Heterogeneous Catalysis Engineering

E. Klemm

Topical Workshop Catalysis
DFG Priority Program 1362
Stuttgart, April 12, 2011

Outline

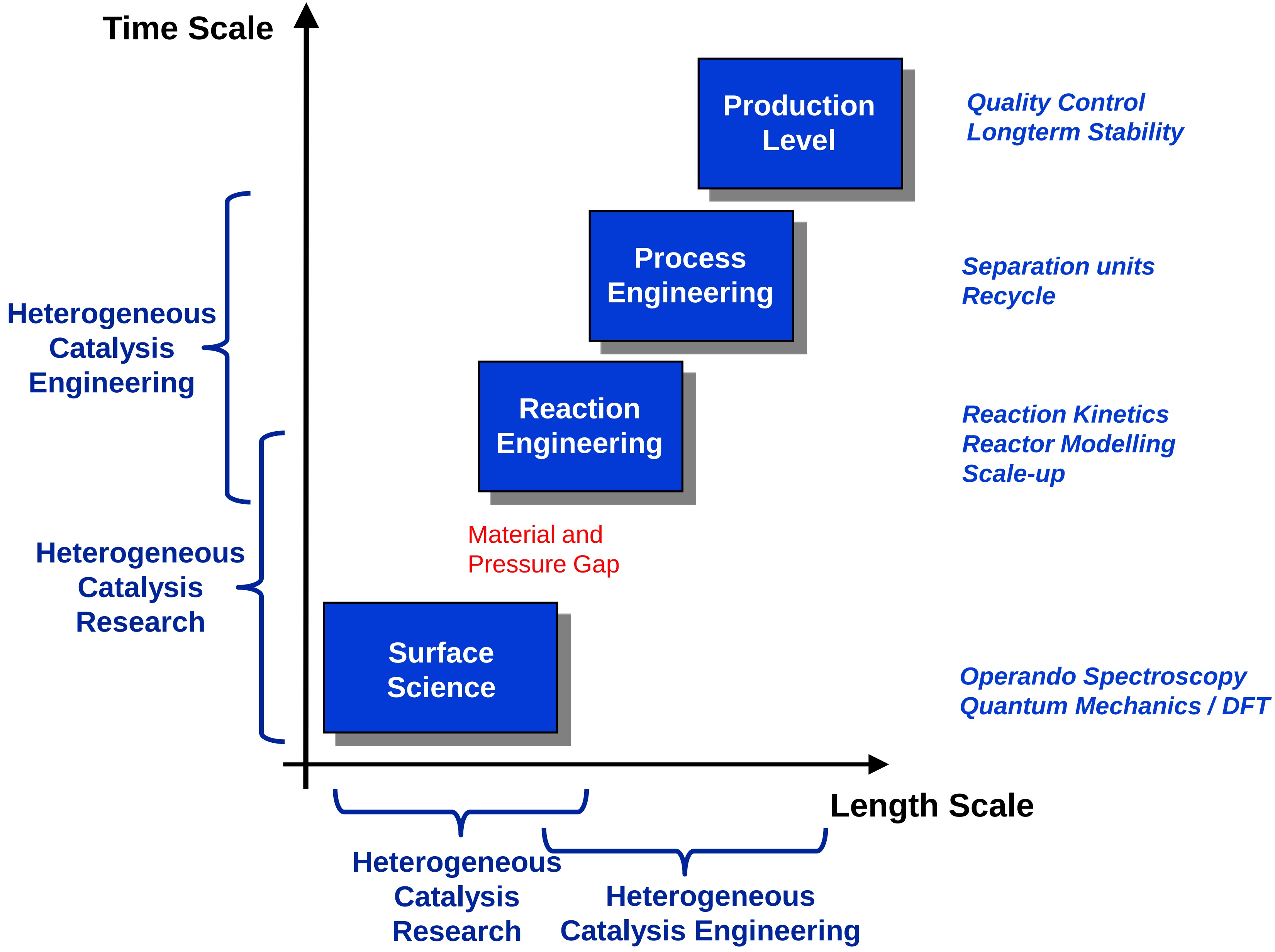
- What is „ Heterogeneous Catalysis Engineering“ ?

- Bulk Chemicals Manufacture
    - Space Time Yield
    - Selectivity-Conversion-Plots
    - Catalyst Life Time

- Fine Chemicals Manufacture
    - Space Time Yield
    - Atom Efficiency (E Factor)
    - Time-to-Market

- Bench Scale Reactors for Het. Cat. Eng.

What is “Heterogeneous Catalysis Engineering” ?



Quality Control
Longterm Stability

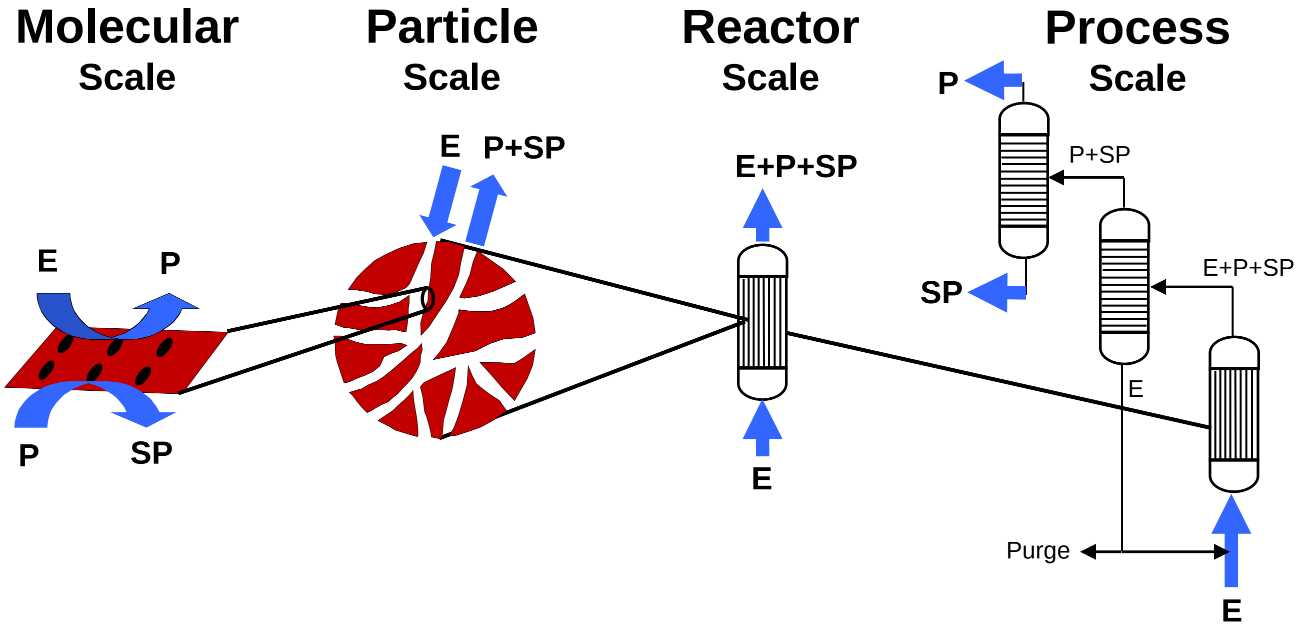
Separation units
Recycle

Reaction Kinetics
Reactor Modelling
Scale-up

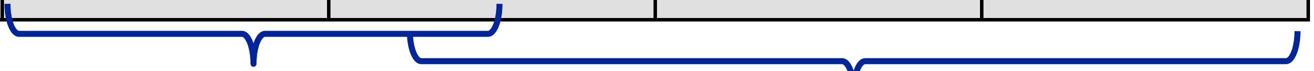
Material and
Pressure Gap

Operando Spectroscopy
Quantum Mechanics / DFT

What is “Heterogeneous Catalysis Engineering” ?



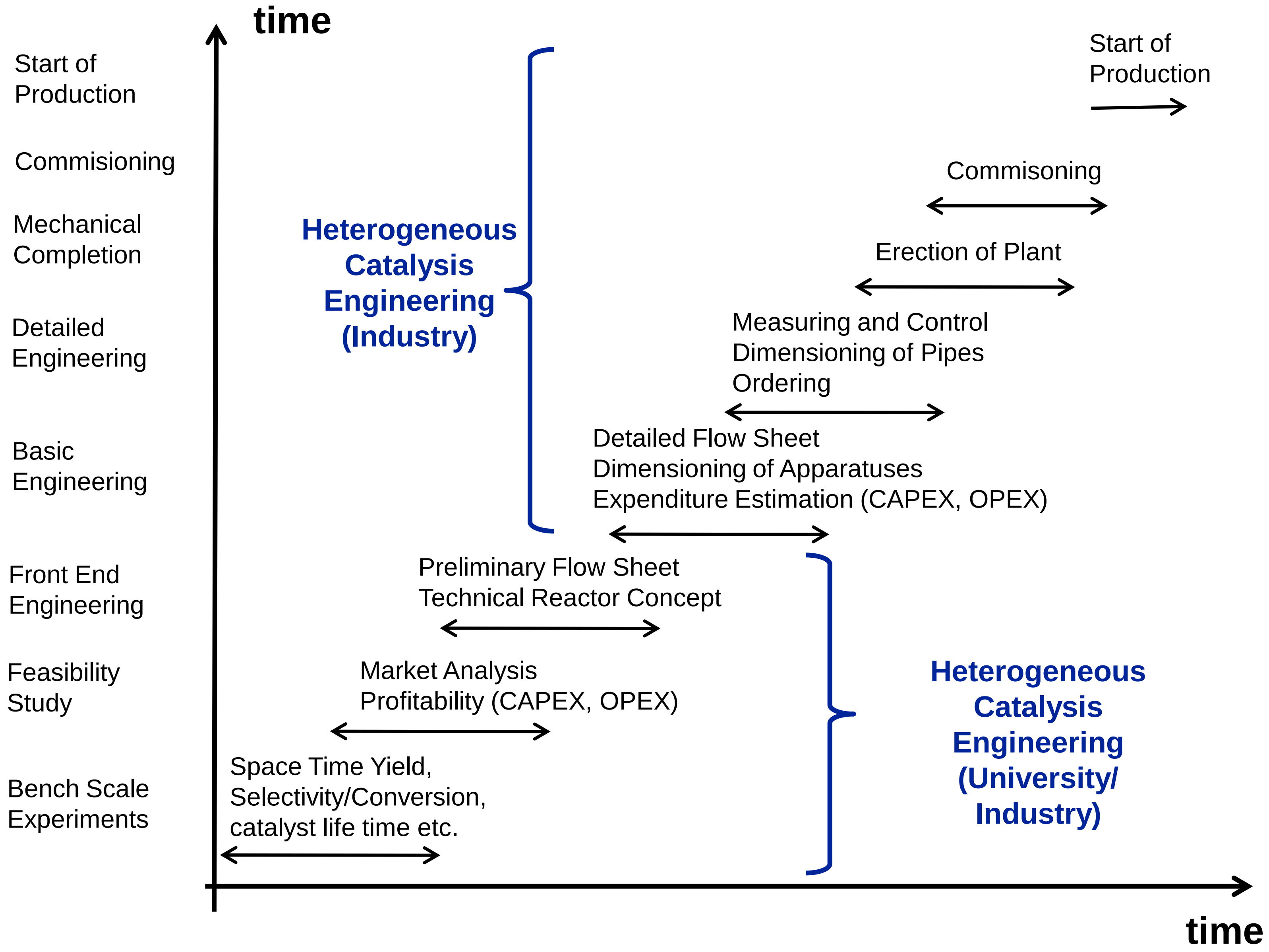
	Active Site	Catalyst Pellet	Reactor	Process
Activity	Turnover Frequency	Effective Reaction Rate	Conversion / Space Time Yield	Process Conversion
Selectivity	Differential Selectivity on Active Site	Differential Selectivity on Pellet	Integral Selectivity	Process Selectivity



Heterogeneous Catalysis Research

Heterogeneous Catalysis Engineering

What is “Heterogeneous Catalysis Engineering” ?



