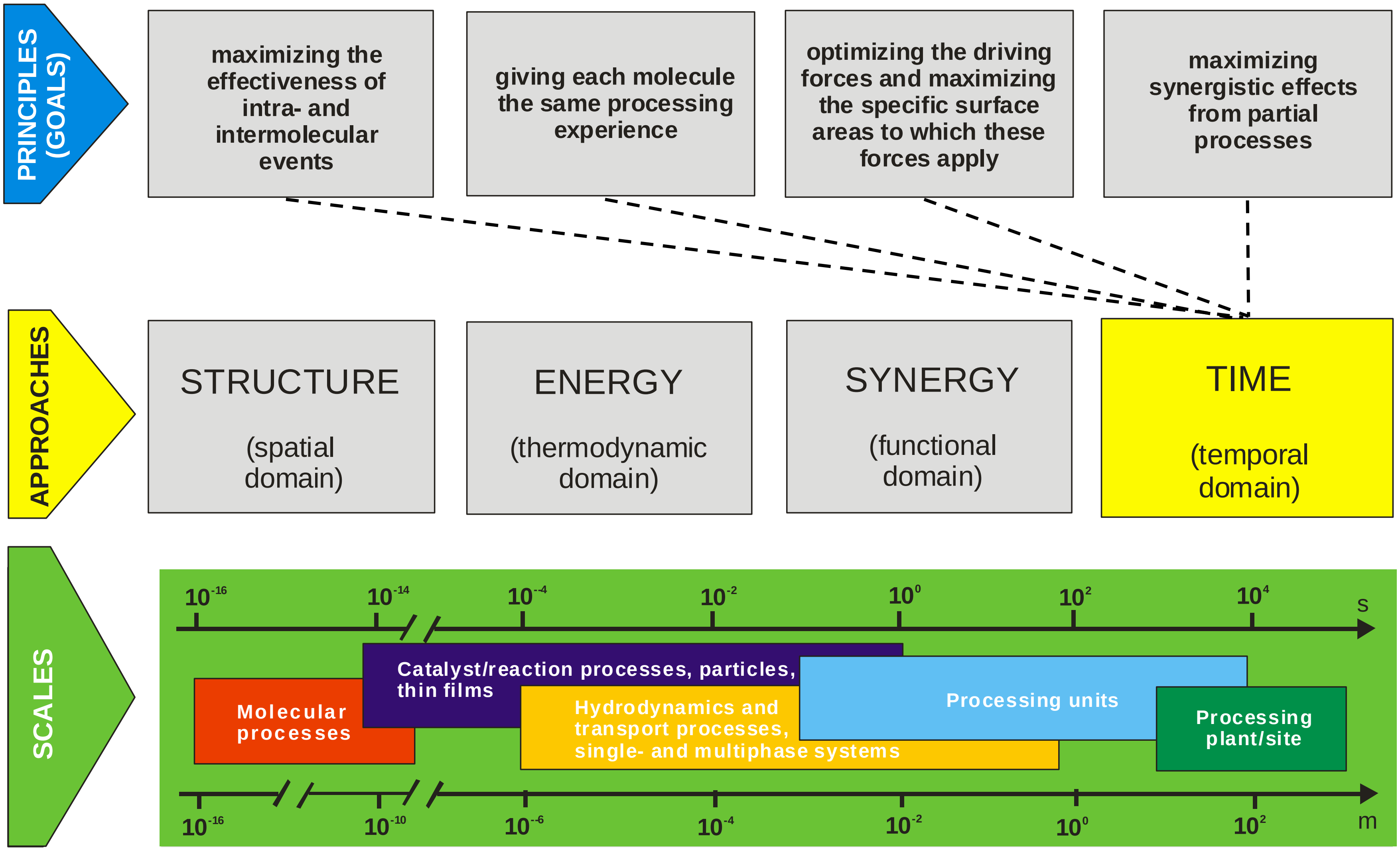
TIME

THE 4TH DIMENSION OF PROCESS INTENSIFICATION

TUDelft

Fundamentals of Process Intensification



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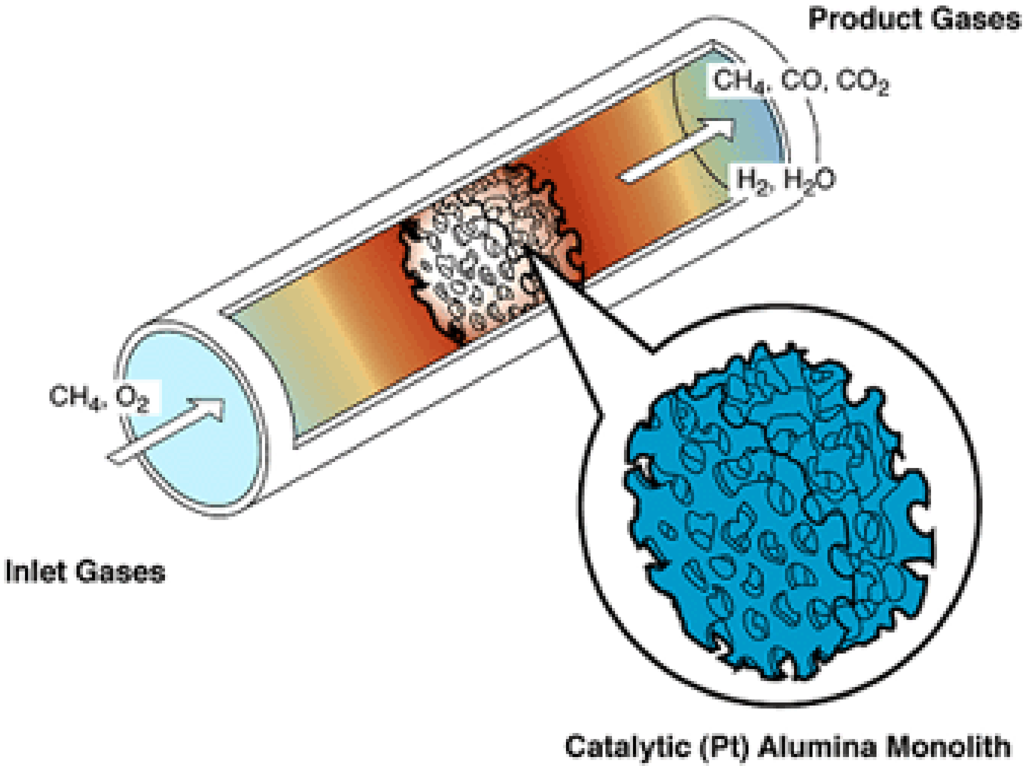
Introducing temporal aspect

- Manipulation of the duration of a process/event
- Introduction of dynamic/transient state in a process (e.g., periodicity)

Minimizing process duration (short contact time reactors)

Microsecond catalytic partial oxidation of alkanes to olefins



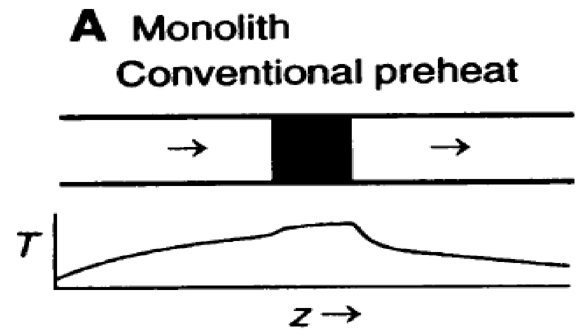
Goal is to avoid complete oxidation, but to form intermediate products by quick heating and cooling

Minimizing process duration

