Countercurrent operation in catalytic hydrotreating – The impact of/on kinetics

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EUROKIN

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www.dct.tudelft.nl/ce

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Literature

- R. Krishna and S. T. Sie
  Strategies for multiphase reactor selection
  Chem.Engng.Sci. **1994**, 49, 4029-4065.
- B. W. van Hasselt, P. J. M. Lebens, H. P. Calis, F. Kapteijn, S. T. Sie, J. A. Moulijn and C. M. van den Bleek
  A numerical comparison of alternative three-phase reactors with a conventional trickle-bed reactor. The advantages of countercurrent flow for hydrodesulfurization
  Chem.Engng.Sci. **1999**, 54, 4791-4799.
- J.W. Gosselink
  Sulfide Catalysts in refineries
  CATTECH **1998**, 2(2), 127-144

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Countercurrent studies TUD

- Paul Lebens - Internally finned monoliths (IFM)
  - Hydrodynamics, flooding, mass transfer, modelling
- Bastiaan van Hasselt - Three-levels of Porosity (TLP)
  - Hydrodynamics, mass transfer, modelling
- Achim Heibel – Monoliths various geometries
  - Hydrodynamics, mass transfer, RTD, modelling, hydrogenation
- Tilman Schildhauer – Structured catalysts
  - Reactive stripping-esterification, modelling

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What will be covered.....

Countercurrent operation
- Why?
- Where?
- How?

Qualitative exploration

Cases
- Reactive stripping - equilibrium limitation & selectivity
- Modeling simple kinetics HDS – mass transfer & inhibition
  - Athena Visual Studio example
    - Co-current PFR – Initial Value problem
    - Countercurrent – Boundary Value problem
- Concluding remarks

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Countercurrent operation

- Equilibrium limitations - maintaining driving force
  - Removal product, shift equilibrium
- Increase productivity – avoid competitive adsorption, secondary reactions
  - Removal inhibiting or deactivating products

- Two-phase operation (GL, LL)
  - Catalytic distillation
  - **Reactive stripping**
  - Catalytic operation

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Where / when do reactive stripping?

Removal of reaction product (byproduct) by means of an inert gas / vapour:

- to 'shift' equilibrium or overcome azeotropes
- to avoid inhibition/catalyst deactivation
- for in-situ cooling by solvent evaporation
- **when reaction and separation conditions (p,T) don't match!**
- e.g. high boiling esters/ethers, polyesters, bisphenol A (Sinopec/Lummus), transesterifications

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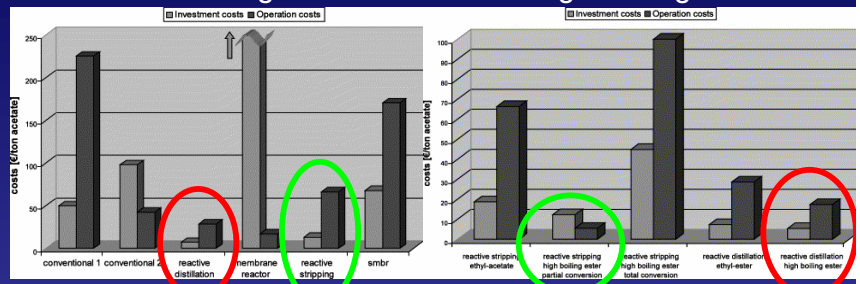
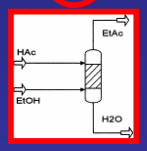
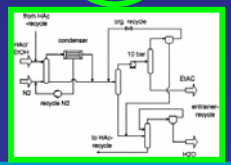
Reactive distillation vs. stripping

Low boiling ester | High boiling ester





from Schembecker and Tlatlik, Chem. Eng. Proc. 42 (2003), 179 - 189



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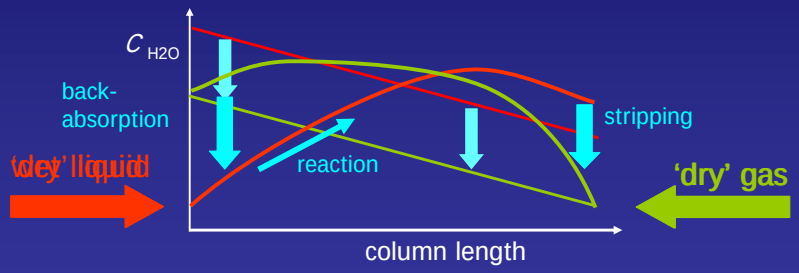
Counter- vs. co-current operation I

- Usually countercurrent operation is more favorable in separation processes
- But with very low entrance concentrations internal loop may occur (reaction)



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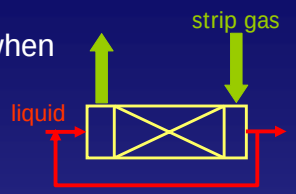
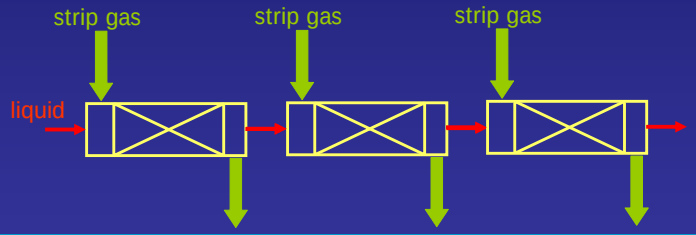
Counter- vs. co-current operation II

- Internal loop no problem, when liquid is recycled partially:



- If necessary, cross flow (cocurrent operation):



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Hydrodynamics essential

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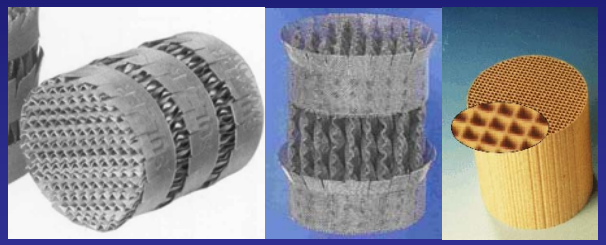
Creating G-L (and L-S) - interfaces

- Maximize G-L (L-S) mass transfer, minimize pressure drop, **balance rates of processes**

→ High Specific surface areas, high voidage

→ **Structured catalysts!**



Sulzer DX (coated with catalyst)

Sulzer katapak-S (filled with catalyst)

Monolith (coated with catalyst)