- Start of Production
- Commisioning
- Mechanical Completion
- Detailed Engineering
- Basic Engineering
- Front End Engineering
- Feasibility Study
- Bench Scale Experiments

Heterogeneous Catalysis Engineering (Industry)

Start of Production

Commisoning

Erection of Plant

Measuring and Control
Dimensioning of Pipes
Ordering

Detailed Flow Sheet
Dimensioning of Apparatuses
Expenditure Estimation (CAPEX, OPEX)

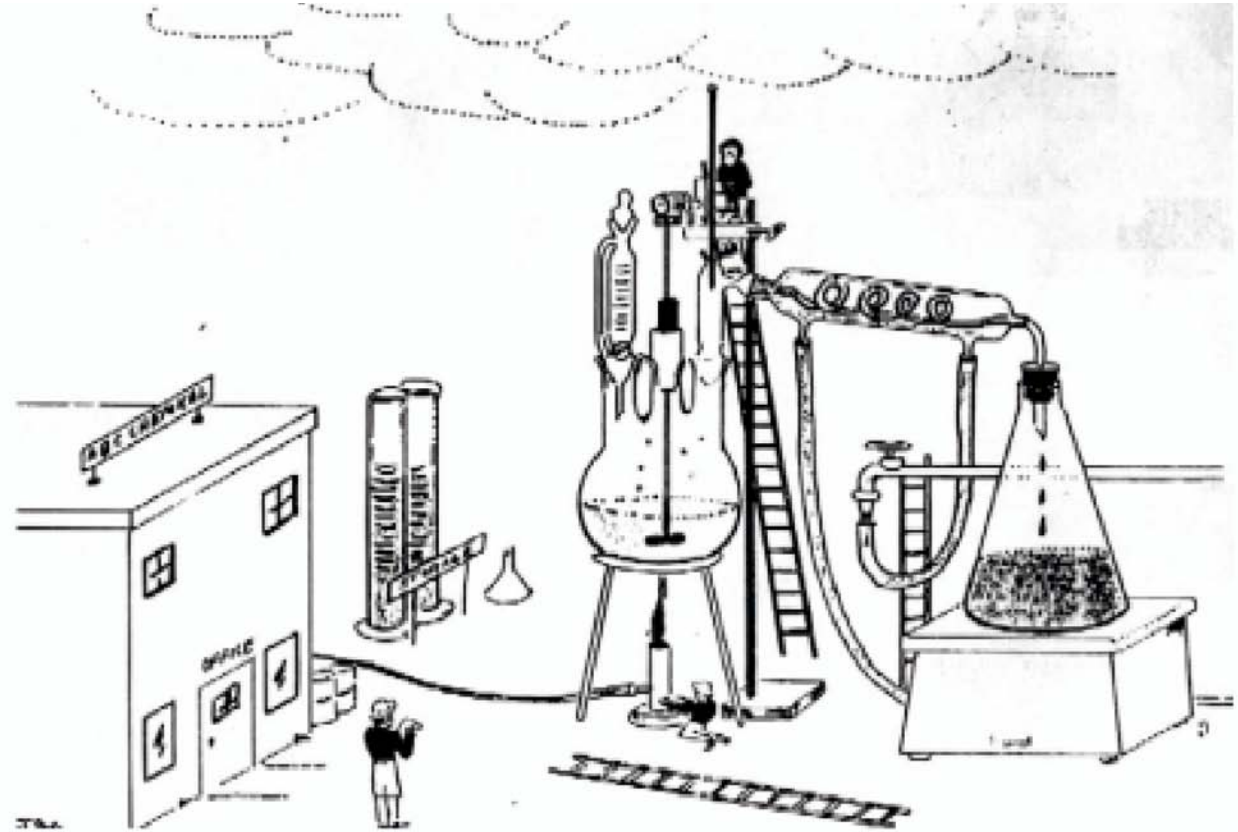
Preliminary Flow Sheet
Technical Reactor Concept

Market Analysis
Profitability (CAPEX, OPEX)

Space Time Yield,
Selectivity/Conversion,
catalyst life time etc.

Heterogeneous Catalysis Engineering (University/ Industry)

What is “Heterogeneous Catalysis Engineering” ?



„The bench scale results were so good that we by-passed the pilot-plant“

aus E.H. Stitt, Chem.Eng.J. 90(2002)47

What is “Heterogeneous Catalysis Engineering” ?

	Bulk Chemicals	**Fine Chemicals**
Plant Capacity	> 10,000 metric tons per year (usually: some 100,000 t/a)	< 10,000 metric tons per year (usually < 1,000 t/a)
Space Time Yield	1-10 kilogram per liter and hour	0.01-1 kilogram per liter and hour
Processing	continuous	batch-wise
Phase	gas (liquid)	liquid
Reactor	typically tube	typically stirred tank
Plant	dedicated	multi-purpose
Product price	< 10 $/kg	> 10 $/kg
Lifecycle of product	long	relatively short
Added value	low	high
Raw materials quote	high	low
kg waste / kg product (E Factor)	relatively low (< 1-5)	high (5-50)

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    - Catalyst-Life-Time

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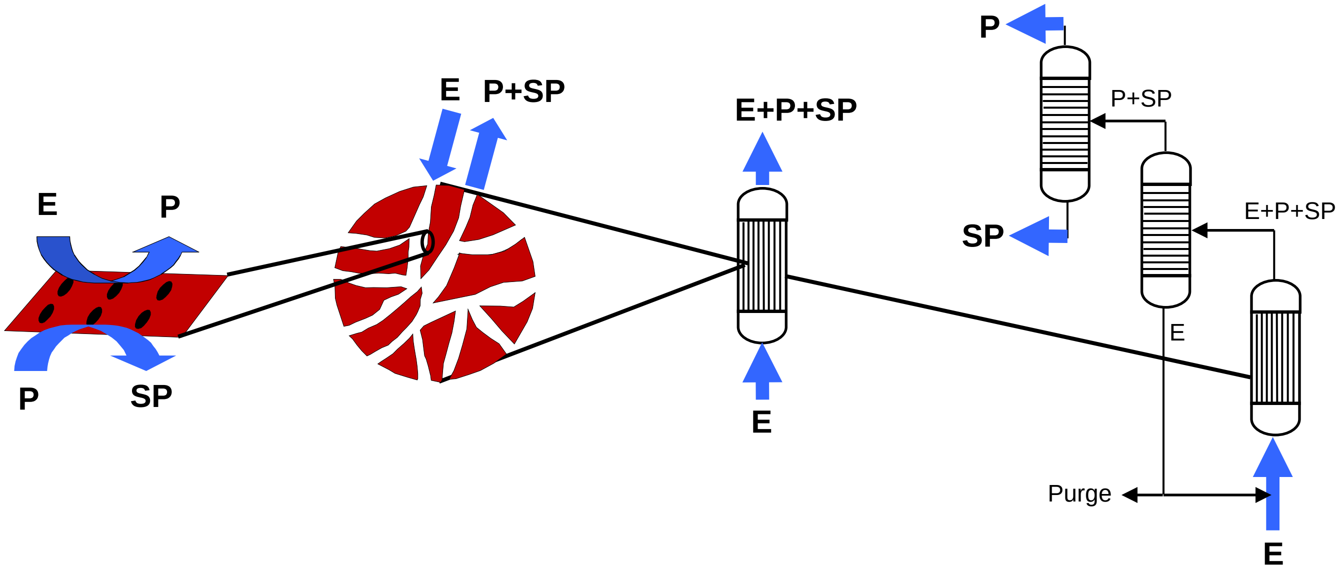
Bulk Chemicals Manufacture

Molecular Scale | **Particle** Scale | **Reactor** Scale | **Process** Scale



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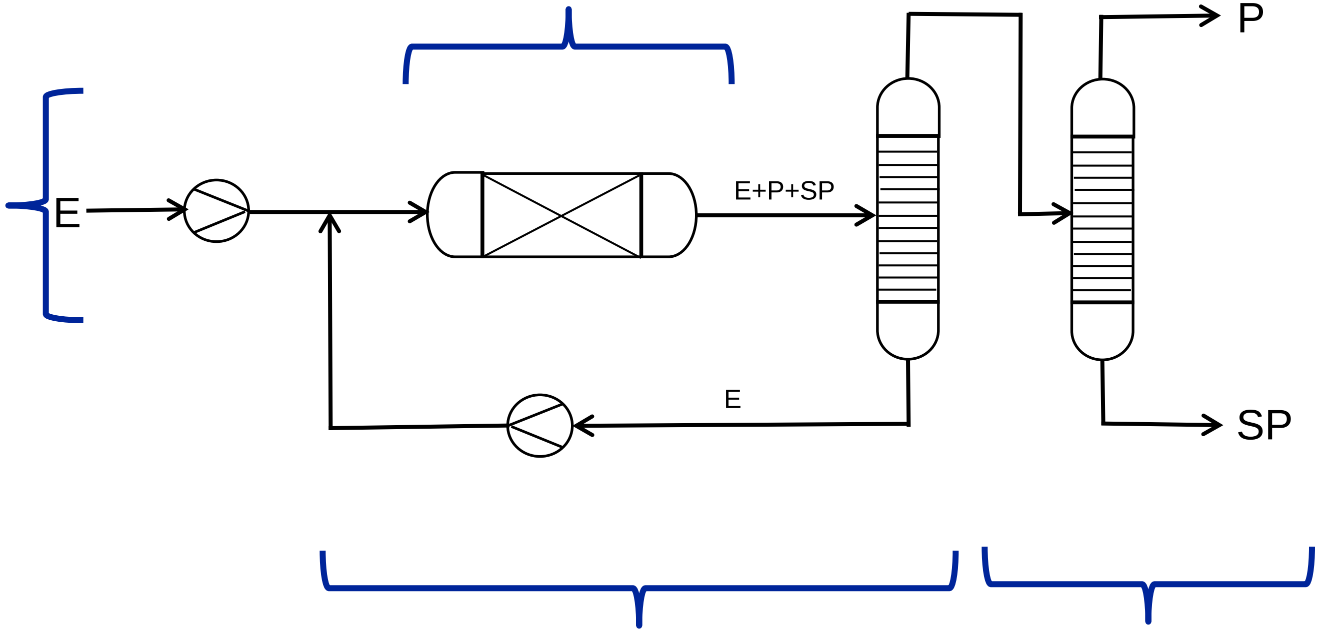
Selectivity	Differential Selectivity on Active Site	Differential Selectivity on Pellet	Integral Selectivity	Process Selectivity