Microsecond catalytic partial oxidation of alkanes

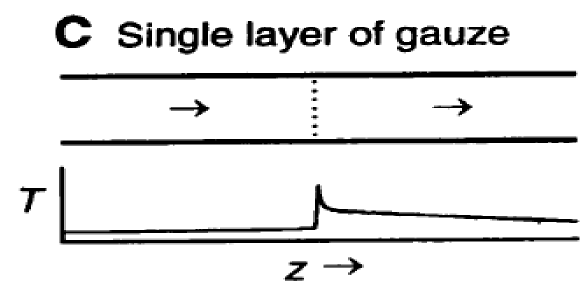
Conventional heating

broad heating/cooling profiles



Microsecond heating

compressed heating/cooling profiles



heating time 5 μs, contact time with catalyst 10 μs, cooling time 200 μs (800°C -> 400°C)

Goetsch et al., Science, 1996

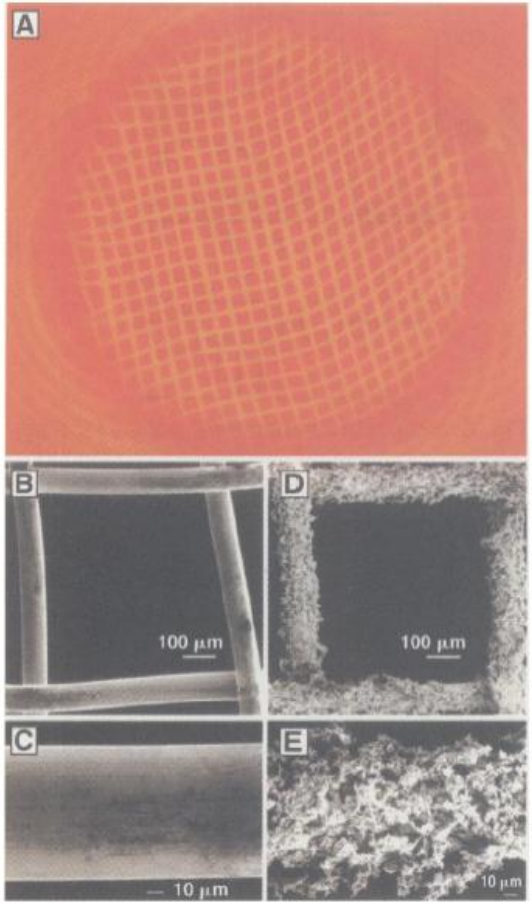
Minimizing process duration

Microsecond catalytic partial oxidation of alkanes

- **High oxygen conversion**
- **High selectivity to POx products**

Table 1. Effect of chain length on alkane oxidation over a single layer of Pt–10% Rh gauze. The conditions were as follows: superficial velocity, 25 cm/s; pressure, 1.4 atm; C/O = 7; and inlet gas temperature, 25°C.