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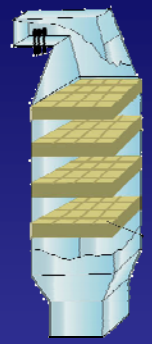
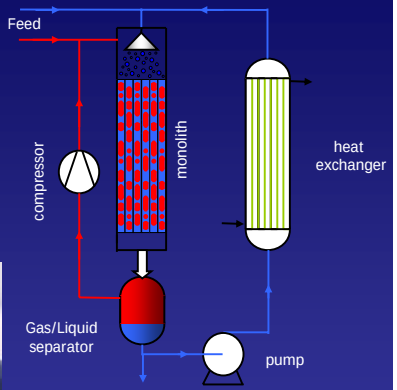
Application of monoliths



deNOx

Removal of VOCs



Three Phase monolith Loop Reactor

Heiszwolf et al, CES, 2001

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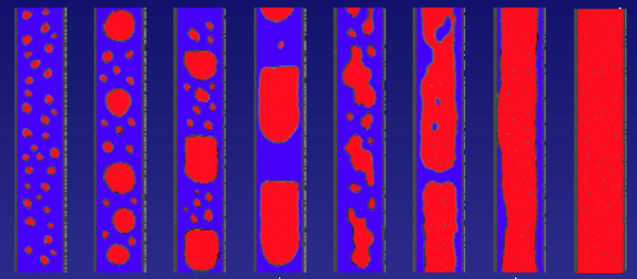
Two-phase flow patterns in capillaries



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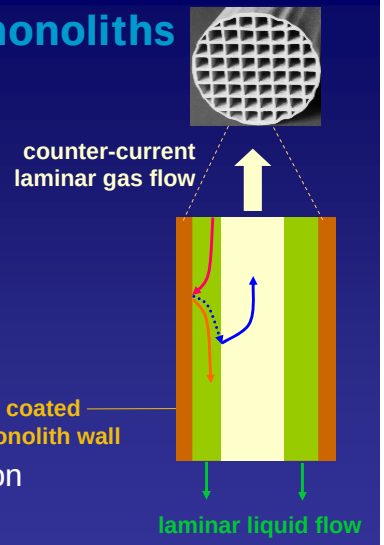
Reactive stripping in monoliths

- Two-phase film flow in monolith channels ($d \geq 2$ mm)
- Low gas-liquid interaction
  → low pressure drop
  → decoupling of mass transfer and hydrodynamics
- No static hold-up
- Issues: flooding, liquid distribution



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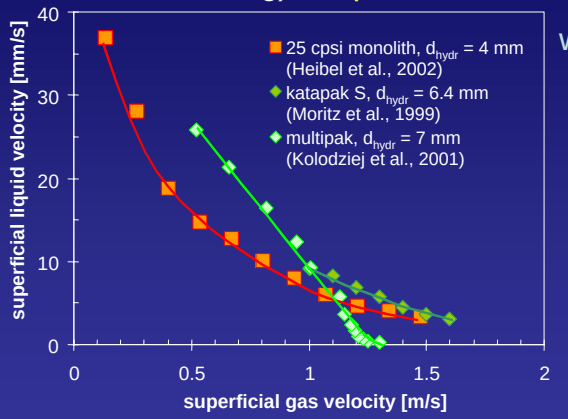
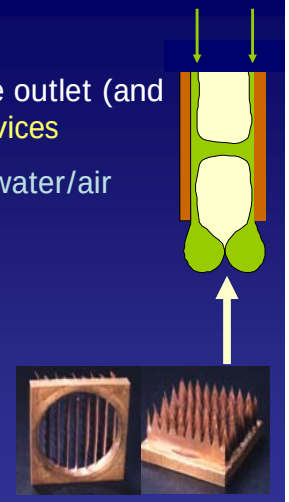
Flooding I

Flooding in monoliths starts mostly at the outlet (and due to bad stacking) → special outlet devices





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A.K. Heibel, F. Kapteijn, J. A.Moulijn, *Ind. Eng. Chem. Res.*, 2002, 41, 6759

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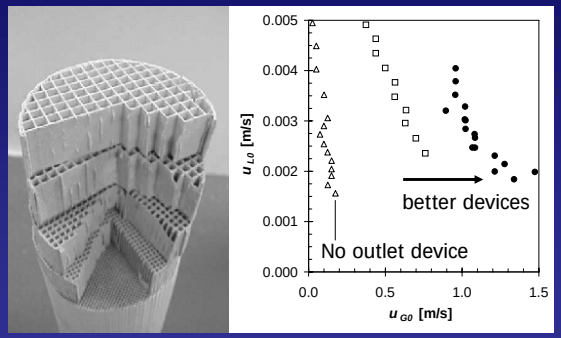
Flooding II

New inlet/outlet design shifts flooding limits!



Flooding limits of 50 cpsi monolith (d_{hydr} = 3 mm) in countercurrent operation

water/air

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T. J. Schildhauer, F. Kapteijn and J. A. Moulijn *Ind.Eng.Chem.Res.* **2005**, *44*, 9556-9560.

Heibel and Jamieson Patent WO03040847, 2003

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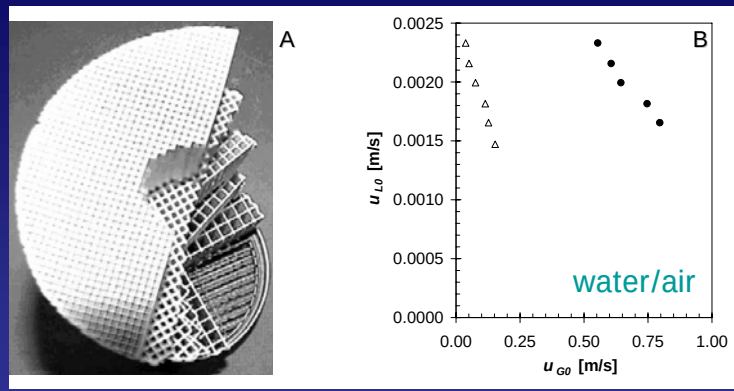
Flooding III



- Optimised outlet device allows countercurrent operation in 200 cpsi monoliths (d_{hydr} = 1.25 mm!)

