



Integrated Catalytic Processes

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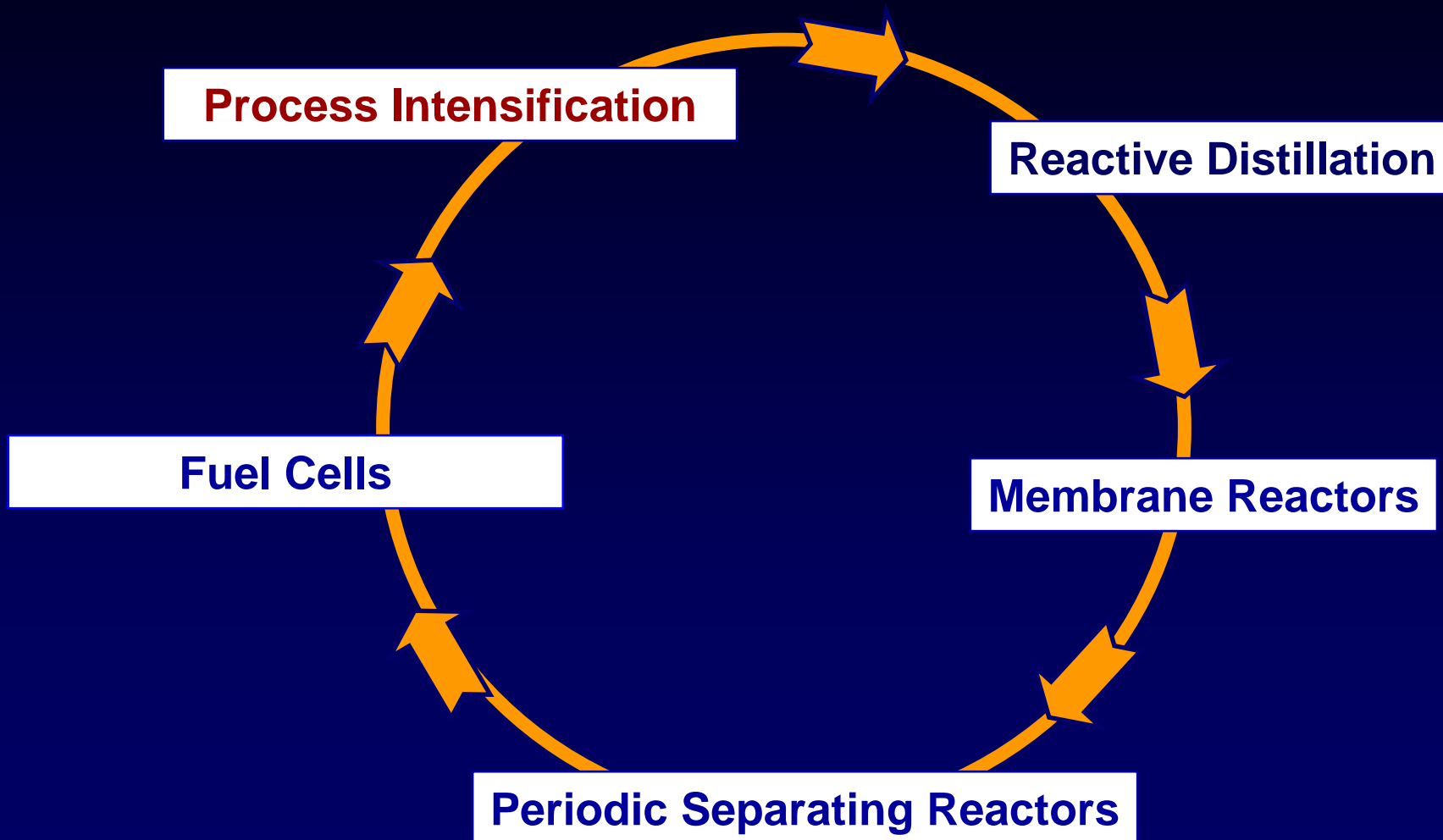
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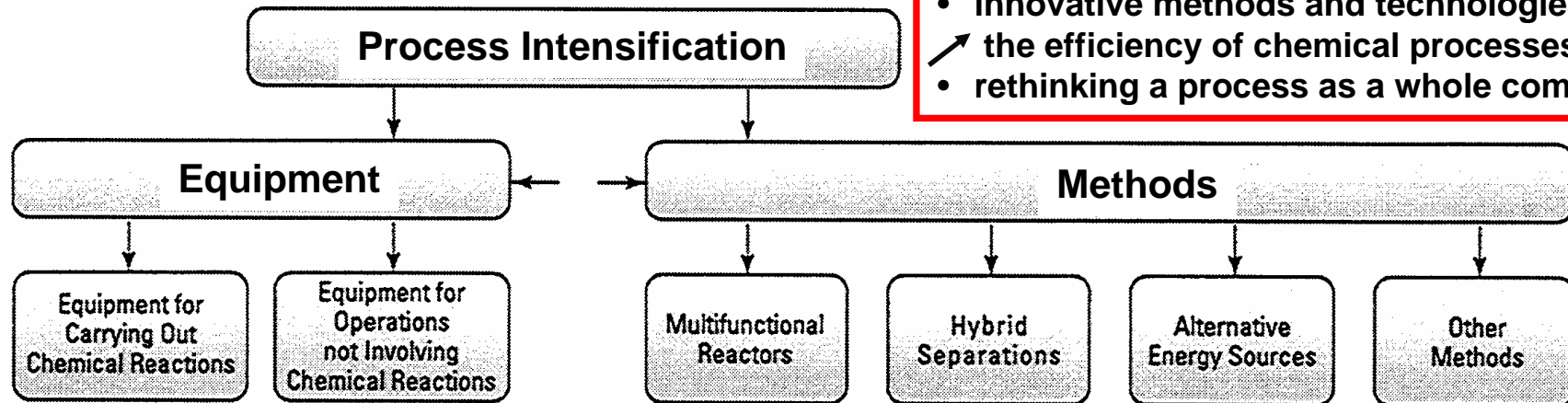
Integrated Catalytic Processes –Lecture Outline





Process Intensification

- innovative methods and technologies
- ↗ the efficiency of chemical processes
- rethinking a process as a whole complex



Examples

Spinning Disk Reactor
Static Mixer Reactor (SMR)
Static Mixing Catalysts (KATAPAKs)
Monolithic Reactors
Microreactors
Heat Exchange (HEX) Reactors
Supersonic Gas/Liquid Reactor
Jet-Impingement Reactor
Rotating Packed-Bed Reactor

Static Mixers
Compact Heat Exchangers
Microchannel Heat Exchangers
Rotor/Stator Mixers
Rotating Packed Beds
Centrifugal Adsorber

Reverse-Flow Reactors
Reactive Distillation
Reactive Extraction
Reactive Crystallization
Chromatographic Reactors
Periodic Separating Reactors
Membrane Reactors
Reactive Extrusion
Reactive Comminution
Fuel Cells

Membrane Absorption
Membrane Distillation
Adsorptive Distillation

Centrifugal Fields
Ultrasound
Solar Energy
Microwaves
Electric Fields
Plasma Technology

Supercritical Fluids
Dynamic (Periodic) Reactor Operation



Potential of Integrated Catalytic Processes

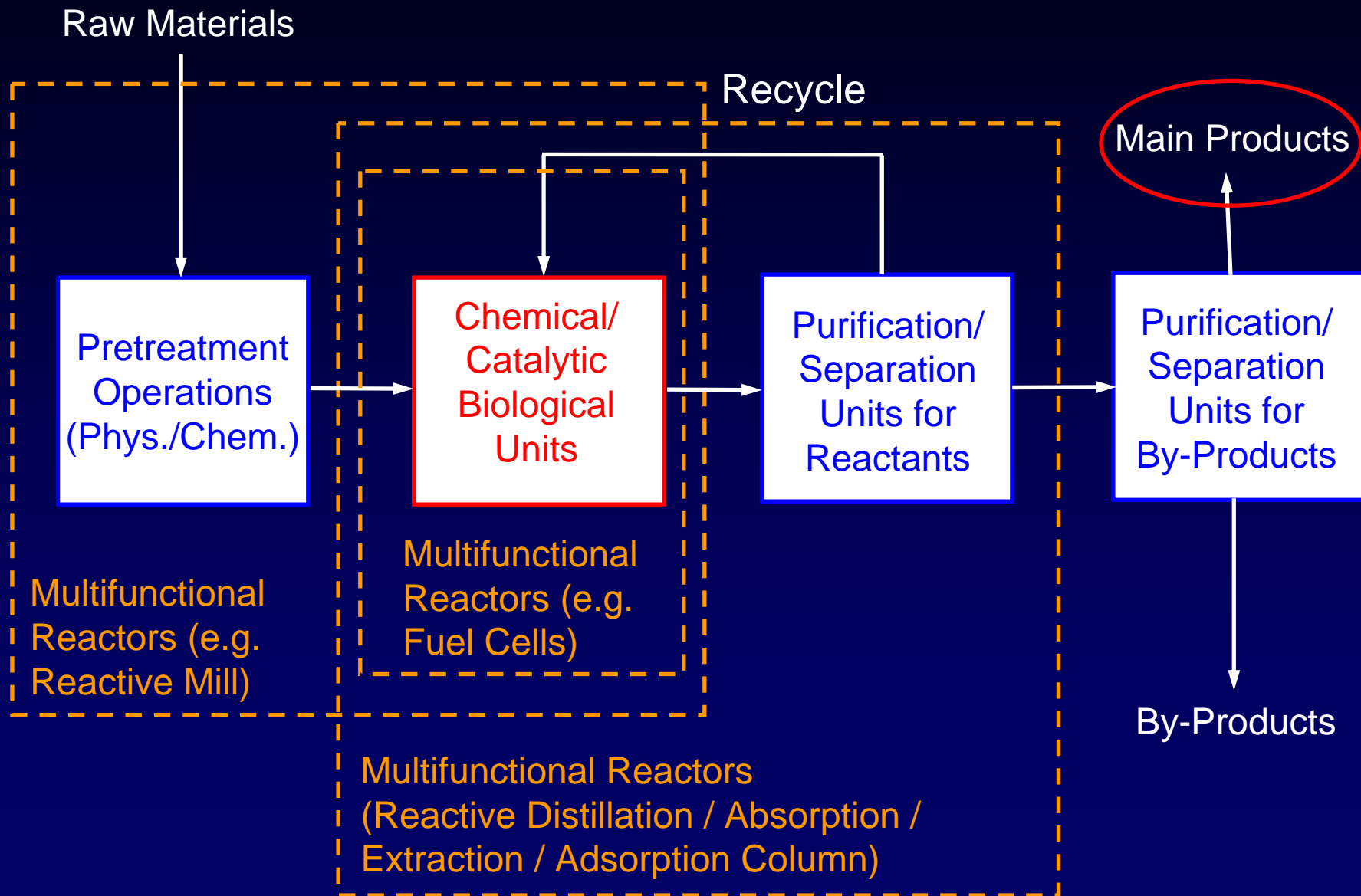


Synergetic interactions of chemical and physical unit operations may lead to:

- ↑ increase of productivity from process intensification
- ↑ increase of selectivity of reactions and/or separations
- ↑ improve separation by „reacting away“ azeotropic mixtures
- ↑ more efficient (in situ) use of energy
- ↑ inherent safety
- ↑ improved environmental compatibility
(e.g. by avoidance of by-products and hazardous solvents).

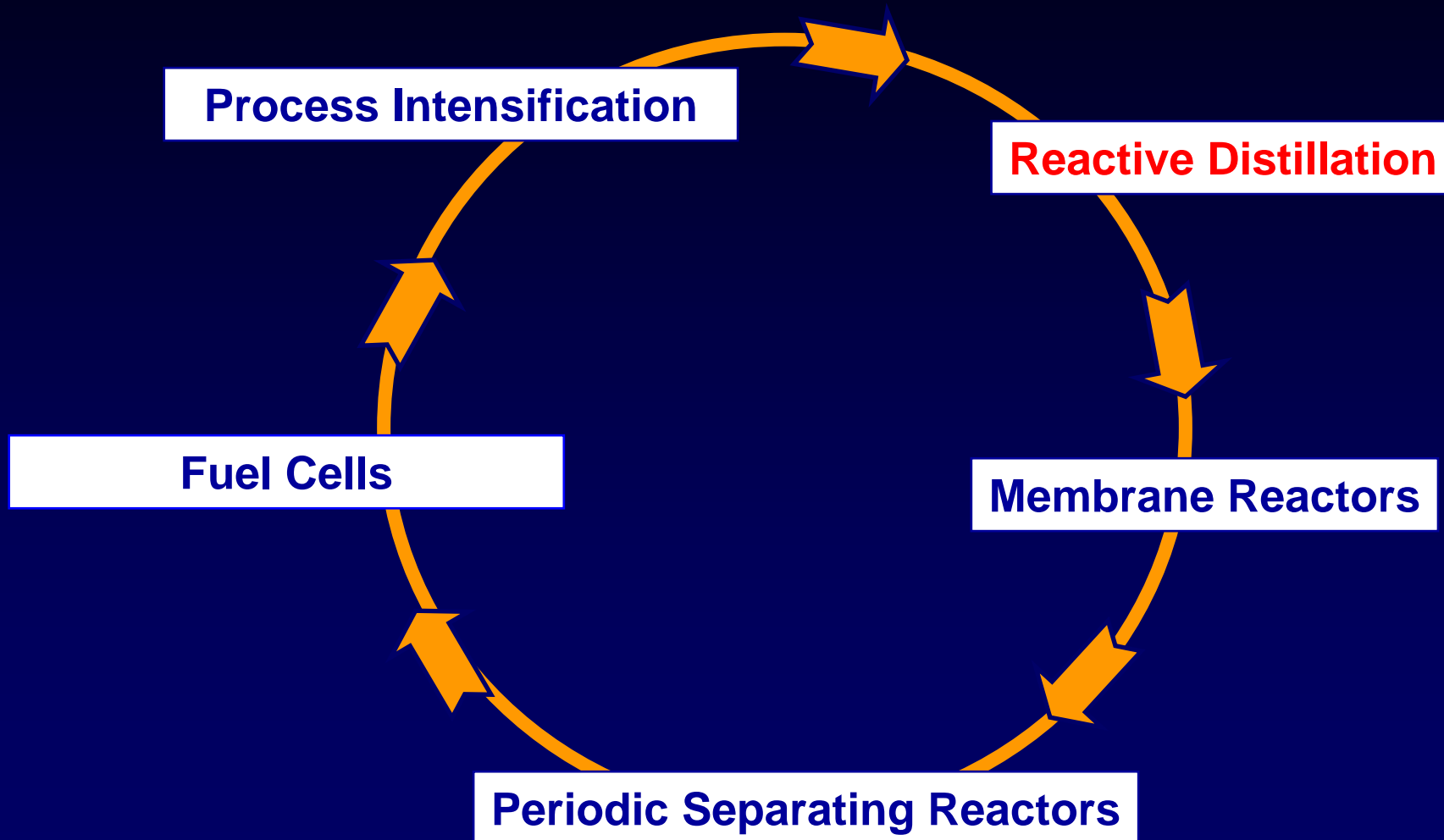


Integration of Unit Operations in Multifunctional Reactors





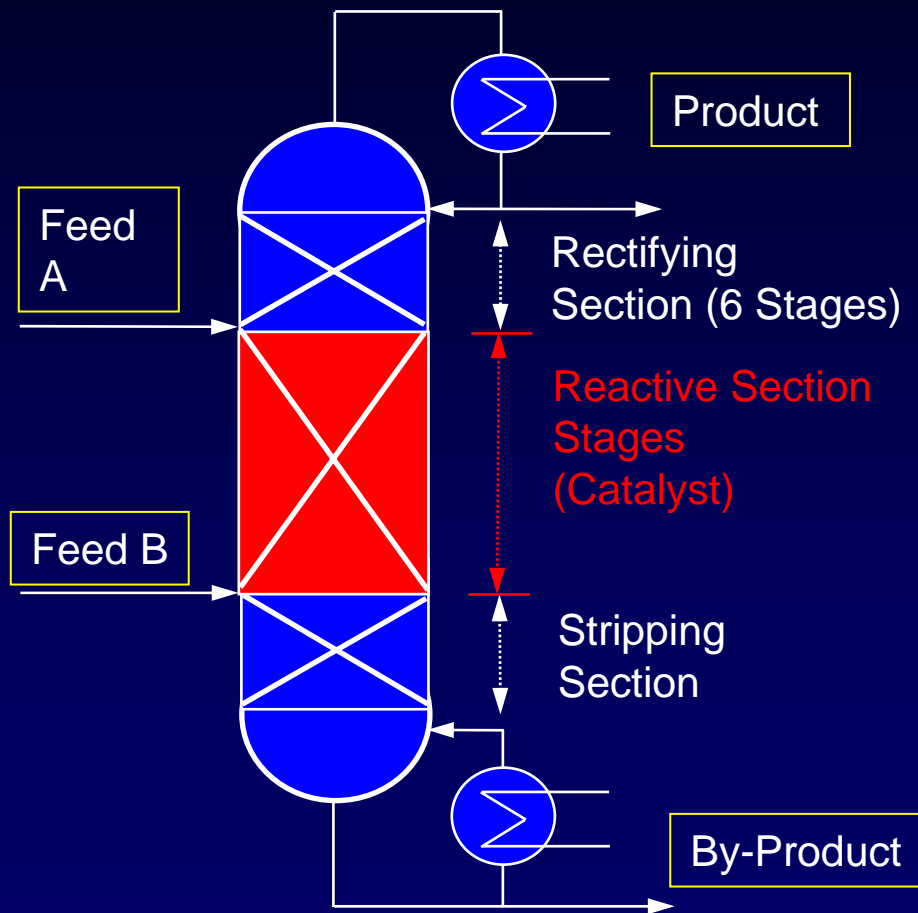
Integrated Catalytic Processes –Lecture Outline





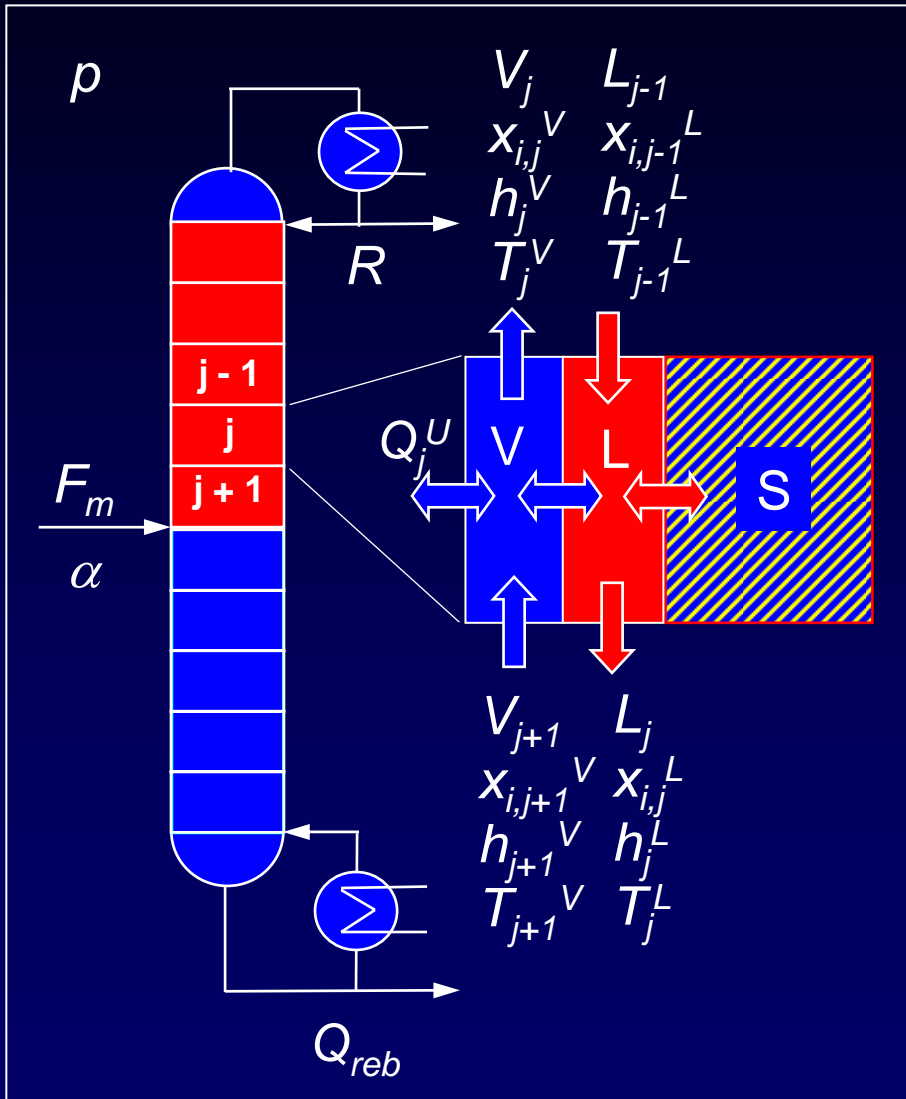
Reactive Distillation

- Combination of a Reactor and a Distillation Unit





Modeling of Catalytic Distillation Column



PSEUDOHOMOGENEOUS MODEL
+ V/L mass transfer model
+ reaction microkinetics

HETEROGENEOUS MODEL
(„Fully rate-based“)
+ V/L mass transfer model
+ reaction microkinetics
+ intraparticle mass transfer
(Maxwell-Stefan-eqs.)

SPECIFICATIONS
+ specifications: p , F ,
Relative volatility α , Q , R



Reactive Batch Distillation: Model Equations



Mass Balances

$$\frac{d x_i}{d \tau} = \underbrace{\left(x_i - y_i(\underline{x}, T) \right)}_{\text{Separation by Distillation}} + Da \cdot \underbrace{\left(\nu_i - x_i \nu \right)}_{\text{Influence of Stoichiometry}} \cdot \underbrace{r^*(\underline{x}, T)}_{\text{Reaction Kinetics}}$$

Damköhler Number

$$Da \equiv \frac{k_+(T_{ref}) \cdot c_{sites} \cdot V_{cat}}{\dot{V}^o}$$

apparent Rate constant

concentration of active sites on catalyst

Boiling Temperature

$$T = T(\underline{x}, p)$$

+ rate control over pressure !
+ T is not a dynamic variable !