Bulk Chemicals Manufacture

Process Profitability =

$$f(\underbrace{\text{Reactor Costs, Separation Costs, Recycle Costs,}}_{\textbf{CAPEX}}\ \underbrace{\text{Feedstock Costs…}}_{\textbf{OPEX}})$$



Reactor Costs
= f(Space Time Yield)

Feedstock Costs
= f(Selectivity)

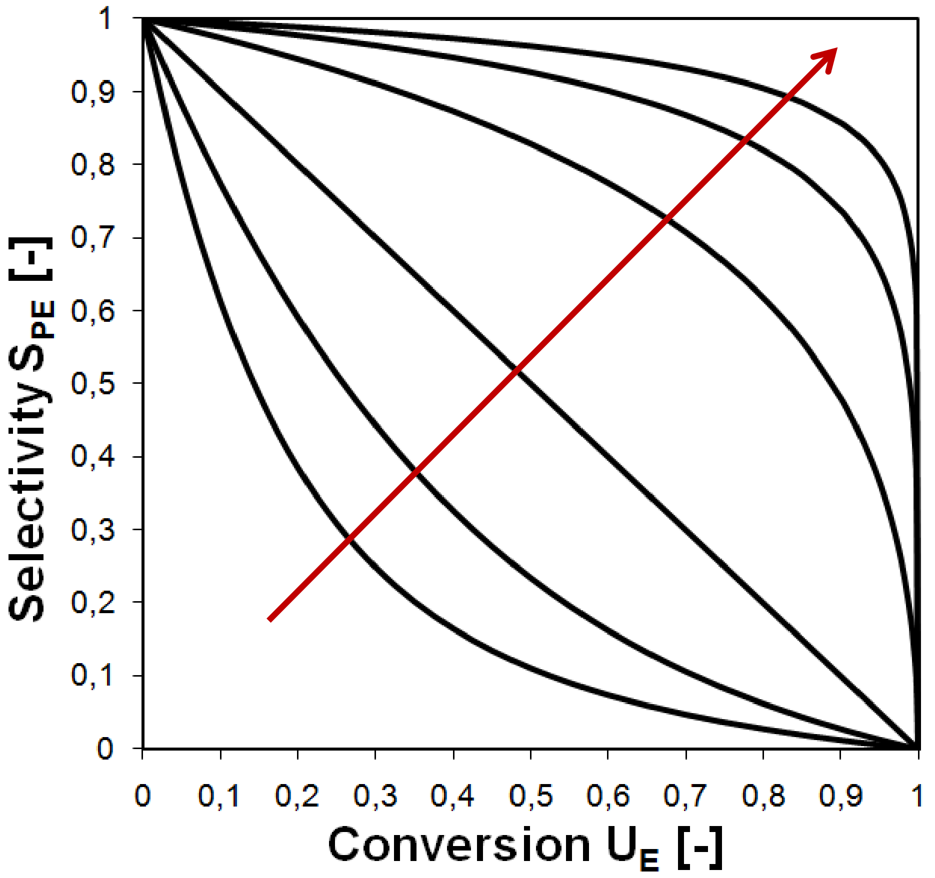
Recycle Costs
= f(Conversion)

Separation Costs
= f(Selectivity)

Bulk Chemicals Manufacture

Process Profitability = f(**Selectivity-Conversion-Plot**, …)

Educt ⟶ **P**roduct ⟶ **S**ide **P**roduct



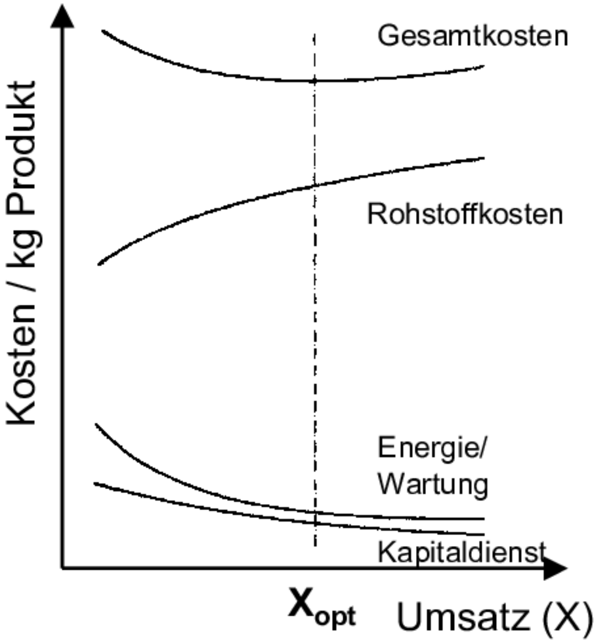
Molecular Scale:
- Turnover Frequencies
- Reducing Formation of Side Products

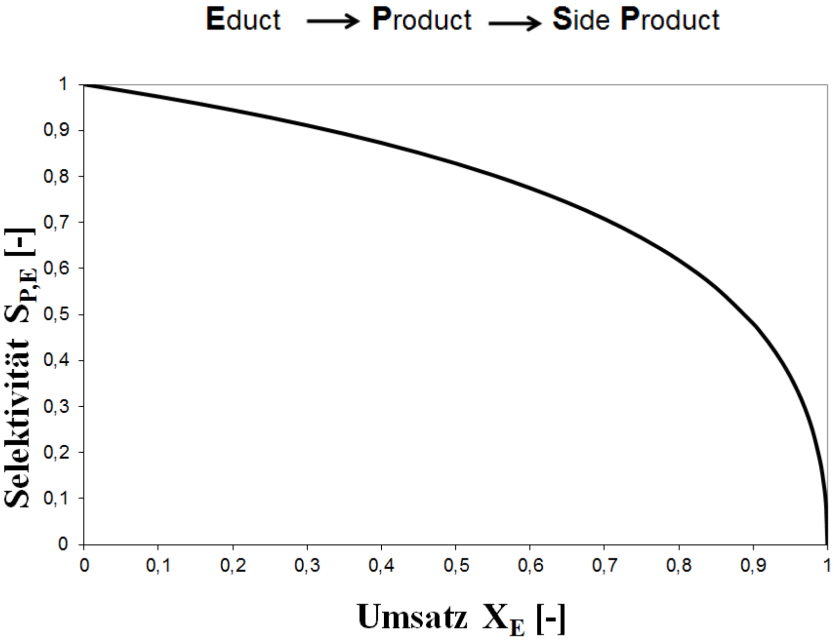
Particle Scale:
- Avoiding Film and Pore Diffusion Limitation
- Utilization of Shape Selective Effects

Reactor Scale:
- Avoiding Backmixing
- Avoiding Hot Spots

Process Scale:
- Recycle of Educt
- Integration of Separation

Bulk Chemicals Manufacture

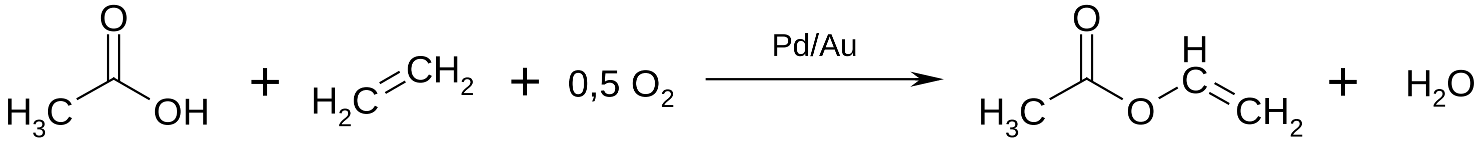




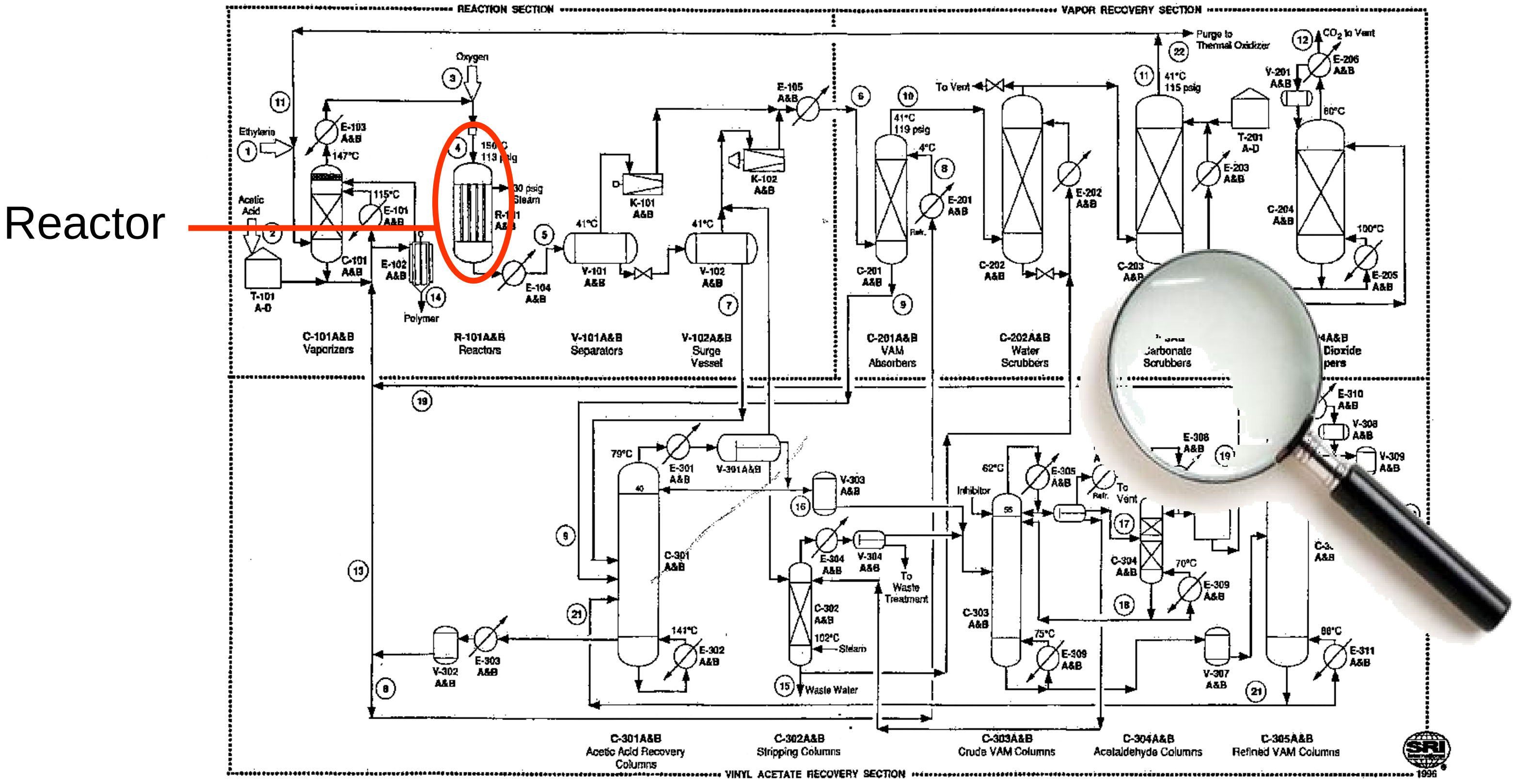
- with increasing conversion the selectivity decreases
  -> feed-stock costs increase
- with increasing conversion less educt has to be separated and recycled
  -> energy costs decrease