	Alkane			
	C_2H_6	C_3H_8	C_4H_{10}	iso-C_4H_{10}
Conversion (%)				
Alkane	34	16	10	3
Oxygen	100	99	90	70
Carbon selectivity (%)				
Olefins	62	58	36	<1
Oxygenates	7	9	40	<0.2
Alkanes	13	10	<1	Trace
$CO + CO_2$	18	23	24	99
Temperature (°C)				
Surface	900	850	800	800
Gas	580	504	400	395



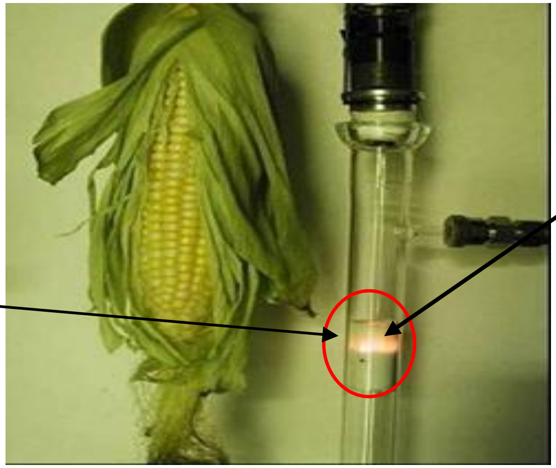
Goetsch et al., Science, 1996

Minimizing process duration

Millisecond biomass gasification

Conventional

Recent invention (U. Minnesota)



Processing 1 kg of biomass / day in a 6 cm^3 reactor!!

- Biomass gasification is a mature technology.
- Tar formation (high molecular weight hydrocarbons) due to slow heat transfer rate is the major problem→ Tars condense and clog the downstream equipment.
- Bulky equipment.

- 50 ms process/ No tar formation

- HUGE IMPACT!
  - Science 2006, 314, 801-804
  - Science 2004, 303, 993-997
  - Nature 2007, 447, 914-915

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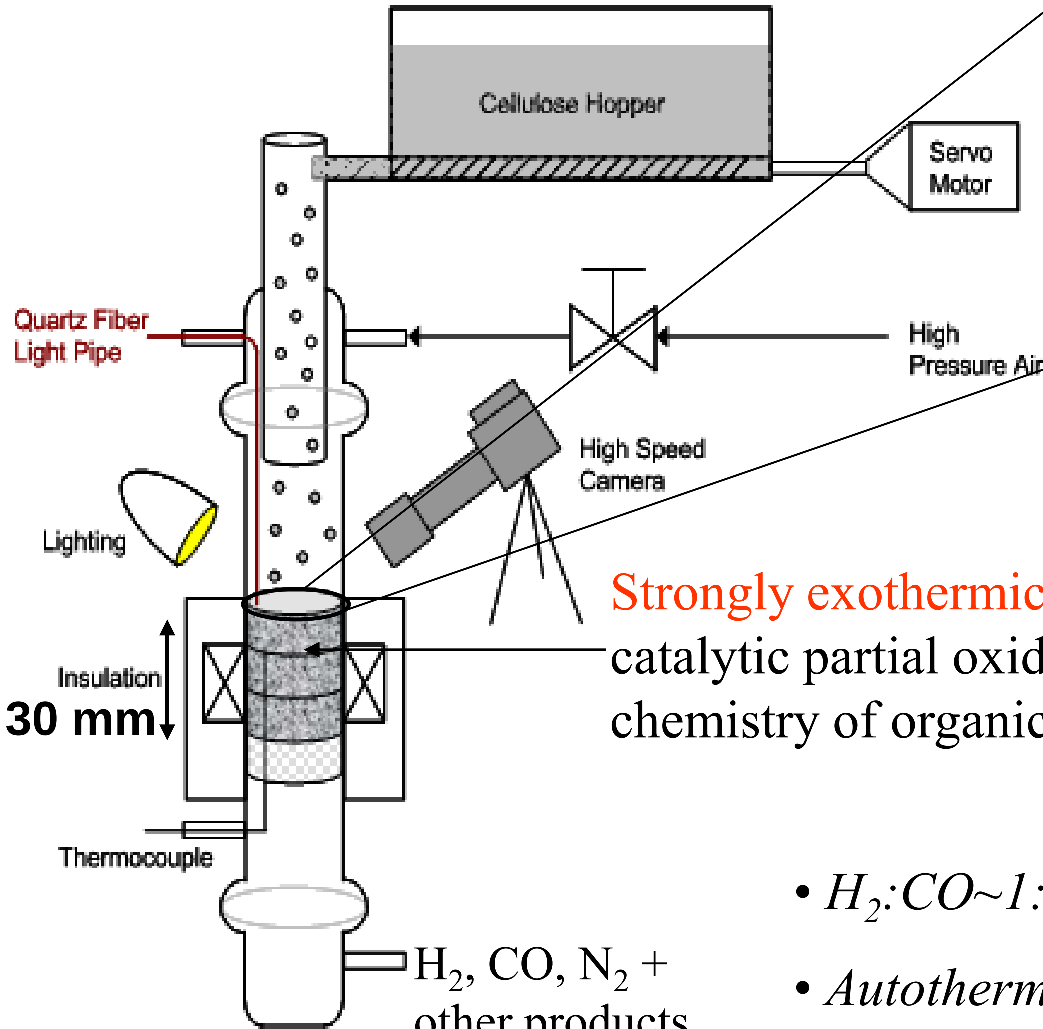
How does it work?