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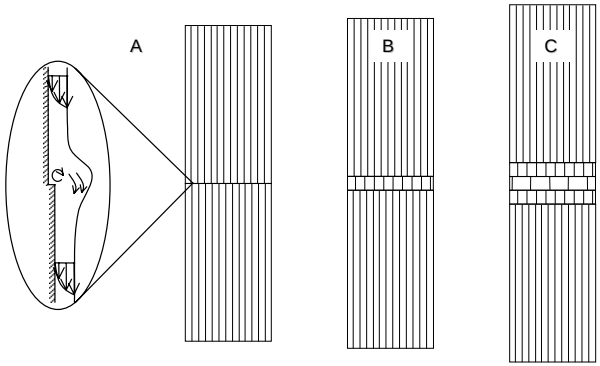
Improved stacking



Better way of stacking monoliths might improve mixing and therefore increase G-L mass transfer without causing flooding

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T. J. Schildhauer, F. Kapteijn and J. A. Moulijn
Ind.Eng.Chem.Res. **2005**, *44*, 9556-9560.
Heibel and Jamieson Patent WO03040847, 2003

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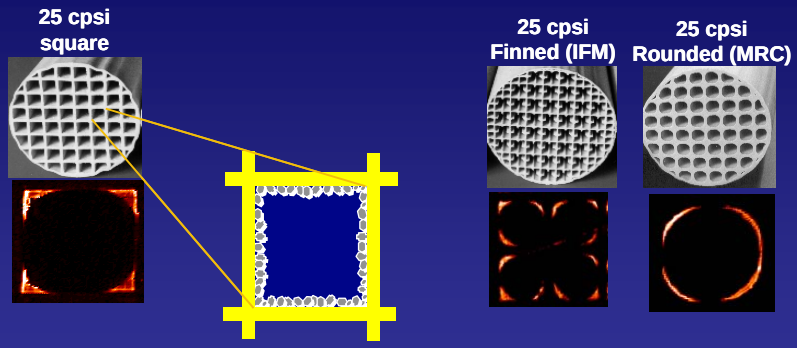
Film flow monoliths with modified geometries

Magnetic Resonance Imaging (MRI)



Channel geometry influences flow distribution and RTD!

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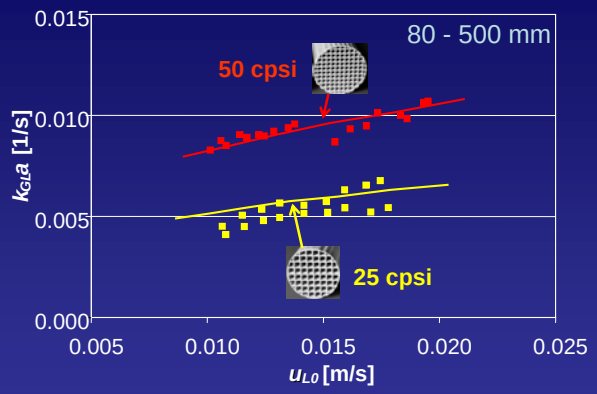
G-L mass transfer – developed flow



Higher *S*/*V* ratio results in better mass transfer

Slight increase with liq. flow due to increased G-L interfacial area

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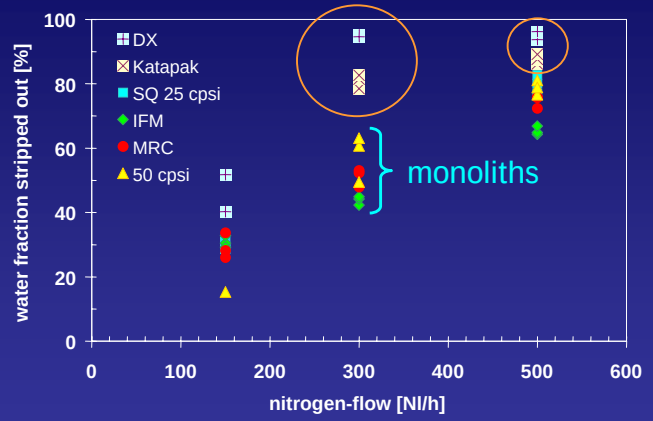
Non-reactive stripping experiments

(160°C, 4 bar, 2m column length, water/ester/cumene)



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Intermediate conclusion I

- Film flow monoliths suited for countercurrent operation
- Flooding performance and liquid distribution can be optimised
- Structured distillation packings show better G-L mass transfer than monoliths with fully developed film flow
- Higher mass transfer rates (and narrower RTD) expected from mixing between stacked monolith pieces

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Model reaction - Esterification

Octanol + Hexanoic acid ↔ Ester + Water

- Solid acid catalyzed (zeolite BEA) reaction:
  - conversion is equilibrium limited
  - water 'inhibits' the catalyst active sites
  - ⇒ water removal by stripping
- Acid itself catalyses reaction
- Cumene as solvent (75%)

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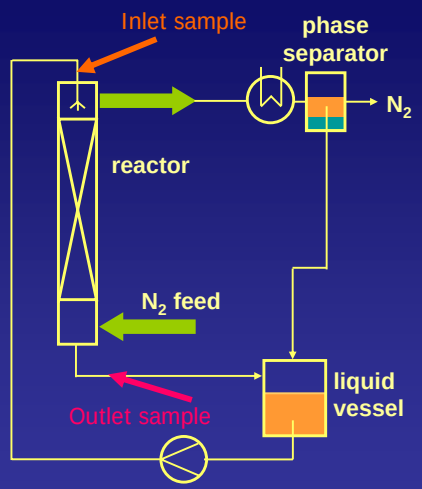
Experiments in pilot-scale plant



$L_{reactor}$	2	m
$\varnothing_{column}$	5	cm
V_{liquid}	15	l
P	4	bar
T	160	°C
liquid feed	25	kg/h
gas feed	500	Nl/h
C_{acid}	12	mol-%
$C_{alcohol}$	12	mol-%

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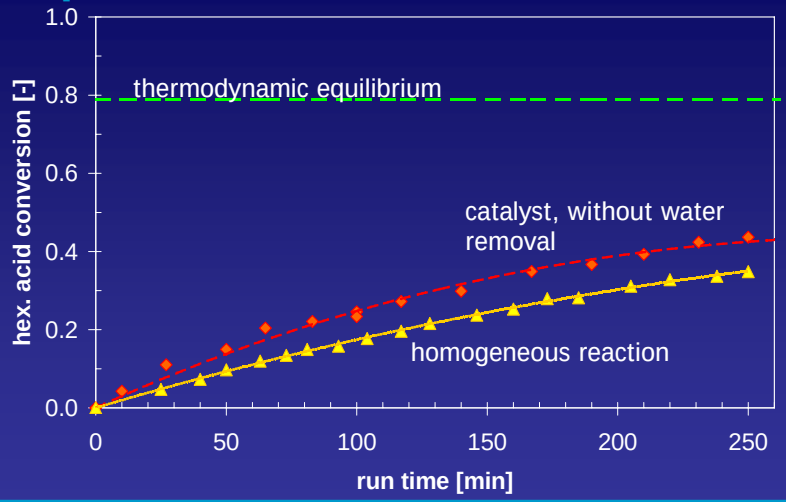
Experimental results