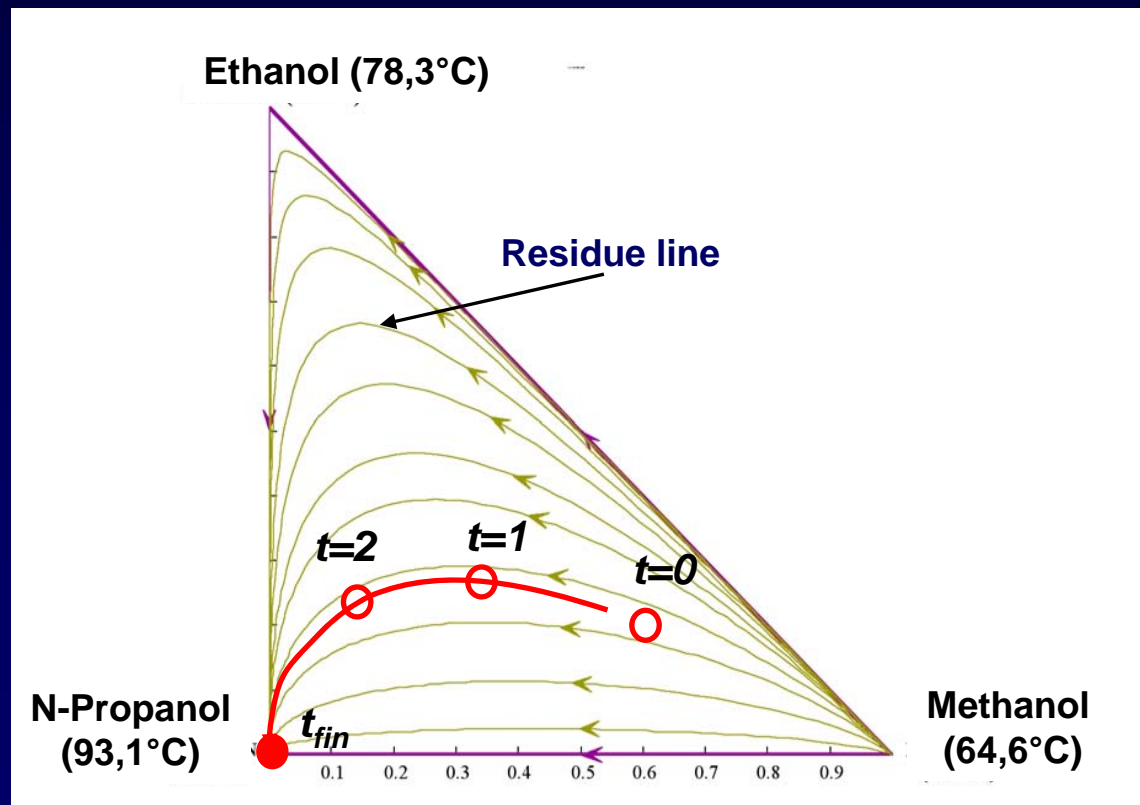
Residue Curve Maps

- Liquid residue composition with time
- 1-stage distillation (batch distillation) with no reflux
- equilibrium relationship of ternary mixtures
- bottom and overhead products
- the feasibility of separation of homogeneous mixtures (stages / energy !)
- the design and operation of a distillation column (azeotropic mixtures)

Example (ideal, no azeotropes)

Starting mixture ($t=0$):

- MeOH 0,6
- EtOH 0,25
- N-PrOH 0,15

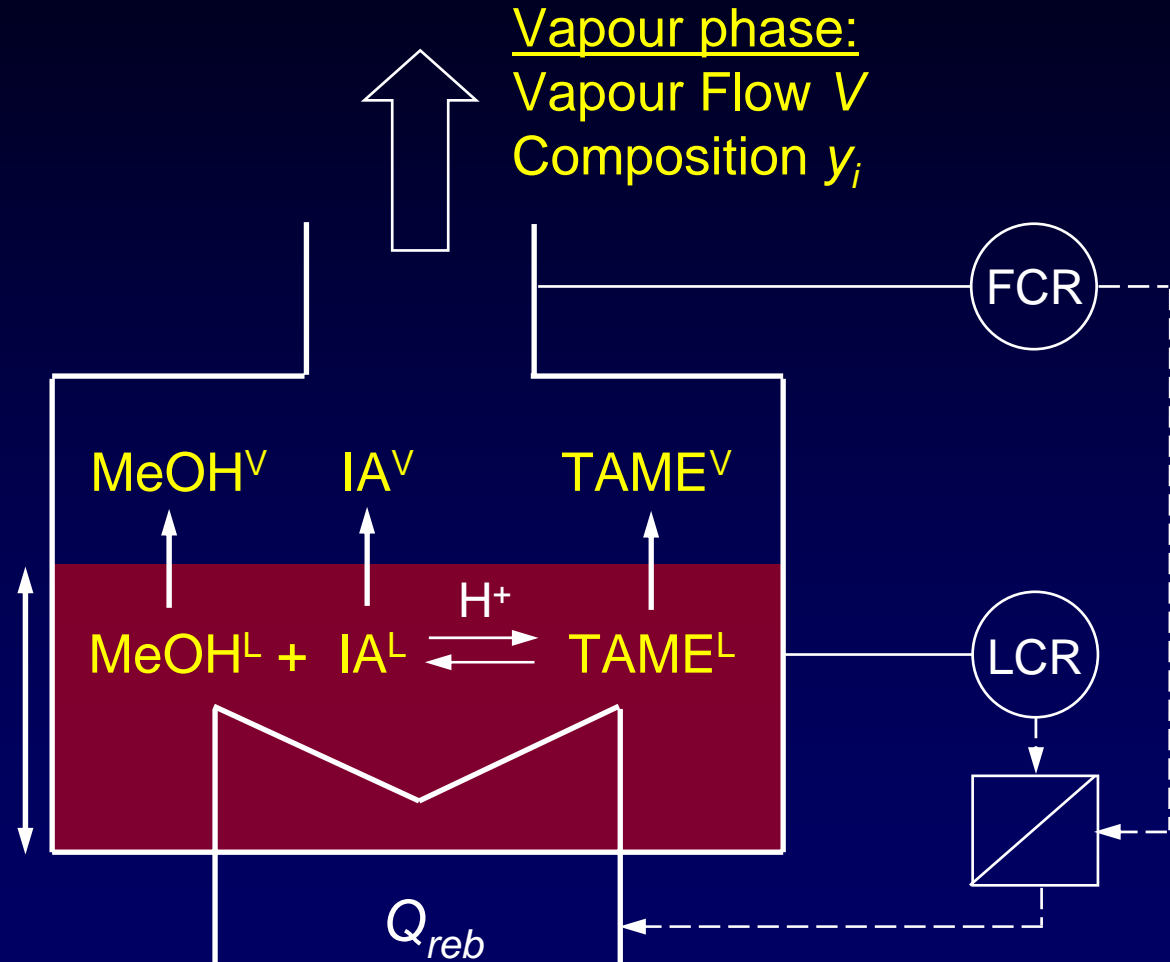




Reactive Batch Distillation: $\text{MeOH} + \text{IA} \rightleftharpoons \text{TAME}$

Heating policy:
 $V / V_0 = H / H_0$

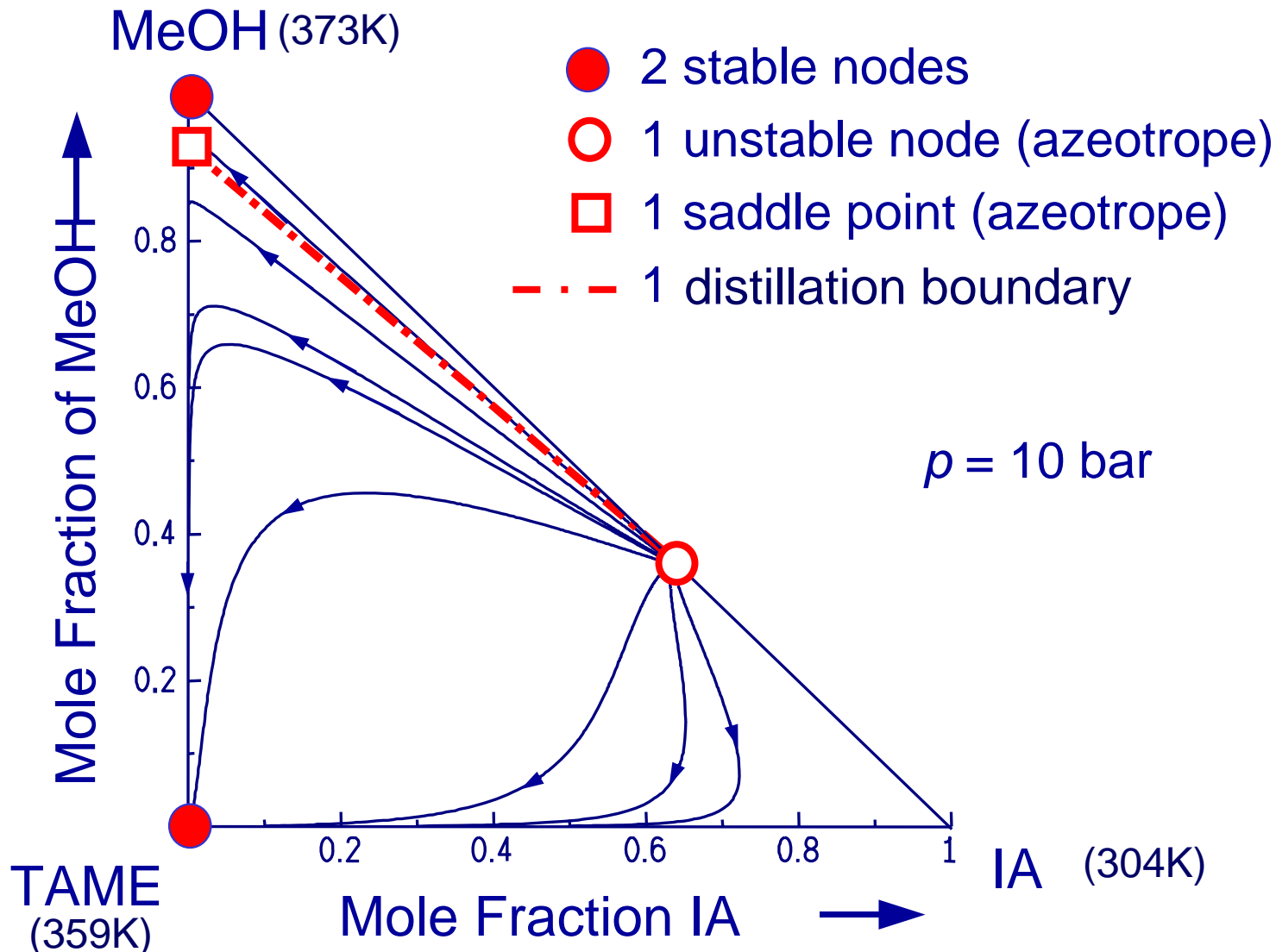
Liquid phase:
Holdup H
Composition x_i



Catalyst: Acidic Ion Exchange Resin (V_{cat}, c_{H^+})

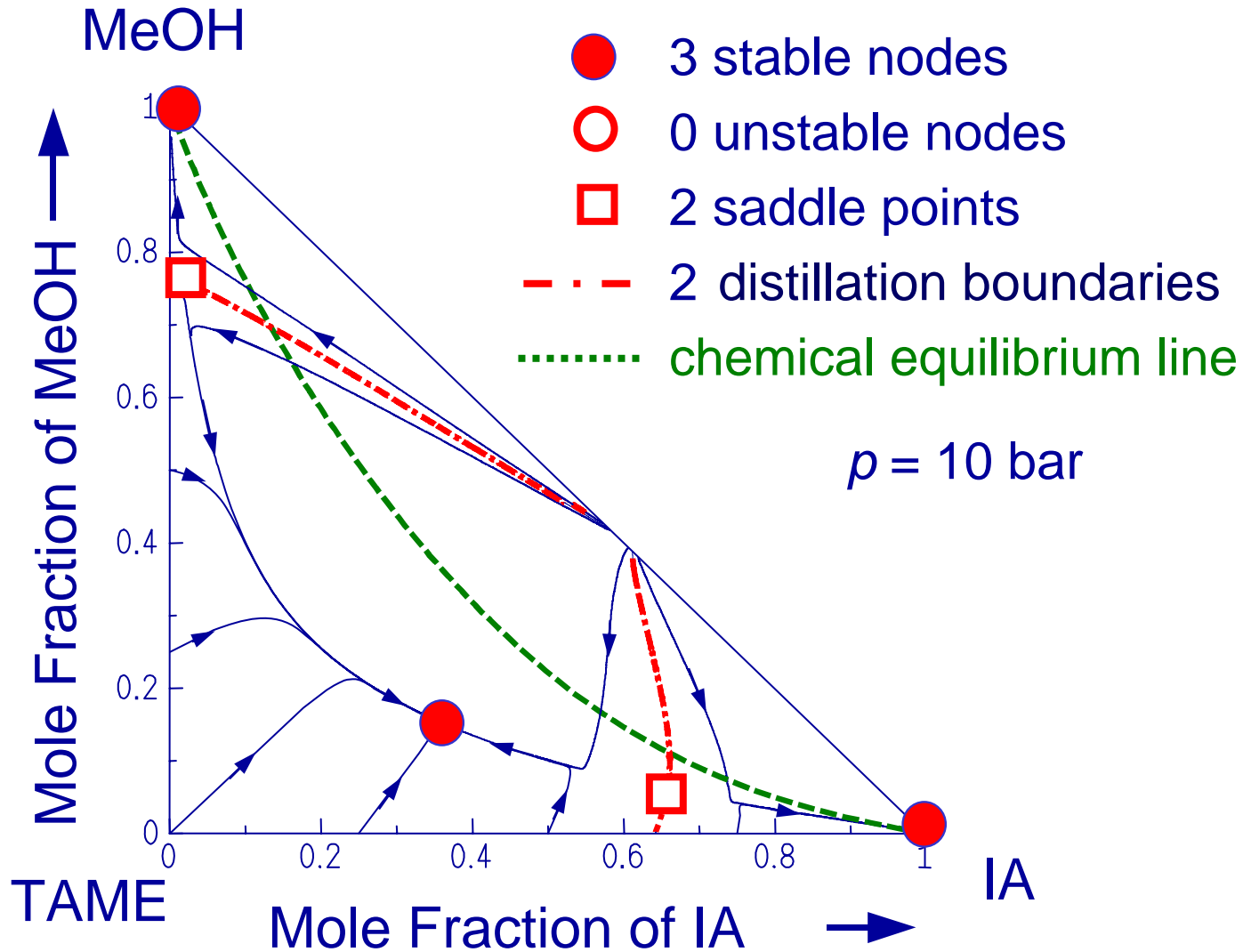


Catalytic Batch Distillation for TAME-Synthesis: No Reaction ($Da = 0$)



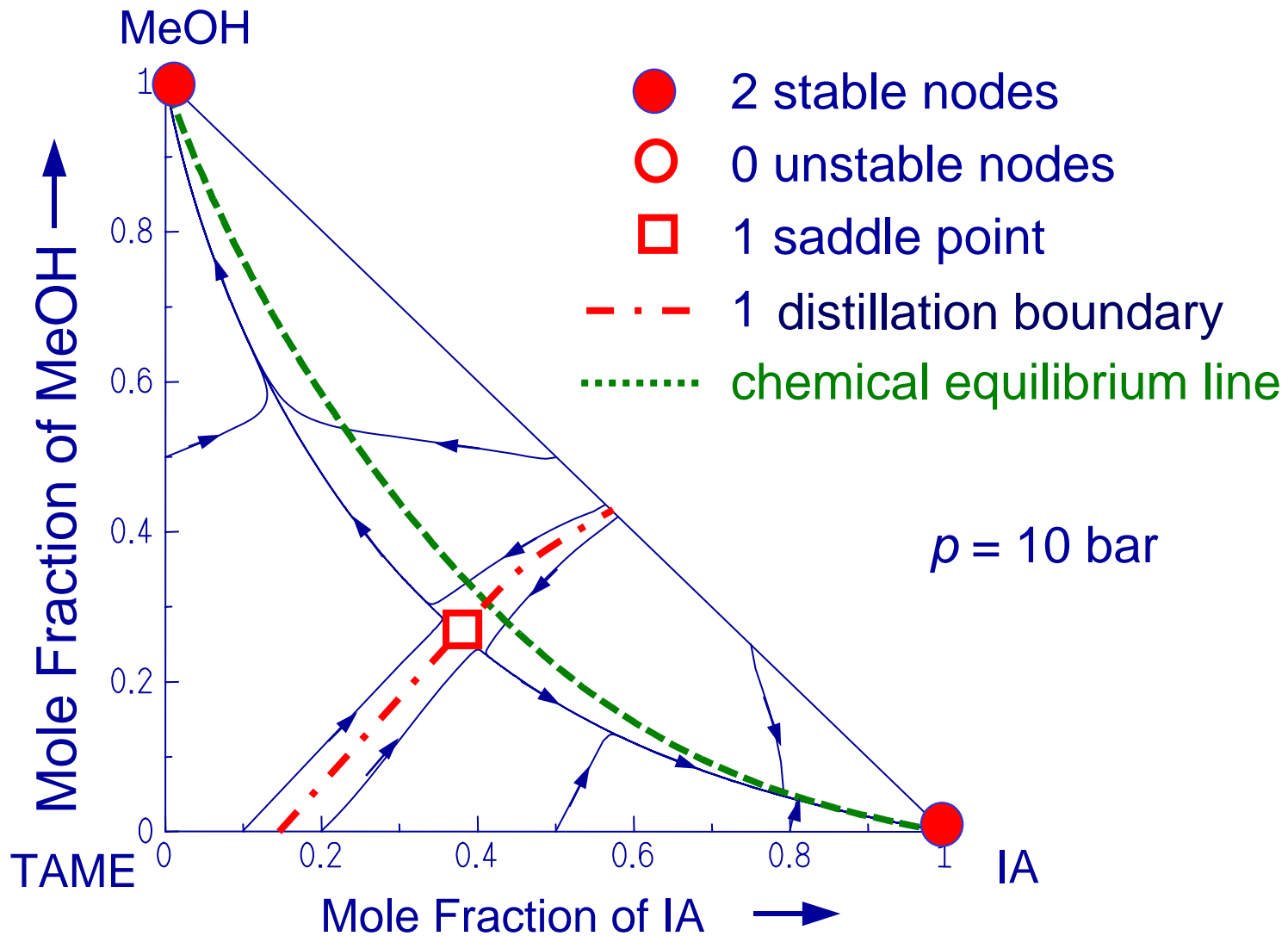


Catalytic Batch Distillation for TAME-Synthesis: Slow Reaction ($Da = 10^{-4}$)



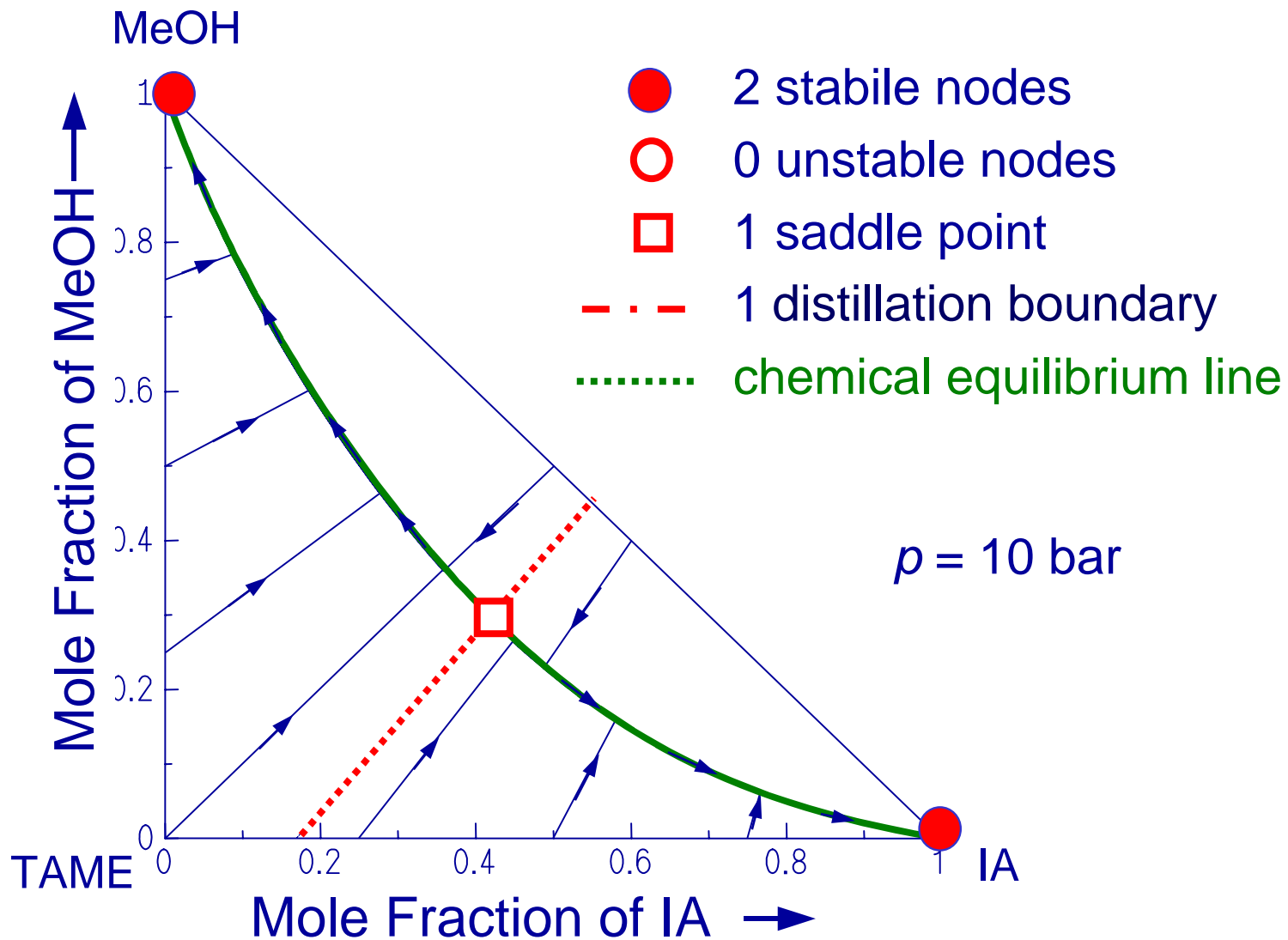


Catalytic Batch Distillation for TAME-Synthesis: Fast Reaction ($Da = 10^{-3}$)