X_{opt}

Bulk Chemicals Manufacture



X_{HAc} = 15-35 % X_{C2H4} = 8-10 % $S_{VAM,C2H4}$ = 88-96 %

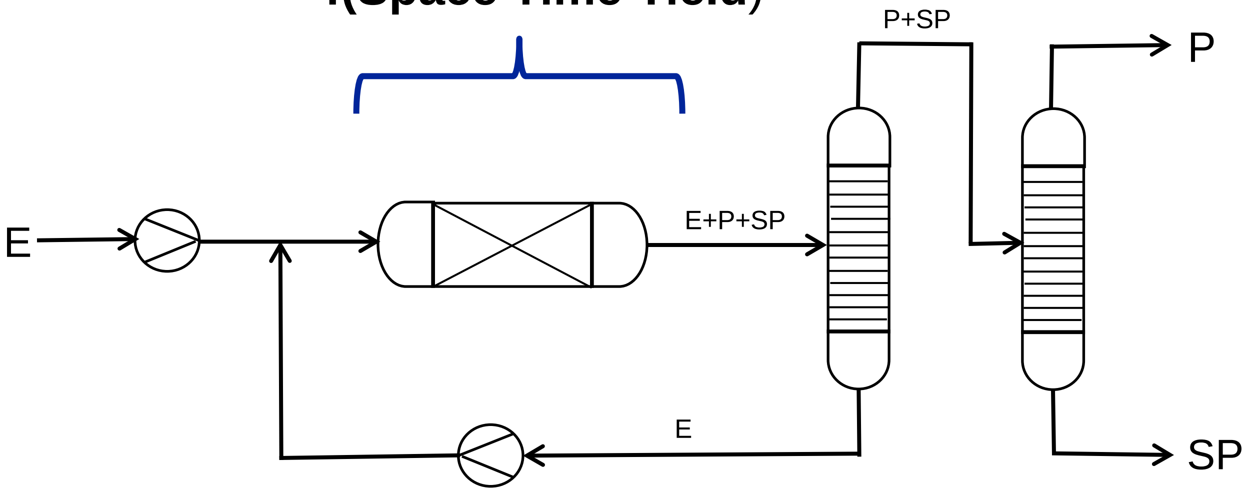


Source: SRI Consulting

Bulk Chemicals Manufacture

Process Profitability = **f(Reactor Costs**,…)

Reactor Costs
= **f(Space Time Yield**)



Bulk Chemicals Manufacture

Process Profitability =
f(**Space Time Yield (STY)**, …)

$$STY = \frac{\dot{m}_P}{V_{\text{reac}}} = \frac{\dot{V} \cdot c_{Eo} \cdot X_E \cdot S_{P,E} \cdot M_P}{V_{\text{reac}}} =$$

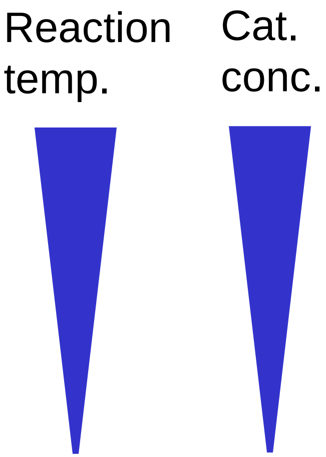
$$= \frac{c_{Eo} \cdot X_E \cdot S_{P,E} \cdot M_P}{\underset{\text{Residence Time}}{\boxed{\tau}}} \quad \left[\frac{kg\ \text{Product}}{l_{\text{Reac}} \cdot \text{h}} \right]$$

Typical Values of STY:
1-10 kg product per 1 liter reaction volume and hour

Bulk Chemicals Manufacture

Space Time Yield (STY): $\frac{\text{kilogram of product}}{\text{liter of reaction volume and hour}}$

Het. Catalysis:	**1-10**	**kg/(l·h)**
Hom. Catalysis:	0.01 – 1	kg/(l·h)
Biocatalysis:	0.001 – 0.01	kg/(l·h)



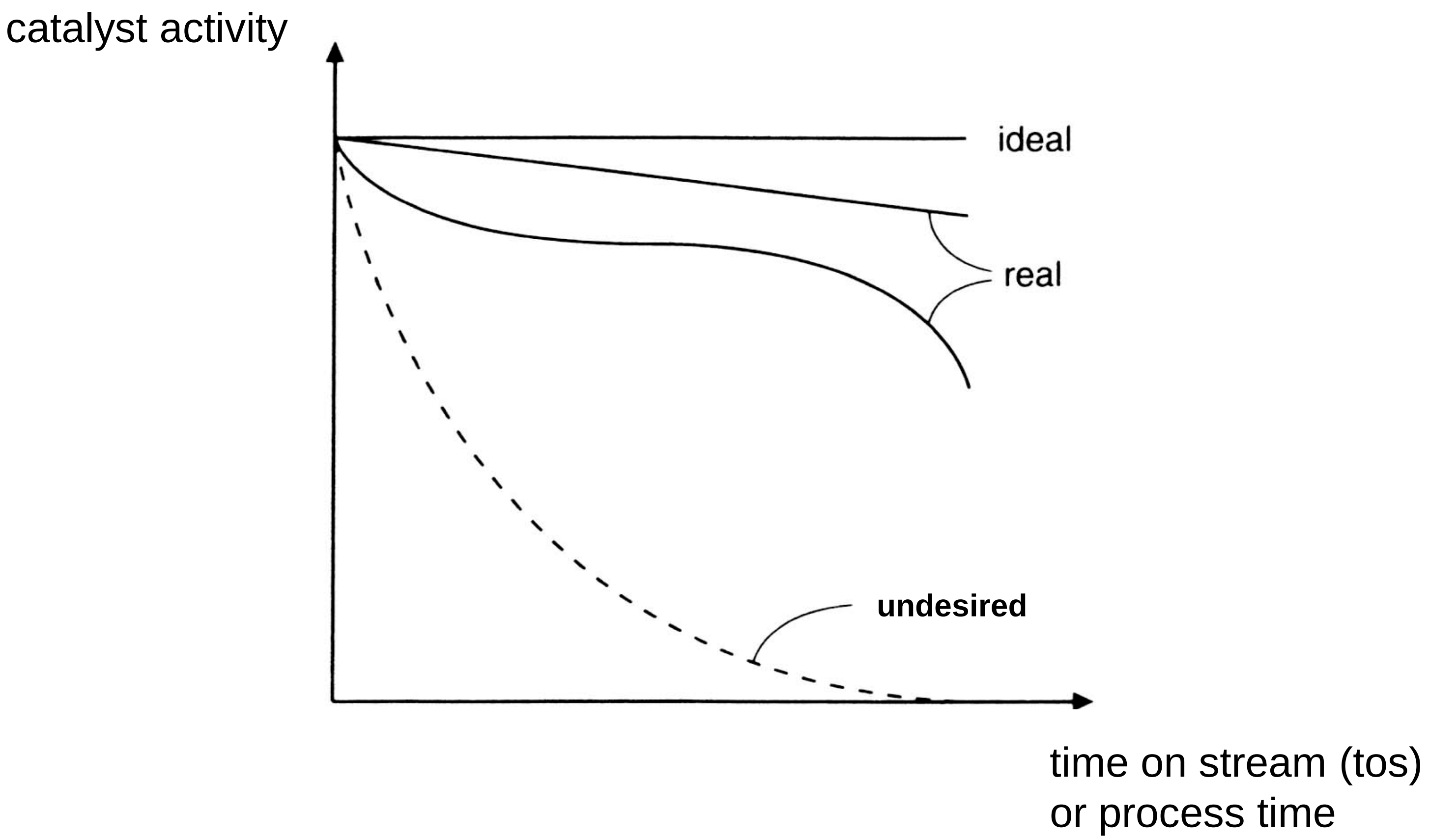
Bulk Chemicals Manufacture

Process Profitability = f(**Space Time Yield (STY)**, …)

Wird beim Arbeiten im Kreislauf jeweils nur ein geringer Umsatz der Reaktionsgase Stickstoff und Wasserstoff erreicht, so ist es ***von größter technischer und wirtschaftlicher Bedeutung****,* ***diese geringfügige Umsetzung noch bei schnellem Durchleiten, also kurzer Berührungszeit der Gase mit dem Katalysator zu erreichen****. Solch reiche* ***„Raum-Zeit-Ausbeute****“ ist nun nur mit Katalysatoren erreichbar, die den um 1905 bekannten an Wirksamkeit um ein Vielfaches überlegen sind.*

Alwin Mittasch, Geschichte der Ammoniaksynthese, Verlag Chemie, Weinheim 1951.