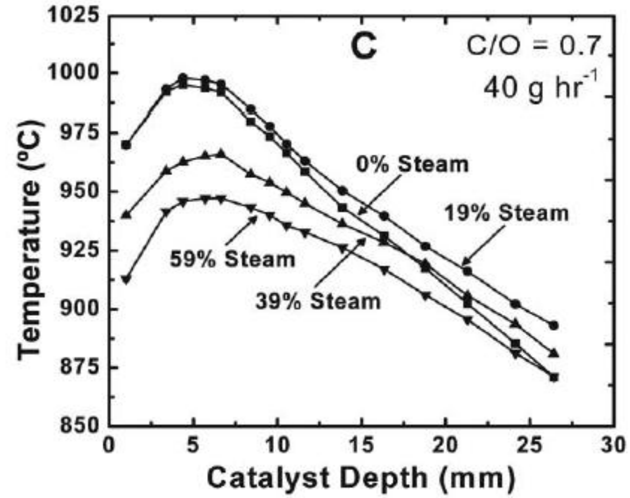
Strongly endothermic flash volatilization of solids at the surface into organic vapors

Strongly exothermic catalytic partial oxidation chemistry of organic vapors

VERY FAST HEAT TRANSFER between the two zones located µm apart enables the process

- *H_2:CO~1:1, conditioned with addition of steam*
- *Autothermal process*

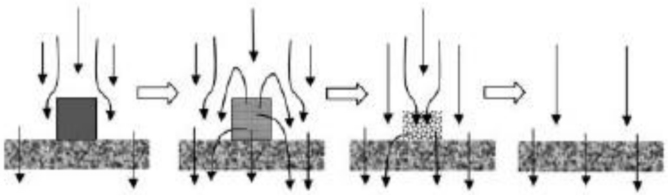
How does it work?



Chemistry

Volatilization: $(C_6H_{10}O_5)_n \rightarrow$ Gases + VOC + Char

Char + $O_2 \rightarrow$ Gases



Oxidation: VOC + $O_2 \rightarrow$ Gases

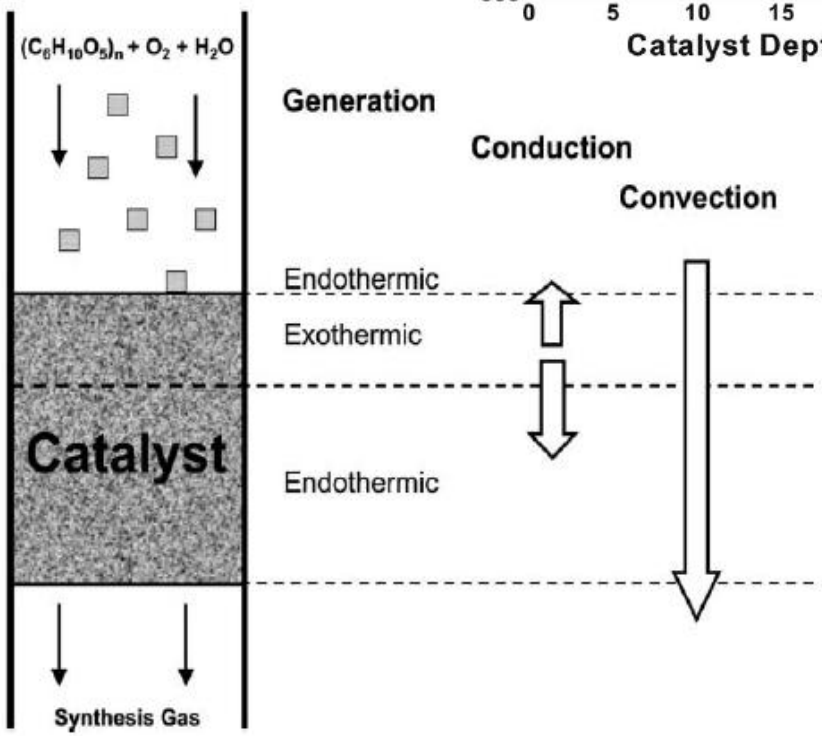
Reforming: VOC + $H_2O \rightarrow$ Gases

