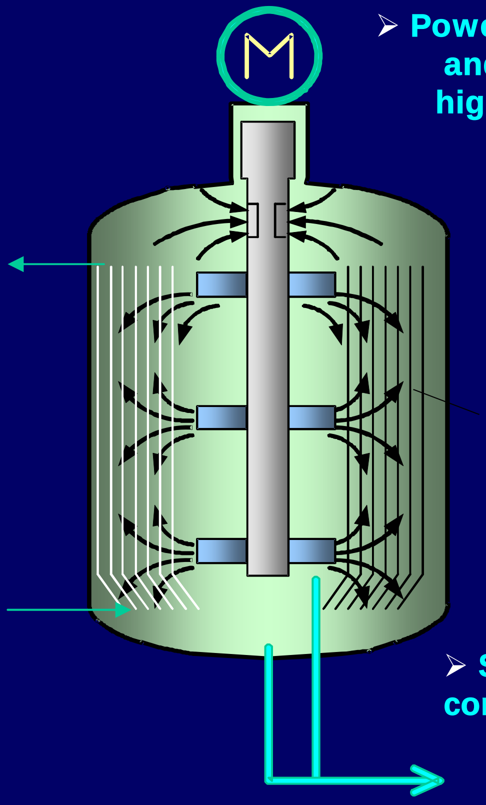
Source: P. L. Mills, R. V. Chaudhari, and P. A. Ramachandran
***Reviews in Chemical Engineering* (1993).**

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
- Inefficient cooling
- Sealing problems



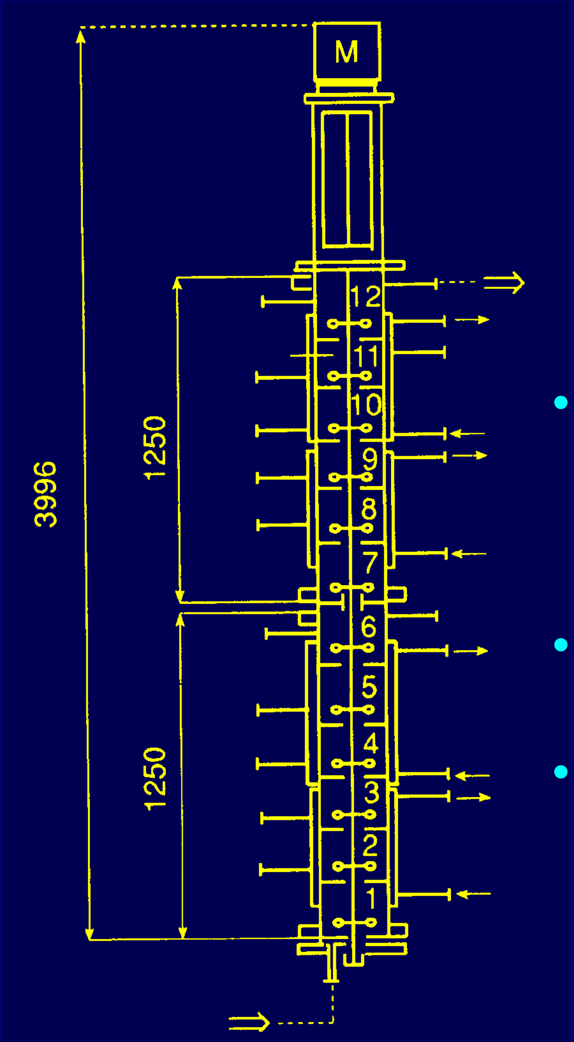
Conventional Reactor



- Powerful gas dispersion and recirculation: high mass transfer
- No heat transfer limitations (up to 20 m^2/m^3)
- Easy catalyst recycling
- Negligible fouling
- Safer than the conventional reactors