Bulk Chemicals Manufacture

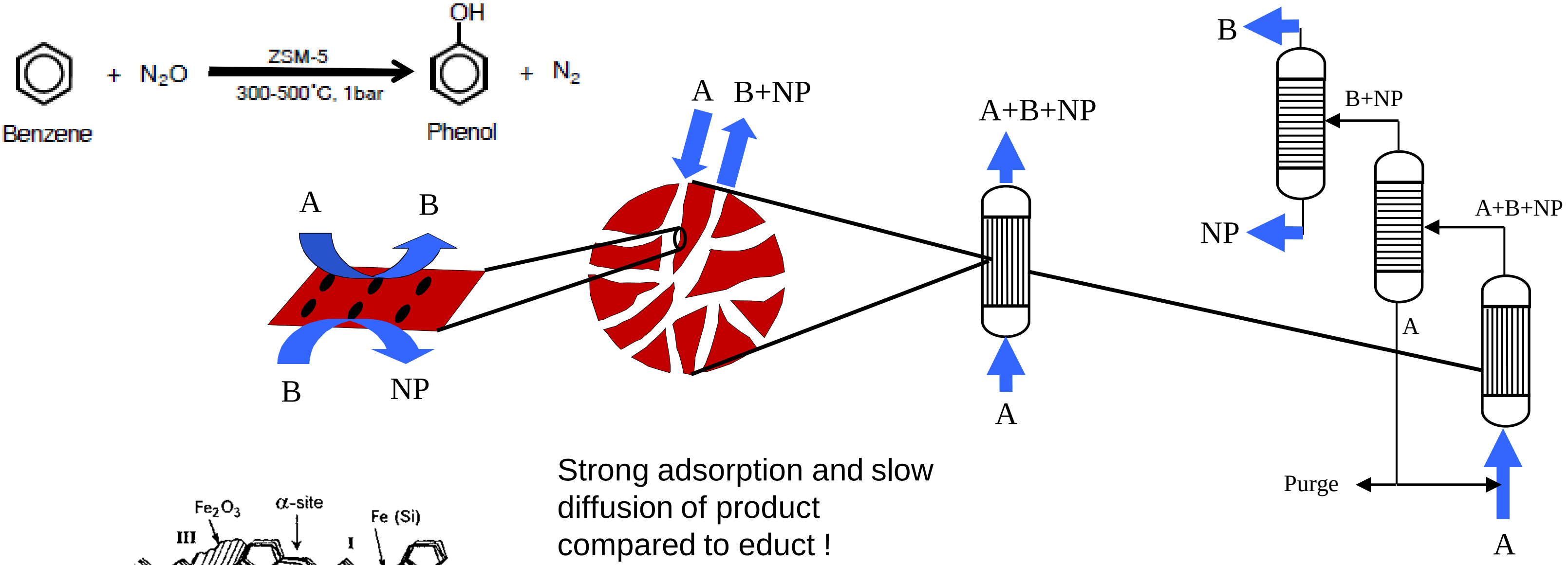


usually:
catalyst life time at least 8.000 hrs. (1 year)

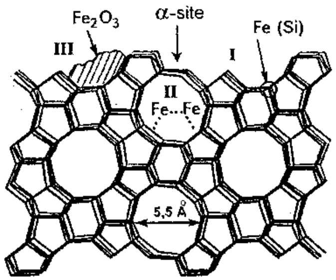
Bulk Chemicals Manufacture (Example I)

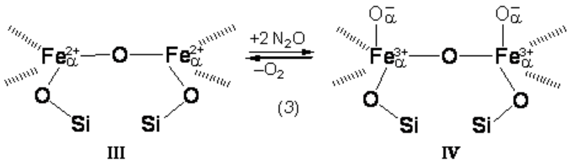
Direct Ring Oxidation of Aromatics with N_2O

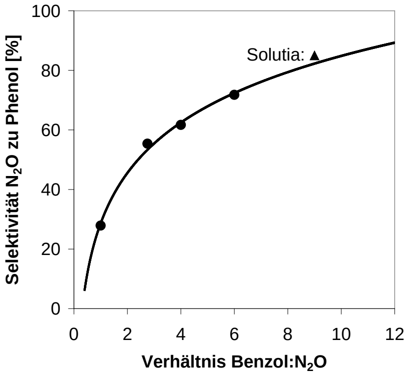
(E. Klemm et al., Direct Ring Oxidation of Aromatics, in: G. Ertl, H. Knözinger, J. Weitkamp (Hg.), Handbook of Heterogeneous Catalysis, 2nd edition, WILEY-VCH, Weinheim, 2008)

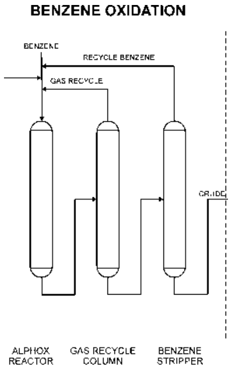


Strong adsorption and slow diffusion of product compared to educt !

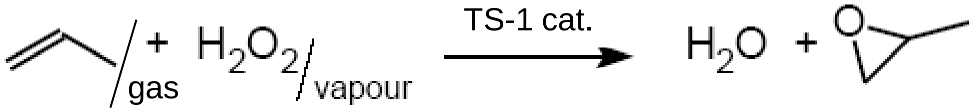






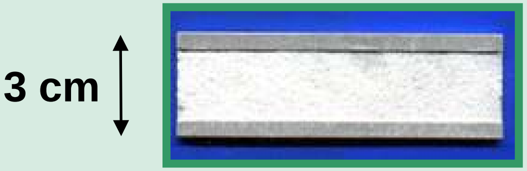


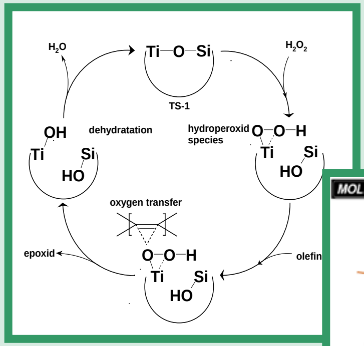
Bulk Chemicals Manufacture (Example II: DEMiS®)



ΔH_R = -220 kJ/mol

Lab Scale





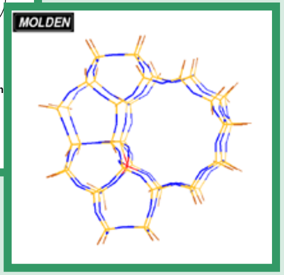
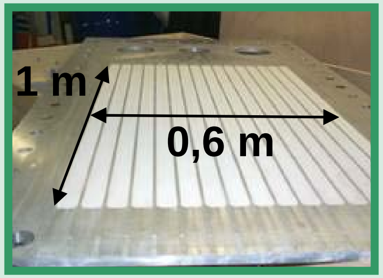


Foto: TU-Chemnitz

Emig · Klemm
Technische Chemie
Einführung in die chemische Reaktionstechnik
Begründet von Erich Fitzer und Werner Fritz
5., aktualisierte und ergänzte Auflage
Springer

equal up

Pilot Scale



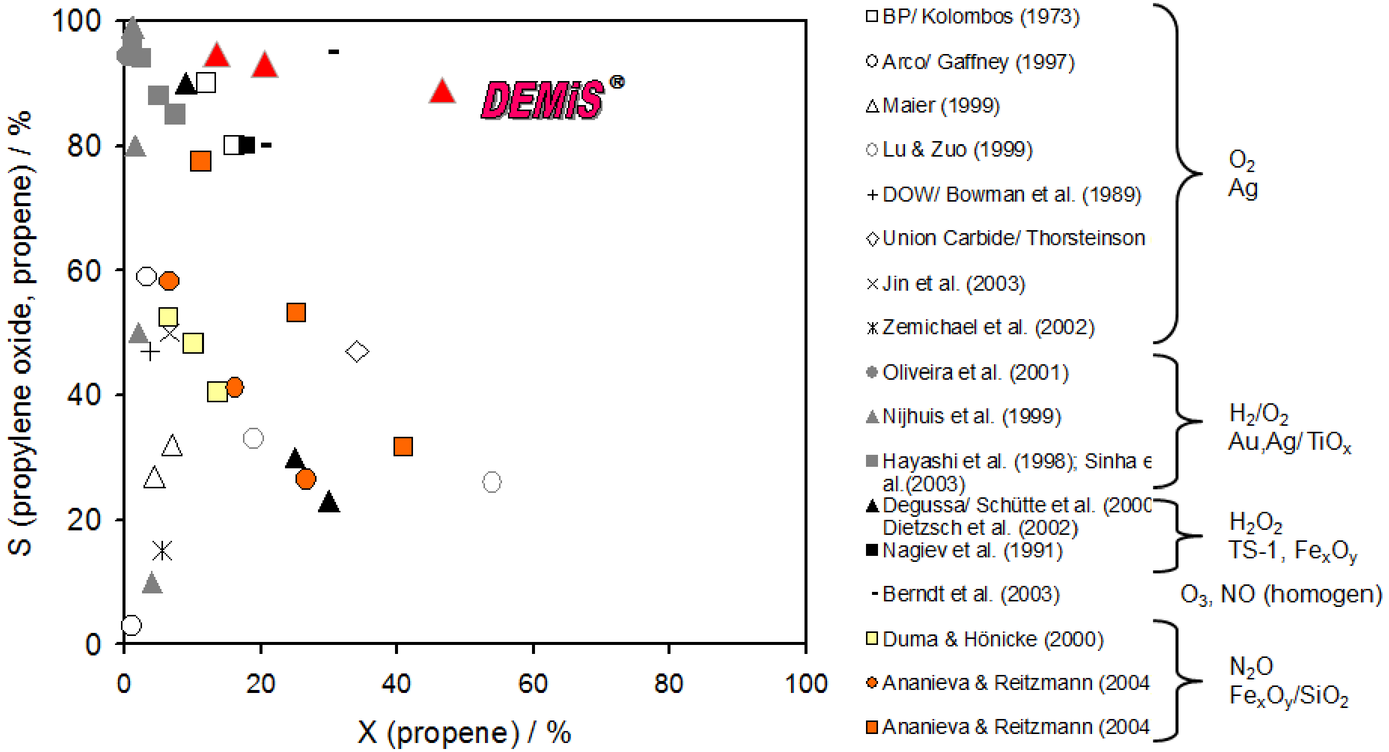
degussa.

Uhde
ThyssenKrupp

Foto: Uhde GmbH / Degussa AG

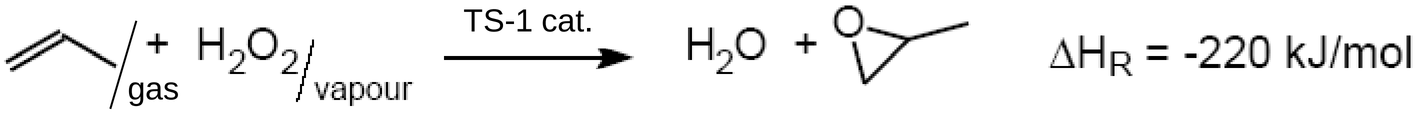
E. Klemm et al., Ind. Eng. Chem. Res. **2008**, *47*, 2086.