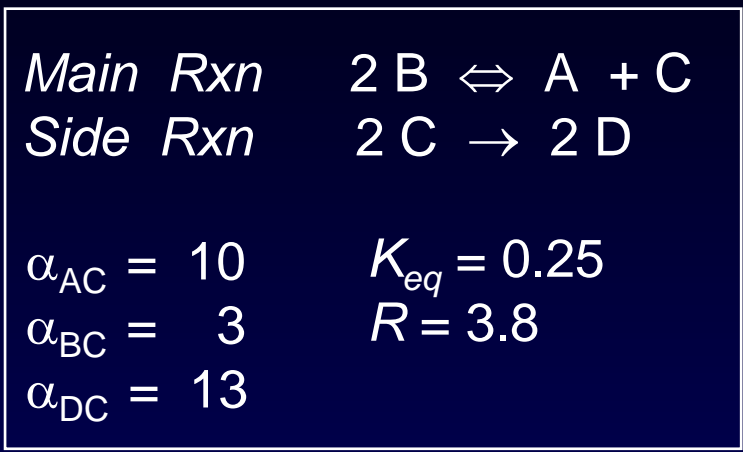


Catalytic Batch Distillation for TAME-Synthesis: Reaction in Equilibrium ($Da > 1$)

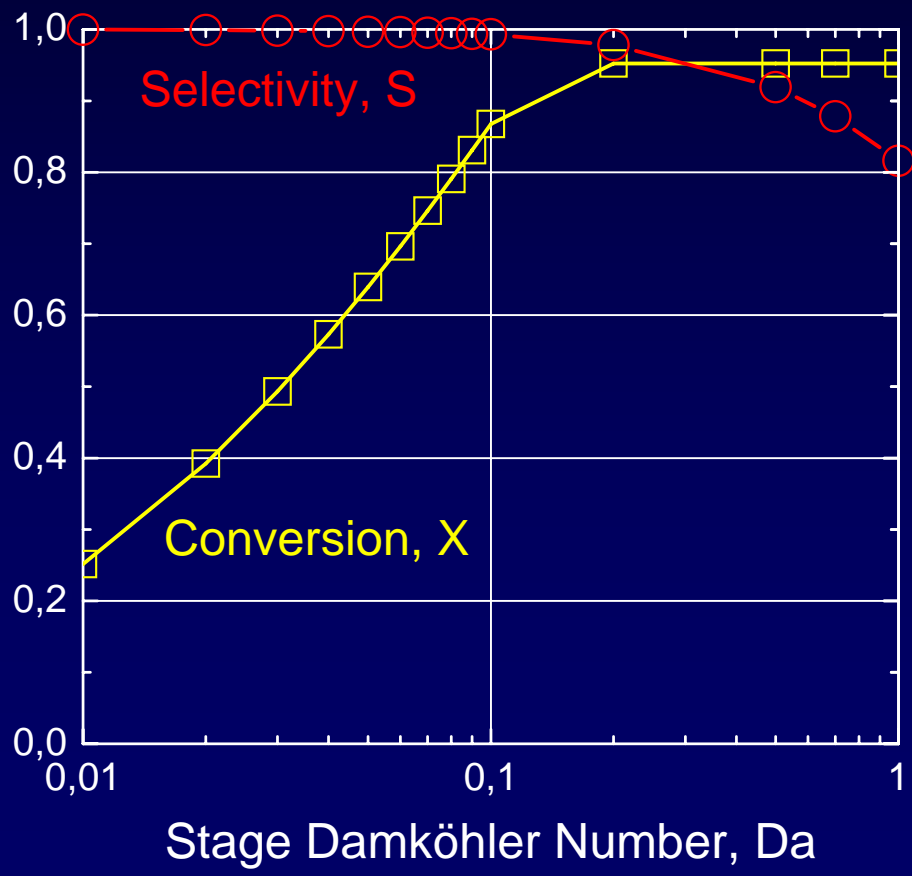
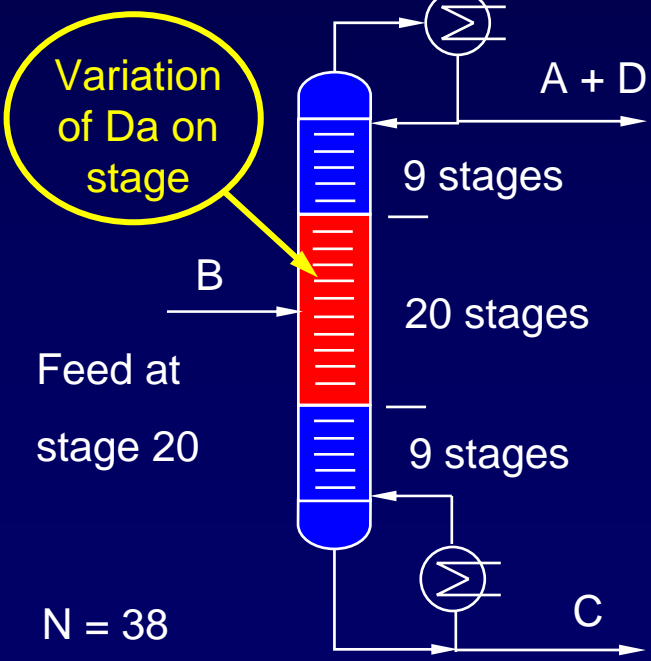




Studies of Side Reactions: Influence of Stage Damköhler Number

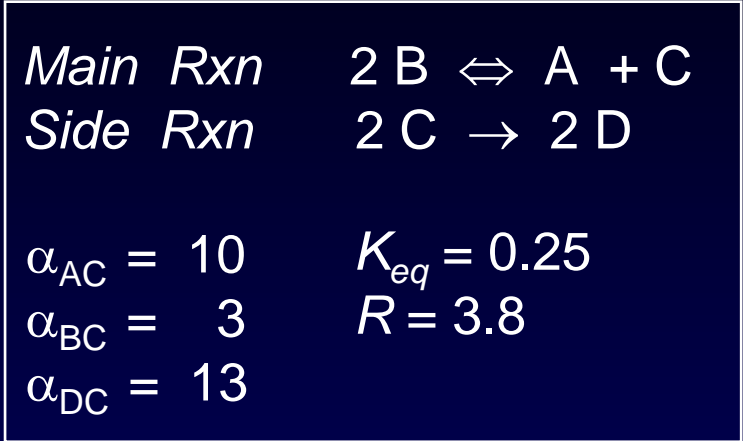


$$r_{main}^* = \frac{x_B^2 - x_A x_C / K_{eq}}{(1 + 5 x_C)^2} \quad r_{side}^* = \frac{0.1 x_C^2}{(1 + 5 x_C)^2}$$

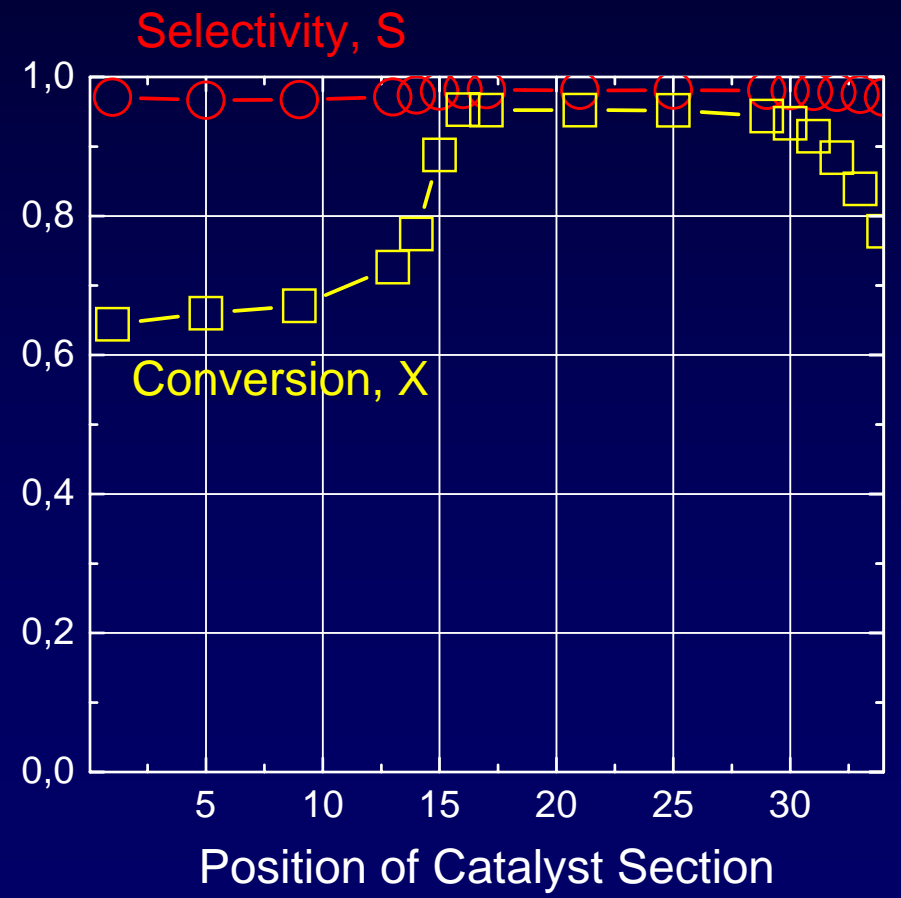
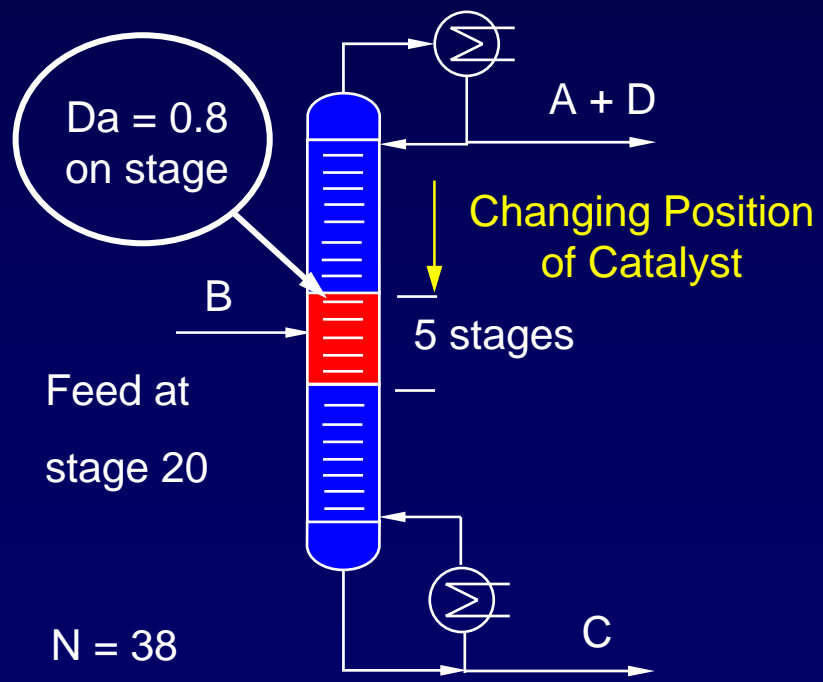




Studies of Side Reactions: Influence of Catalyst Position



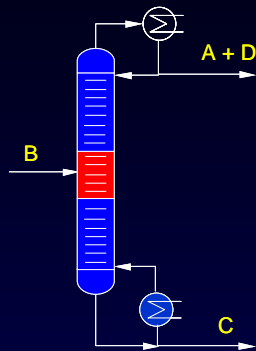
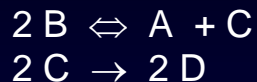
$$r_{main}^* = \frac{x_B^2 - x_A x_C / K_{eq}}{(1 + 5 x_C)^2} \quad r_{side}^* = \frac{0.1 x_C^2}{(1 + 5 x_C)^2}$$



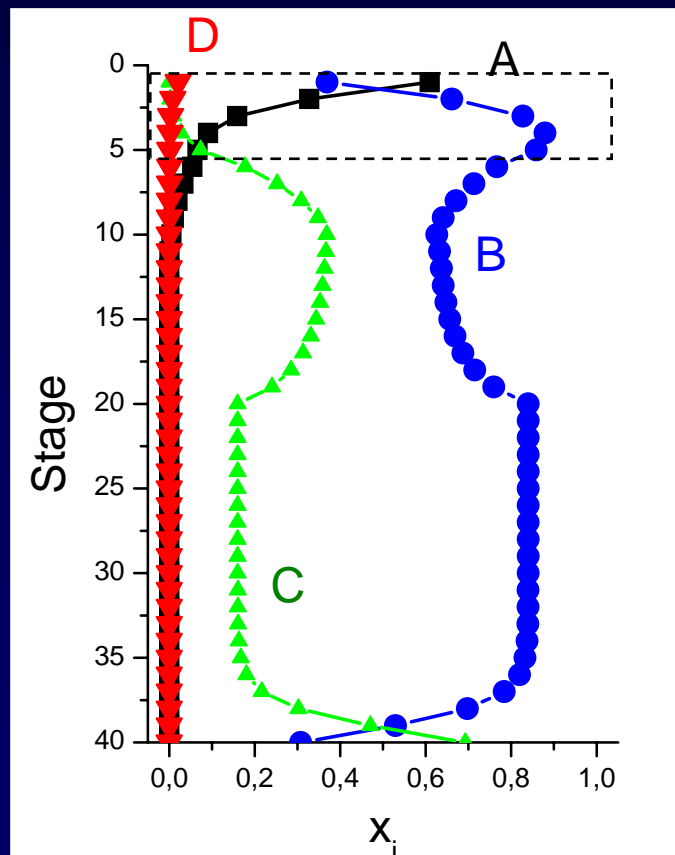
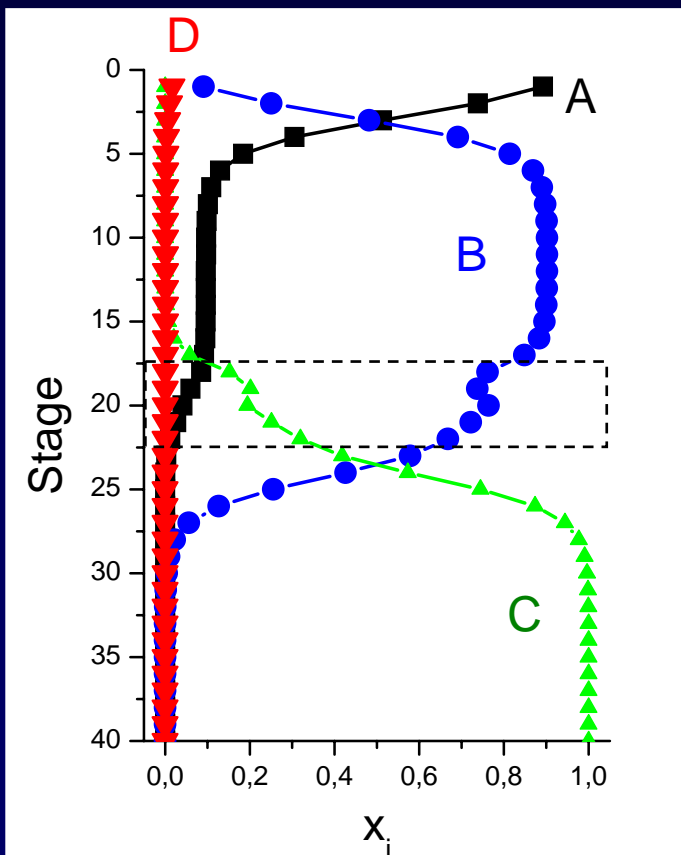
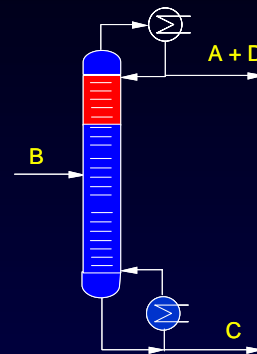


Studies of Side Reactions: Influence of Catalyst Position

(Da = 0.2, Reactive Stages = 5)



$$\frac{r_{main}^*}{r_{side}^*} \sim \frac{x_B^2 - x_A x_C / K_{eq}}{x_C^2}$$

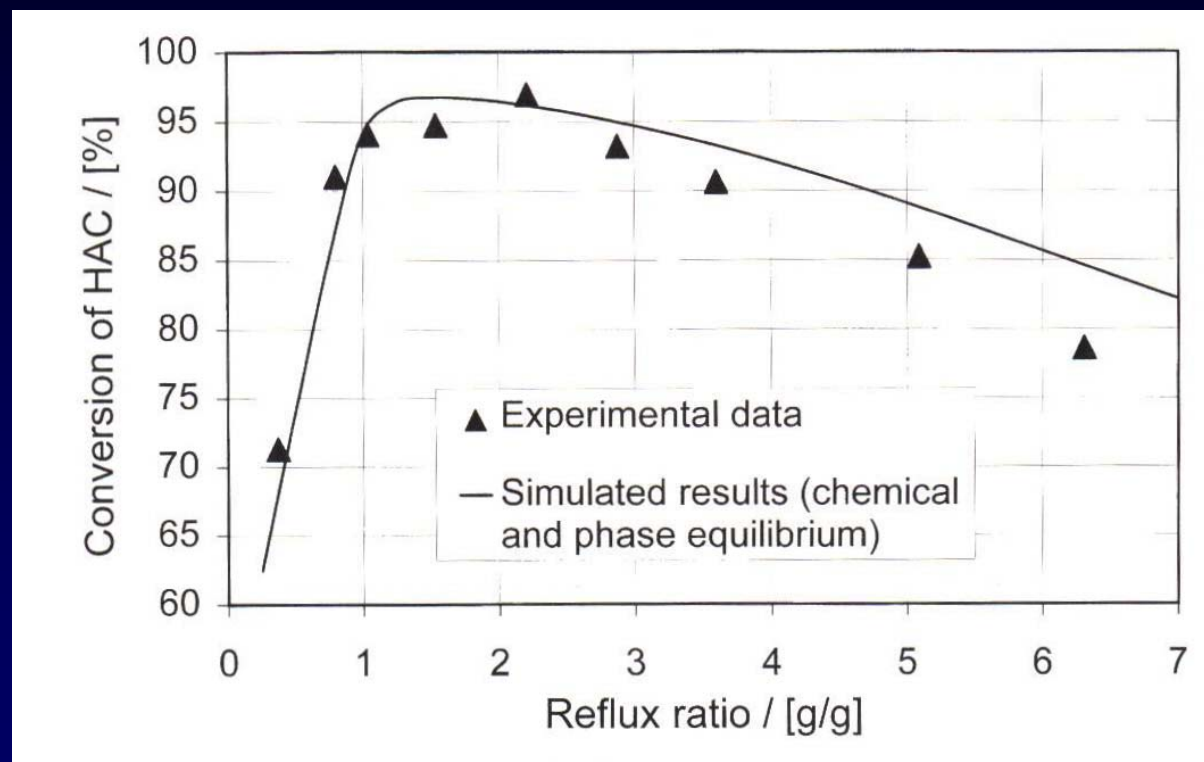
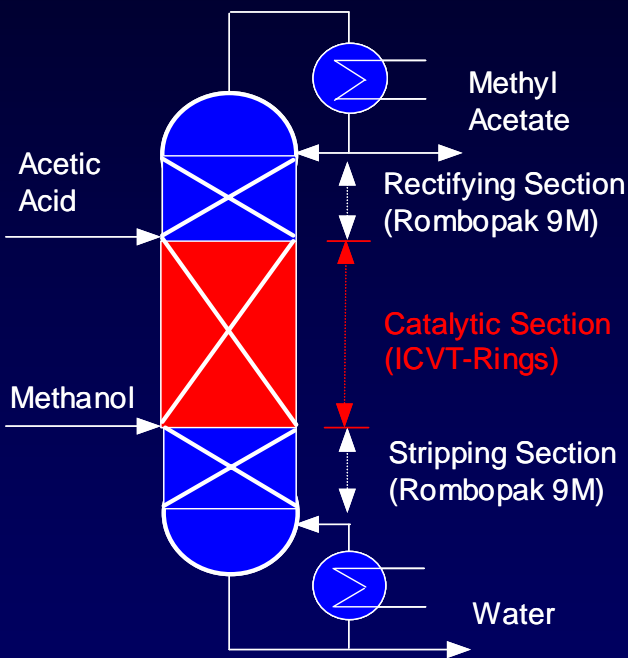




Influence of Reflux Ratio on Conversion



Conversion of Acetic Acid



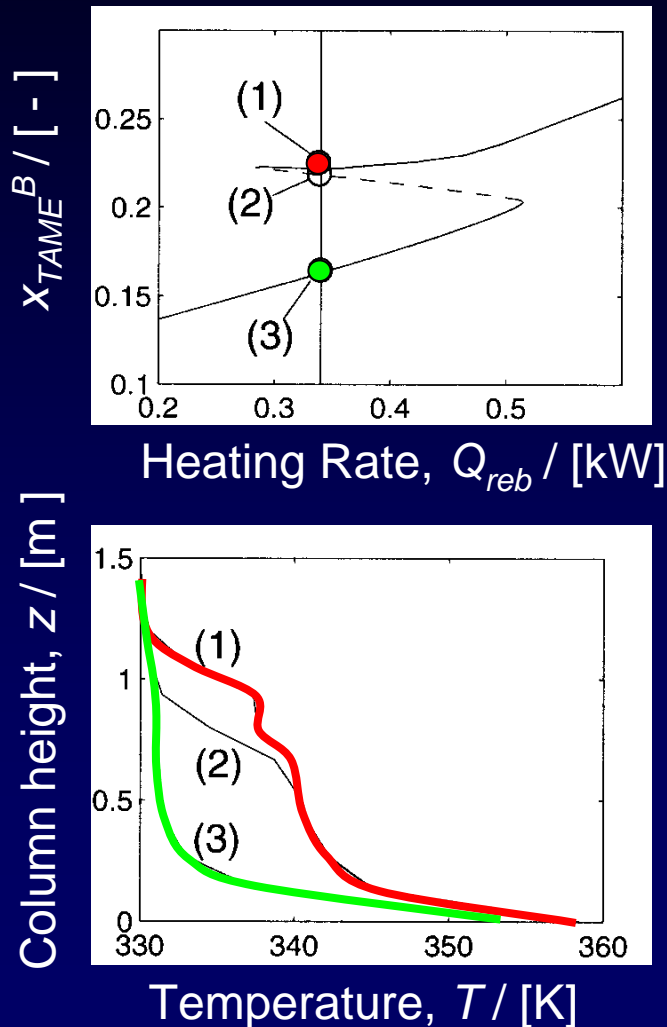
There is an optimal reflux ratio !