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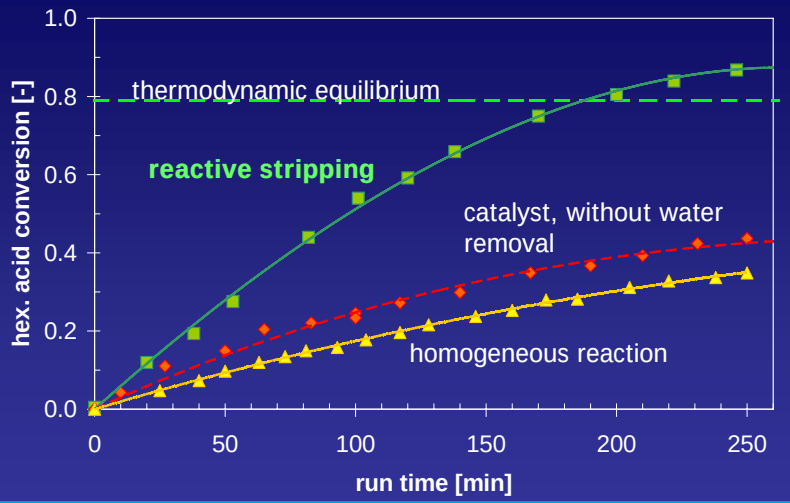
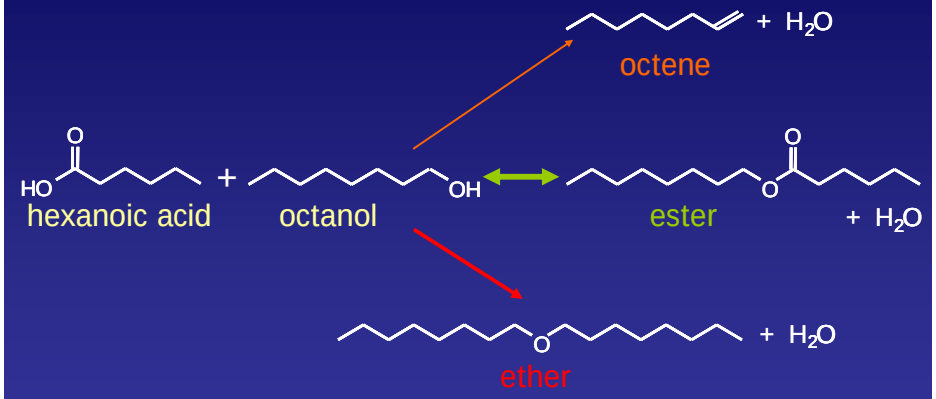
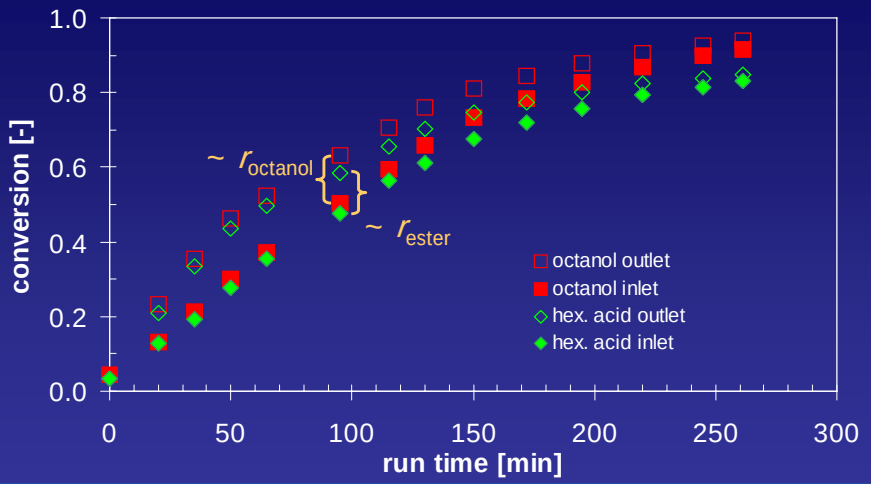
It works!



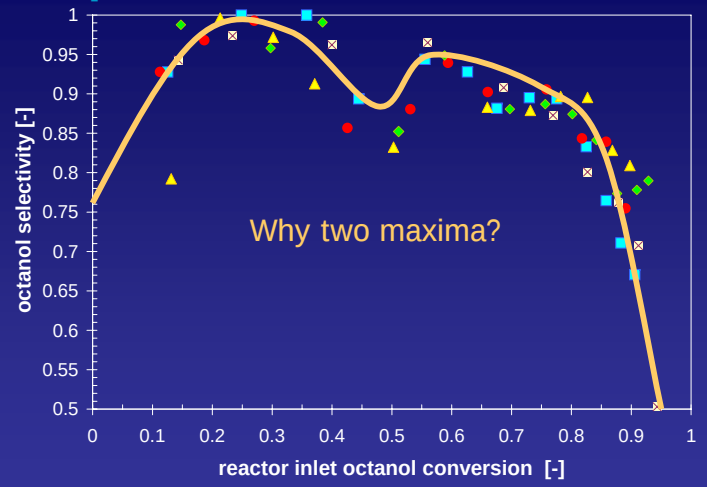
Model reaction – Side reactions



Selectivity



Comparison inst. selectivities (5 internals)