Bulk Chemicals Manufacture (Example II: DEMiS®)

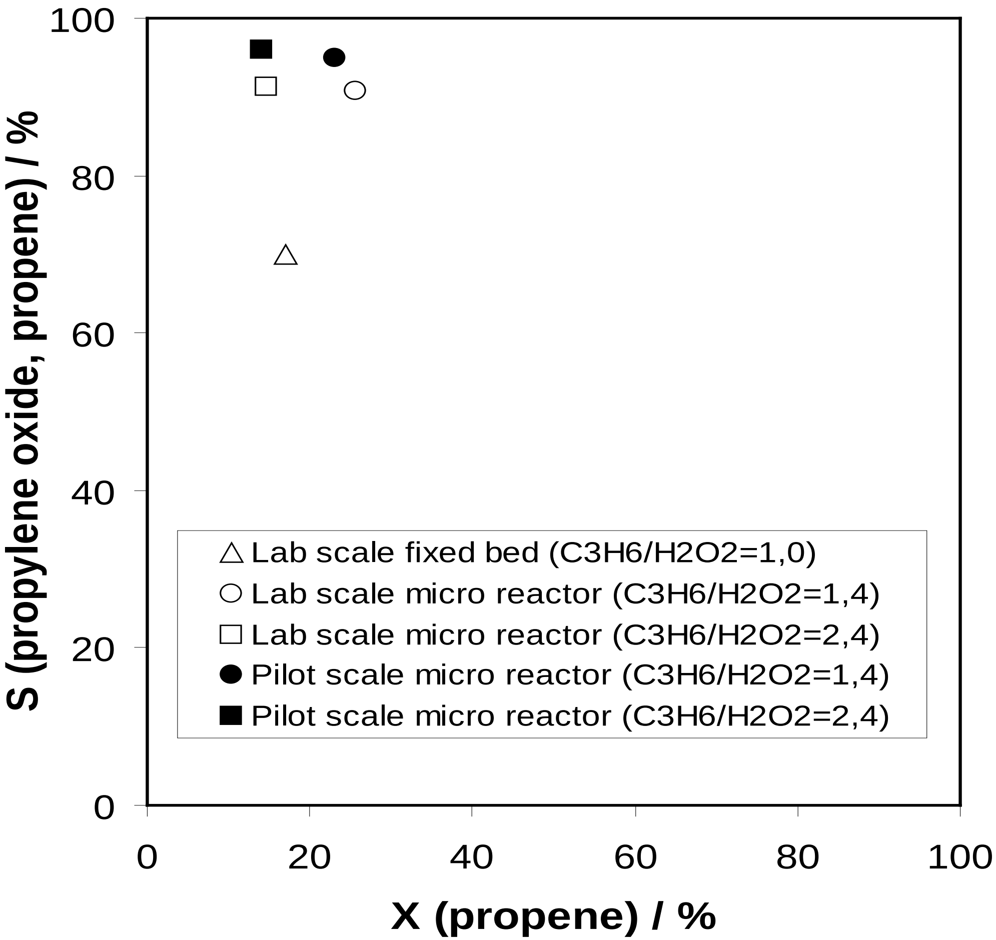


According to: E. Ananieva, A. Reitzmann, Chem. Eng. Sci., **59** (2004) 5509 - 5517

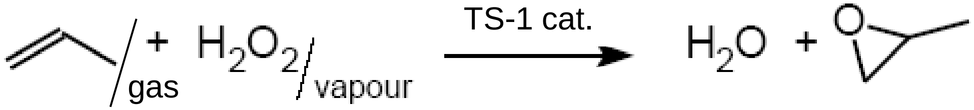
Bulk Chemicals Manufacture (Example II: DEMiS®)



Catalyst TS-1	
Reaction conditions	
reaction temperature [°C]	100-150
reaction pressure [bar]	1
substrate/hydrogen peroxide	>1
hydrogen peroxide in gas [vol%]	3 – 8



Bulk Chemicals Manufacture (Example II: DEMiS®)



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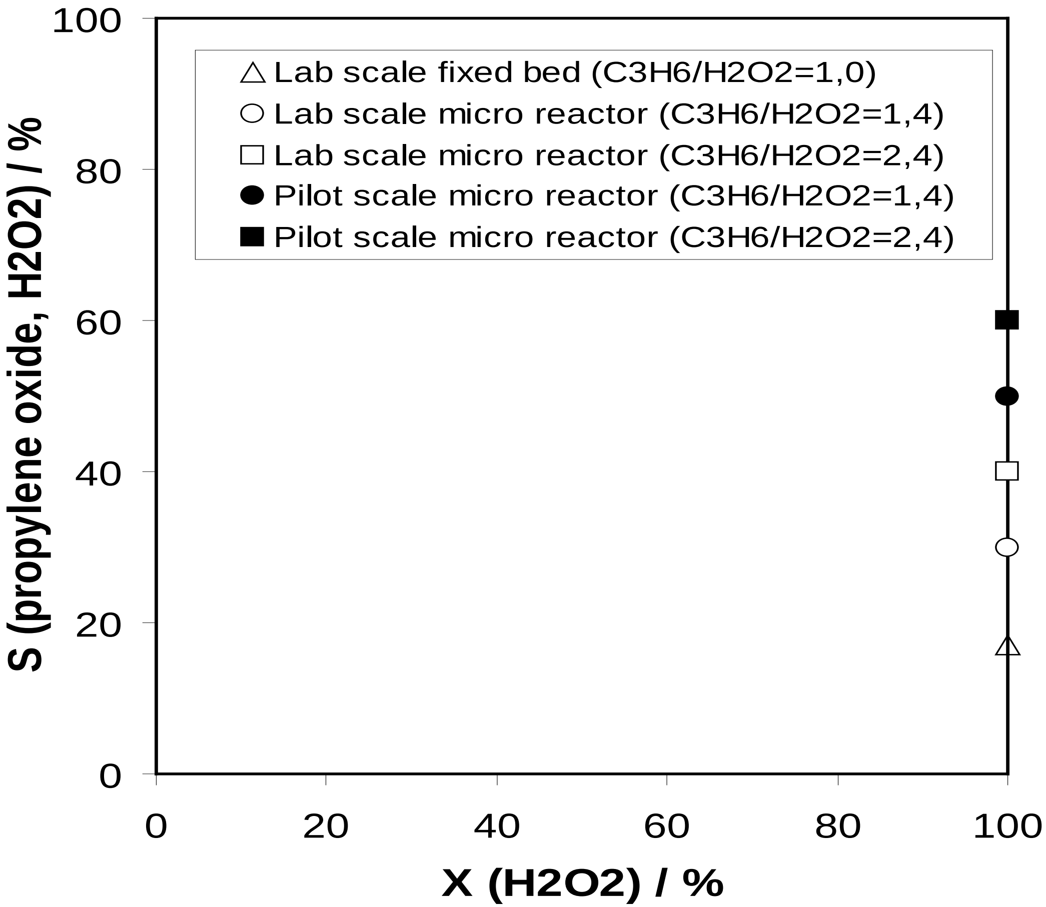
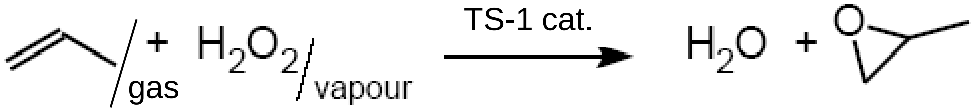


Bulk Chemicals Manufacture (Example II: DEMiS®)



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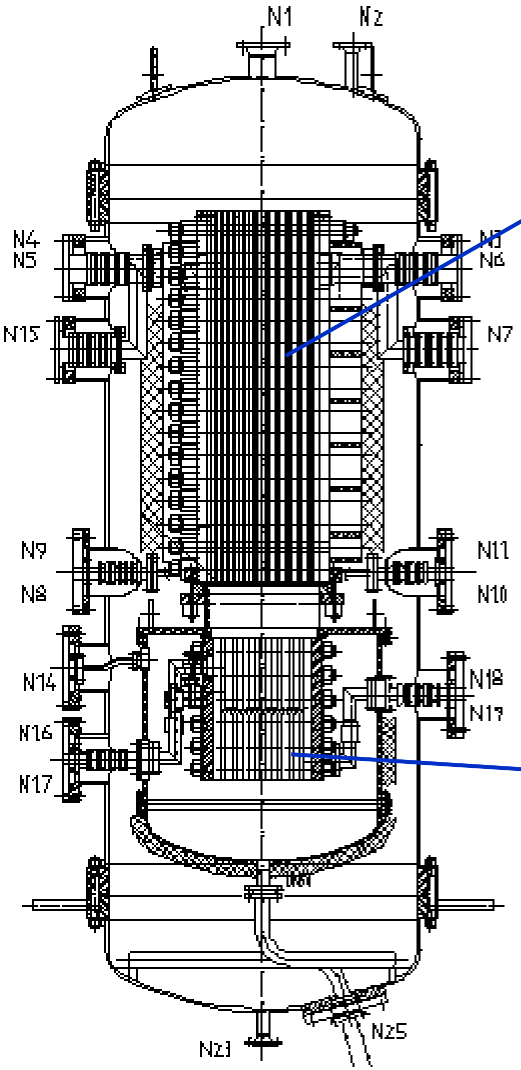


E. Klemm et al., Ind. Eng. Chem. Res. **2008**, *47*, 2086.

S. Heinrich, M. Plettig, E. Klemm,
Role of the Ti(IV)-Superoxide Species in the Selective Oxidation of Alkanes with Hydrogen Peroxide in the Gas Phase on Titanium Silicalite-1 – an In-Situ EPR Investigation – Catal. Lett. 141(2011)251.

T. Schwarz, S. Schirrmeister, H. Döring, E. Klemm,
Herstellung von Wandkatalysatoren für Mikrostrukturreaktoren mittels der Niederdruckspritztechnologie, Chem. Ing. Tech. 82(2010)921.

S. Schirrmeister, K. Büker, M. Schmitz-Niederau, B. Langanke, A. Geißelmann, F. Becker, R. Machnik, G. Markowz, T. Schwarz, E. Klemm,
Katalytisch beschichtete Träger, Verfahren zu dessen Herstellung und damit ausgestatteter Reaktor sowie dessen Verwendung,
Disclosure DE 10 2005 019 000 A1, 26.10.2006.

E. Klemm, G. Mathivanan, T. Schwarz, S. Schirrmeister,
Evaporation of Hydrogen Peroxide with a Microstructured Falling Film, Chem. Eng. Proc, submitted.

E. Klemm et al.,
Method for Obtaining a Gaseoues Phase From a Liquid Medium and Device for Carrying Out the Same, Disclosure WO 2004/036137 A2, 29.04.2004.