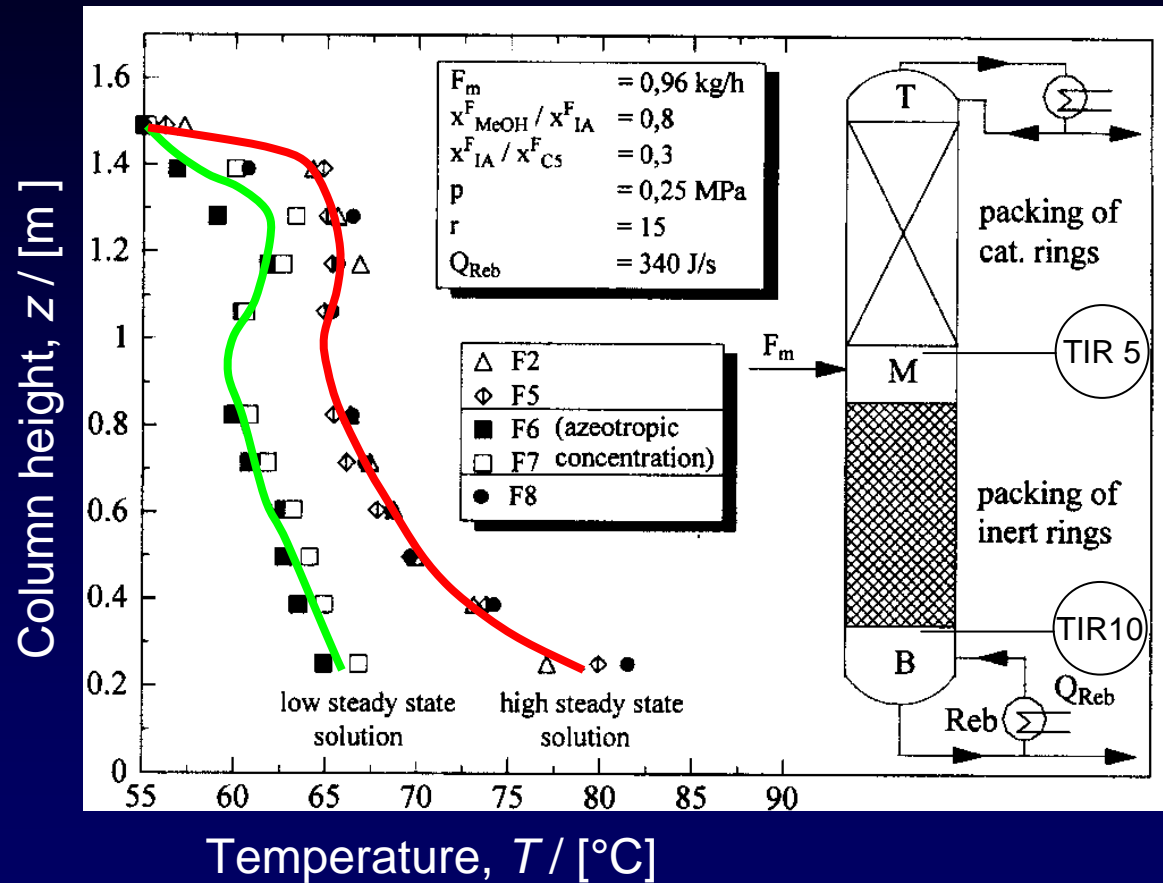
Multiple Steady States of TAME CD Column: Model Predictions and Experimental Results



Model Predictions

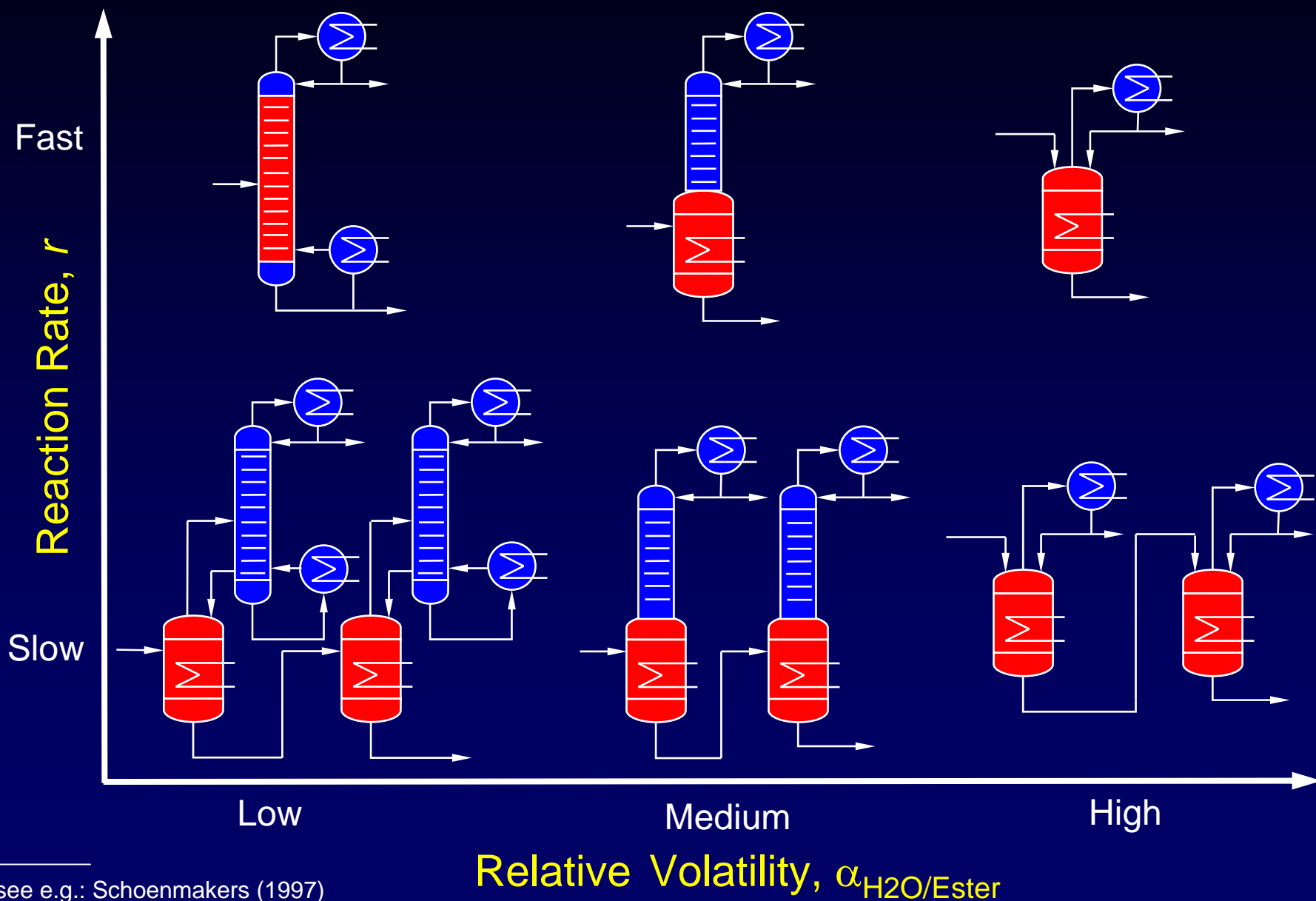


Experimental Liquid Phase Temperatures





Mapping of Reactor-Separator Systems for Esterification: Alcohol + Acid \rightleftharpoons Ester + H₂O





Simple Guideline for CD Reactor Selection



□ Slow reactions: $Da \ll 1$

- + reaction kinetics is limiting
- + high residence time
- + hom. catalysis: high liquid holdup
- + het. catalysis: high catalyst holdup

□ Solution

- + tray column (bubble caps)
- + packed column with random packing
- + column with external side reactors

□ Fast reactions: $Da \geq 1$

- + mass transfer is limiting
- + low residence time sufficient
- + hom. catalysis: low liquid holdup
- + het. catalysis: low catalyst holdup

□ Solution

- + packed column
- + tray column with low holdup





Catalytic Distillation Processes



Process Examples of Catalytic Distillation



Motives for Application of Reactive Distillation



	Motives	Examples
Reaction Problems	Overcoming Limitations of Chemical Equilibrium	Methanol + Acetic Acid \Leftrightarrow Methyl Acetate + H ₂ O Methanol + Isobutene \Leftrightarrow Methyl- <i>tert.</i> -butylether (MTBE) Formaldehyde + 2 Methanol \Leftrightarrow Methylal + H ₂ O
	Increase of Selectivity	Chlorohydrins \rightarrow Propylene Oxide + H ₂ O \rightarrow Propylene Glycol 2 Acetone \rightarrow Diacetone Alcohol \rightarrow Mesityl Oxide + H ₂ O Isobutane + 1-Butene \rightarrow Isooctane + 1-Butene \rightarrow C ₁₂ H ₂₄
	Use of Heat of Reaction	Propene + Benzene \rightarrow Cumene Ethylene Oxide + H ₂ O \rightarrow Ethylene Glycol
Separation Problems	Separation of Closely Boiling Mixtures	m-Xylene / p-Xylene (Reactive Entrainer: Na-p-Xylene) Cyclohexene / Cyclohexane (Reactive Entrainer: Formic Acid) 1-Butene / Isobutene (Reactive Entrainer: Methanol / Water)
	Breaking of Azeotropes	Methyl Acetate / Water ; Methyl Acetate / Methanol (Entrainer: Acetic Acid)
	High Purity Separation	Hexamethylene Diamine / Water (in Nylon 6,6 process) (Reactive Entrainer: Adipic Acid)



Production of Methyl Acetate



Reaction:



Catalysts: H_2SO_4 / Acidic Ion Exchange Resin

Chemical Equilibrium Constant: $K_x(25^\circ\text{C}) = 5.2$

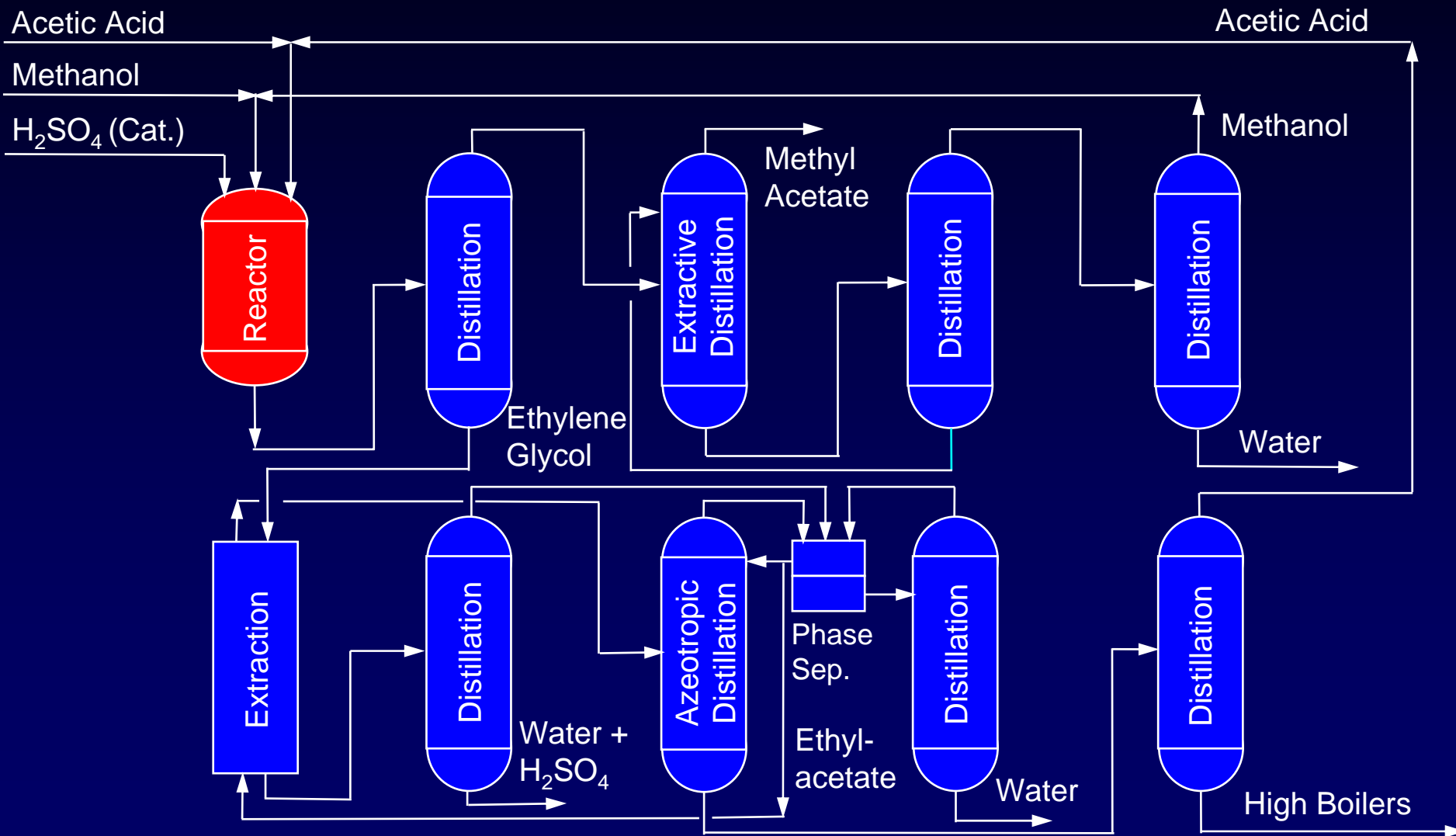
Boiling Sequence at $p = 0.1$ MPa:

hom. azeotrope MeAc/Methanol	53.8 °C
hom. azeotrope MeAc/Water	56.7 °C
Methylacetate (MeAc)	56.9 °C
Methanol	64.6 °C
Water	100.0 °C
Acetic Acid	118.0 °C

L/L-phase splitting: in ternary system MeAc/Methanol/Water



Production of Methyl Acetate (Conventional Process)

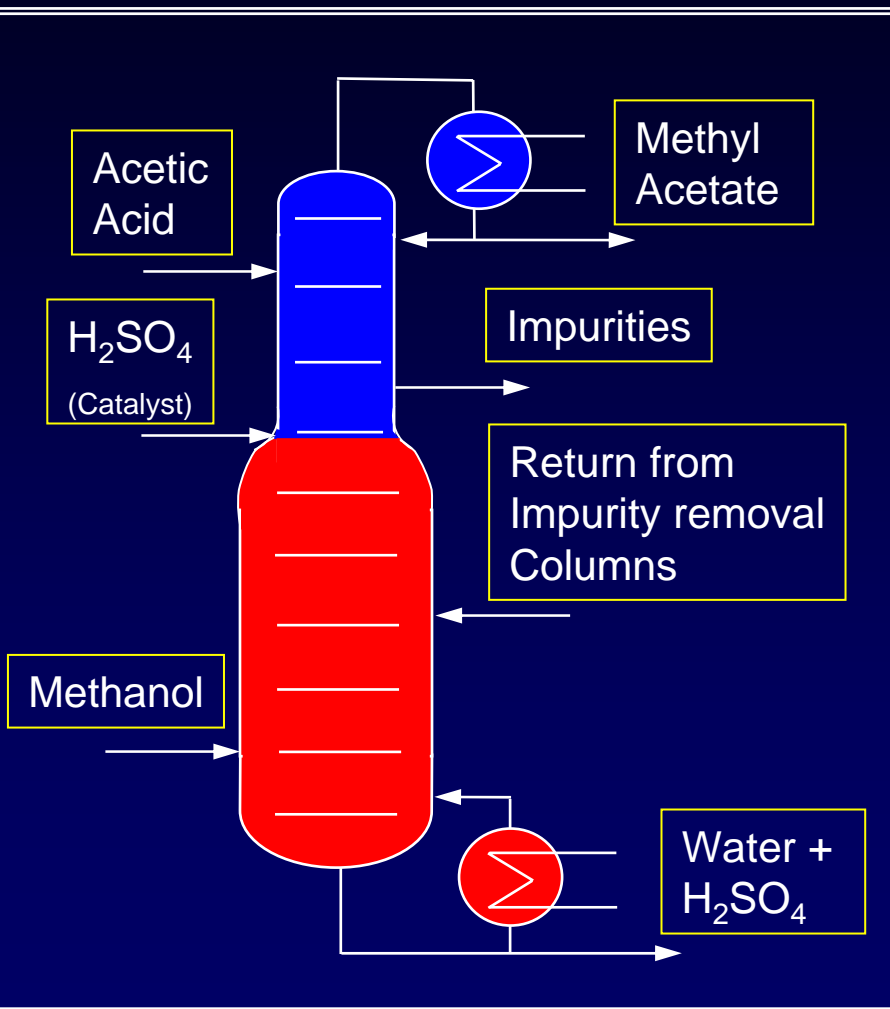




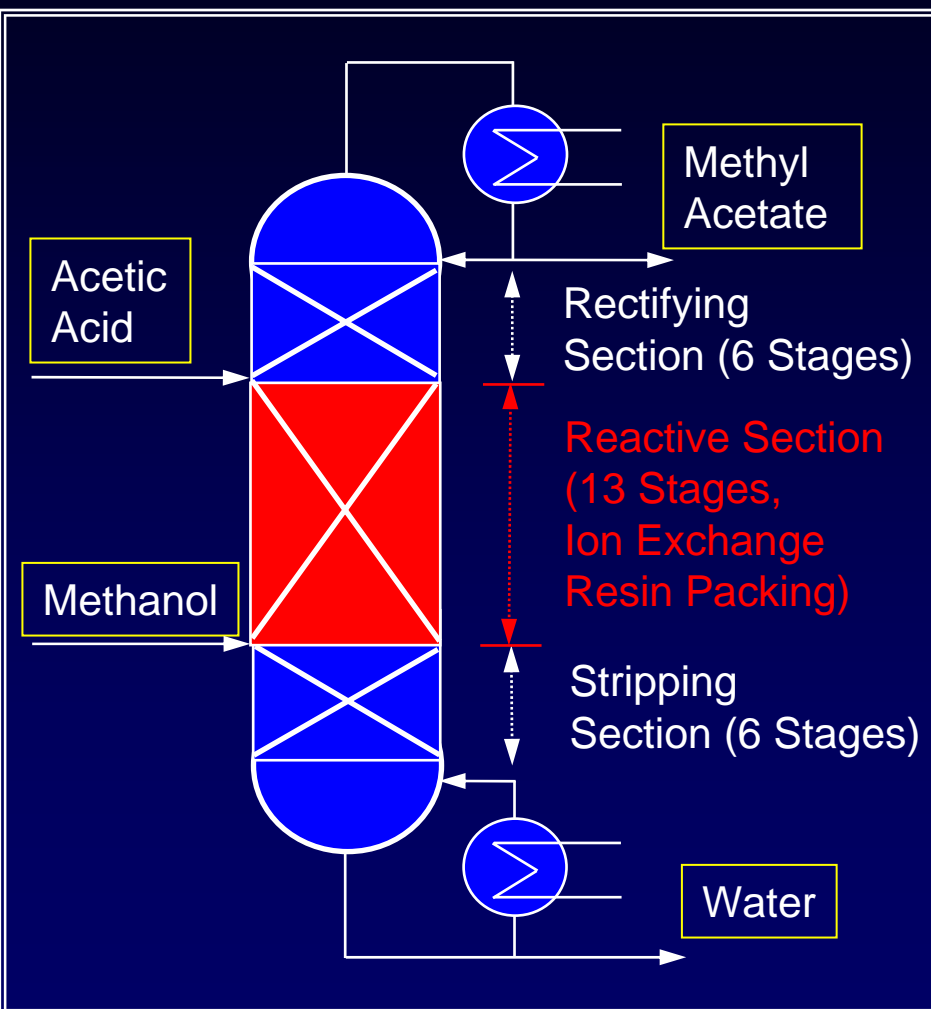
Production of Methyl Acetate (CD Processes)



Homogeneously Catalyzed Reaction*



Heterogeneously Catalyzed Reaction**



* Agreda, V.H.; Partin, L.R., US Patent No. 4,435,595 (1984, Eastman-Kodak-Process)

Bessling, B.; Löning, J.-M.; Ohligschläger, A.; Schembecker, G.; Sundmacher, K., *Chem. Eng. Technol.* **21 (1998) 393-400.