$CO + H_2O \leftrightarrow CO_2 + H_2$

Global Chemistry:

$(C_6H_{10}O_5)_n + O_2 + H_2O \rightarrow CO + CO_2 + H_2 + H_2O$

Reactor



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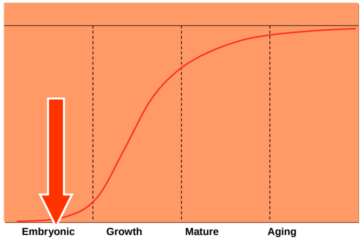
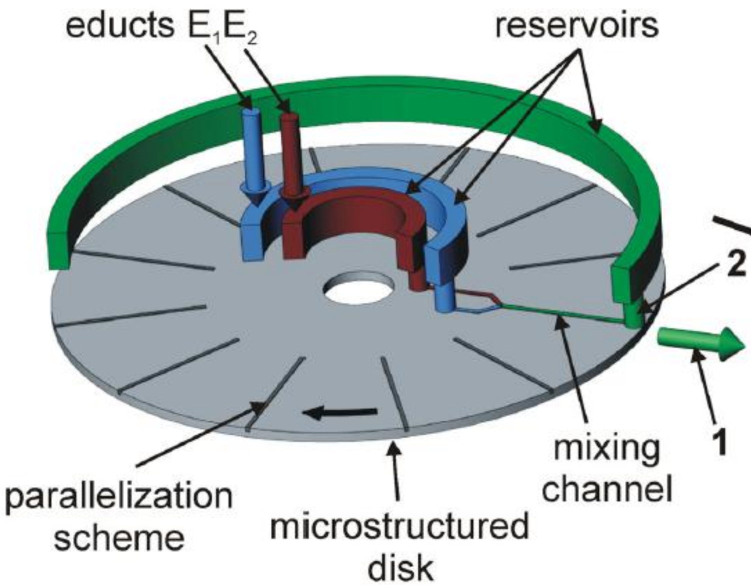
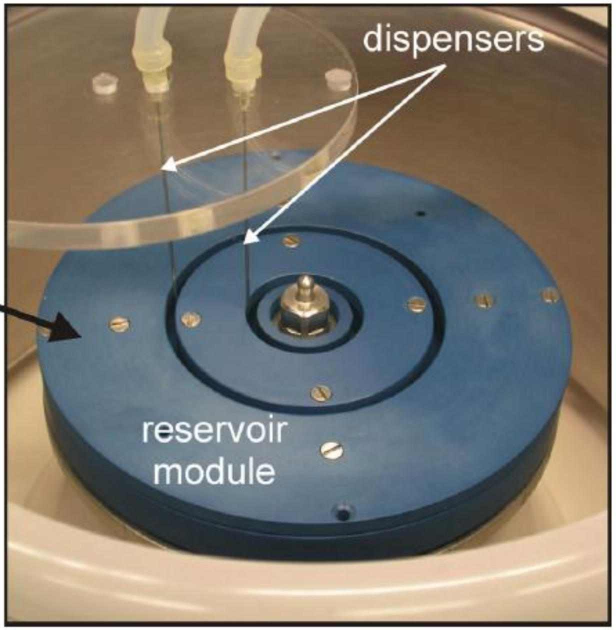
Manipulation of time



High-gravity field induces rapid mixing in straight channels





- J. Ducrée et al. (2006): **shortening of the mixing time by up to 2 orders of magnitude**

(J. Ducrée, et al., Microfluid Nanofluid, 2, 97-105 (2006))

Introducing temporal aspect

- Manipulation of the duration of a process/event
- Introduction of dynamic/transient state in a process (e.g., periodicity)

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Natural periodicity in "stationary" reactors

Time scale	Examples
<Nanoseconds	Active sites, molecular level
0.001–0.1 s	Bubbles, drops, film transfer
0.1–1 s	Monoliths, pulsed trickle bed
Seconds	Risers
Seconds to minutes	Fluidized beds
Minutes to hours	Moving beds
Hours to days	Bioreactors, batch processes

Forced Dynamic Operation of Chemical Reactors

Via dynamic operation (pulsing) one can:

- influence kinetics of the adsorption-reaction-desorption processes on the catalyst surface (e.g. by pulsing concentrations, pressures, temperatures or pulsing electric and electromagnetic fields)

- increase interfacial mass transfer rates (e.g. pulsing operation of trickle-bed reactors or pulsing bubble columns)

- shift the process beyond the equilibrium limitation or improve energy utilization efficiency (regenerative processes, e.g. Reverse Flow Reactors)

- improve mixing characteristics of the system (e.g. variable volume operation of CSTRs and Oscillatory Flow Reactors)