Kinetic model (Beers et al., $K_{ads,\ H2O}$ by I. Hoek)

equilibrium limitation

Esterification

$$r_{esterification} = \frac{k_c \cdot C_{acid} \cdot C_{cat} \cdot [1 - \frac{C_{ester} \cdot C_{water}}{K_{eq} \cdot C_{acid} \cdot C_{alcohol}}]}{[1 + (...) + K_W \cdot C_{water}]}$$

water adsorption

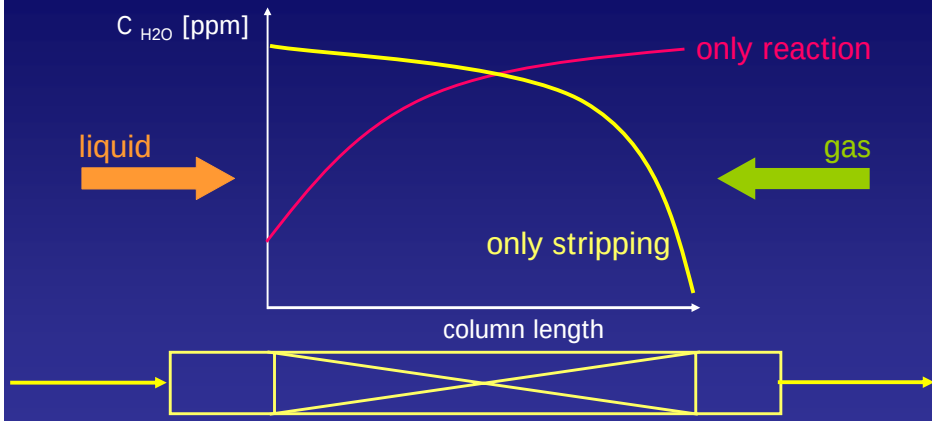
Etherification

2nd order

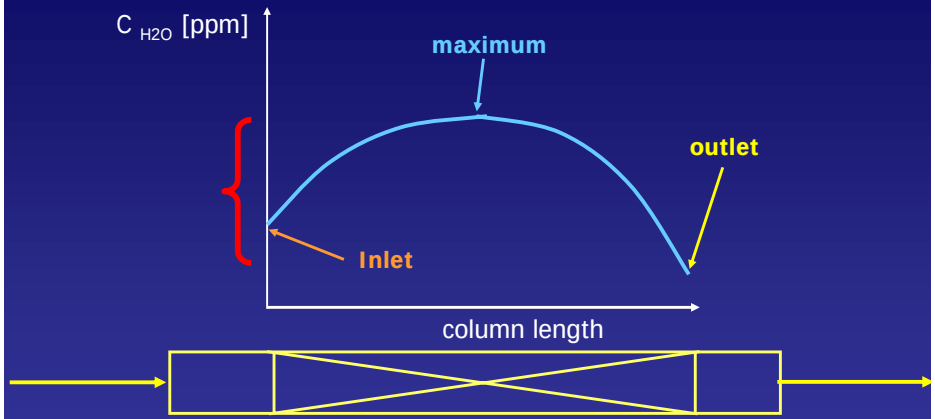
two sites involved

$$r_{etherification} = \frac{k_A \cdot C_{alcohol}^{2} \cdot C_{cat}}{[1 + (...) + K_W \cdot C_{water}]^{2}}$$

Column profile water concentration



Column profile water concentration



Intermediate conclusions II

- Reactive stripping can intensify processes
- Film flow monoliths are suitable reactor internals
- Selectivities can be explained qualitatively from interplay between kinetics and mass transfer

Countercurrent operation

- Equilibrium limitations - maintaining driving force
  - Removal product, shift equilibrium
- Increase productivity – avoid competitive adsorption, secondary reactions
  - Removal inhibiting or deactivating products

- Two-phase operation (GL, LL)
  - Catalytic distillation
  - Reactive stripping
  - **Catalytic operation**

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Model case study

- Co-current versus counter-current – plug flow
- Gas-Liquid system (solid catalyst) – hydrotreating
  - HDS, isothermal
  - Gas-liquid mass transfer
  - Conditions:
    - 638K, 80 bar, 400 mol/m^3, 352 mol H_2/s, 432 m^3
    - Pure hydrogen feed, inlet liquid no hydrogen
  - Kinetics
    - First order in both reactants
    - With & without inhibition

$$r = \frac{k c_{H_2} c_S}{1 + K_S c_S + K_{H_2S} c_{H_2S}}$$

v.Hasselt, Lebens *et al.* Chem.Engng.Sci. 54 (1999) 4791-4799

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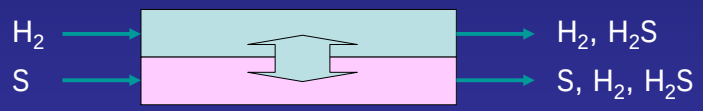
Co-current

- Effect mass transfer
  - No inhibition
  - Only H_2S inhibition
  - H_2S and organics inhibition



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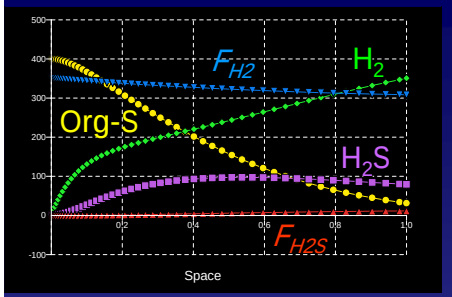
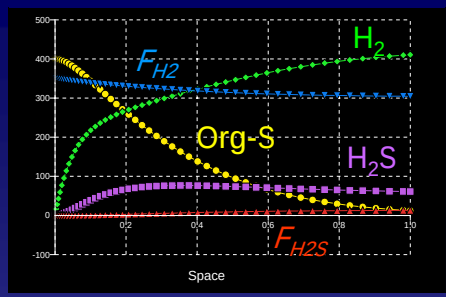


$k_La = 5*10^{-4}\ s^{-1}$



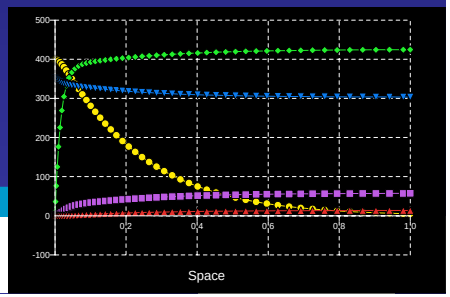
$k_La = 1*10^{-3}\ s^{-1}$

Co-current

- mass transfer
- no inhibition

$k_La = 5*10^{-3}\ s^{-1}$

$k = 10^{-6}$ $K_{H2S} = K_S = 0$



Changing order
Hydrogen availability

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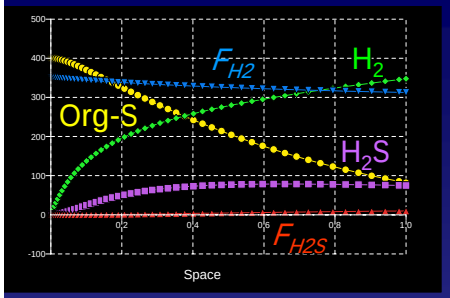
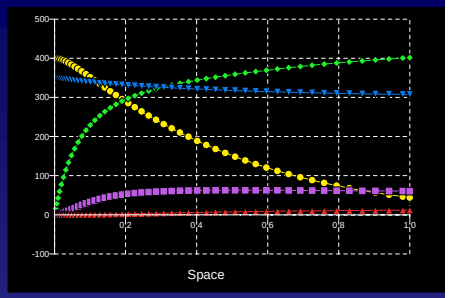