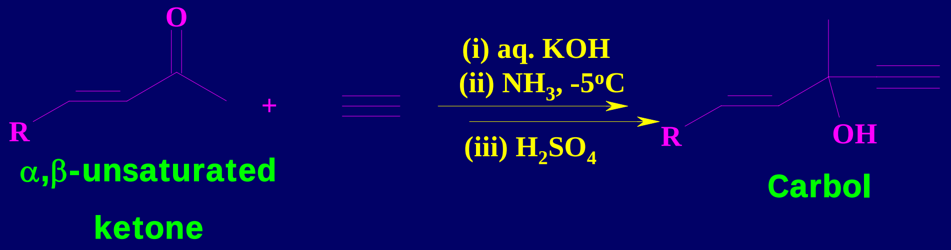
BIAZZI Reactor

Multistage Agitated Column for Synthesis "Carbol"-Pharmaceutical Intermediate



Volume = 120 Liters

Stirred Chambers = 12



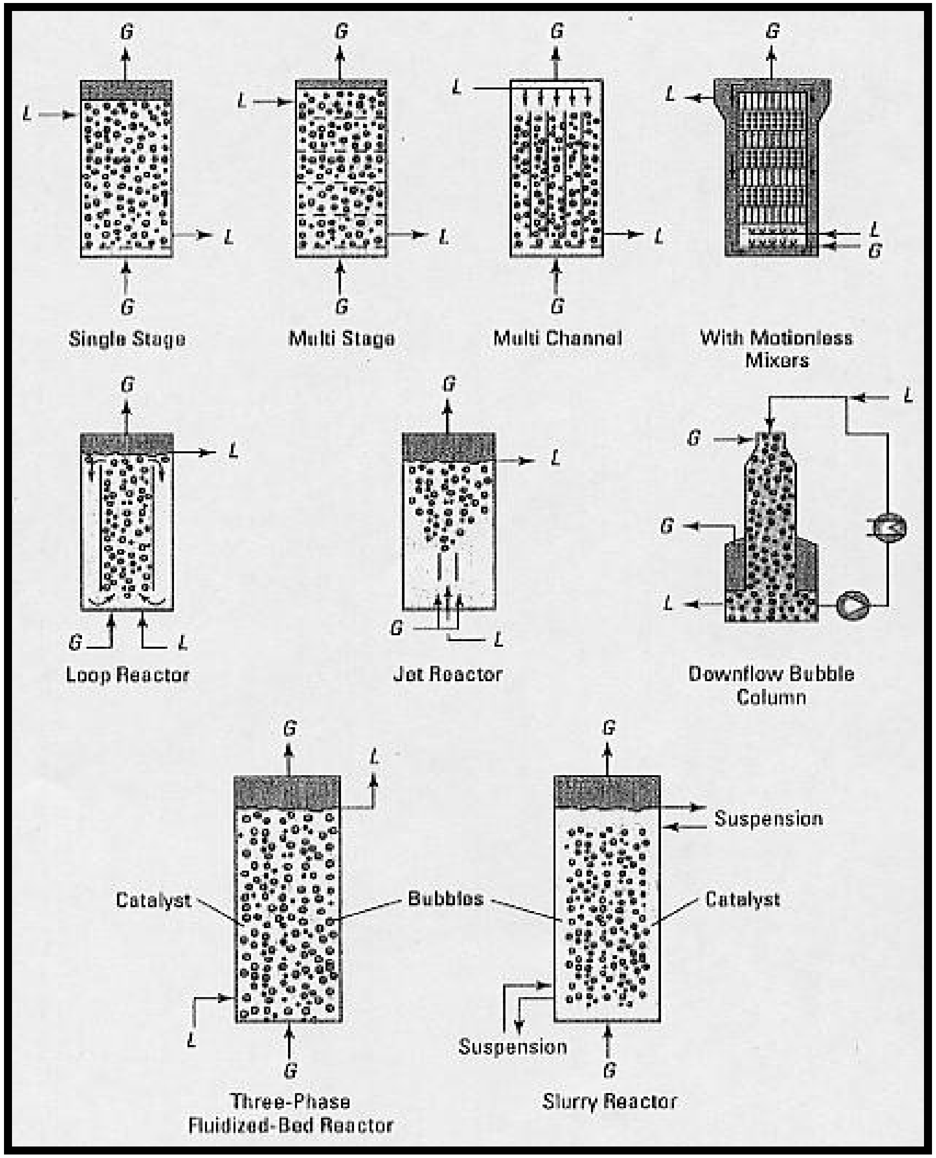
α,β-unsaturated ketone

Carbol

- 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

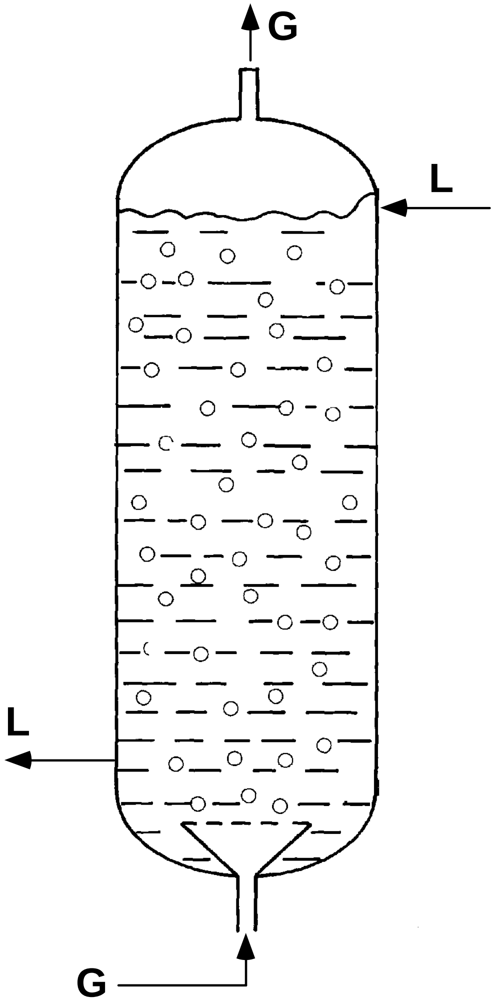
Chem. Eng. Sci., 43, 1783, 1988

Bubble Column Reactors at a Glance

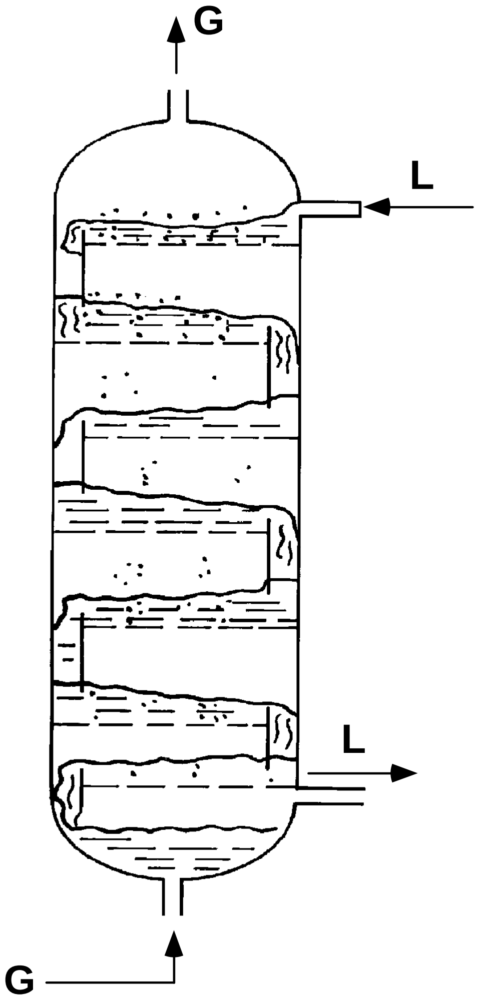


Tarhan (1983)

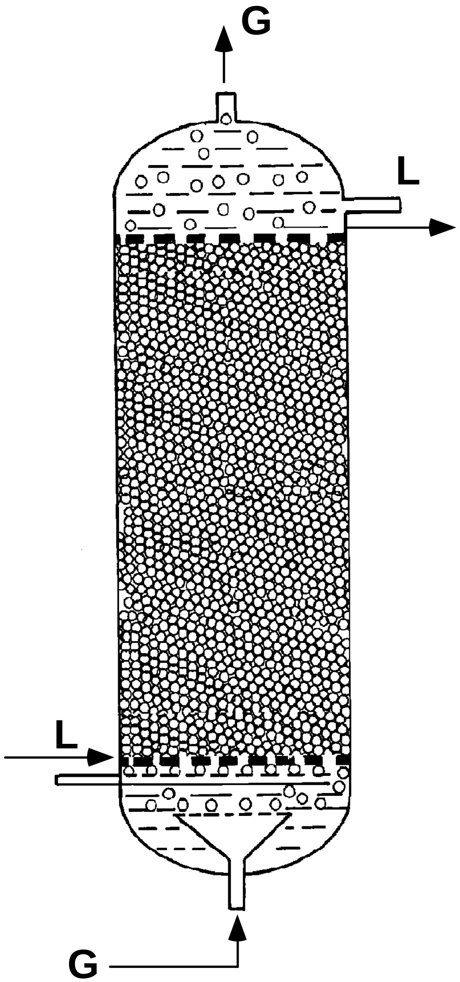
Key Types of Bubble Columns



(a) Empty
Semi - Batch
or Continuous



(b) Plate
Continuous



(c) Packed
Semi - Batch
or Continuous

Bubble Column Reactors
- Pros and Cons -

Pros

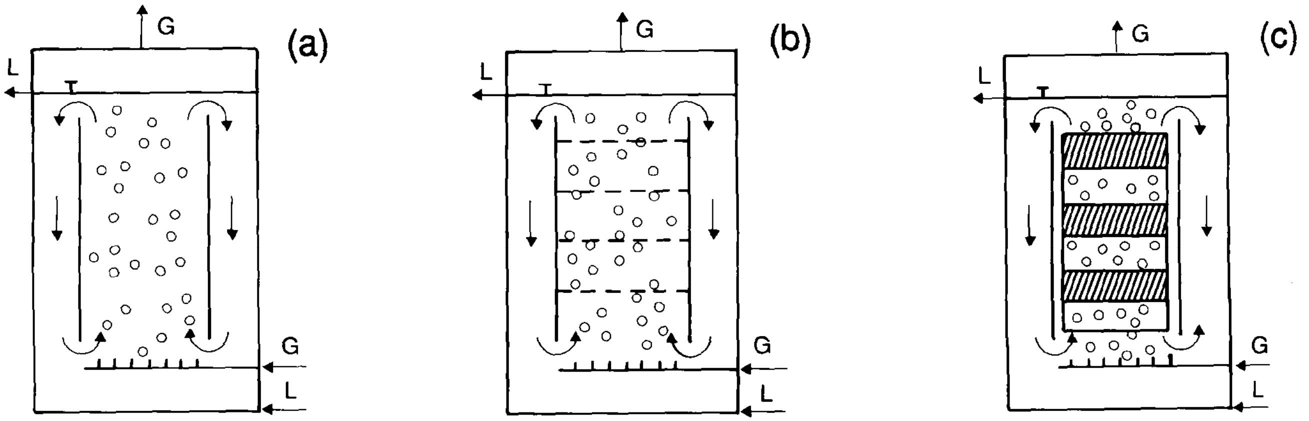
- Small catalyst particles
- High effectiveness factor
- Highly active catalysts
- Well-mixed liquid
- Nearly isothermal
- Lower power consumption
- High pressure operation

Cons

- Catalyst handling
- Catalyst fines carryover
- Catalyst loading limitations
- Homogeneous reactions
- Selectivity Control
- No guidelines for internals
- More complex scaleup

Source: P. L. Mills, R. V. Chaudhari, and P. A. Ramachandran
Reviews in Chemical Engineering **(1993).**