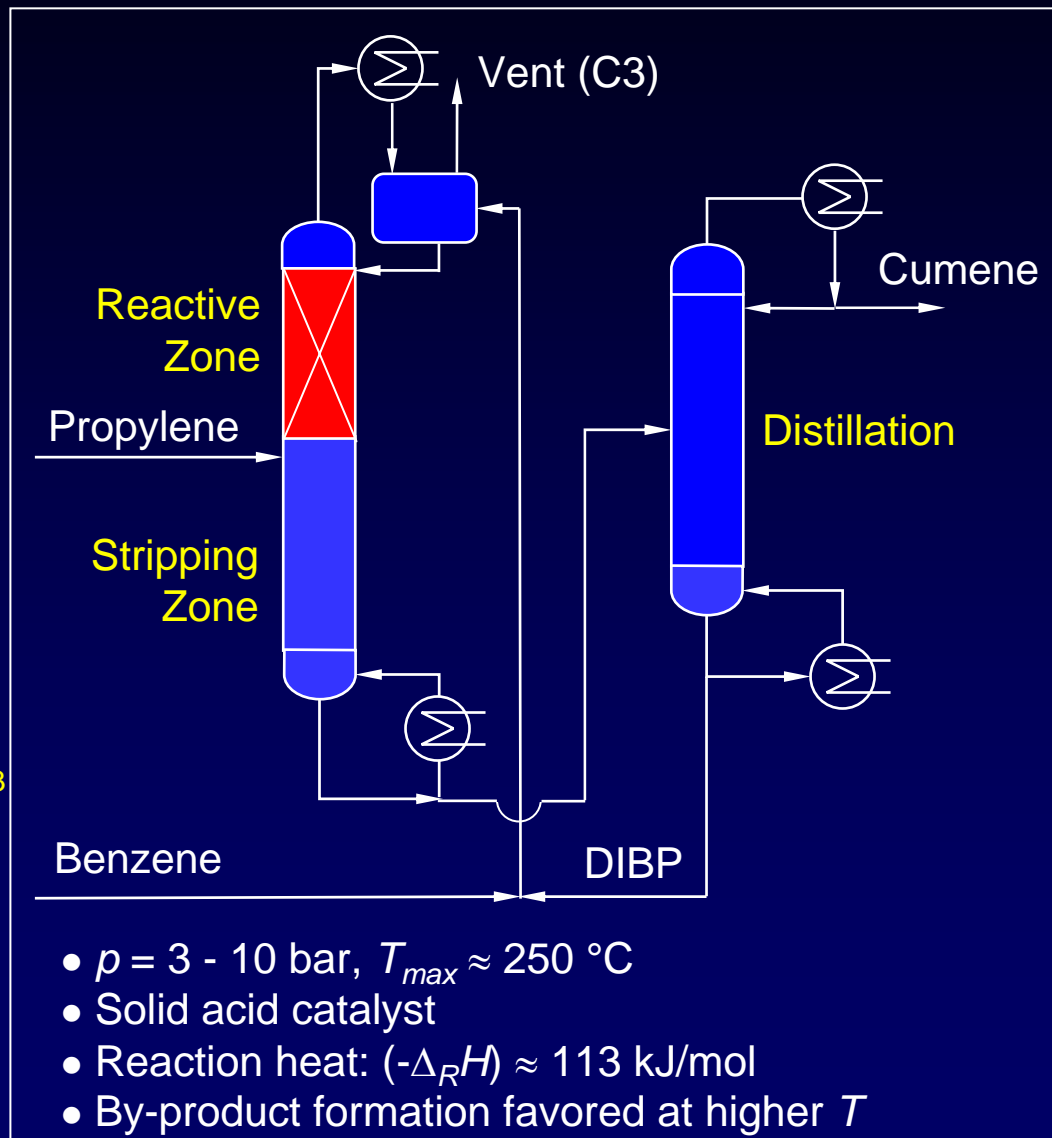
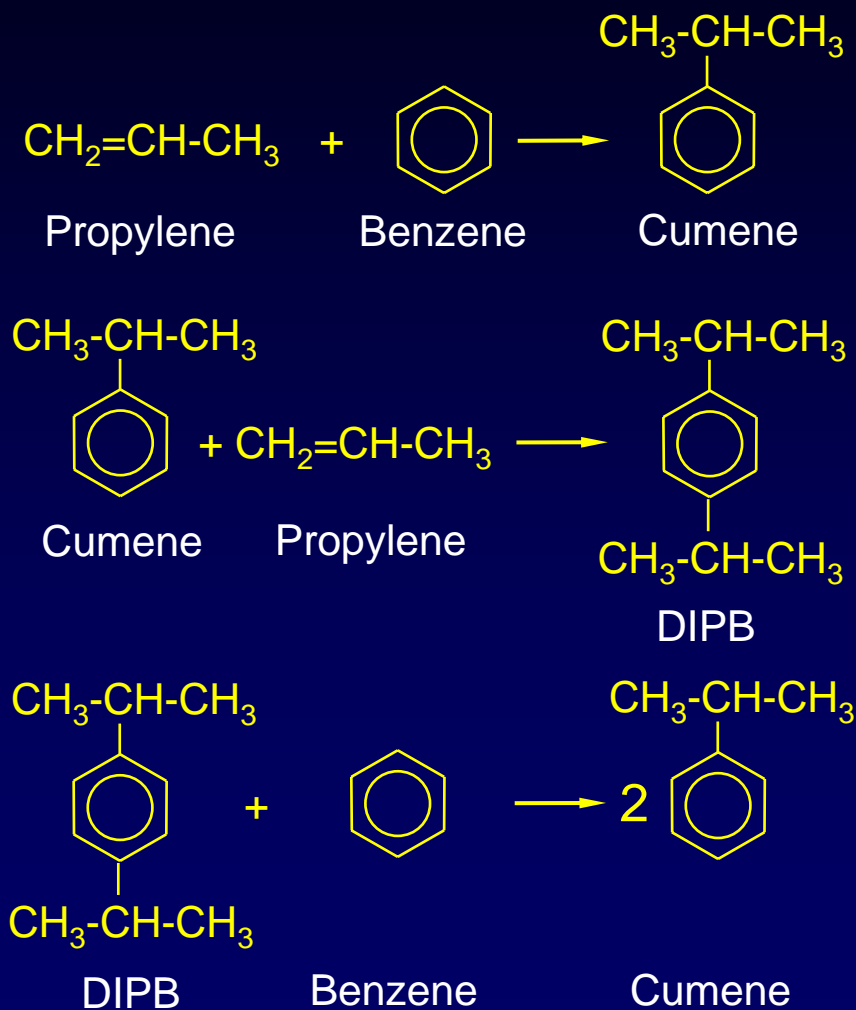


CD Application for Highly Exothermic Reactions

Example: Cumene Production



Reaction Scheme





RD Application for High Purity Separation, Example: C4-Separation (Hüls-UOP*)



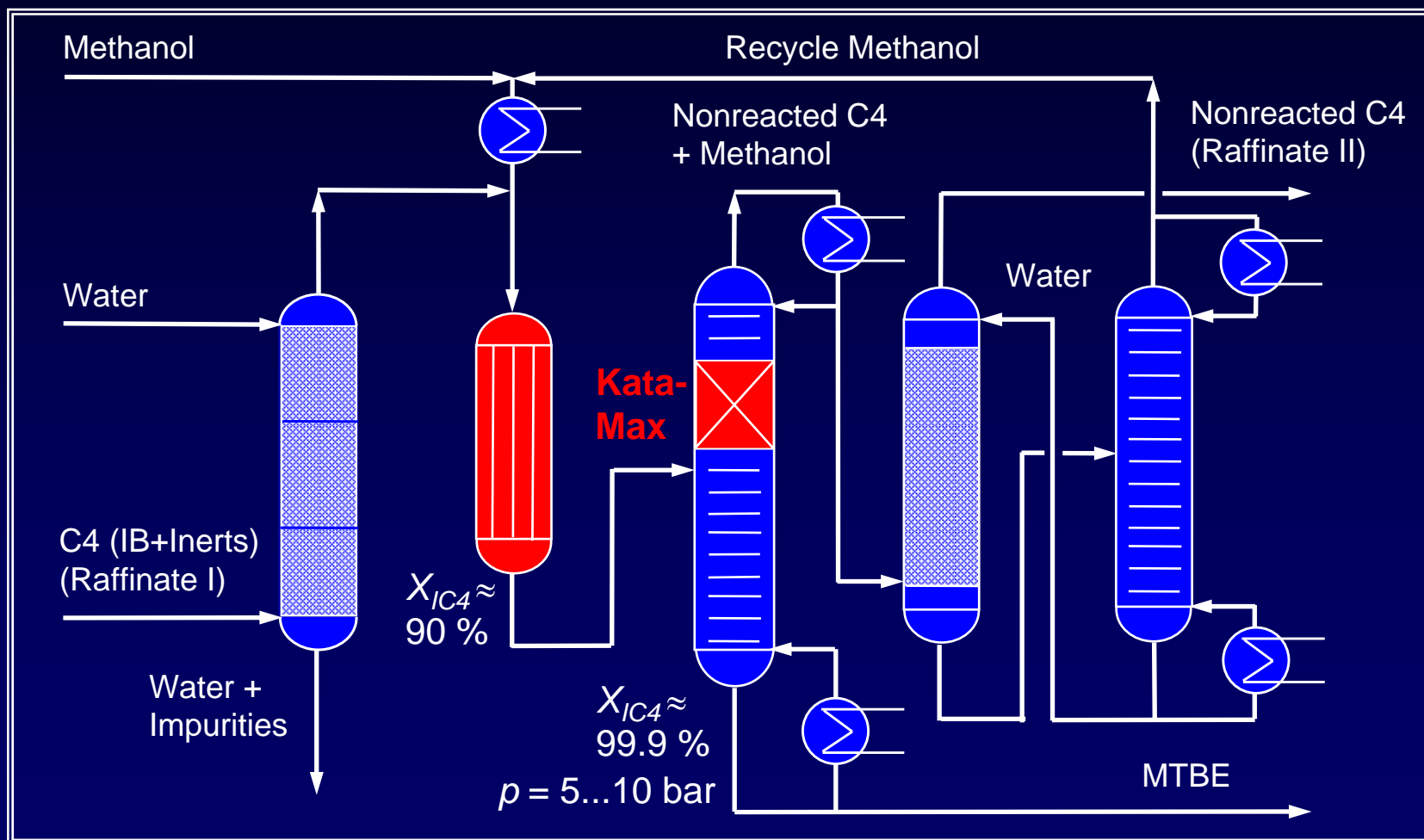
Feed
Wash

Fixed Bed
Tubular
Reactor

Reactive
Distillation
Column

Methanol
Extraction

Methanol/
Water
Distillation

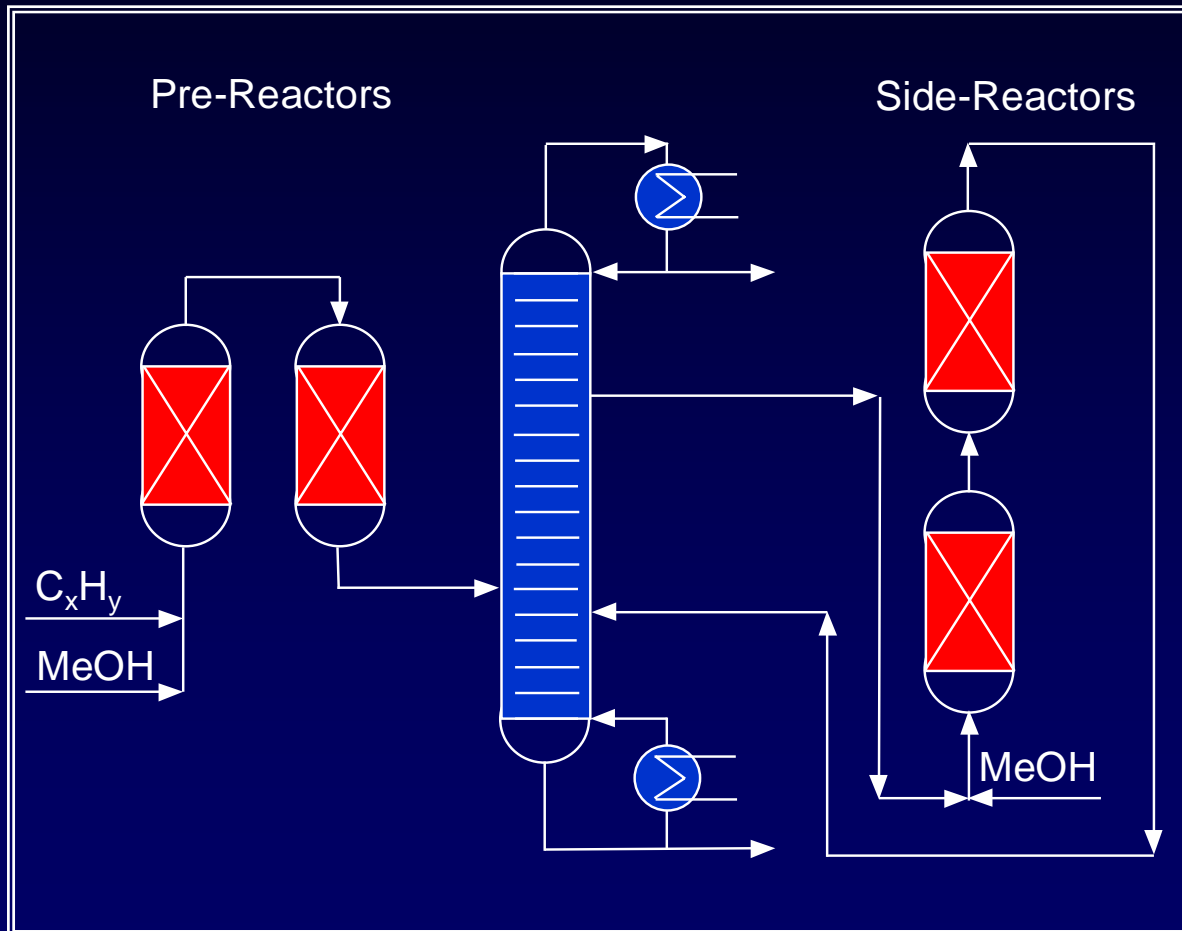




RD System based on Pre- and Side Reactors



Ether Production Flow Scheme (Neste Oil)



Advantages

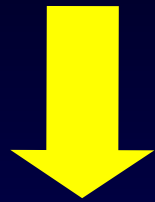
- easy catalyst replacement
- easy control of reactant-ratio
- independent of specific catalyst packing
- distillation column hydraulics and mass transfer not affected by catalyst structure
- high Da/N -ratio achievable



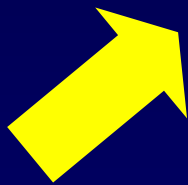
Catalytic Packings: Aspects of Selection



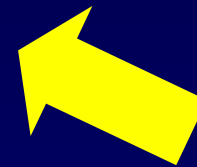
Reaction Rate
(Catalyst Holdup: ε_{cat})



Catalytic Packing
in CD Columns



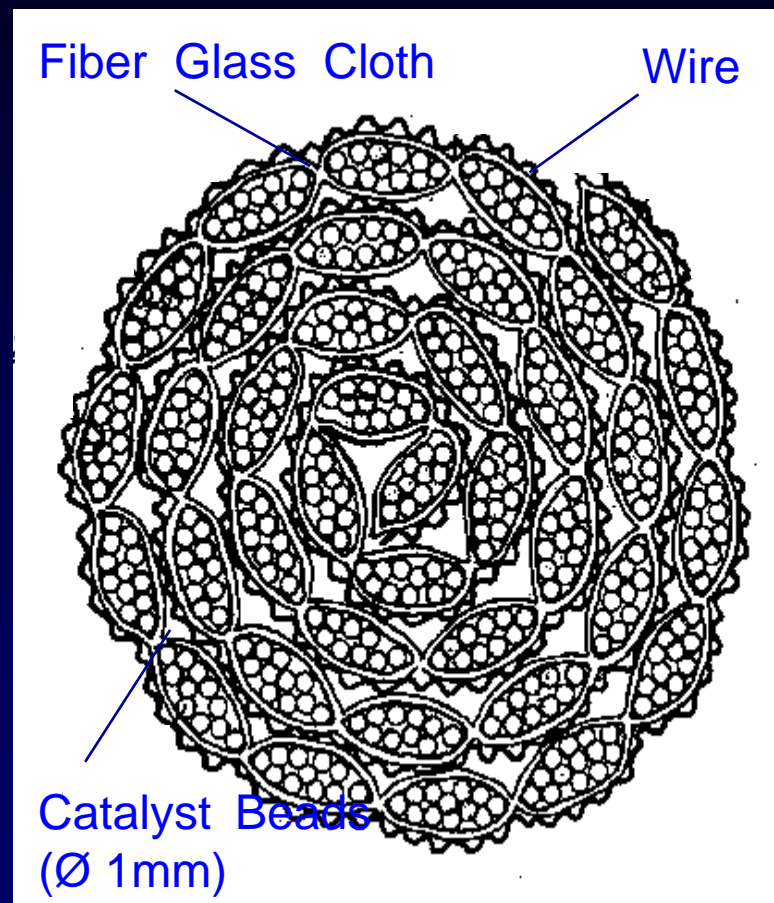
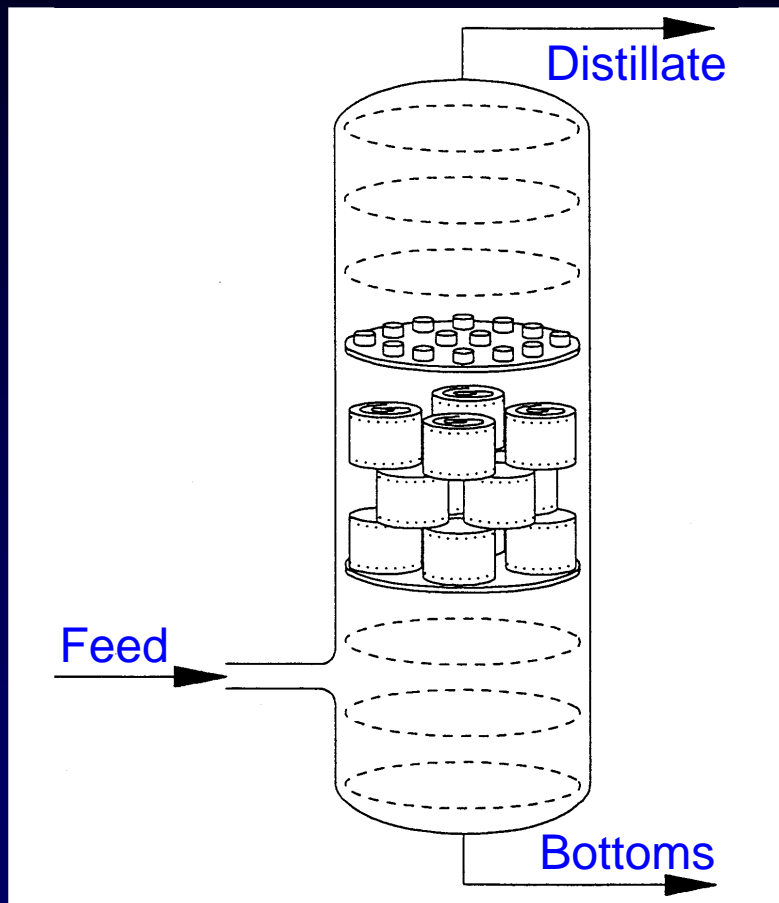
Hydraulic Capacity
(Void Fraction: $1 - \varepsilon_{\text{cat}}$)



Mass Transfer
Efficiency
(Number of Theoretical
Stages: NTSM)



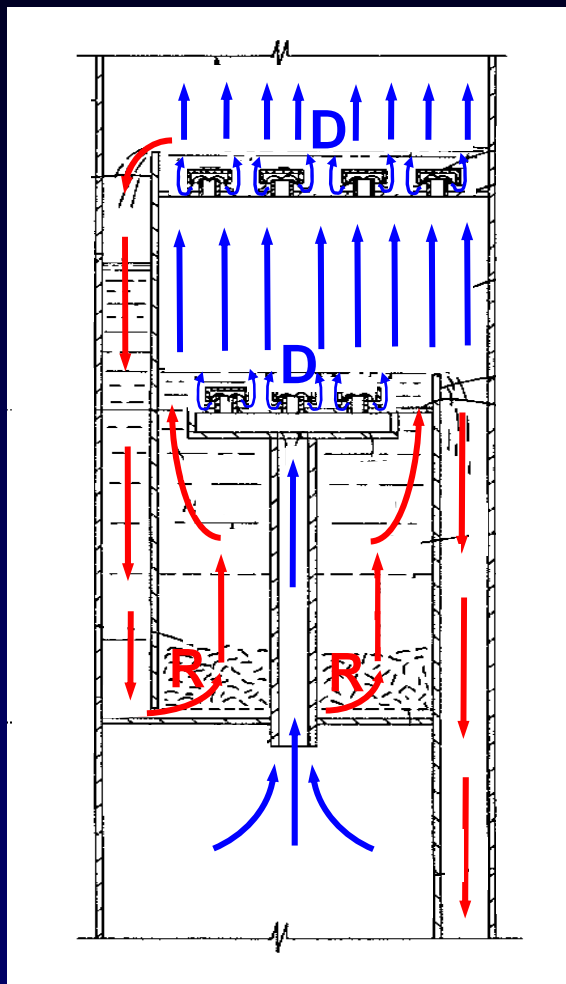
Catalytic Bales (CD Tech)



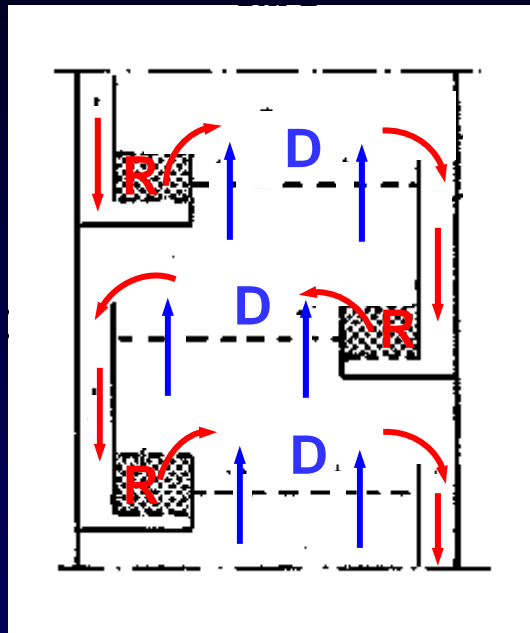


Catalytic Distillation Trays

CR & L

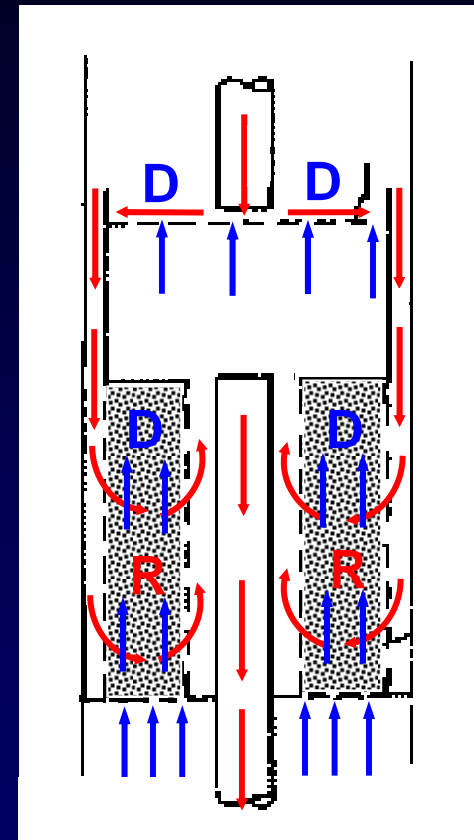


IFP



Lionel, A. *et al.*, US 5368691 (1994)

SNAMPROGETTI



Domenico, S. *et al.*, US 5493059 (1996)

Jones Jr., Edward M., US 5130102 (1992)



Structured Catalytic Packings



KATAPAK-S (Sulzer Chemtech)