$k_La = 5*10^{-4}\ s^{-1}$



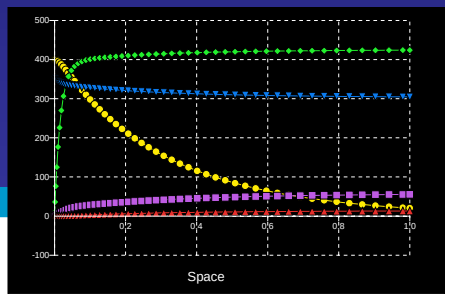
$k_La = 1*10^{-3}\ s^{-1}$

Co-current

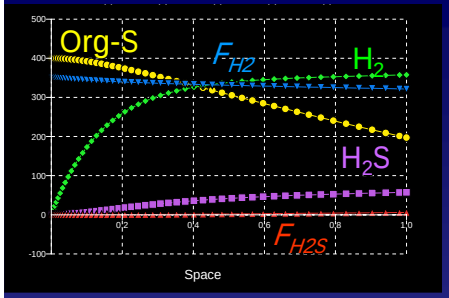
$k_La = 5*10^{-3}\ s^{-1}$

- mass transfer
- H_2S inhibition

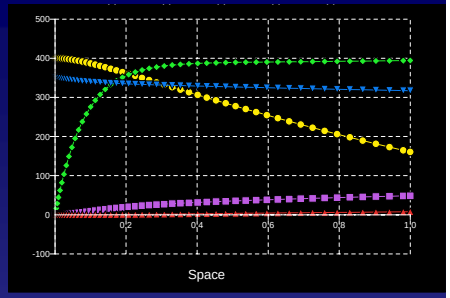
$k = 10^{-6}$ $K_{H2S} = 1.09*10^{-2}$ $K_S = 0$



Changing order to 0
Lower conversion



$k_La = 5*10^{-4}\ s^{-1}$



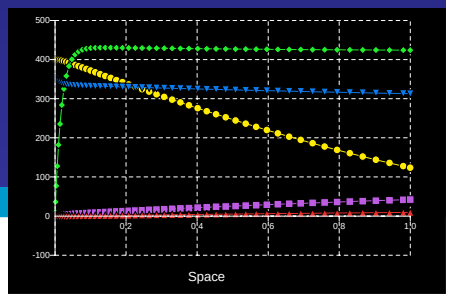
$k_La = 1*10^{-3}\ s^{-1}$

Co-current

$k_La = 5*10^{-3}\ s^{-1}$

- mass transfer
- H_2S, Org-S inhibition

$k = 10^{-6}$ $K_{H2S} = K_S = 1.09*10^{-2}$



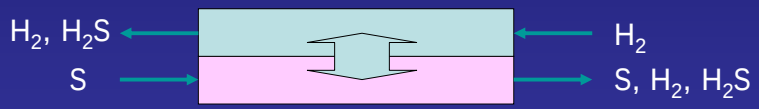
Order 0 to negative
Low conversions

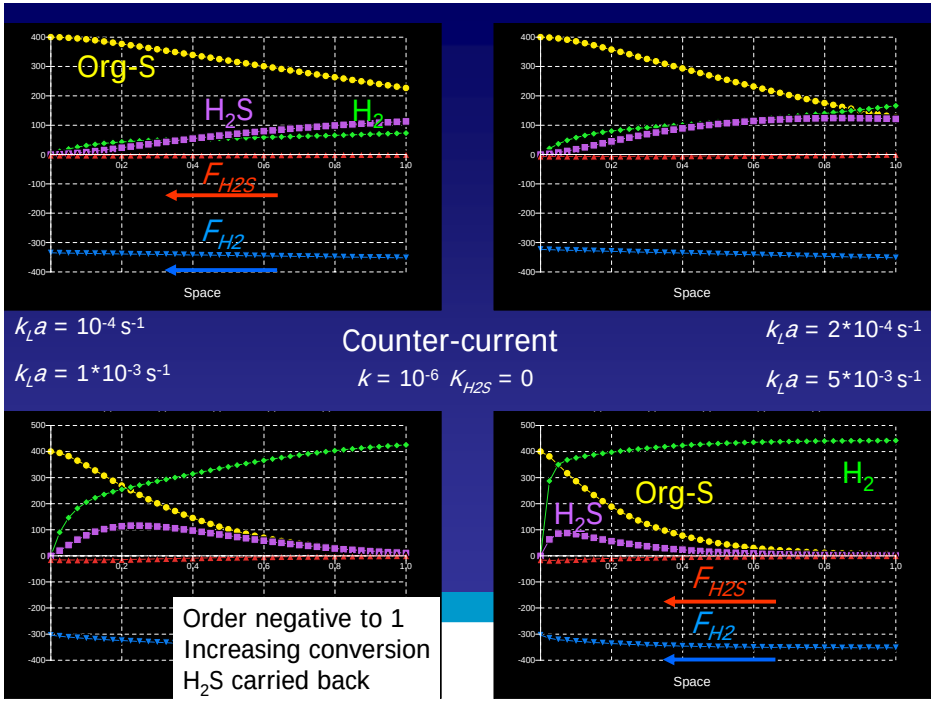
Co-current operation

- Inhibition
  - Lowers conversion
  - Change from apparent 1st to 0th (neg.) order
- Mass transfer improves conversion
  - apparent reaction order increases with k_La
  - Poor mass transfer yields negative order