Draft Tube and Loop Reactors

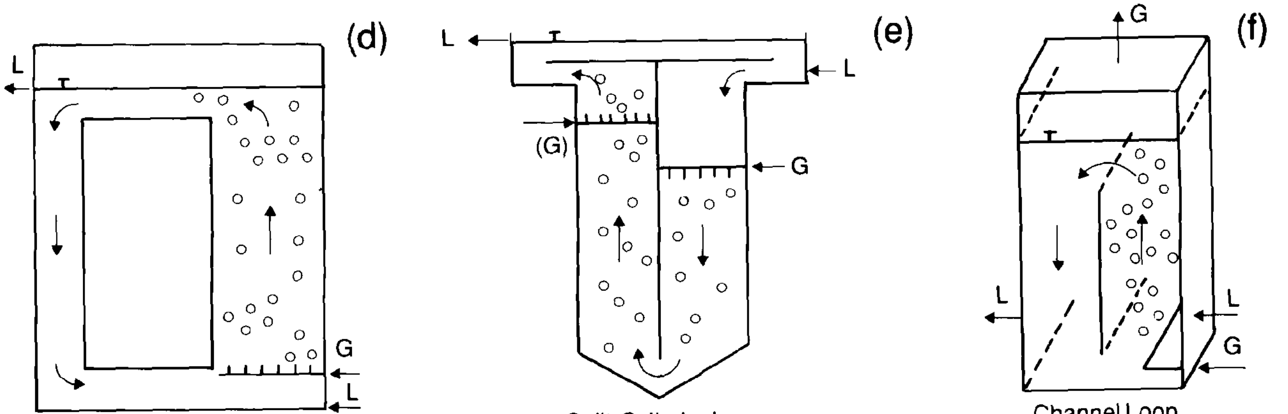


Concentric Draft Tube Loop

Concentric Draft Tube with Baffles

Concentric Draft Tube with Static Mixers

Internal Circulation



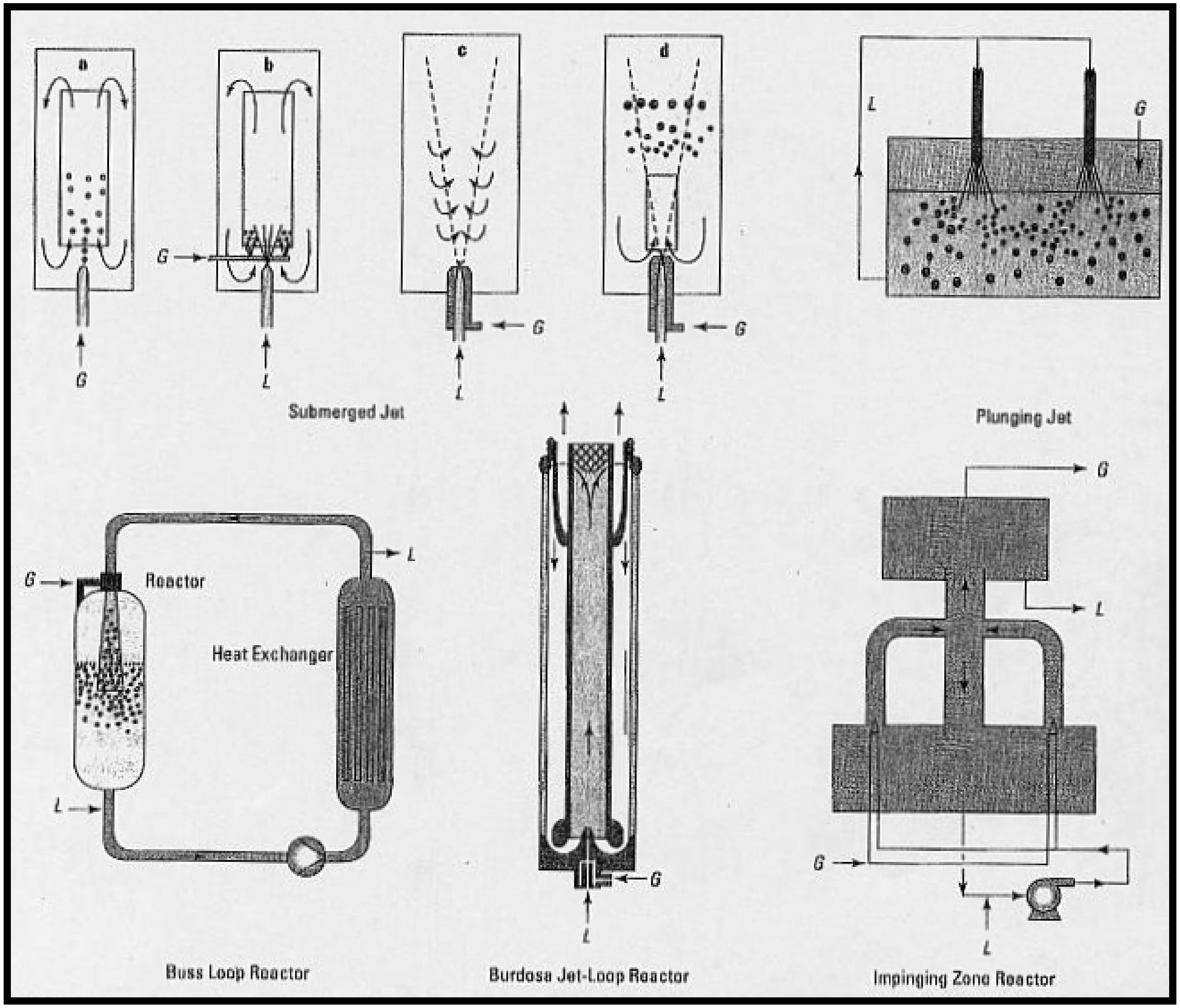
Tubular Loop

Split-Cylinder Loop (Deep-shaft (ICI))