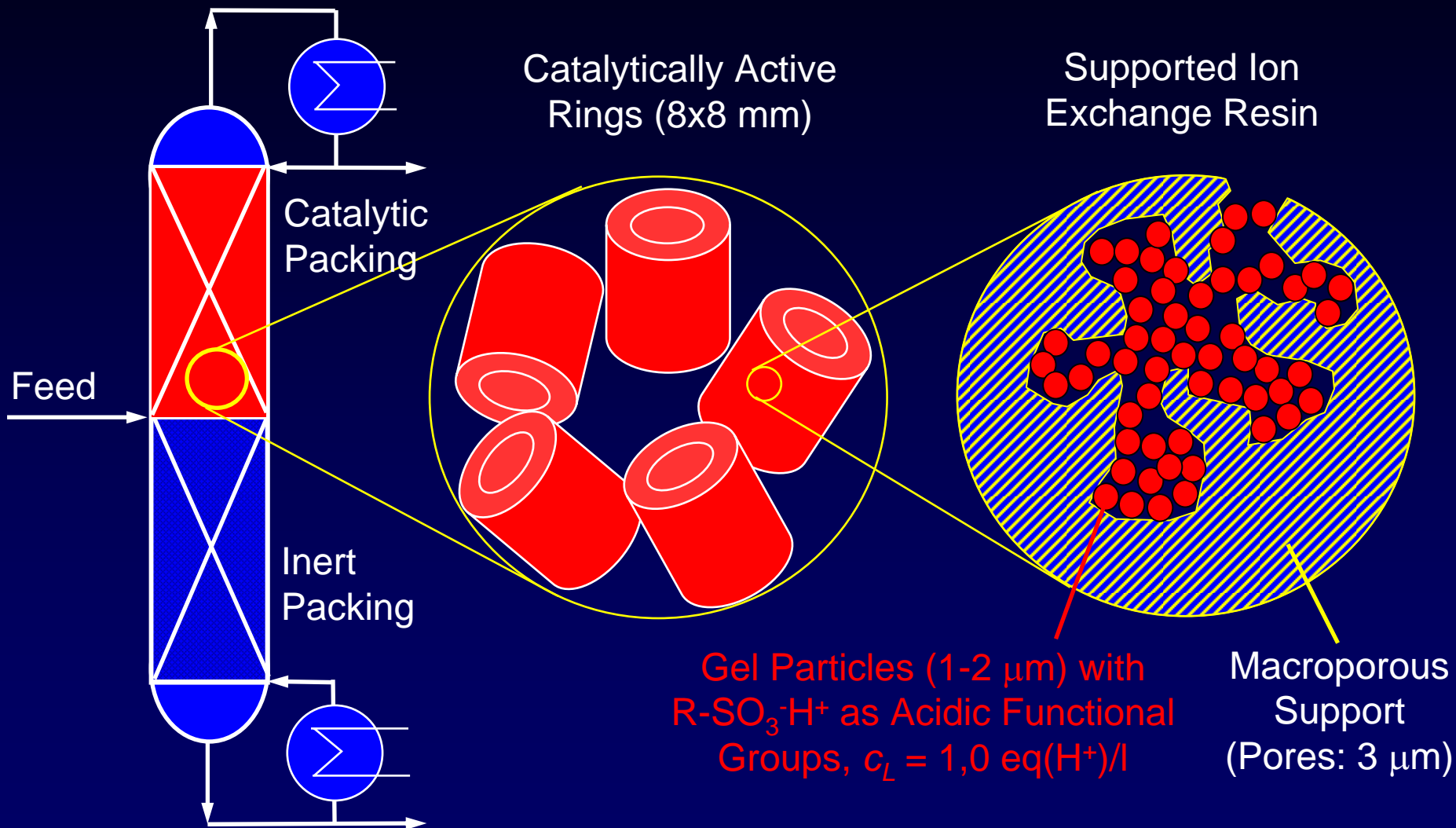
MULTIPAK (Julius Montz)

Stringaro, J.P., EP 631813 A1 (1993)

Gorak, A., Kreul., L. U., DE 197 01 045 A1 (1998)

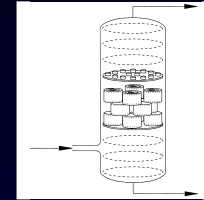


Catalytic Distillation Process for Fuel Ether Production (TU Clausthal)





Some Properties of Catalytic Packings



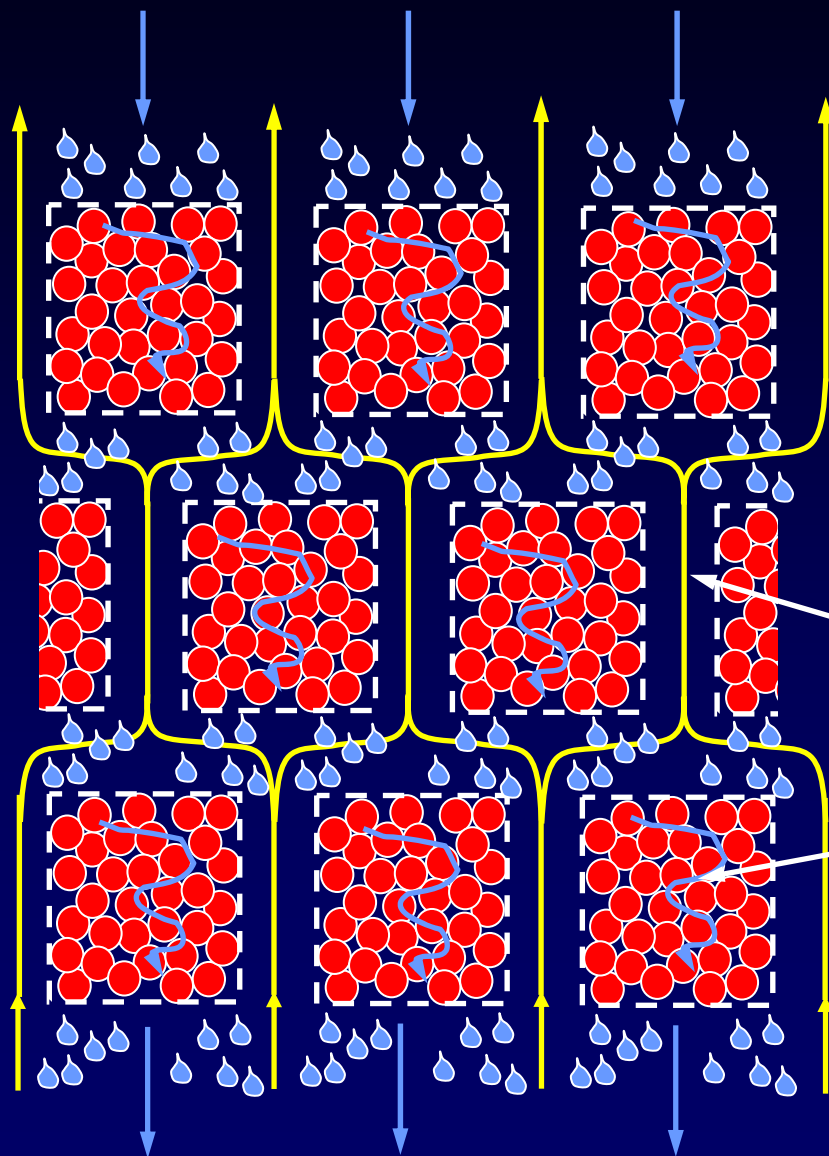
Katapak

Void Fraction	$[m^3/m_{col}^3]$	0.49	0.75*	0.75*
Catalyst Loading	$[m_{cat}^3/m_{col}^3]$	0.51	0.20*	0.20*
Catalyst Surface-to-Volume Ratio	$[m_{cat}^2/m_{cat}^3]$	1129	4000*	4000*
Packing Surface-to-Volume Ratio	$[m_{cat}^2/m_{col}^3]$	576	800*	800*

* See: Lebens, P. J. M., Kapteijn, F., Sie, T.N., Moulijn, J.A., *Chem. Eng. Sci.* 54 (1997) 1359-1365.

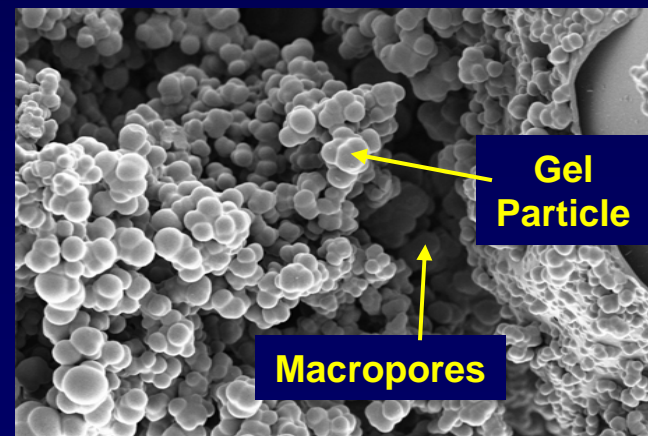


Three-Levels-of-Porosity Concept



Three Pore Levels:

- I. Pores inside catalytic particles
- II. mm-Pores between catalytic particles
- III. cm-Pores between the catalytic pockets



see e.g.: Krishna, R., Sie, S.T.,
Chem. Eng. Sci **49** (1994) 4029-4065.



Summary RD

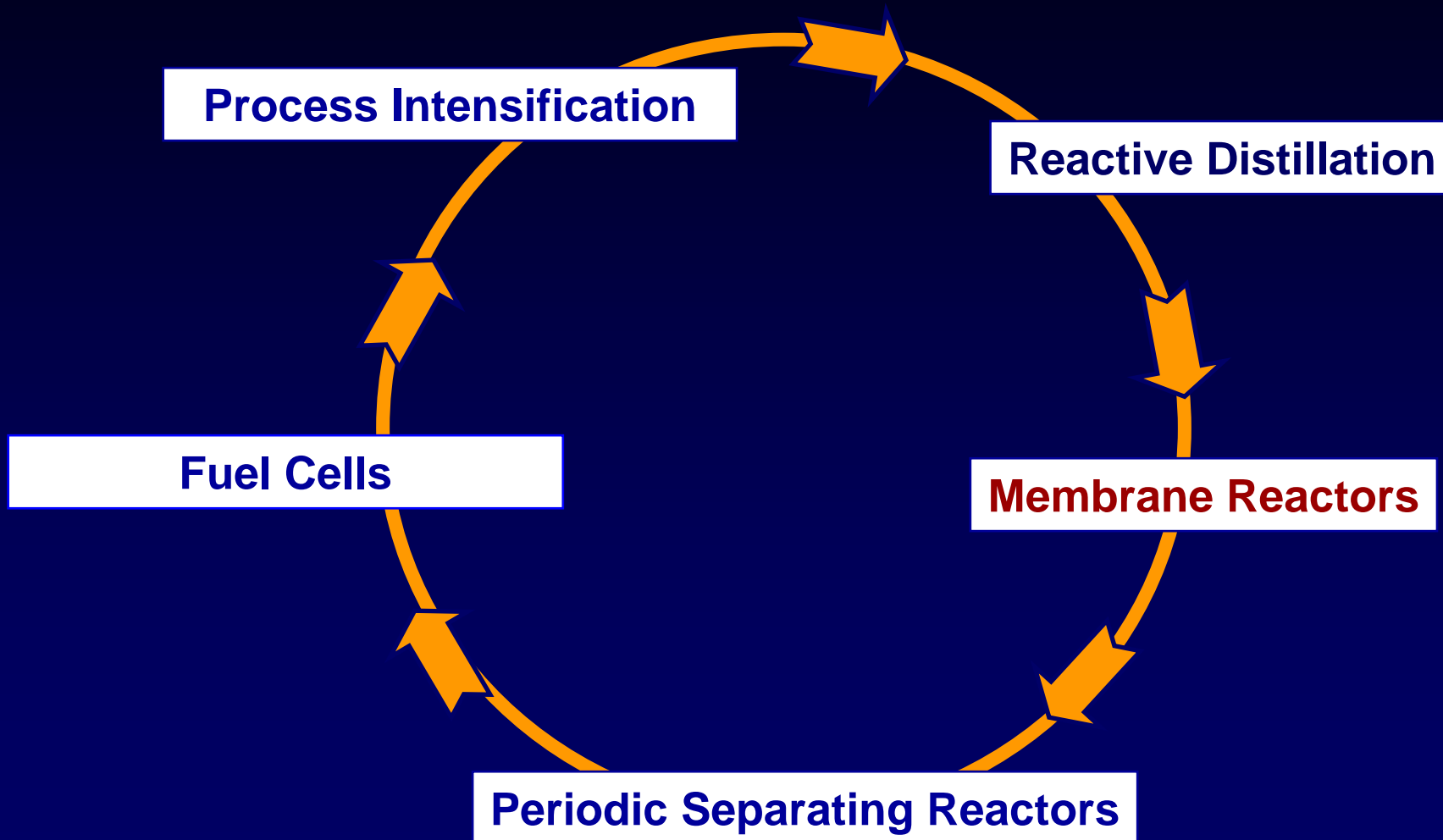


- Reduced downstream processing
 - Overcoming limitations of thermodynamic equilibrium
 - Breaking of azeotropes
 - Increasing selectivity
 - Utilisation of the ΔH_r for evaporation
 - Separation of isomeric mixtures
-

- Compatible T - p range
- Very slow reactions
- Gas-liquid reaction (high T and p)
- Catalyst life time



Integrated Catalytic Processes –Lecture Outline

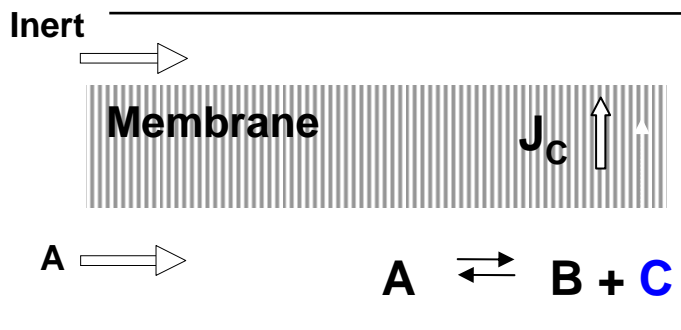




Catalytic Membrane Processes



Selective product removal („Extractor“)

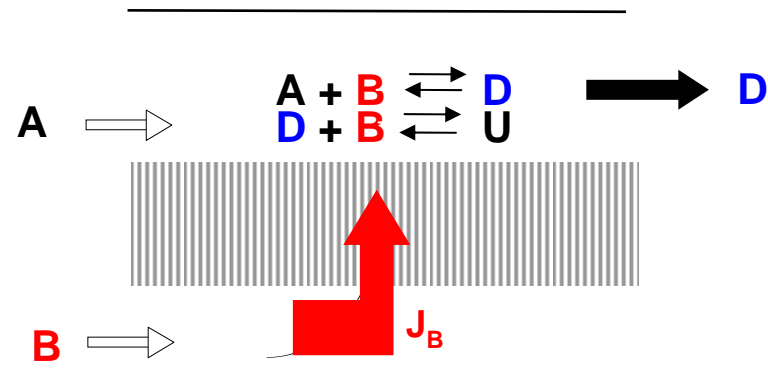


- enhanced conversion of reversible reactions

Advantages:

- „overcome“ equilibrium
- suppress unwanted subseq. reaction
- controlled reaction, hot spots
- cogeneration of electric power (EMR)

Controlled reactant dosing („Distributor“)



- dosing of critical reactants
- selectivity improvements
- cleaning of B from impurities

Challenges:

- reactor size/productability
- materials
- costs
- optimal dosing

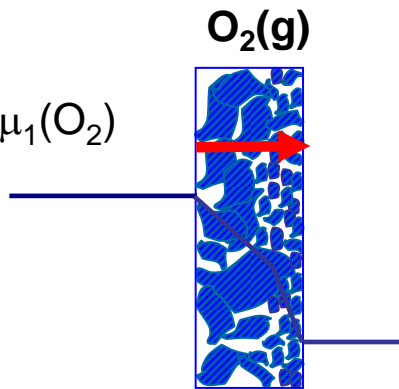


Electrochemical Membrane Reactor

Porous Membranes

- gaseous oxygen
- nonselective
- permselective microporous

- alumina
- silica
- zeolites

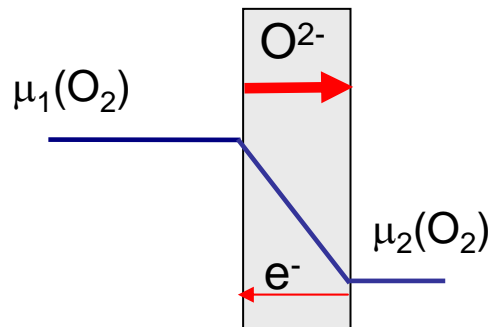


Ceramic Dense Membranes

- oxygen transfer as ion O^{2-}
- good permselectivity towards oxygen
- reactor efficiency limited by permeability (T!)

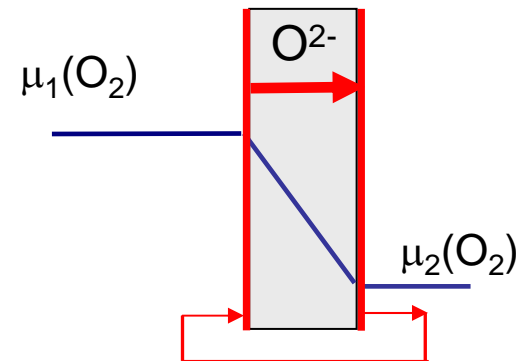
Mixed Ion Electron Conducting Membranes

- σ_{ion} and σ_{el} high
- internal circuit for electrons
- simple construction as reactor



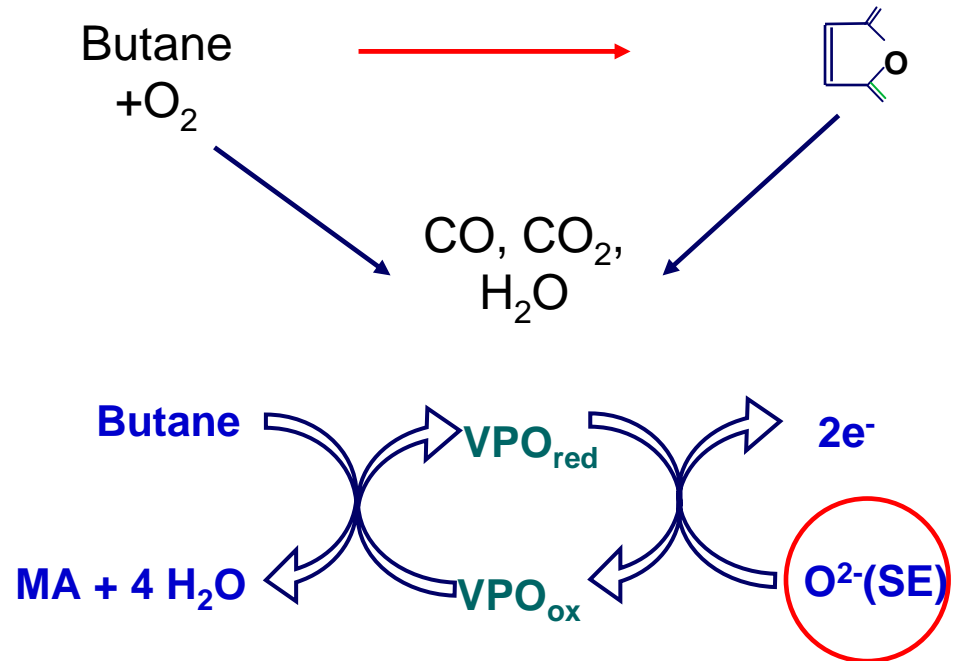
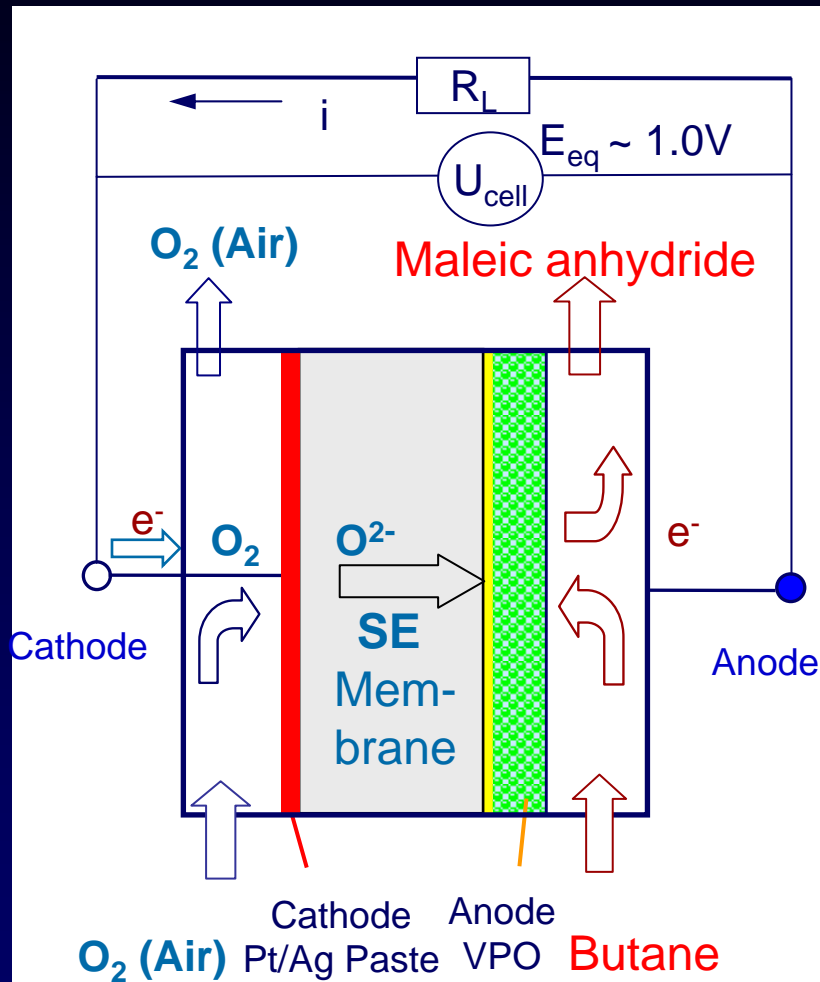
Oxygen Ion Conducting Solid Electrolytes (SE)

- σ_{ion} high and σ_{el} low
- external circuit for electrons
- complex construction





EMR in Butane Partial Oxidation

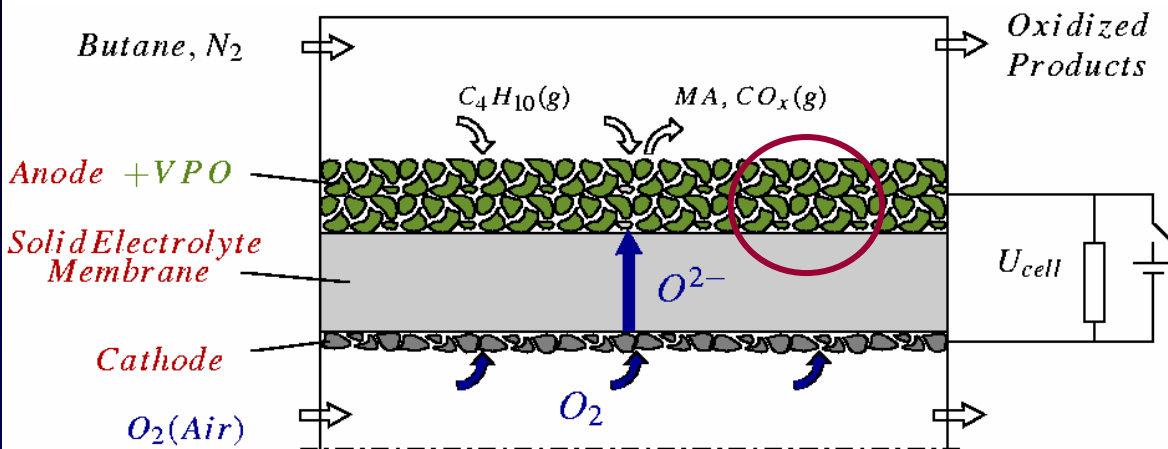


Electrochemical process:

- reoxidation of catalyst electrochemically
- + control of catalyst oxidation state
- + no gas phase oxygen
- + total oxidation suppressed