Fine Chemicals Manufacture

Virtual, but realistic example:

Fine chemical synthesis with $Y_{P,E}$=80 %, c_{Eo} = 1 mol/l and M_P = 100 g/mol
(assuming stirred tank reactor witch V_{reac} = 2 m^3)

3-shift batch-wise operation:

$$m_{\mathrm{Product/day}} = 3 \cdot V_{reac} \cdot c_{Eo} \cdot Y_{P,E} \cdot M_{\mathrm{P}} =$$

$$= 3 \cdot 2{,}000\, l \cdot 1\, mol/l \cdot 0.8 \cdot 100\, g/mol =$$

$$= 480\, kg/day$$

Production Capacity: ca. 170 t / a
Space Time Yield: ca. 0.01 kg per liter and hour

Fine Chemicals Manufacture

Process Profitability =
f(**Space Time Yield (STY)**, …)

$$STY = \frac{m_P}{V_{\mathrm{Reac}} \cdot t} = \frac{V_{\mathrm{Reac}} \cdot c_{Eo} \cdot Y_{P,E} \cdot M_P}{V_{\mathrm{Reac}} \cdot t} =$$

$$= \frac{c_{Eo} \cdot Y_{P,E} \cdot M_P}{\enclose{circle}{t}} \quad \left[\frac{kg\ \mathrm{Product}}{l_{\mathrm{Reac}} \cdot \mathrm{h}}\right]$$

Process Time for batch-wise operation

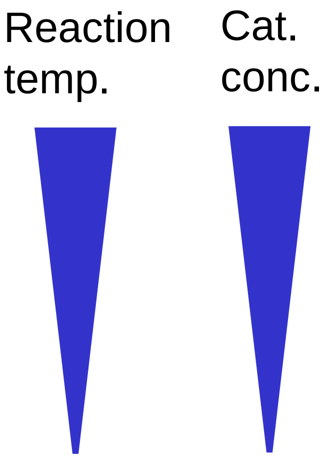
Typical Values of STY:
0.01 – 1 kg product per 1 liter reaction volume and hour

Fine Chemicals Manufacture

Space Time Yield (STY):

$$\frac{\text{kilogram of product}}{\text{liter of reaction volume and hour}}$$

Het. Catalysis:	1-10	kg/(l·h)
Hom. Catalysis:	**0.01 – 1**	**kg/(l·h)**
Biocatalysis:	0.001 – 0.01	kg/(l·h)



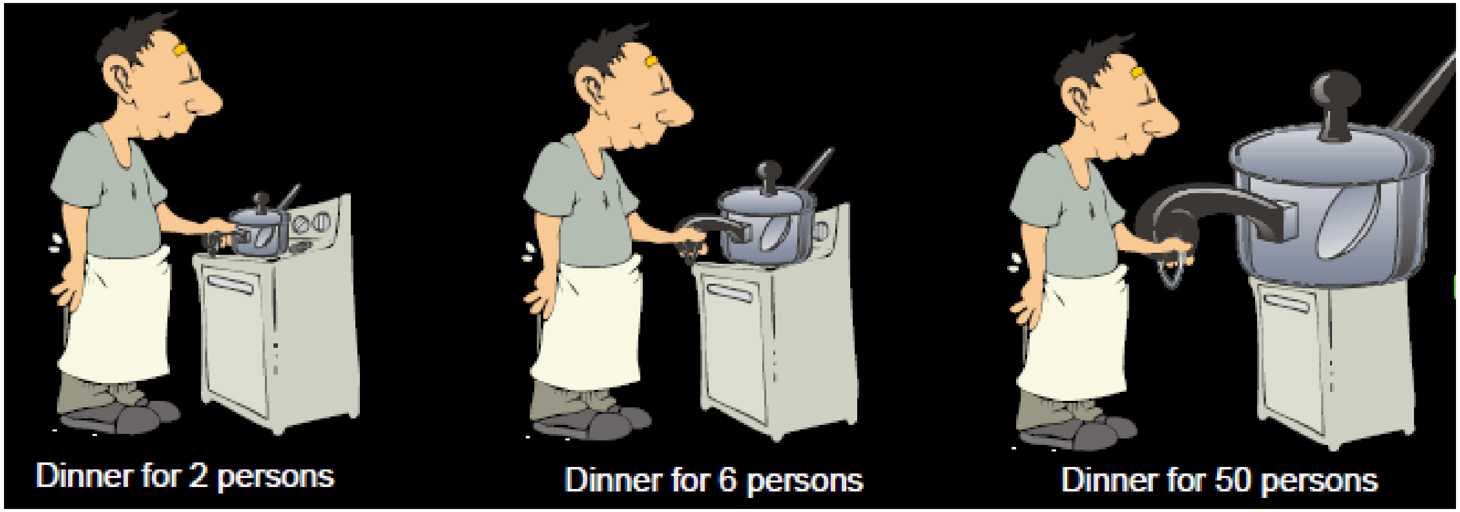
Fine Chemicals Manufacture

	Plant Capacity	E Factor (kg waste / kg product)
Oil Refining	> 1 Mio t / year	< 0.1
Bulk Chemicals	10.000 t / year up to 1 Mio t / year	< 1-5
Fine Chemicals	< 10.000 t / year	5-50
Pharmaceuticals	< 1 t / year	25-100

According to: R.A. Sheldon, *The E factor: fifteen years on*, Green Chemistry 9 (2007) 1273.

Process Development for the Reduction of the **E factor** in Fine Chemicals and Pharmaceuticals Manufacture due to …
… reduction of negative environmental impact
… reduction of cost of disposing of waste

Fine Chemicals Manufacture

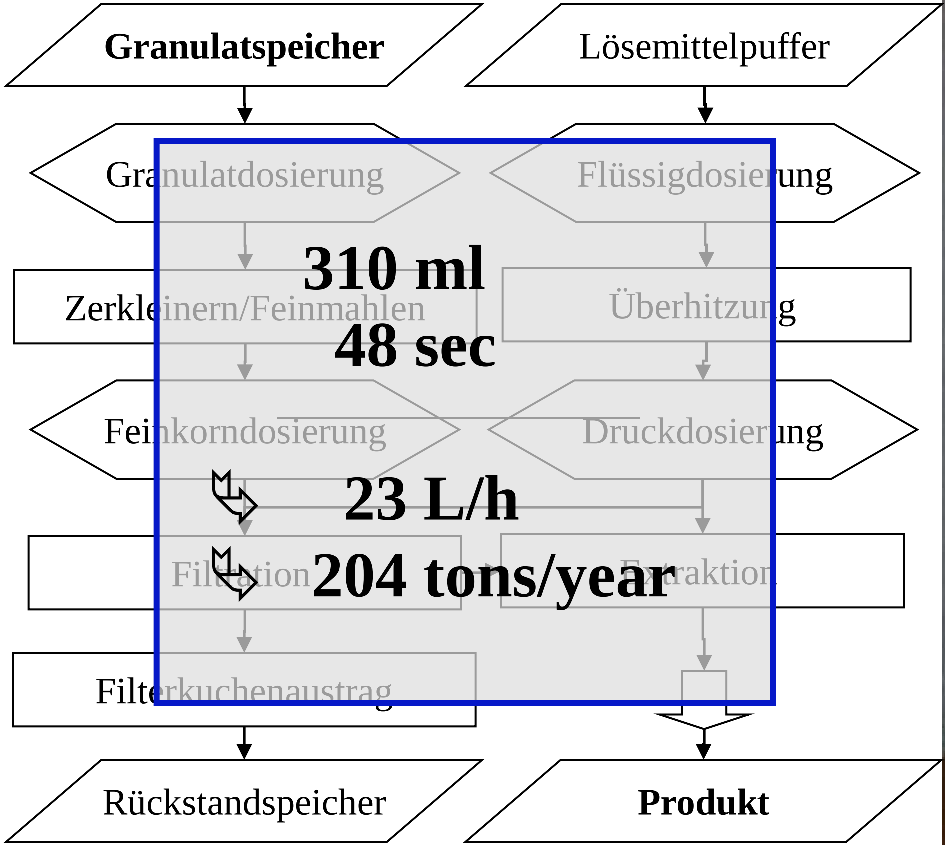


From: A. Stankiewicz, Process Intensification Workshop, DECHEMA, 29.05.2006.

Process time in batch-wise fine chemical manufacture is mostly limited by heat and mass, and not by the chemical reaction itself.

Due to increasing V and decreasing A/V, **process time** increases when scaling up from bench to production scale.

Fine Chemicals Manufacture



Granulatspeicher

Lösemittelpuffer

Granulatdosierung

Flüssigdosierung

Zerkleinern/Feinmahlen

Überhitzung

Feinkorndosierung

Druckdosierung

Filtration

Extraktion

Filterkuchenaustrag

Rückstandspeicher

Produkt

310 ml

48 sec

23 L/h

204 tons/year

V=ca. 40 l

From: Dr. J. Lang, Evonik Degussa

Fine Chemicals Manufacture

Shifting from batch-wise to continuous operation:

Fine chemical synthesis with $Y_{P,E}$=80 %, c_{E0} = 1 mol/l and M_P = 100 g/mol
(assuming continuous reactor with V_{reac} = 40 l and reaction time of 1 min):

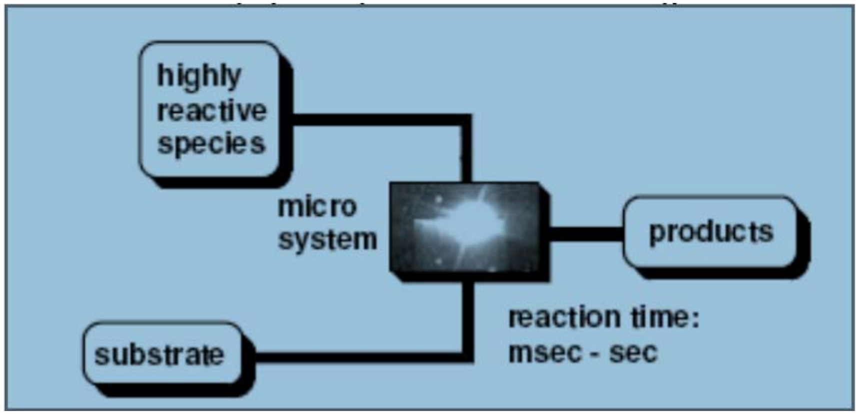
$$\dot{m}_{\mathrm{Product}} = \frac{V_{\mathrm{reac}} \cdot c_{Eo} \cdot Y_{P,E} \cdot M_{\mathrm{P}}}{\tau} =$$