Channel Loop

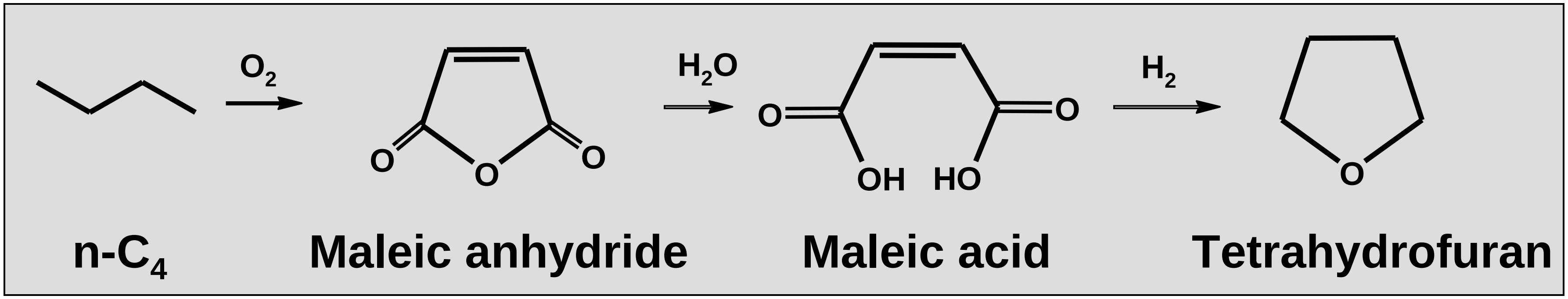
External Circulation

Venturi Loop Reactors



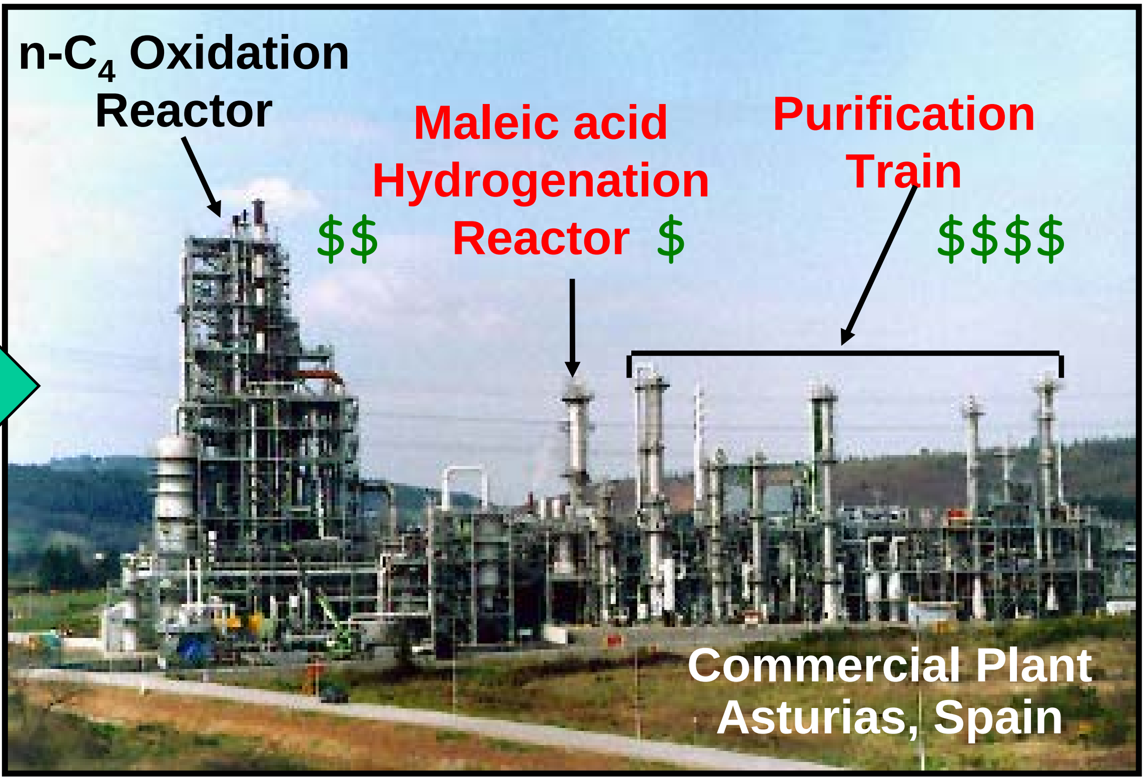
Cramers et al. (1994)

Example: DuPont Butane to THF Process



n-C_4 Maleic anhydride Maleic acid Tetrahydrofuran

Pilot Plant Reactor
Ponca City, OK



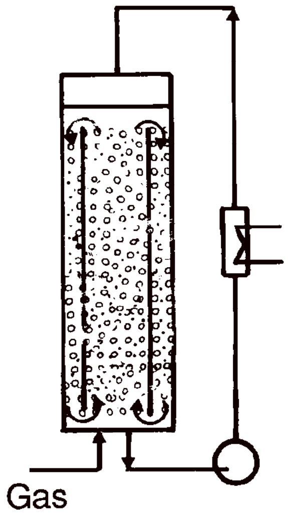
n-C_4 Oxidation Reactor $$

Maleic acid Hydrogenation Reactor $

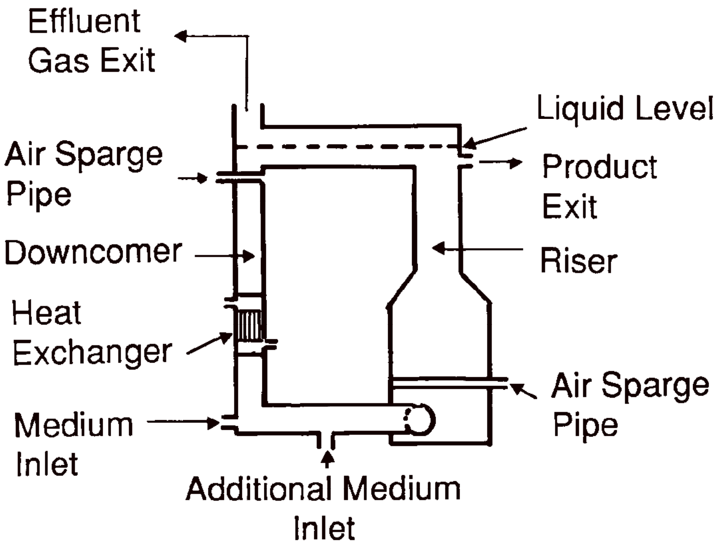
Purification Train $$$$

Commercial Plant
Asturias, Spain

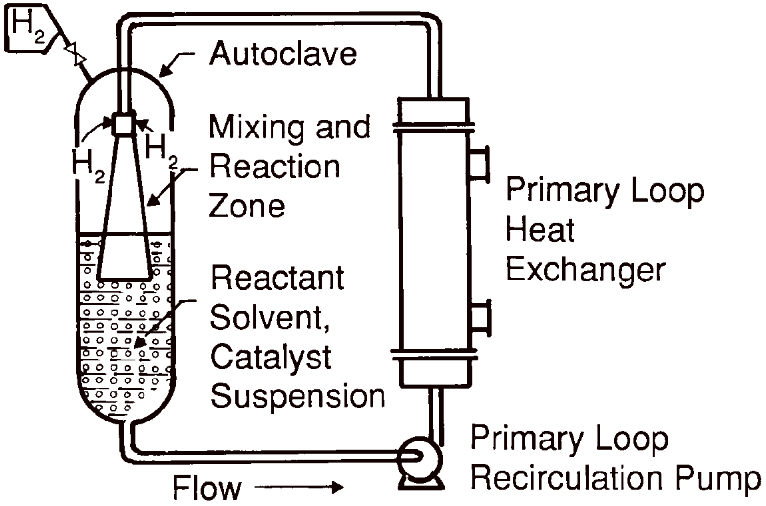
Other Types of Loop Reactors



(a)



(b)



(c)