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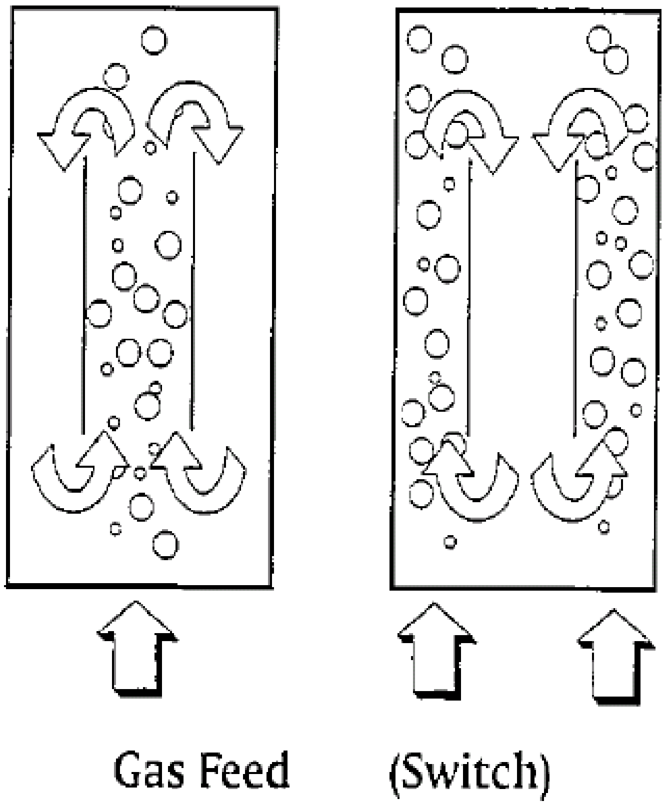
Forced Dynamic Operation of Chemical Reactors

Purposeful dynamic operation to intensify mass transfer

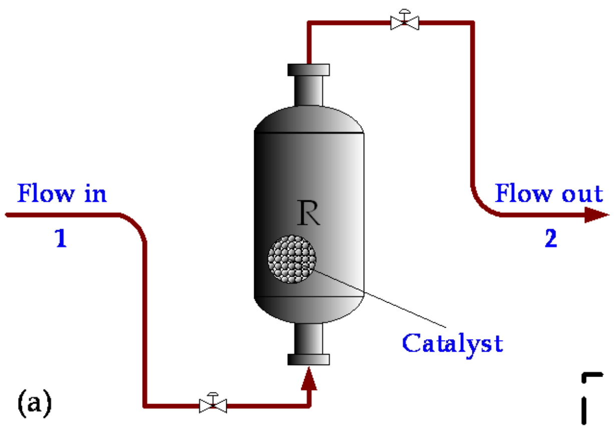
e.g. in gas-liquid (bubble-column) or gas-liquid-solid (trickle-bed) reactors

Periodical sparger switching led to 30% increase in mass transfer coefficients (Dehua et al., 1992)

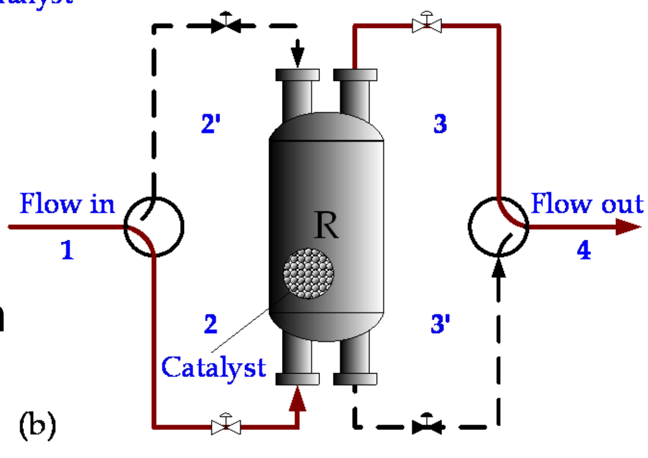


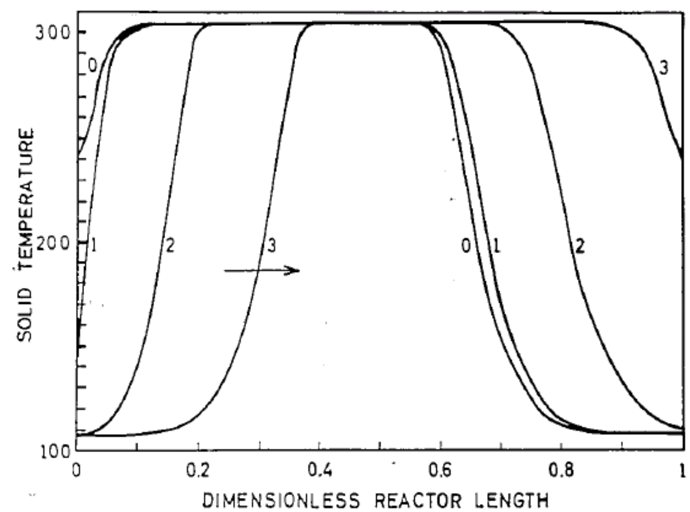
Forced Dynamic Operation of Chemical Reactors