Counter-current

- Effect mass transfer
  - No inhibition
  - Only H_2S
  - Both H_2S and reactant





k_La = 10^{-4} s^{-1}

k_La = $1*10^{-3}$ s^{-1}

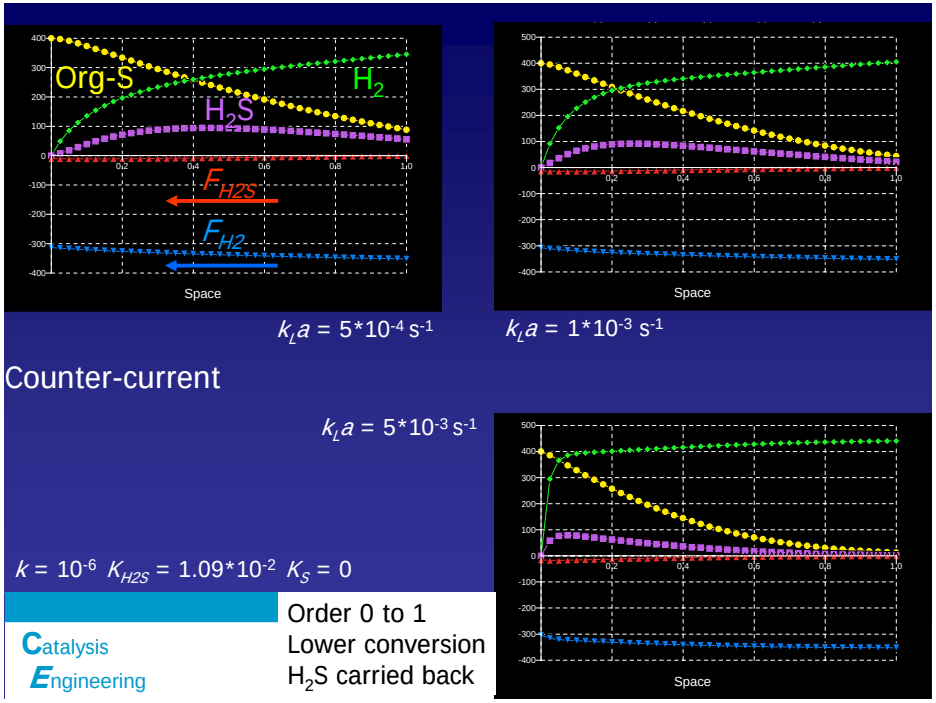
Counter-current

k = 10^{-6} K_{H2S} = 0

k_La = $2*10^{-4}$ s^{-1}

k_La = $5*10^{-3}$ s^{-1}

Order negative to 1
Increasing conversion
H_2S carried back



k_La = $5*10^{-4}$ s^{-1}

k_La = $1*10^{-3}$ s^{-1}

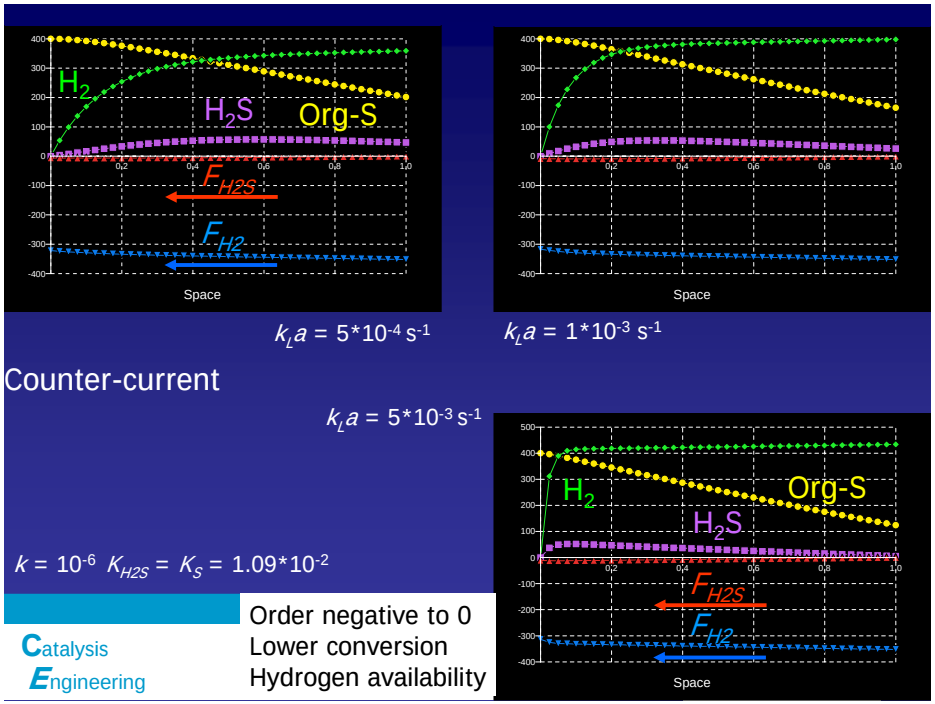
Counter-current

k_La = $5*10^{-3}$ s^{-1}

k = 10^{-6} K_{H2S} = $1.09*10^{-2}$ K_S = 0

Catalysis Engineering

Order 0 to 1
Lower conversion
H_2S carried back



k_La = $5*10^{-4}$ s^{-1}

k_La = $1*10^{-3}$ s^{-1}

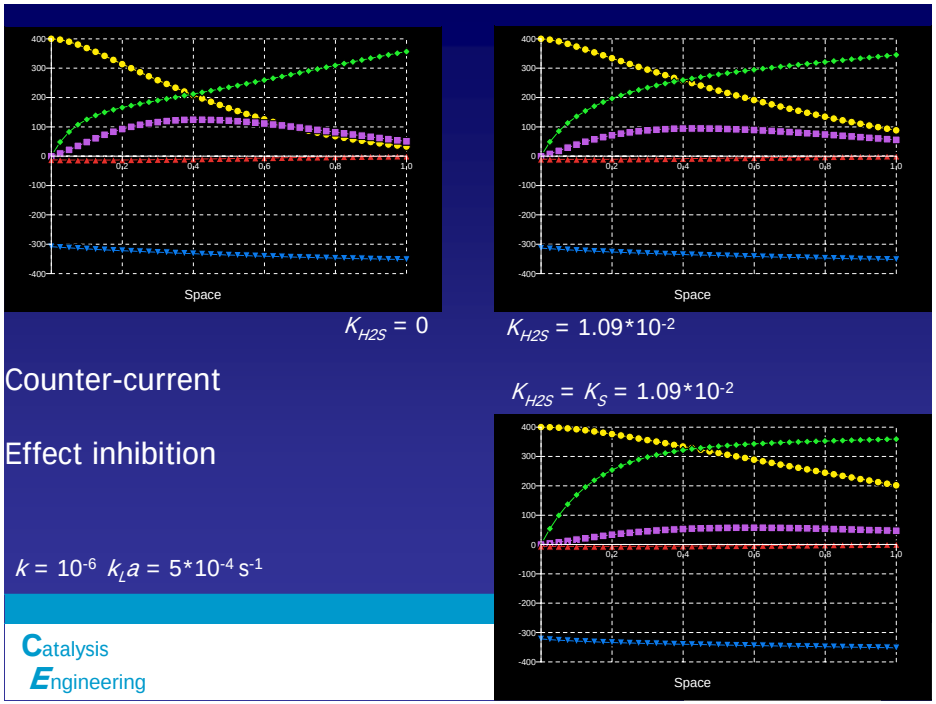
Counter-current

k_La = $5*10^{-3}$ s^{-1}

k = 10^{-6} K_{H2S} = K_S = $1.09*10^{-2}$

Catalysis Engineering

Order negative to 0
Lower conversion
Hydrogen availability



K_{H2S} = 0

K_{H2S} = $1.09*10^{-2}$

Counter-current

Effect inhibition

K_{H2S} = K_S = $1.09*10^{-2}$

k = 10^{-6} k_La = $5*10^{-4}$ s^{-1}

Catalysis Engineering

Counter-current

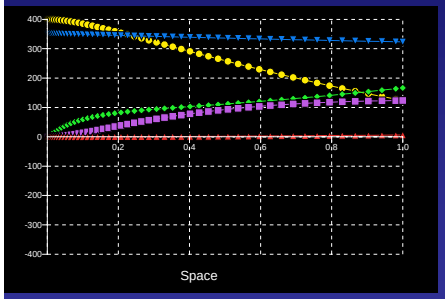
- Inhibition
  - Lowers conversion
  - Change apparent order (~from 1st to 0th)
- Mass transfer
  - Increases conversion
  - Changes apparent order (~from neg. to pos.)
- H_2S
  - Liquid concentration through maximum
  - Leaves reactor in liquid phase

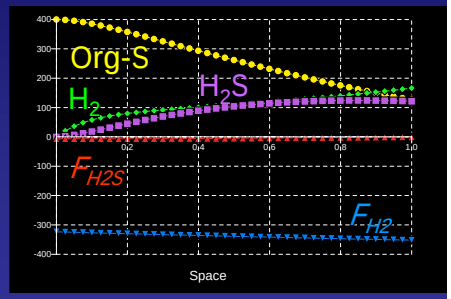
Co- versus Counter-current

- Effect mass transfer
  - No inhibition

$k = 10^{-6}$
$k_La = 2*10^{-4}\ s^{-1}$
$K_{H2S} = 0$