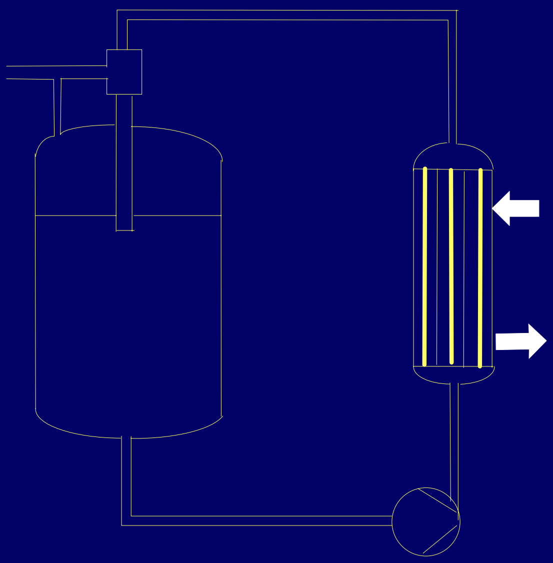
Internal Recirculation

External Recirculation

Jet Loop with External Recirculation

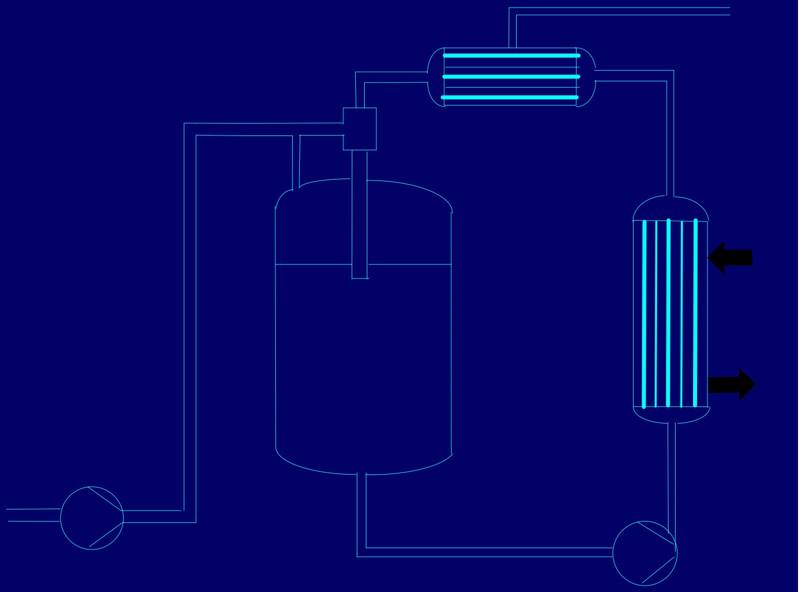
Jet Loop Recycle Reactors

Batch Operation



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

Continuous Operation



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

Source : Davy Process Technology

Gas-lift and Loop Reactors
- Pros and Cons -

Pros

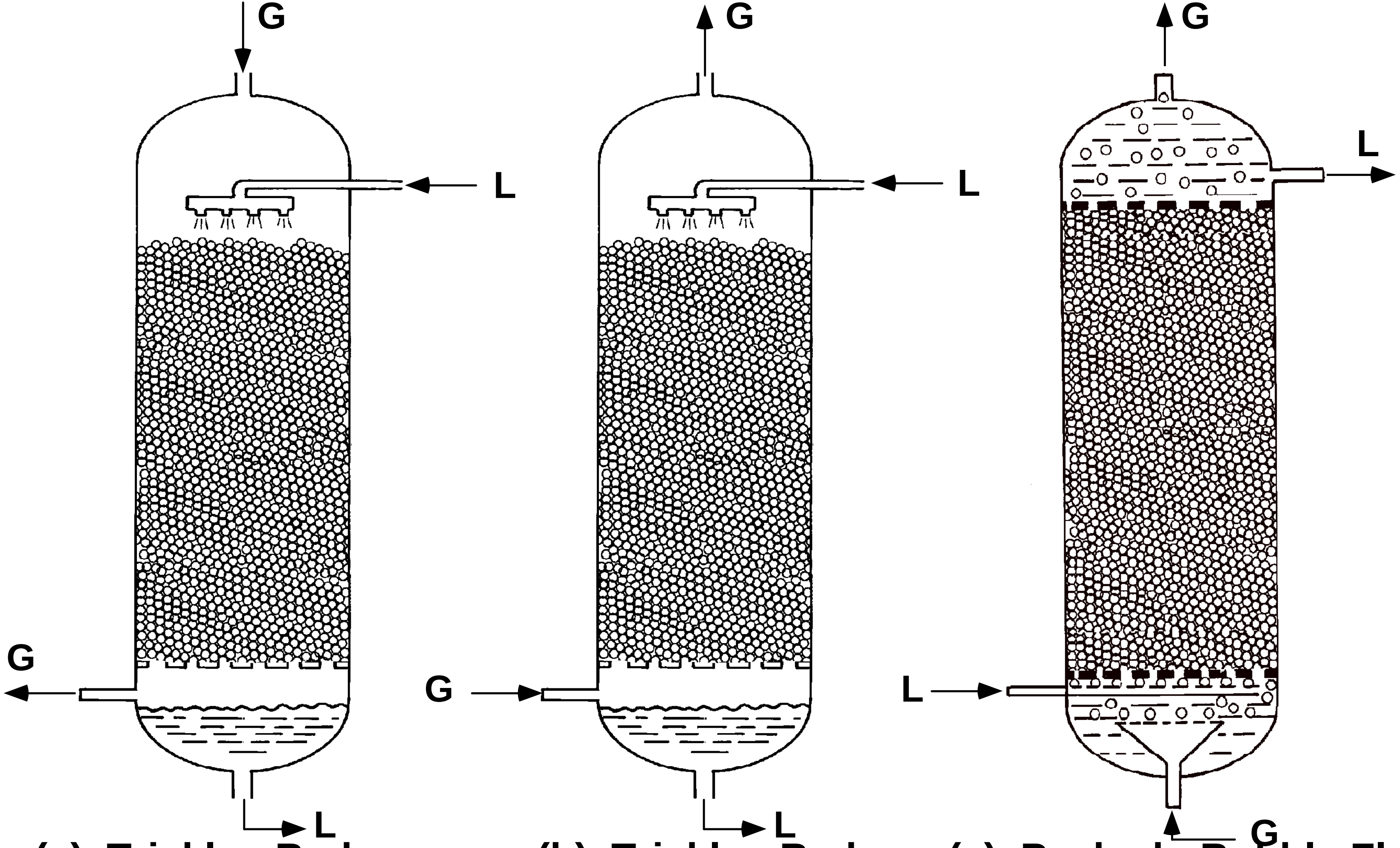
- Small catalyst particles
- High effectiveness factor
- Highly active catalysts
- Well-mixed liquid
- Nearly isothermal
- High pressure operation (Gas-lift reactor)
- Process flexibility
- Modular design

Cons

- Catalyst handling
- Catalyst fines carryover
- Catalyst loading limitations
- Homogeneous reactions
- Selectivity control
- Possible pressure limitations (Loop reactor)
- Greater power consumption (Loop reactor)
- Catalyst attrition

Source: P. L. Mills, R. V. Chaudhari, and P. A. Ramachandran
Reviews in Chemical Engineering **(1993).**

Fixed-Bed Multiphase Reactors



(a) Trickle - Bed
Cocurrent downflow

(b) Trickle - Bed
Countercurrent flow

(c) Packed - Bubble Flow
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 maldisdribution
- Higher heat and mass transfer rates

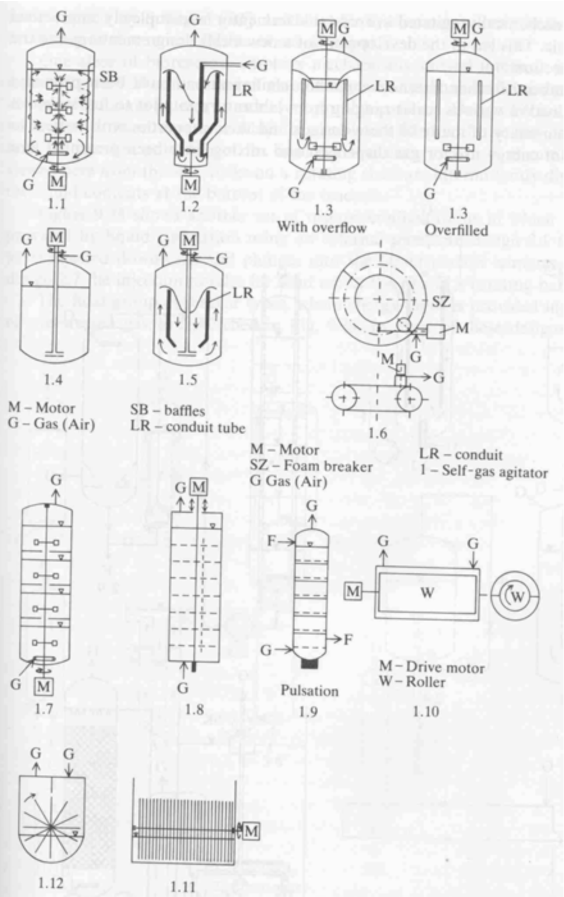
Packed Bubble Flow Reactors
- Disadvantages -

- Higher dissipated power than in TBR
- Throughput limited by bed fluidization velocity
- Increased potential for runaway
- Promotion of undesired homogeneous reactions
- Greater pressure drop

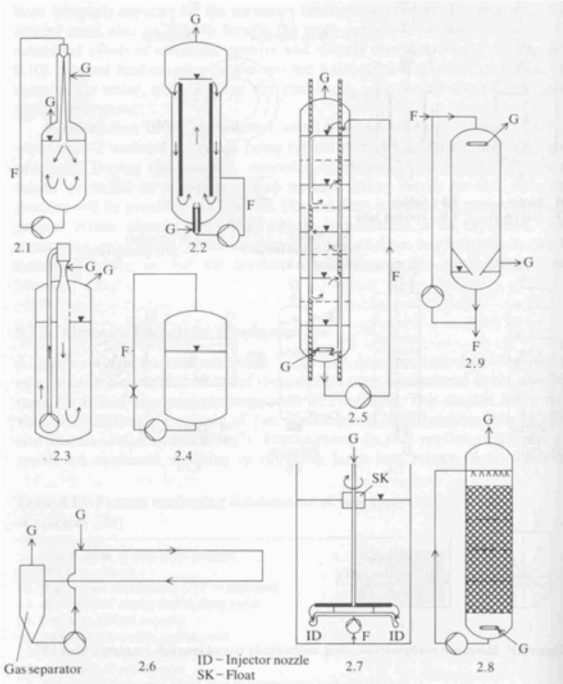
Bioreactor Types

(After Bailey and Ollis, 1986)