Purposeful dynamic operation to utilize the reaction heat in an optimal manner.



reverse-flow reactors





Chronological segregation between heat generation and consumption

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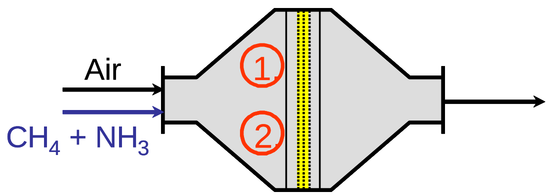
Heat exchange integration in industrial reactions

HCN synthesis

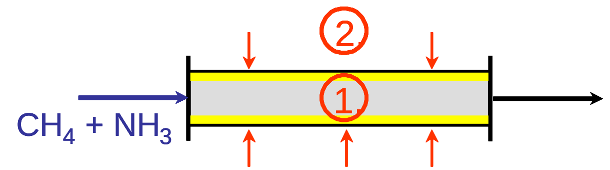
1. Synthesis reaction: $CH_4 + NH_3 \xrightarrow{1200\ °C} HCN + 3\ H_2$; $\Delta_r H = +\ 256$ kJ/mol

2. Heat generation: $3\ H_2 + 1{,}5\ O_2 \longrightarrow 3\ H_2O$; $\Delta_r H = -\ 726$ kJ/mol

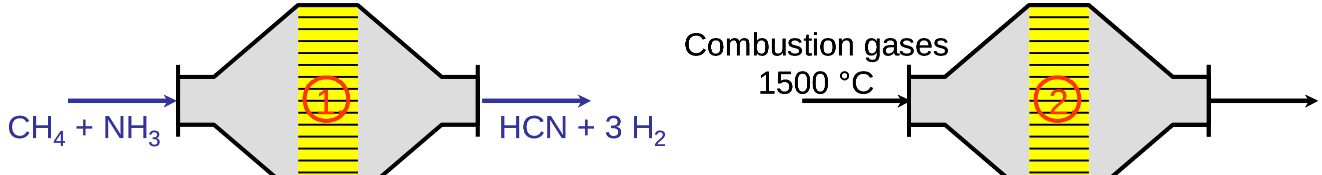
1. Andrussow-Process



2. BMA-Process



3. Regenerator-Reactor
(regenerative heat exchange)



D. Agar (1999), Chem.Engng.Sci. 54:1299-1305

(source: D. Agar, in: *Re-Engineering the Chemical Processing Plant*, Marcel Dekker, 2003)

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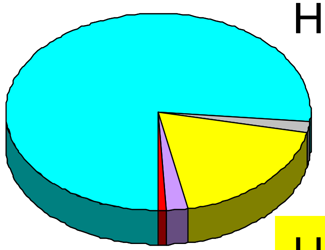
Heat exchange integration in industrial reactions

Andrussow

BMA



Comparison of reactor concepts

Process	Andrussow	BMA	Regenerator-Reactor
Catalyst	Pt/Rh-gauze	Pt-layer on tube wall	Supported Pt-cat. Fixed bed
Temp. [°C]	1100	1250	1200
C-Yield	60 %	91 %	91 %
N-Yield	65 %	82 %	82 %
HCN-Concn.	6 %	23 %	23 %
Energy demand [MJ/kg HCN]	~ 60	~ 60	< 50
$\eta_{thermal}$ of reactor	> 90 %	> 50 %	> 90 %
Reactor construction	simple, robust	ceramic, fragile	simple, robust

(source: D. Agar, in: *Re-Engineering the Chemical Processing Plant*, Marcel Dekker, 2003)

Reverse-flow reactors

Pros and Cons:

+ High energy utilization efficiency
+ No heat exchange surface in reactor-compactness
+ Higher throughputs compared to steady state operation
+ Operation at leaner combustible mixtures

– Difficult to exactly regulate temperature profiles

– Need for bifunctional catalyst for exo-/endothermic reactions

– Not applicable to gaseous chemistries (*does not hold for microreactors*)