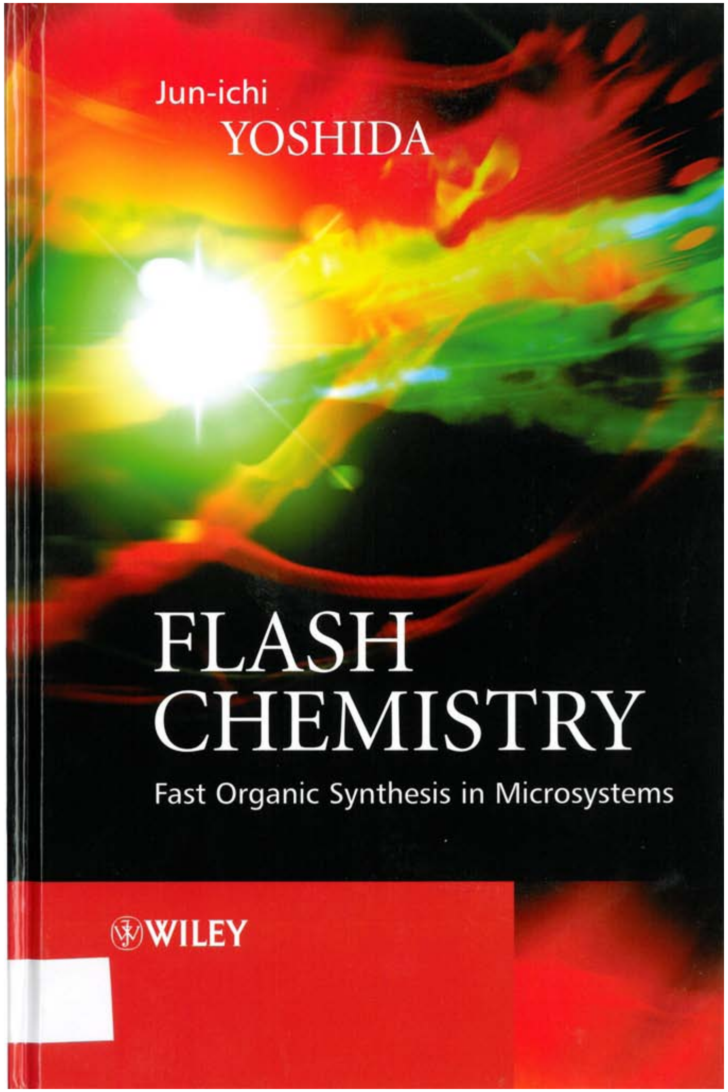
$$= \frac{40\,l \cdot 1\,mol/l \cdot 0.8 \cdot 100\,g/mol}{1\,\mathrm{min}} =$$

$$= 4{,}608\,kg/day = 4{,}6\,t/day$$

Production Capacity: ca. 1,533 t / a
Space Time Yield: ca. 4.8 kg per liter and hour
→ higher capacity or shorter time-to-market

Fine Chemicals Manufacture



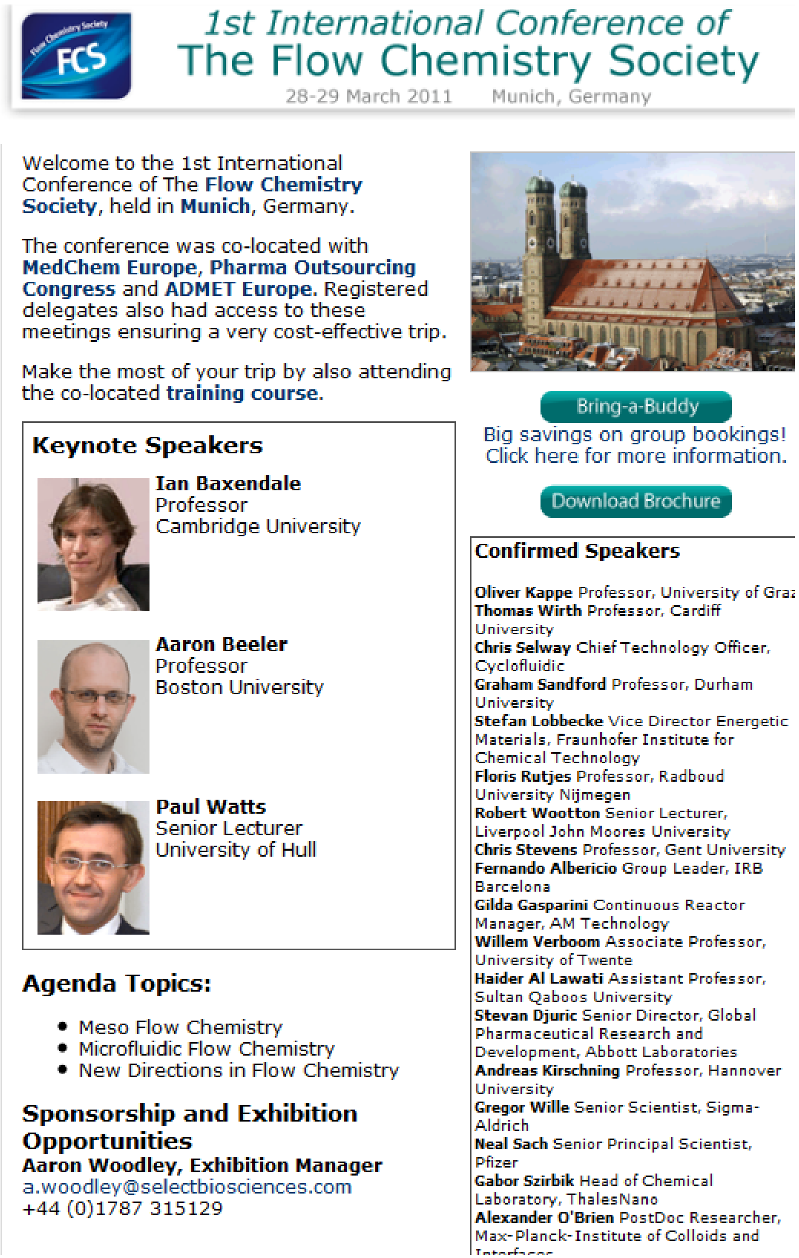

Jun-ichi
YOSHIDA

FLASH
CHEMISTRY
Fast Organic Synthesis in Microsystems

WILEY

J. Yoshida, A. Naganki, T. Yamada, Chem. Euro. J. 14(2008)7450.

Fine Chemicals Manufacture



1st International Conference of
The Flow Chemistry Society
28-29 March 2011 Munich, Germany

Welcome to the 1st International Conference of The **Flow Chemistry Society**, held in **Munich**, Germany.

The conference was co-located with **MedChem Europe**, **Pharma Outsourcing Congress** and **ADMET Europe.** Registered delegates also had access to these meetings ensuring a very cost-effective trip.

Make the most of your trip by also attending the co-located **training course**.

Keynote Speakers

Ian Baxendale
Professor
Cambridge University

Aaron Beeler
Professor
Boston University

Paul Watts
Senior Lecturer
University of Hull

Agenda Topics:

- Meso Flow Chemistry
- Microfluidic Flow Chemistry
- New Directions in Flow Chemistry

Sponsorship and Exhibition Opportunities
Aaron Woodley, Exhibition Manager
a.woodley@selectbiosciences.com
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Big savings on group bookings!
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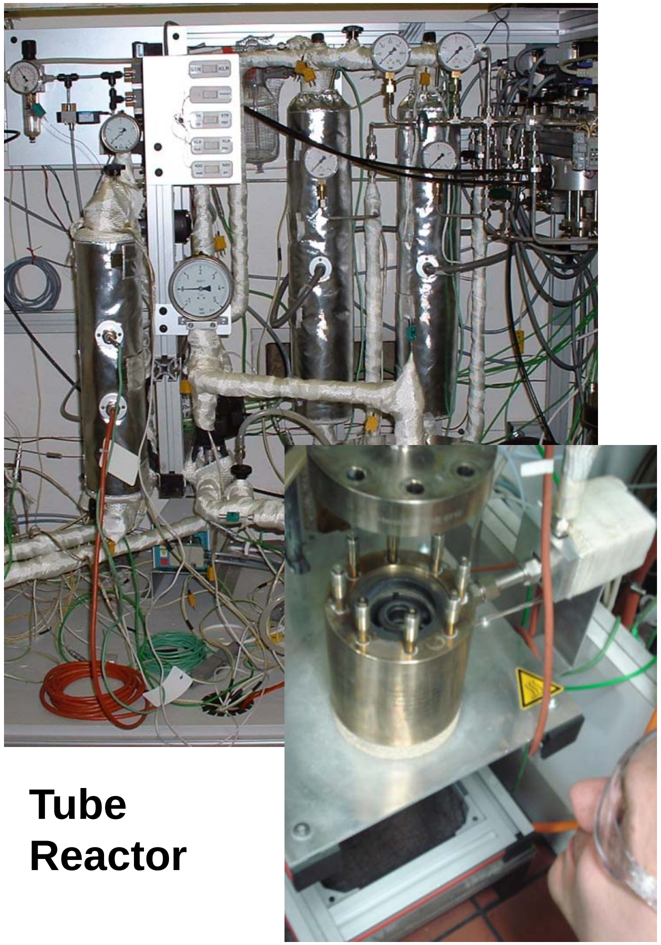
Confirmed Speakers

Oliver Kappe Professor, University of Graz
Thomas Wirth Professor, Cardiff University
Chris Selway Chief Technology Officer, Cyclofluidic
Graham Sandford Professor, Durham University
Stefan Lobbecke Vice Director Energetic Materials, Fraunhofer Institute for Chemical Technology
Floris Rutjes Professor, Radboud University Nijmegen
Robert Wootton Senior Lecturer, Liverpool John Moores University
Chris Stevens Professor, Gent University
Fernando Albericio Group Leader, IRB Barcelona
Gilda Gasparini Continuous Reactor Manager, AM Technology
Willem Verboom Associate Professor, University of Twente
Haider Al Lawati Assistant Professor, Sultan Qaboos University
Stevan Djuric Senior Director, Global Pharmaceutical Research and Development, Abbott Laboratories
Andreas Kirschning Professor, Hannover University
Gregor Wille Senior Scientist, Sigma-Aldrich
Neal Sach Senior Principal Scientist, Pfizer
Gabor Szirbik Head of Chemical Laboratory, ThalesNano
Alexander O'Brien PostDoc Researcher, Max-Planck-Institute of Colloids and

Bench Scale Reactors for Heterogeneous Catalysis

Catalytic Wall Reactors



Tube Reactor

Recycle Reactor (Type Berty)

Stirred Autoclave Reactor

Slug Flow Reactor

Source:
Lehrstuhl Technische Chemie,
Universität Erlangen-Nürnberg
Universität Stuttgart

List of Symbols

Symbol	Dimension	Description
$c_{E,0}$	$\mathrm{mol \cdot m^{-3}}$	concentration of educt species E at the beginning of the reaction
M_E	$\mathrm{g \cdot mol^{-1}}$	molar mass of educt E
$\dot{m}_P$	$\mathrm{kg \cdot s^{-1}}$	productivity (mass flow of the product P)
$S_{P,E}$	-	selectivity to product P related to educt E
t	s	process time
V_{reac}	$\mathrm{m^3}$	reaction volume
$\dot{V}$	$\mathrm{m^3 \cdot s^{-1}}$	volumetric flow rate
X_E	-	conversion of educt E
$Y_{P,E}$	-	yield of product P related to educt E
τ	s	residence time