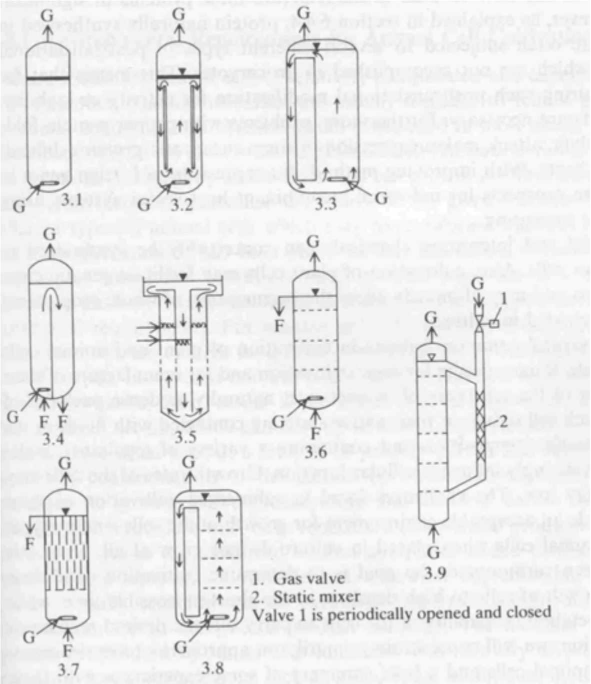
Mechanical agitation



External pumping



Gas agitation



Commercial or Planned Bioprocesses
High Volume Products

Product	Carbon source	Production, t/year
Lactic acid	corn syrup, whey permeate, agric. waste	300,000
Citric acid	molasses, glucose	550,000
Amino acids lysine, glutamic acid	molasses, glucose, corn syrup	250,000
Ethanol	molasses, corn syrup, cellulose, agric. waste	28,000,000[a]
Single cell protein	methane	50,000[b]
1,3 Propane diol	corn syrup	NA
Penicillin	glucose, corn steep liquor	25,000
Detergent enzymes[c]	glucose, maltose, starch	

[a] for fuels only (US production $14.5\text{x}10^6$ t/year in 1996)

[b] a target of 500,000 t/year is projected for Europe for 2010

[c] yearly product value in excess of 10^9 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 O_2 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.

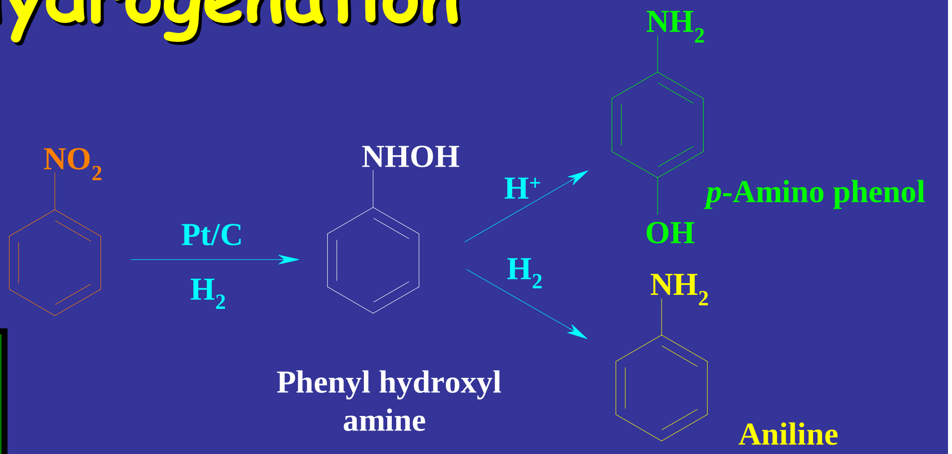
- The global stoichiometry changes with operating conditions and feed composition; Kinetics and stoichiometry obtained from steady-state (chemostat) data cannot be used reliably over a wide range of conditions unless fundamental models are employed

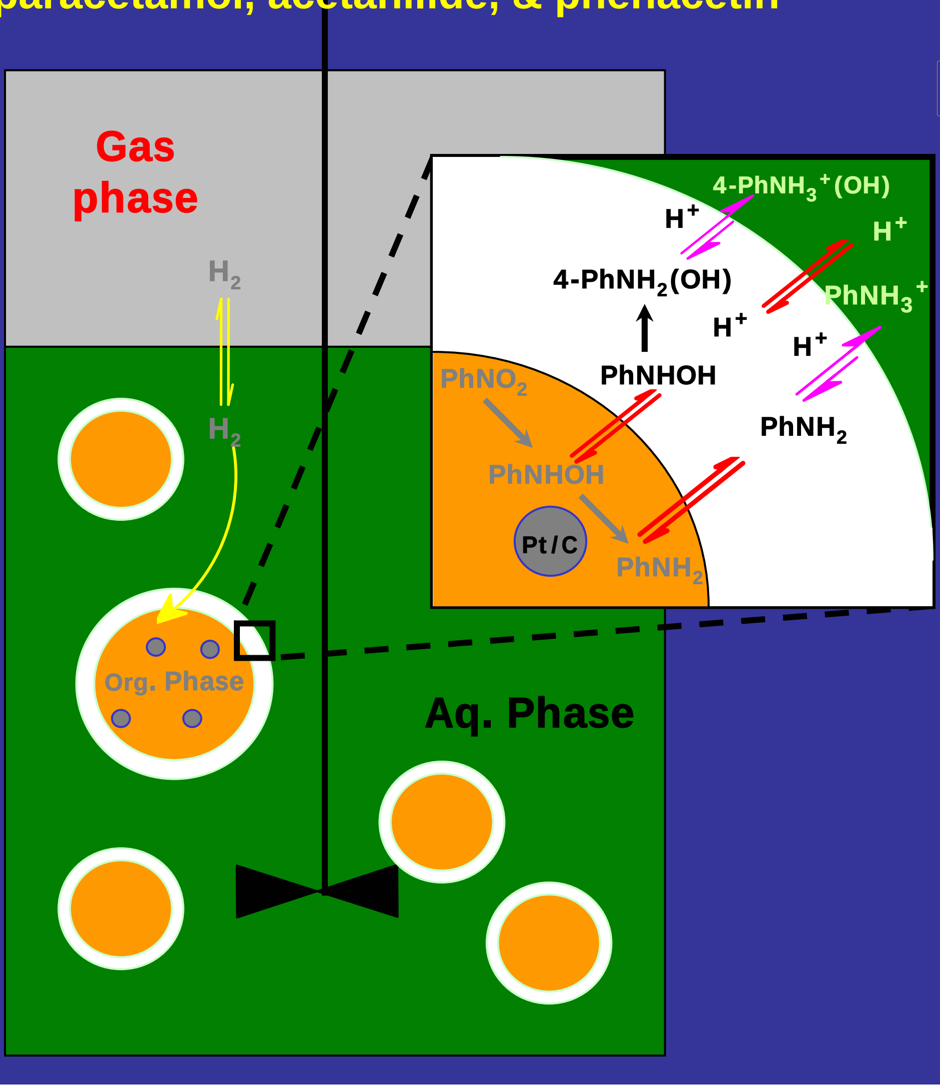
- Long term adaptations (mutations) may occur in response to environment changes, that can alter completely the product distribution

