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

Freek Kapteijn
Catalysis Engineering TUDelft
The Netherlands

10th Anniversary Symposium
IFP Solaize, France
19-20 May 2008

Literature

• R. Krishna and S. T. Sie
  Strategies for multiphase reactor selection

• 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

• J. W. Gosselink
  Sulfide Catalysts in refineries
  CATTECH 1998, 2(2), 127-144

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

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
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

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

Reactive distillation vs. stripping

Low boiling ester  High boiling ester


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)
Counter- vs. co-current operation II

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

- If necessary, cross flow (cocurrent operation):

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!

Application of monoliths

Two-phase flow patterns in capillaries

Removal of VOCs

Three Phase monolith Loop Reactor
Heiszwohl et al, CES, 2001
Reactive stripping in monoliths

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

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

Flooding II
New inlet/outlet design shifts flooding limits!

Flooding III
Optimised outlet device allows countercurrent operation in 200 cpsi monoliths (d_{hydr} = 1.25 mm)
Improved stacking

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

Film flow monoliths with modified geometries

Channel geometry influences flow distribution and RTD!

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

Non-reactive stripping experiments

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

Model reaction - Esterification

\[
\text{Octanol} + \text{Hexanoic acid} \leftrightarrow \text{Ester} + \text{Water}
\]

- 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%)

Experiments in pilot-scale plant

- Reactor:
  - \(L_{\text{reactor}} = 2\) m
  - \(\theta_{\text{column}} = 5\) cm
  - \(V_{\text{liquid}} = 15\) l
  - \(P = 4\) bar
  - \(T = 160\) °C
- Gas feed:
  - \(\text{gas feed} = 500\) Nl/h
- Liquid feed:
  - \(C_{\text{acid}} = 12\) mol-%
  - \(C_{\text{alcohol}} = 12\) mol-%

Experimental results

- thermodynamic equilibrium
- catalyst, without water removal
- homogeneous reaction

\[
\begin{align*}
\text{hex. acid conversion} & \\
\text{run time [min]} & \\
0 & 0.0 \\
50 & 0.2 \\
100 & 0.4 \\
150 & 0.6 \\
200 & 0.8 \\
250 & 1.0
\end{align*}
\]
**It works!**

- Thermodynamic equilibrium
- Reactive stripping
- Catalyst, without water removal
- Homogeneous reaction

**Model reaction - Side reactions**

```
\[
\text{hexanoic acid} + \text{octanol} \rightarrow \text{ester} + \text{H}_2\text{O} \\
\text{octene} + \text{H}_2\text{O} \rightarrow \text{ether}
\]
```

**Selectivity**

- Selectivity vs. run time

**Comparison inst. selectivities (5 internals)**

- Why two maxima?
**Kinetic model** (Beers et al., $K_{\text{eq}, \text{H}_2\text{O}}$ by I. Hoek)

Esterification

$$r_{\text{esterification}} = \frac{k_e \cdot C_{\text{acid}} \cdot C_{\text{water}}}{[1 + (\ldots) + K_w \cdot C_{\text{water}}]} \left[1 - \frac{C_{\text{ester}} \cdot C_{\text{water}}}{K_{\text{eq}} \cdot C_{\text{acid}} \cdot C_{\text{alcohol}}} \right]$$

 Etherification

$$r_{\text{etherification}} = \frac{k_A \cdot C_{\text{alcohol}} \cdot C_{\text{water}}}{[1 + (\ldots) + K_w \cdot C_{\text{water}}]}$$

- Two sites involved
- Water adsorption
- Equilibrium limitation
- 2nd order

**Column profile water concentration**

- Only reaction
- Only stripping

**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

**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/m³, 352 mol H₂/s, 432 m³
    - Pure hydrogen feed, inlet liquid no hydrogen
  - Kinetics
    - First order in both reactants
    - With & without inhibition
      \[ r = \frac{k c_{H_2} c_S}{1 + K_S c_S + K_{H_2} c_{H_2} S} \]

**Co-current**

- Effect mass transfer
  - No inhibition
  - Only H₂S inhibition
  - H₂S and organics inhibition

**Changing order**

\[ F_{H_2} \quad H_2 \quad F_{H_2} \]

\[ F_{H_2} \quad H_2 \quad F_{H_2} \]

\[ F_{H_2} \quad H_2 \quad F_{H_2} \]

**Hydrogen availability**

\[ F_{H_2} \quad H_2 \quad F_{H_2} \]

\[ F_{H_2} \quad H_2 \quad F_{H_2} \]
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

\[ k_{La} = 5 \times 10^{-4} \ \text{s}^{-1} \]
\[ k_{La} = 1 \times 10^{-3} \ \text{s}^{-1} \]
\[ k = 10^{-6} \ \text{K}_{H_2S} = 1.09 \times 10^{-2} \ \text{K}_S = 0 \]
$k_i a = 10^{-4} \text{s}^{-1}$  
$k_i a = 1 \times 10^{-3} \text{s}^{-1}$  
$k_i a = 5 \times 10^{-3} \text{s}^{-1}$  

Counter-current

$k_i a = 2 \times 10^{-4} \text{s}^{-1}$  
$k_i a = 1 \times 10^{-3} \text{s}^{-1}$  

Counter-current

$k_i a = 5 \times 10^{-3} \text{s}^{-1}$  

Counter-current

$k_i a = 10^{-6}$  

Counter-current

$k_i a = 5 \times 10^{-4} \text{s}^{-1}$  

Counter-current

Counter-current

Order negative to 1
Increasing conversion
H$_2$S carried back

Order negative to 0
Lower conversion
Hydrogen availability

Effect inhibition

Order 0 to 1
Lower conversion
H$_2$S carried back

$k = 10^{-6}$  

$k = 10^{-6}$  

$k = 10^{-6}$  

$k = 10^{-6}$
Counter-current

- Inhibition
  - Lowers conversion
  - Change apparent order (from 1st to 0th)
- Mass transfer
  - Increases conversion
  - Changes apparent order (from neg. to pos.)
- H₂S
  - Liquid concentration through maximum
  - Leaves reactor in liquid phase

Co- versus Counter-current

- Effect mass transfer
  - No inhibition

\[
k = 10^{-6} \\
k_{2,a} = 2 \times 10^{-4} \text{ s}^{-1} \\
K_{H2S} = 0
\]
Co- versus Counter-current

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

- Effect mass transfer
  - H₂S inhibition

\[
\begin{align*}
  k &= 10^{-6} \\
  k_a &= 5 \times 10^{-4} \text{s}^{-1} \\
  K_{H2S} &= 1.09 \times 10^{-2}
\end{align*}
\]
Co- versus Counter-current

- No inhibition:
  - Low mass transfer: co-current preferred
  - High mass transfer: countercurrent preference
- H₂S inhibition:
  - Changeover at higher mass transfer rates
    - Higher H₂, lower H₂S 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 H₂S
  - Catalyst grading not attractive
- Apparent reaction order: negative to positive
  - Decreases with inhibition and poorer H₂ availability
  - Increases with increasing mass transfer
  - Countercurrent stronger order decrease

Thanks!
Any question?