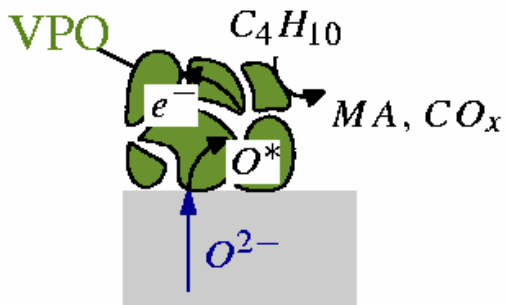
EMR Electrode Construction



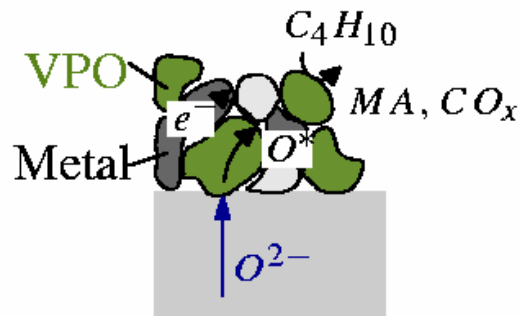
Advantages:

- no prior air separation units
- faradaic coupling of oxygen feed to cell current
→ forced periodic operation
- driving force $\Delta_R G \sim U_{cell}^0$
(fuel cell mode)
→ cogeneration of electricity

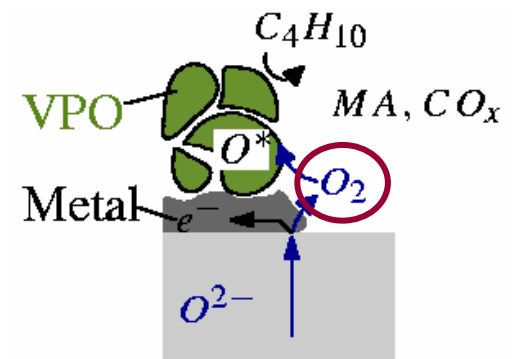
Optimal case: Anode mixed (O^{2-} and e^-) conducting



Composite anode



Present study:

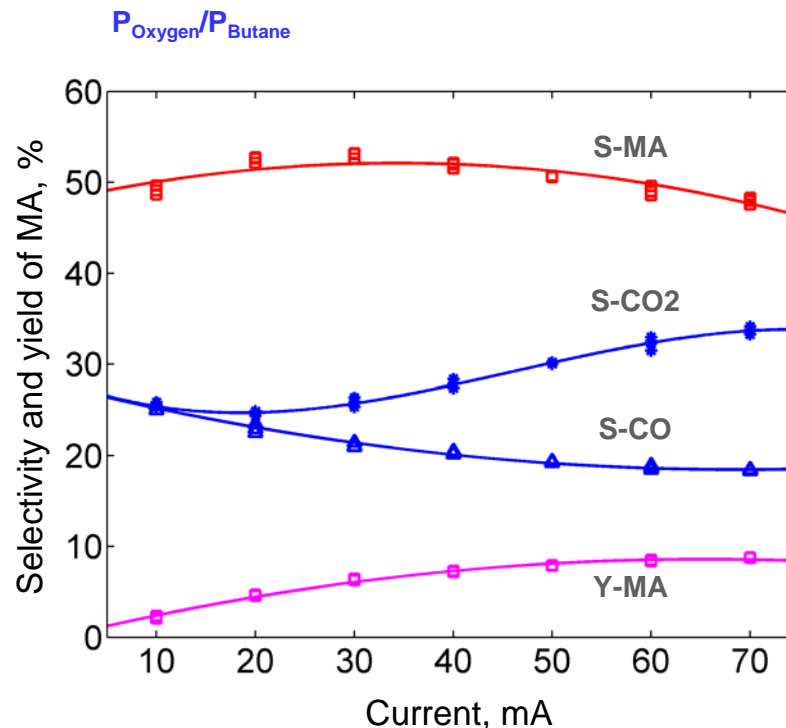
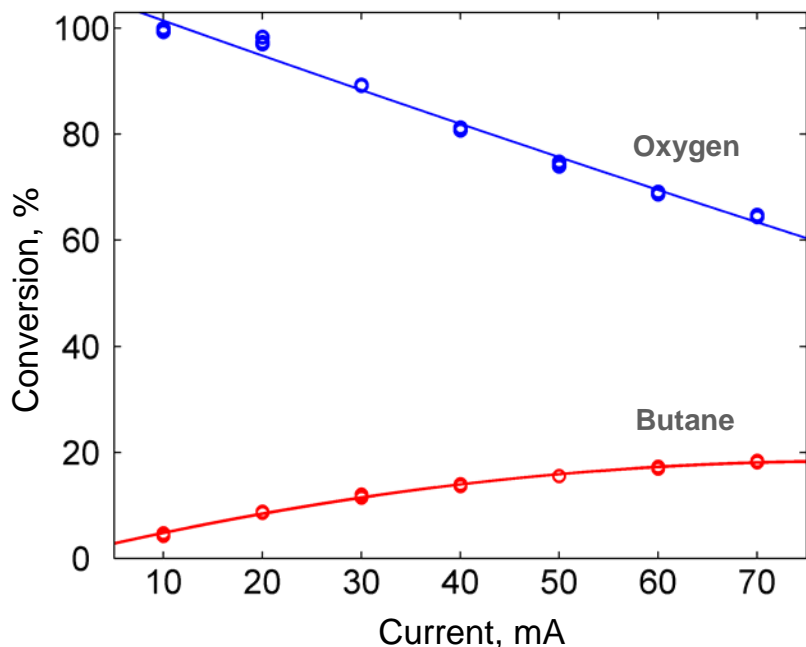
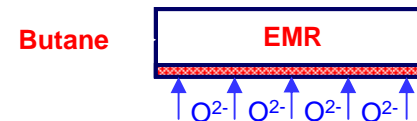




Current Effect in EMR

Experimental condition:

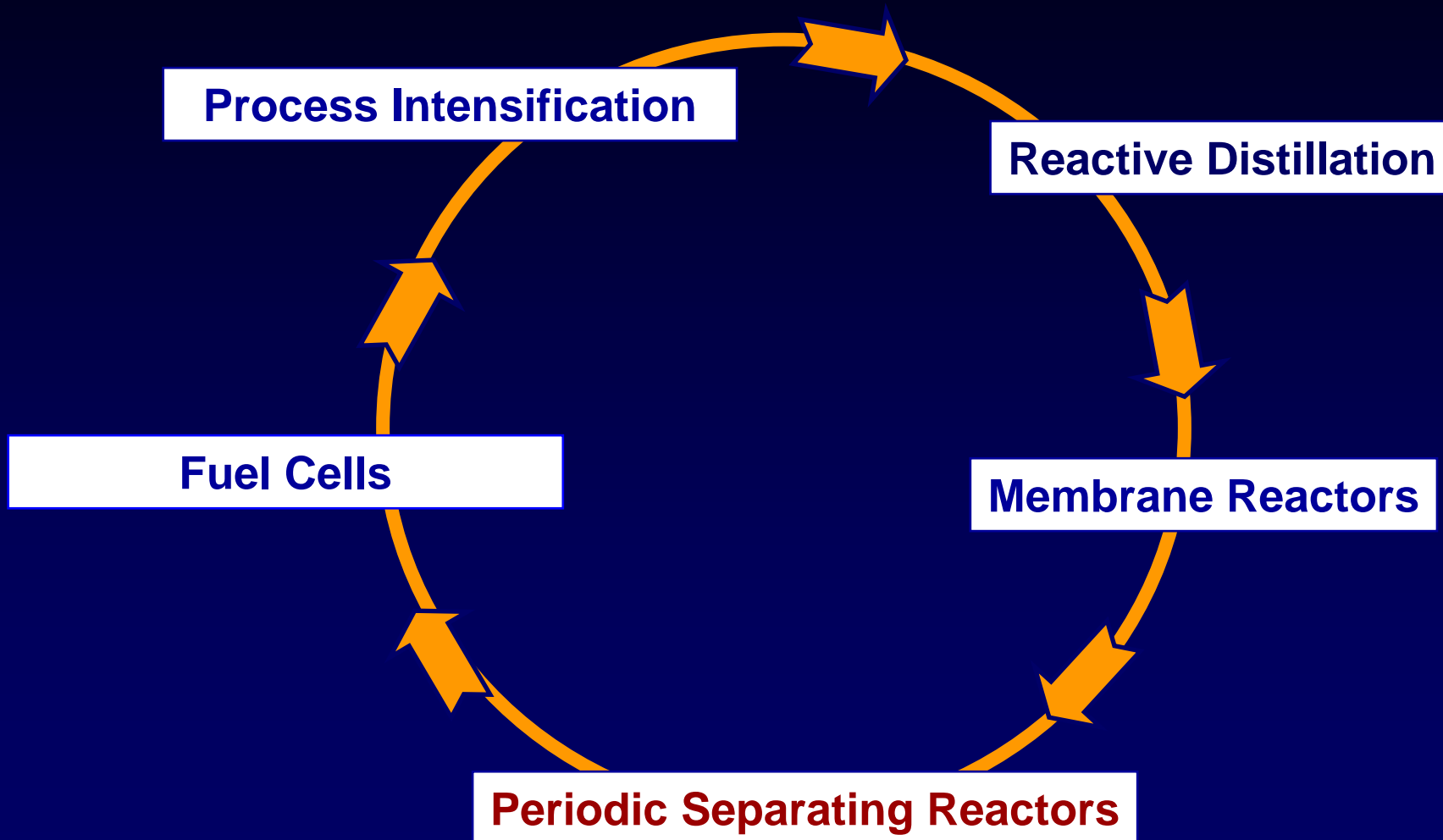
$T=480\text{ }^{\circ}\text{C}$; $P_{\text{Butane}}=0.55\text{ kPa}$; $F=35\text{ ml/min}$; $I=0.44\text{--}3.1\text{ mA/cm}^2$



- High current is favorable for butane conversion and MA yield
- S_{MA} has a maximum w.r.t. current

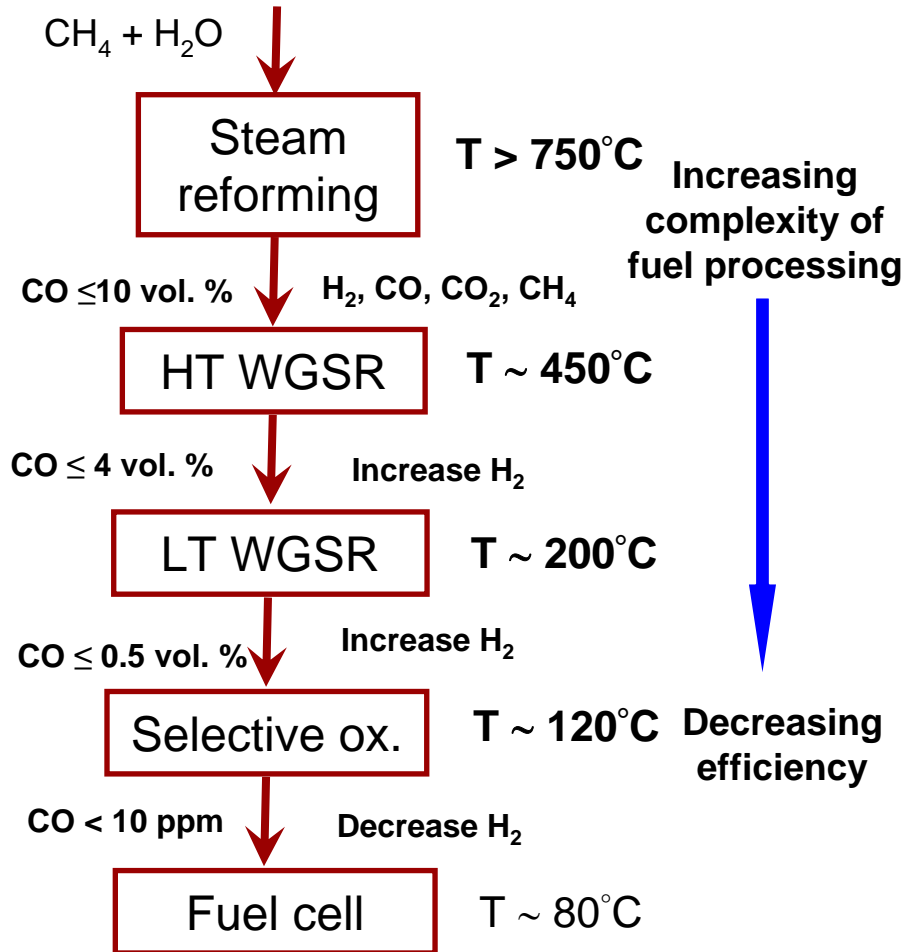


Integrated Catalytic Processes –Lecture Outline

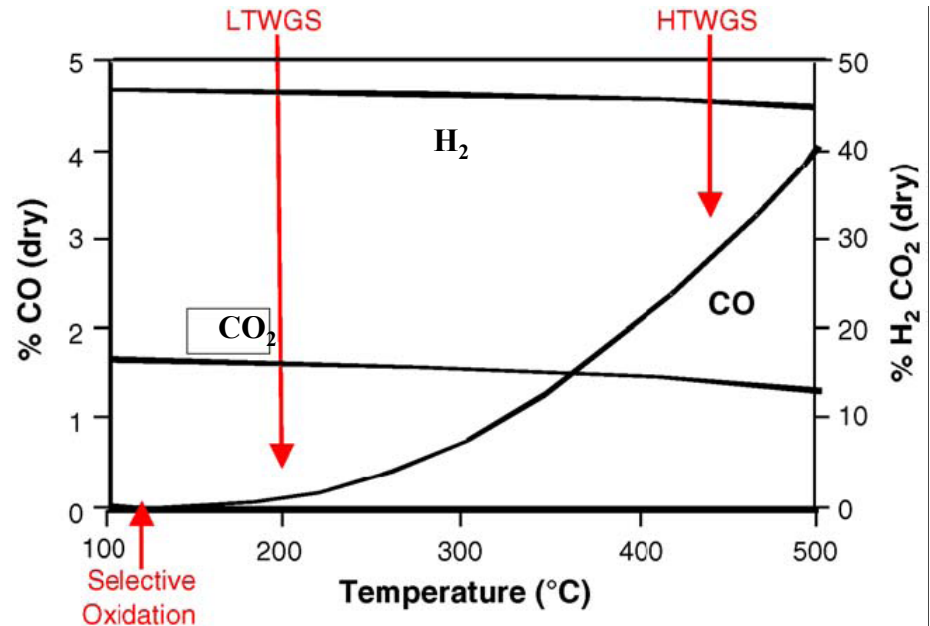




Water Gas Shift (WGS) Reaction



Equilibrium concentrations in WGS as a function of temperature

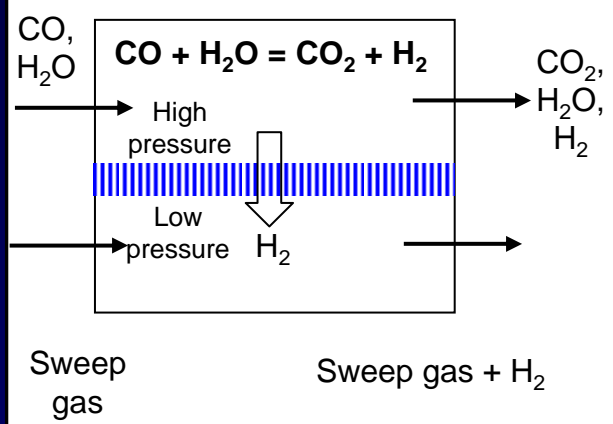




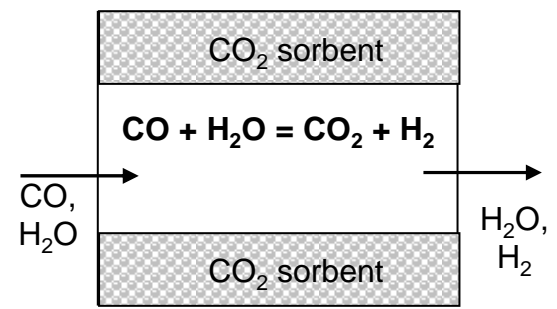
Hydrogen Purification- single step processes



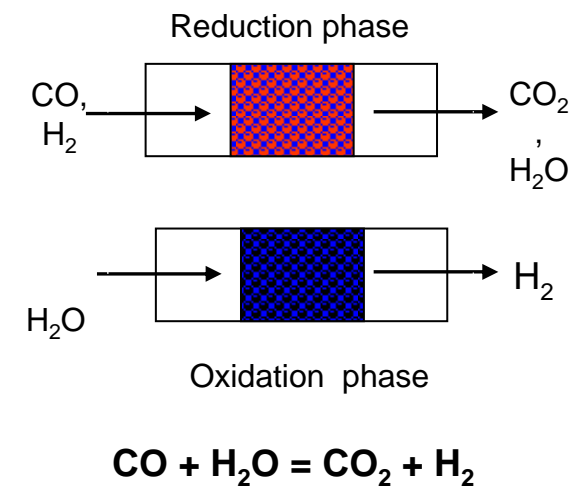
WGS with H₂-separating membrane



WGS with CO₂ capture



WGS with periodic separating reactor

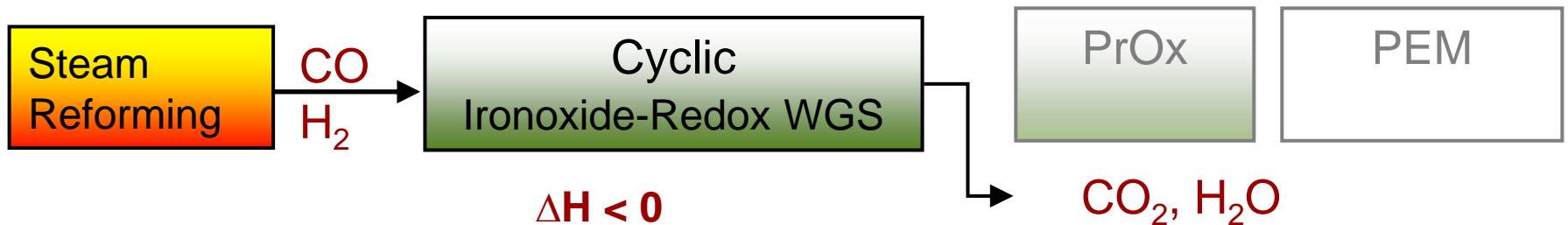




Periodic Separating Reactor

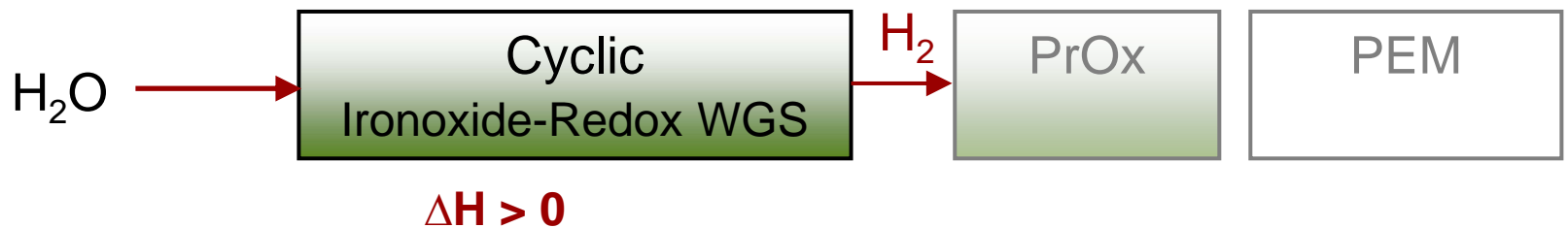


Phase 1: Reduction of Iron oxide
 $\text{Gas (CO, H}_2\text{)} + \text{Fe}_3\text{O}_4 \rightarrow \text{FeO}_x + \text{CO}_2 + \text{H}_2\text{O}$



Phase 2: Re-Oxidation with Steam
 $\text{H}_2\text{O} + \text{FeO}_x \rightarrow \text{Fe}_3\text{O}_4 + \text{H}_2$

Overall reaction
 $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$
 $\Delta H = -41 \text{ kJ/mol}$

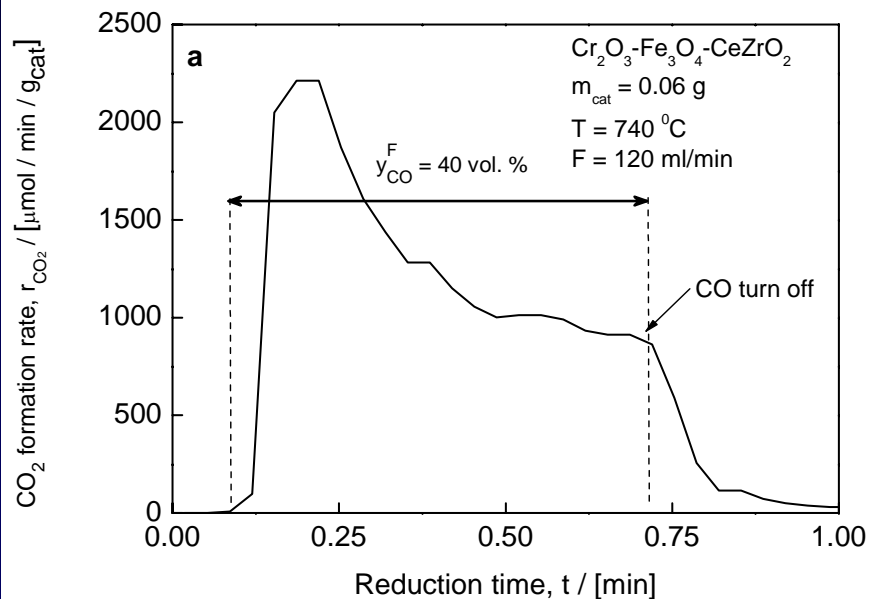




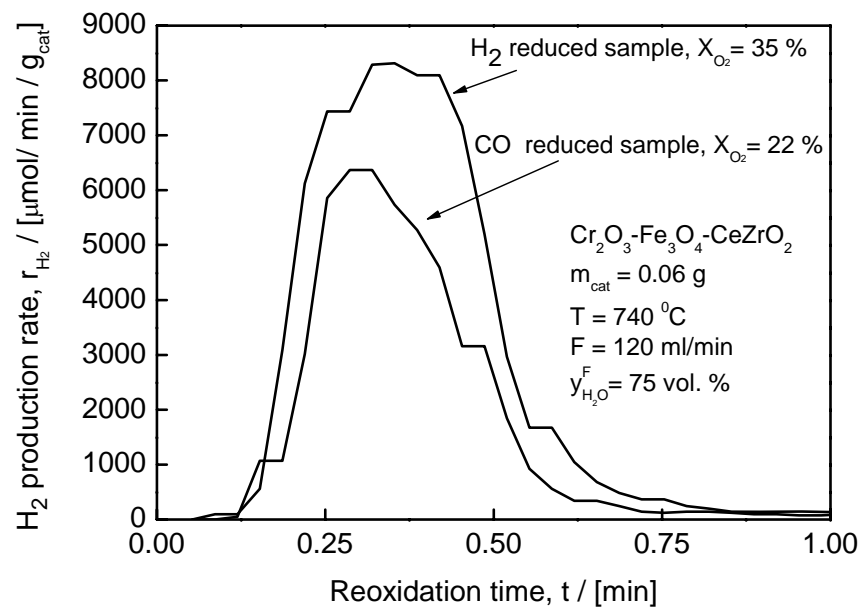
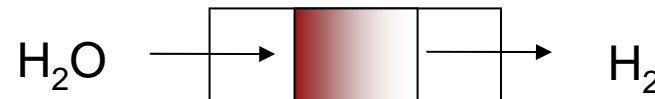
Feasibility of Cyclic WGS