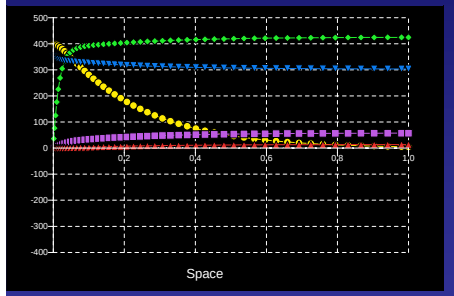
Co-current > Counter-current

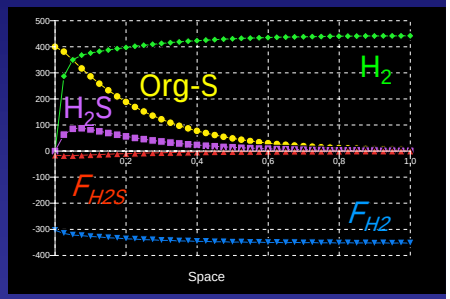




$k = 10^{-6}$
$k_La = 5*10^{-3}\ s^{-1}$
$K_{H2S} = 0$

Co-current < Counter-current





Co- versus Counter-current

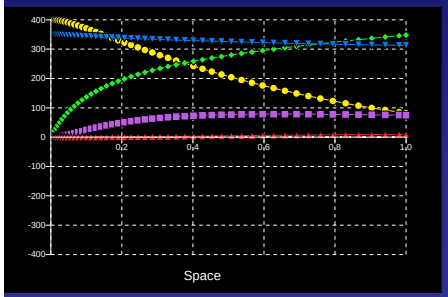
- No inhibition:
  - Low mass transfer: co-current preferred
  - High mass transfer: countercurrent preference
    - Hydrogen availability

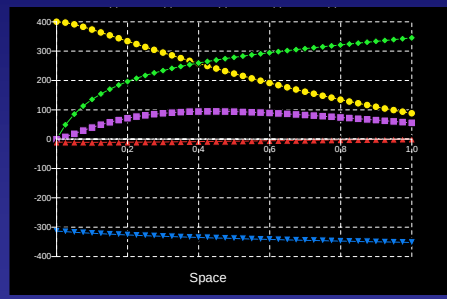
Co- versus Counter-current

- Effect mass transfer
  - H_2S inhibition

$k = 10^{-6}$
$k_La = 5*10^{-4}\ s^{-1}$
$K_{H2S} = 1.09*10^{-2}$

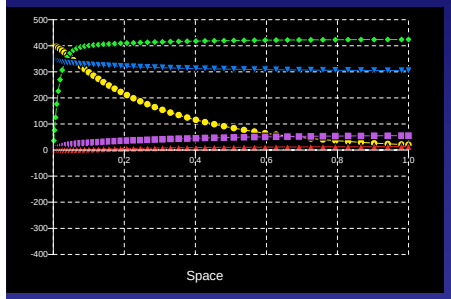
Co-current > Counter-current

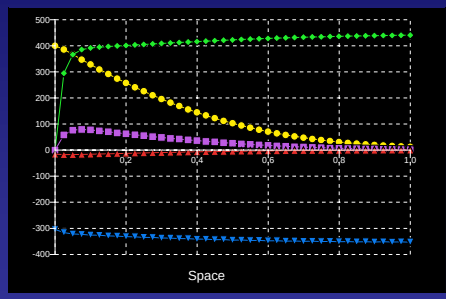




$k = 10^{-6}$
$k_La = 5*10^{-3}\ s^{-1}$
$K_{H2S} = 1.09*10^{-2}$

Co-current < Counter-current





Co- versus Counter-current

- No inhibition:
  - Low mass transfer: co-current preferred
  - High mass transfer: countercurrent preference
- H_2S inhibition:
  - Changeover at higher mass transfer rates
    - Higher H_2, lower H_2S concentration at end
    - Only at high conversion

Conclusions modeling - single reactor

- Countercurrent only better at high conversions
- Inhibition requires higher mass transfer rates for advantage
- Liquid phase not necessarily free of H_2S
  - Catalyst grading not attractive
- Apparent reaction order: negative to positive
  - Decreases with inhibition and poorer H_2 availability
  - Increases with increasing mass transfer
  - Countercurrent stronger order decrease

Thanks!

Any question?