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



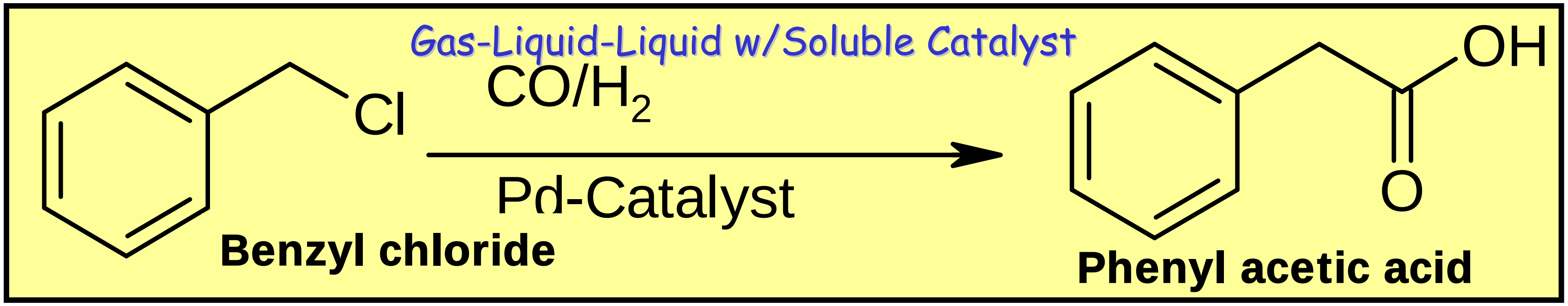


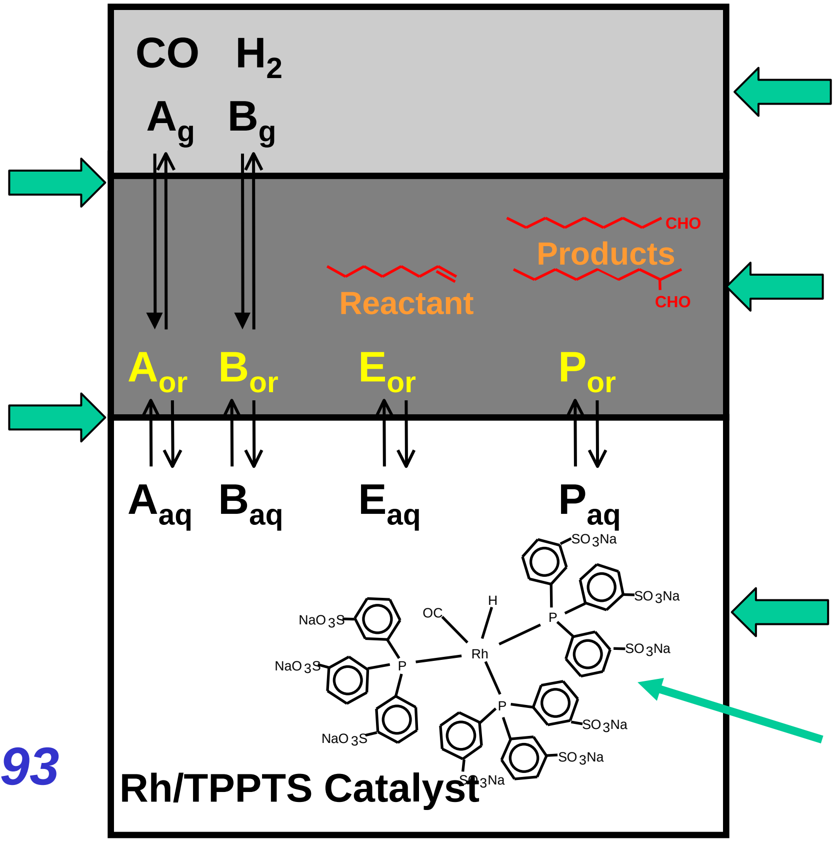
- **Single step process**
- **Intermediate phenylhydroxylamine rearranged by interfacial reaction to *para*-aminophenol**
- **Selectivity determined by competing hydrogenation in organic phase and & interfacial rearrangement with aqueous acid catalyst**

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





Gas - Organic Phase Interface

Aqueous-Organic Phase Interface

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

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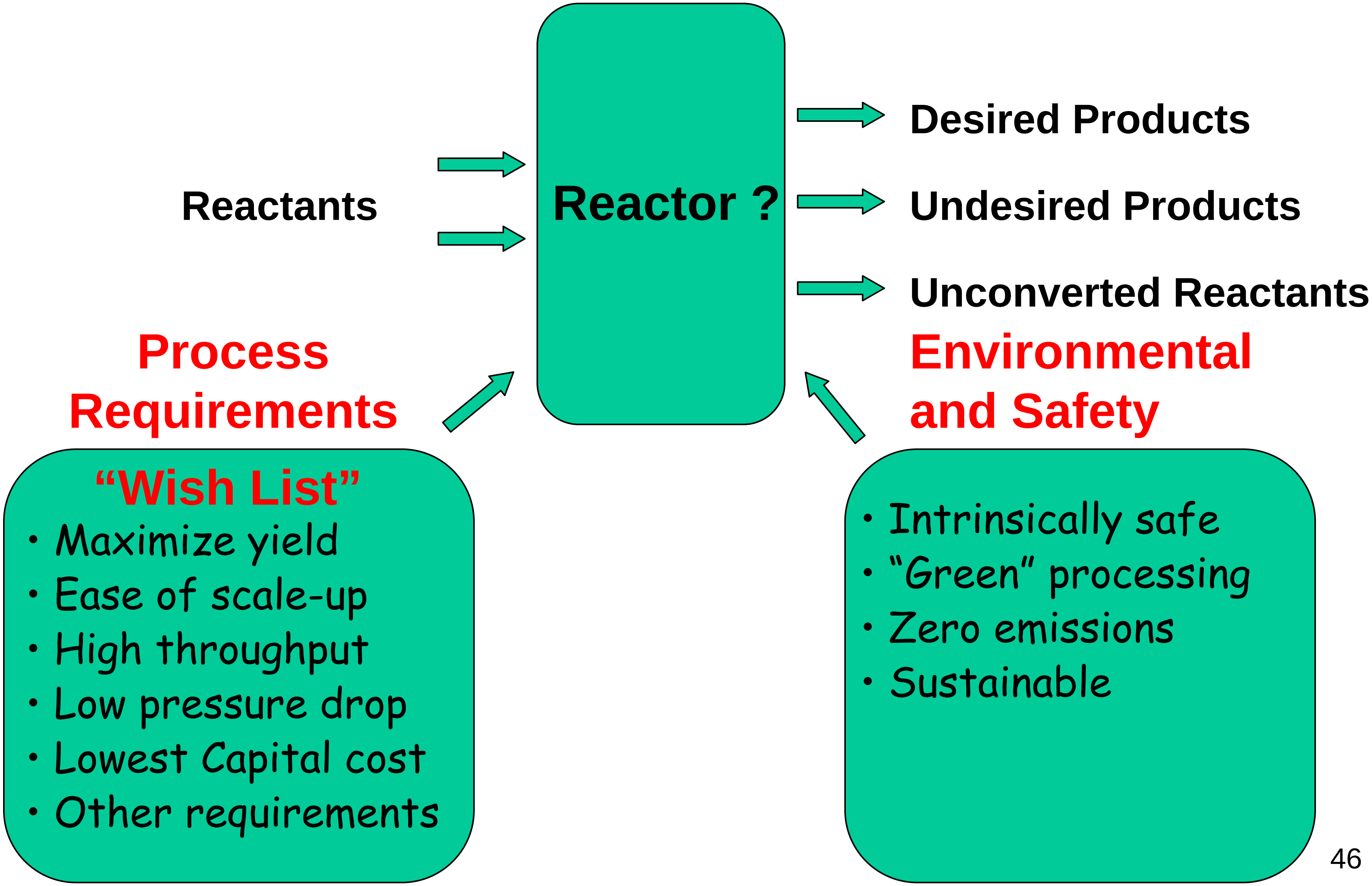


Reactants

Reactor ?