Reduction with CO

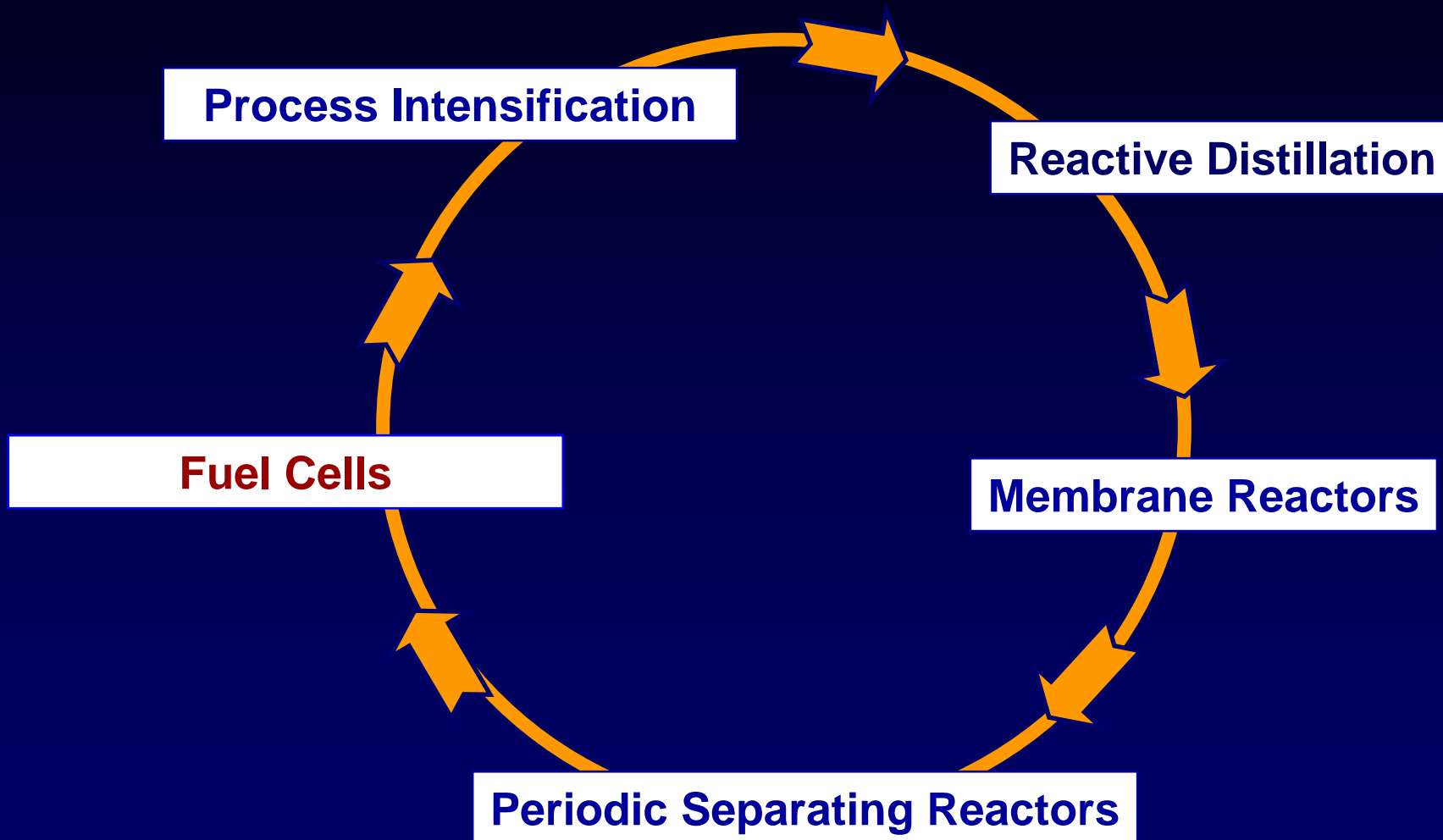


Re-Oxidation with H₂O





Integrated Catalytic Processes –Lecture Outline





HT Fuel Cells

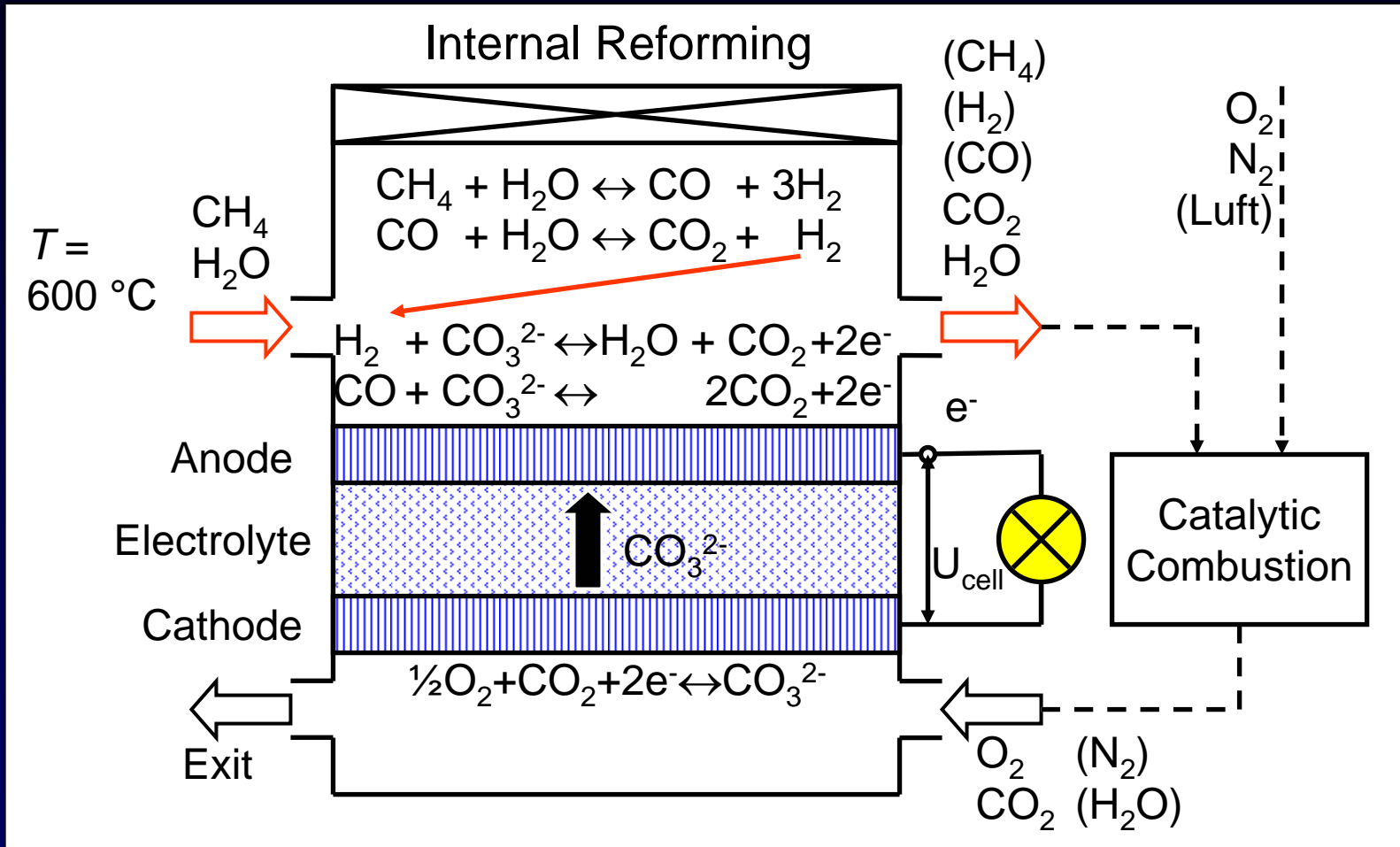
HotModule in Magdeburg University

- Developed by MTU CFC Solutions GmbH
- Start in October 2002
- Molten-Carbonate Fuel Cell (MCFC)
- Feed natural gas

HotModule bei der IPF in Magdeburg



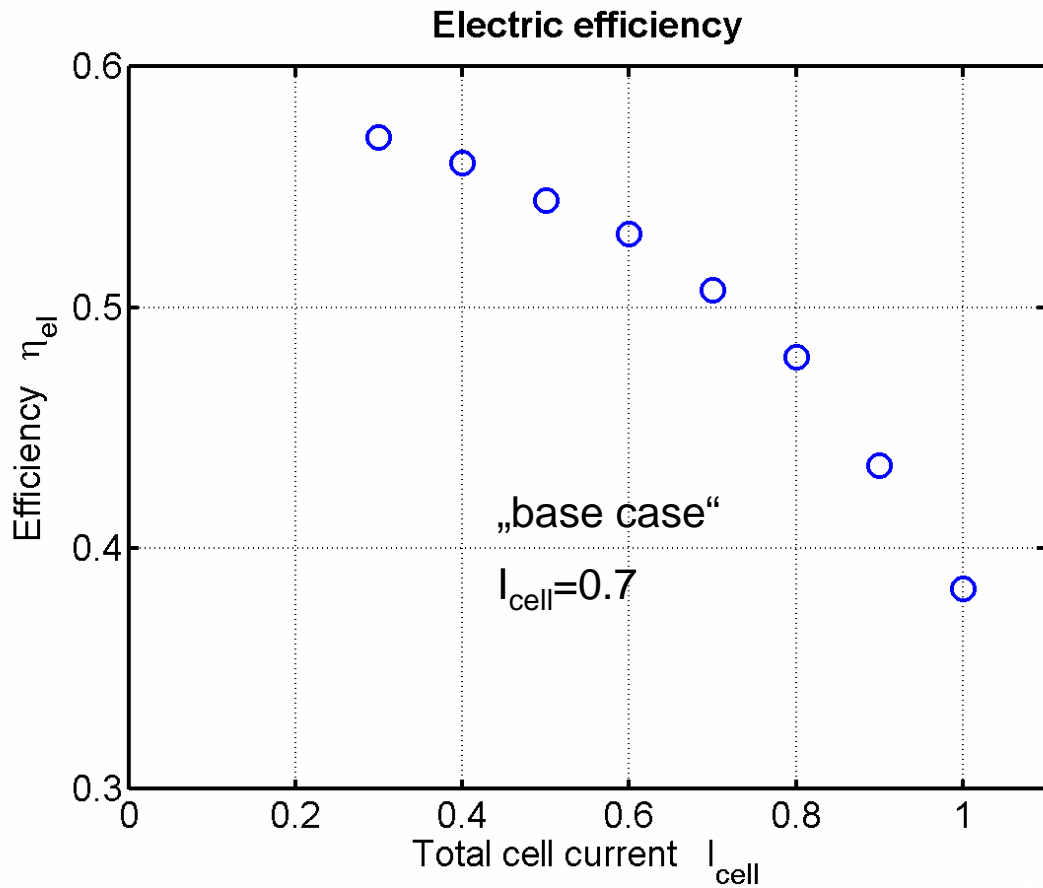
Optimized Internal Reforming in MCFC



- Mass coupling (reforming + WGS + electrochemical Oxidation)
- Energetical coupling (ΔH_r)

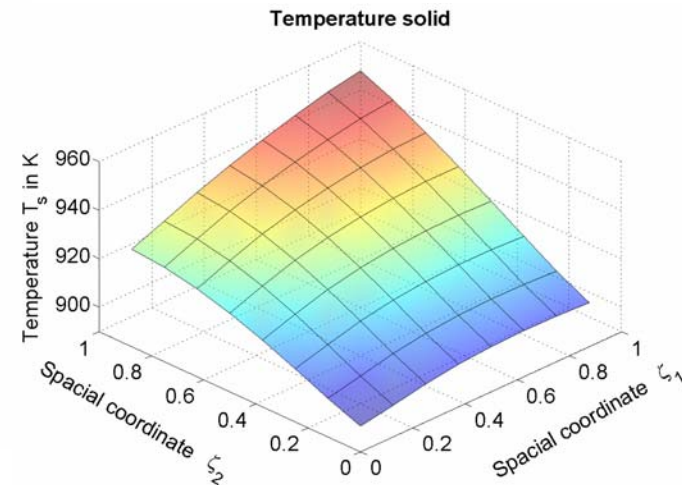
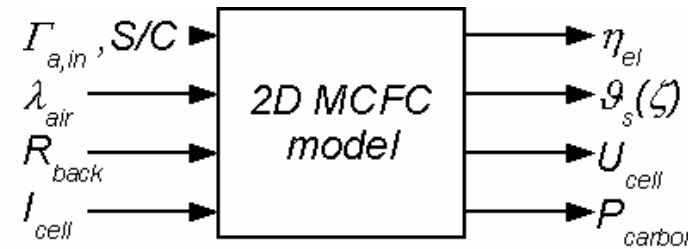


Optimization of operating conditions



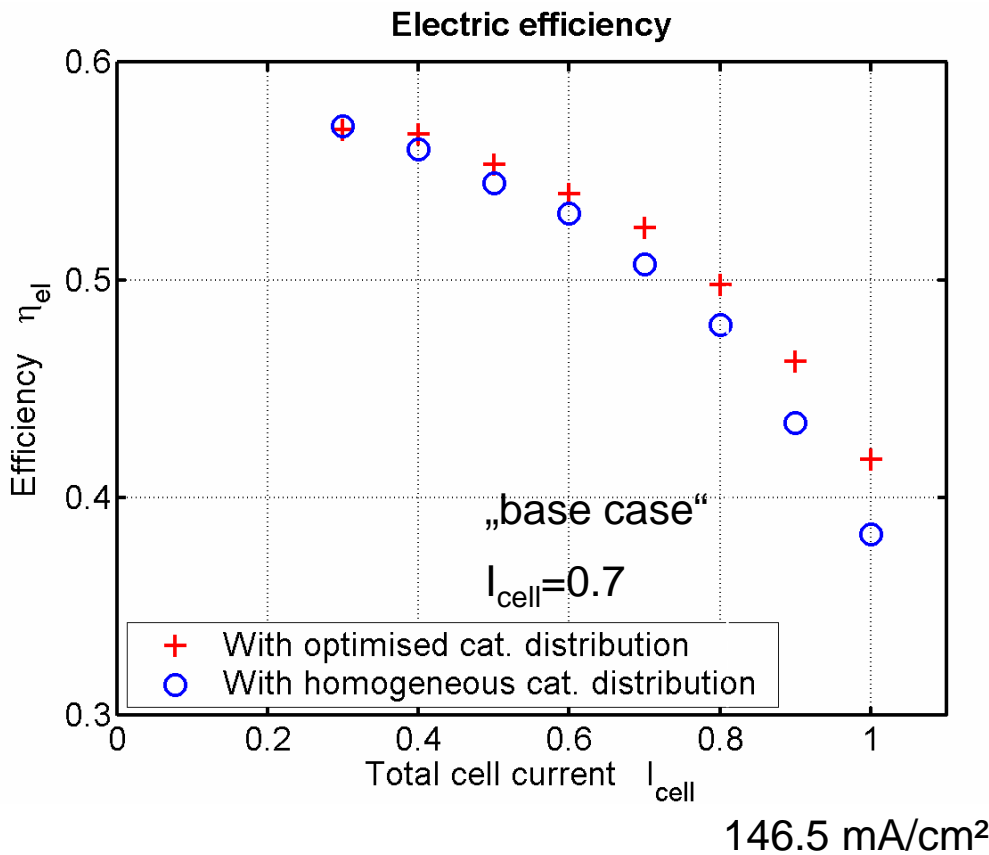
146.5 mA/cm²

$$\eta_{el}(\Gamma_{a,in}, S/C, \lambda_{air}, R_{back}) \rightarrow \max!$$

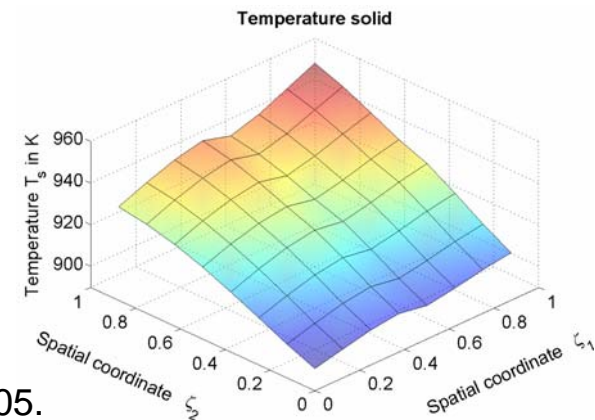
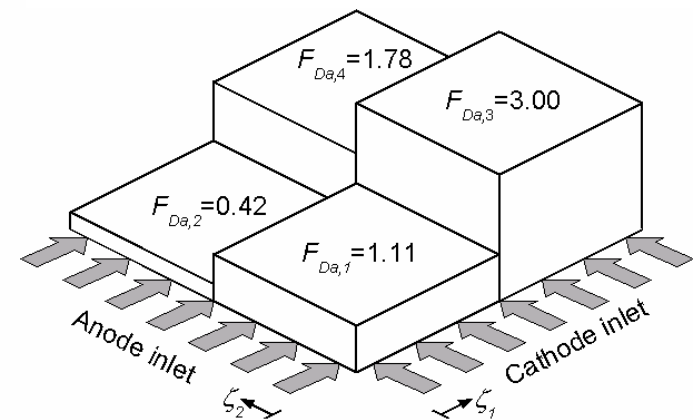




Optimization of reforming catalyst distribution



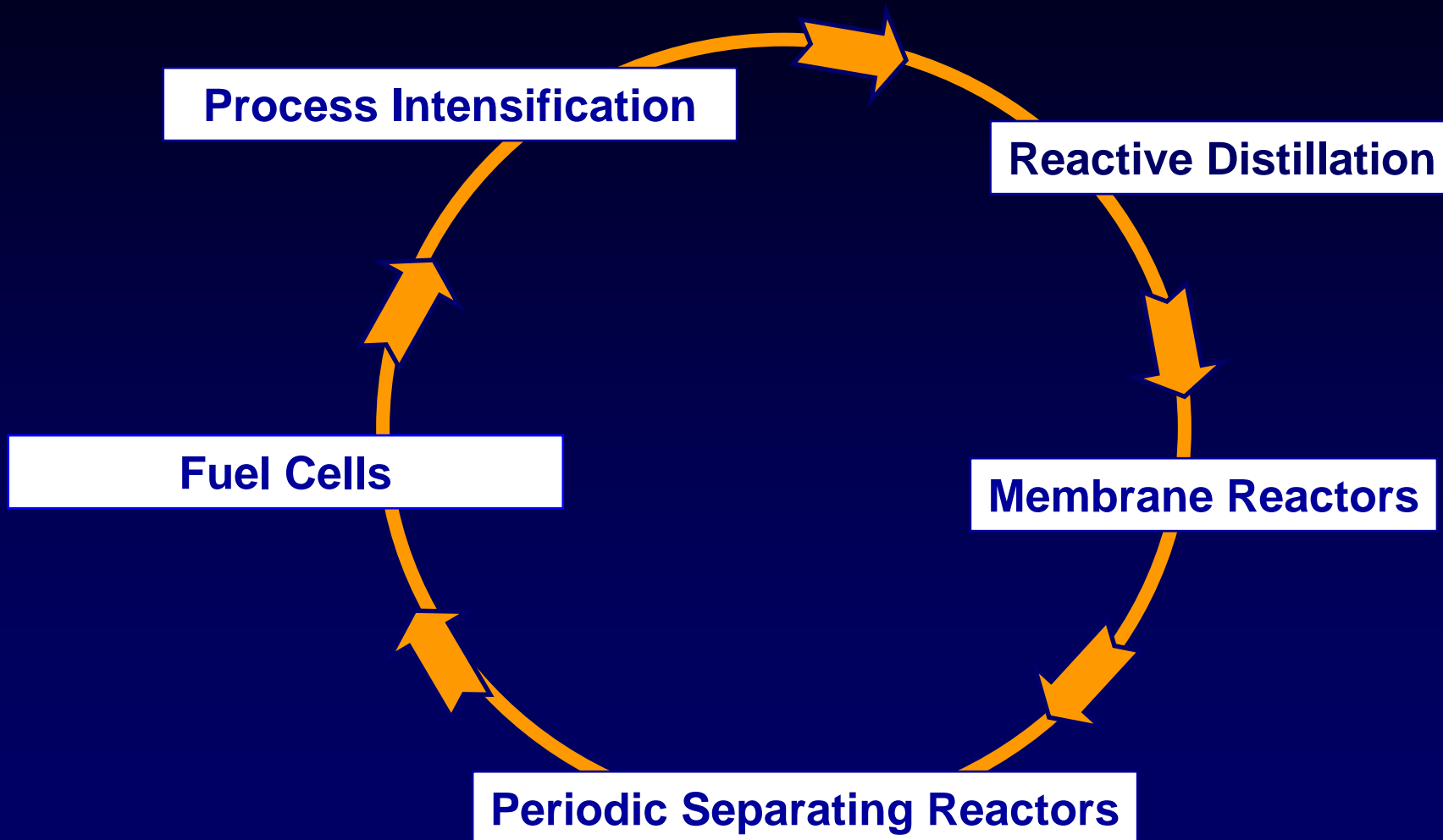
$$\eta_{el}(\Gamma_{a,in}, S/C, \lambda_{air}, R_{back}, F_{Da}) \rightarrow \max!$$



P. Heidebrecht, Fortschritt-Berichte, VDI-Verlag, Düsseldorf, 2005.
P. Heidebrecht, K. Sundmacher, Ind. Eng. Chem. Res.44 (10), 2005



Integrated Catalytic Processes –Lecture Outline





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