Desired Products

Undesired Products

Unconverted Reactants

Process Requirements

"Wish List"

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

Environmental and Safety

- Intrinsically safe
- "Green" processing
- Zero emissions
- Sustainable

Summary: Distinguishing Features of Multiphase Reactors

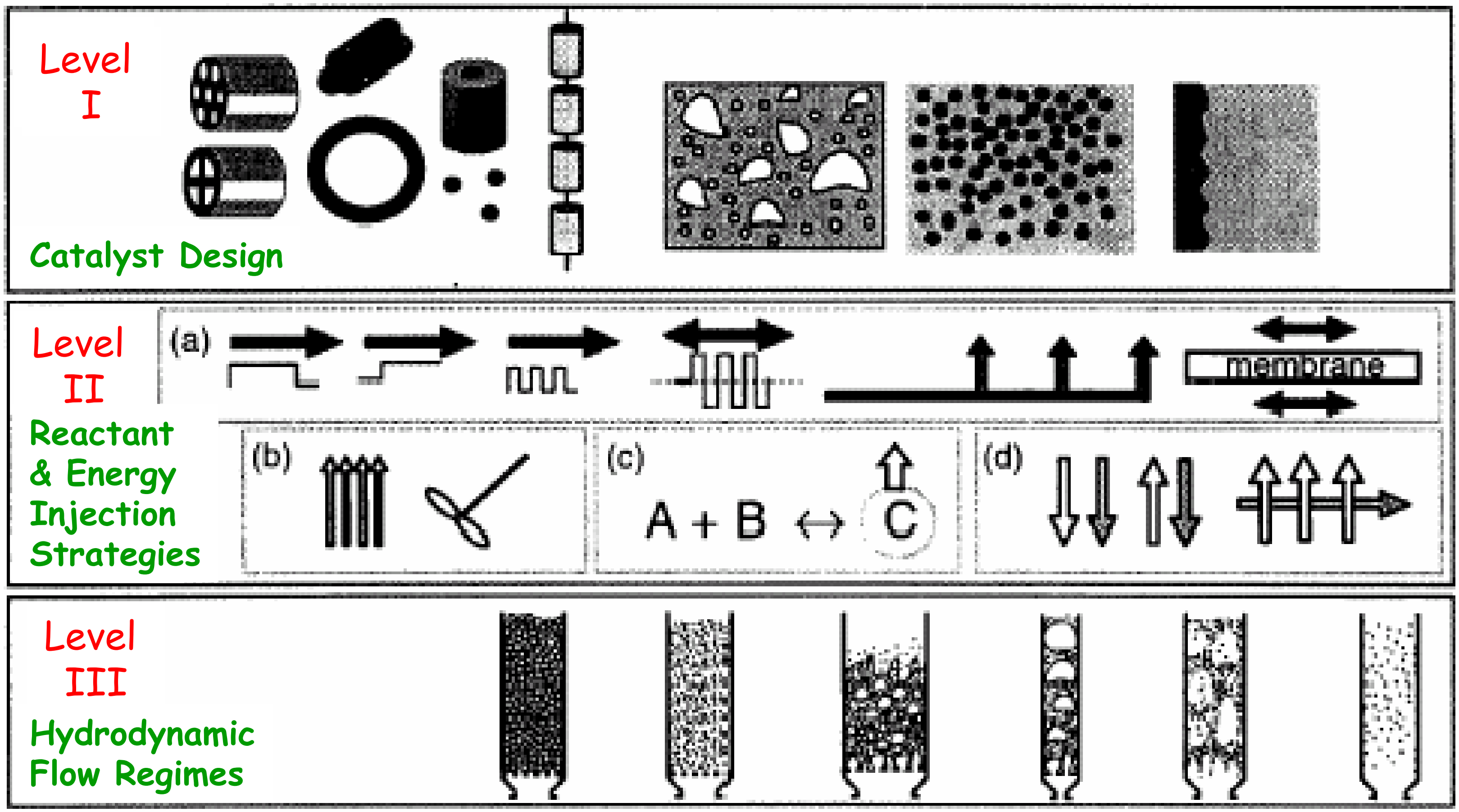
- ***Efficient contacting*** **of reactive phases and separation of product phases** ***is key*** **to safety, operability and performance**

- ***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**

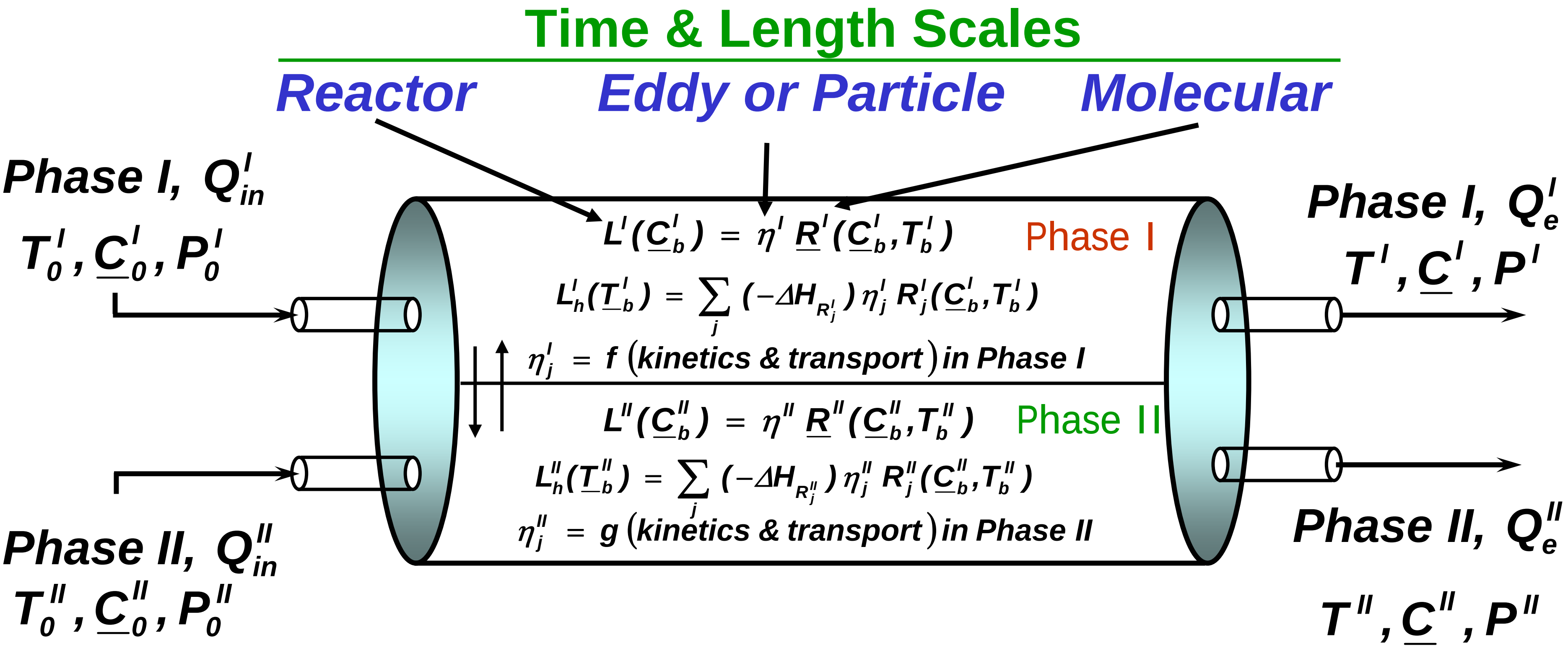
Three-Level Strategy for Reactor Selection



- 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^I_{in}

$T^I_0, \underline{C}^I_0, P^I_0$

Phase II, Q^{II}_{in}

$T^{II}_0, \underline{C}^{II}_0, P^{II}_0$

$L^I(\underline{C}^I_b) = \eta^I \, \underline{R}^I(\underline{C}^I_b, T^I_b)$ Phase I

$L^I_h(\underline{T}^I_b) = \sum_j (-\Delta H_{R^I_j}) \, \eta^I_j \, R^I_j(\underline{C}^I_b, T^I_b)$

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

$L^{II}(\underline{C}^{II}_b) = \eta^{II} \, \underline{R}^{II}(\underline{C}^{II}_b, T^{II}_b)$ Phase II

$L^{II}_h(\underline{T}^{II}_b) = \sum_j (-\Delta H_{R^{II}_j}) \, \eta^{II}_j \, R^{II}_j(\underline{C}^{II}_b, T^{II}_b)$

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

Phase I, Q^I_e

$T^I, \underline{C}^I, P^I$

Phase II, Q^{II}_e

$T^{II}, \underline{C}^{II}, P^{II}$

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