"Wrong-way behavior" may arise upon flow reversal

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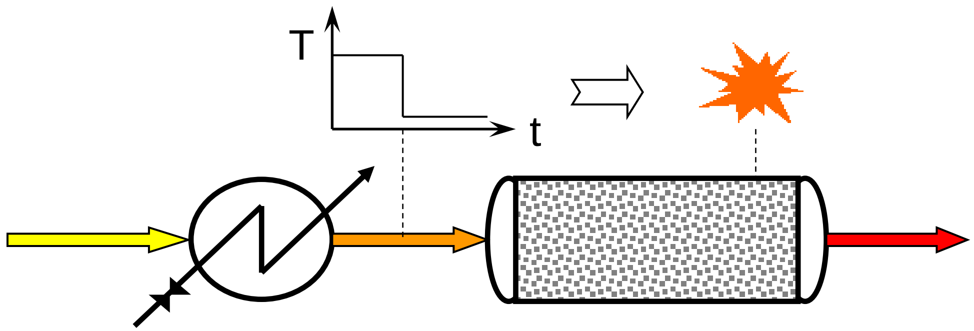
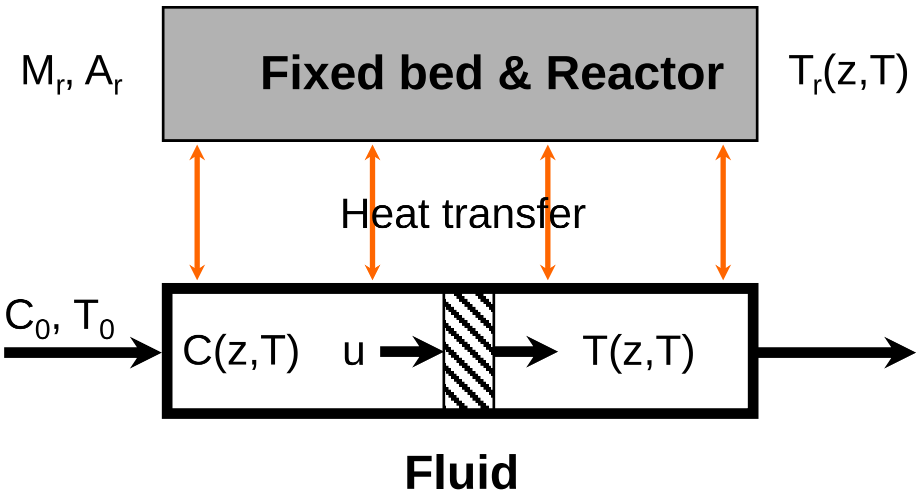
Wrong-way behavior



Despite reduction of inlet temperature, the transitional temperature within the reactor can increase considerably

- Concentration change: propagates with fluid velocity

- Temperature change: propagates much more slowly due to heat regeneration: $T_{Max} > T_o + \Delta T_{Ad}$! (*convection vs. conduction time scale*)



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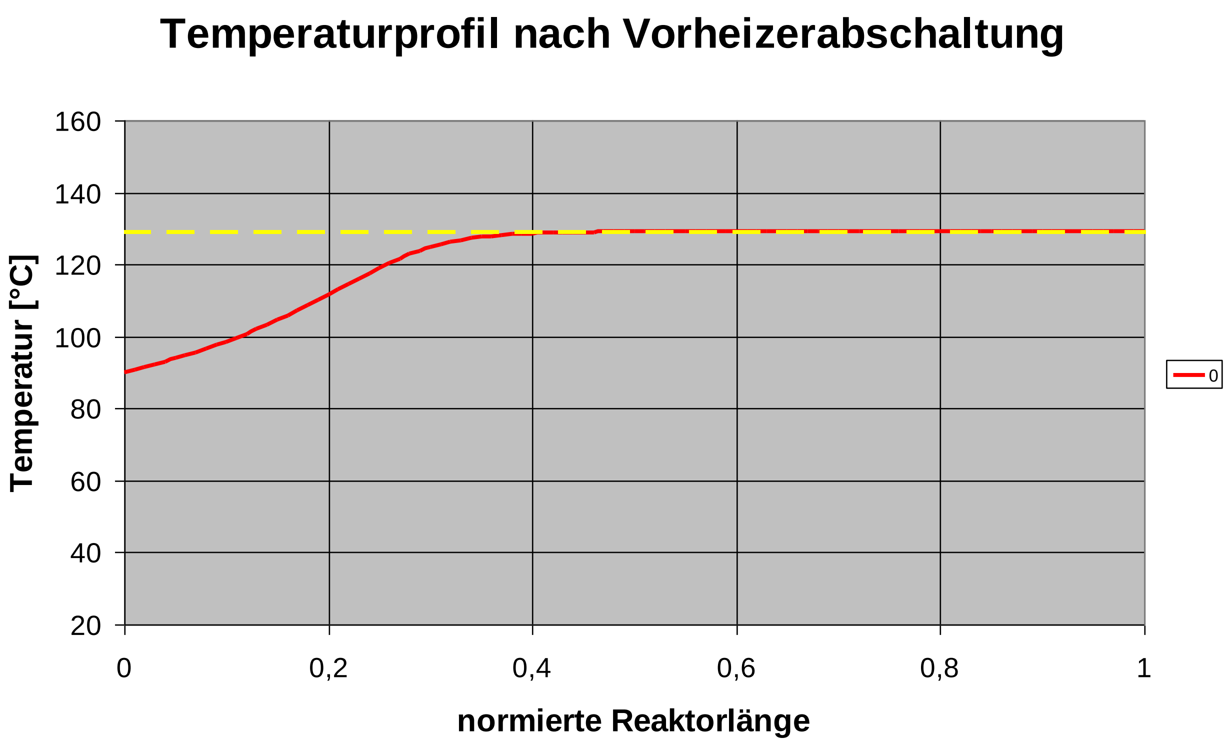

(source: D. Agar)

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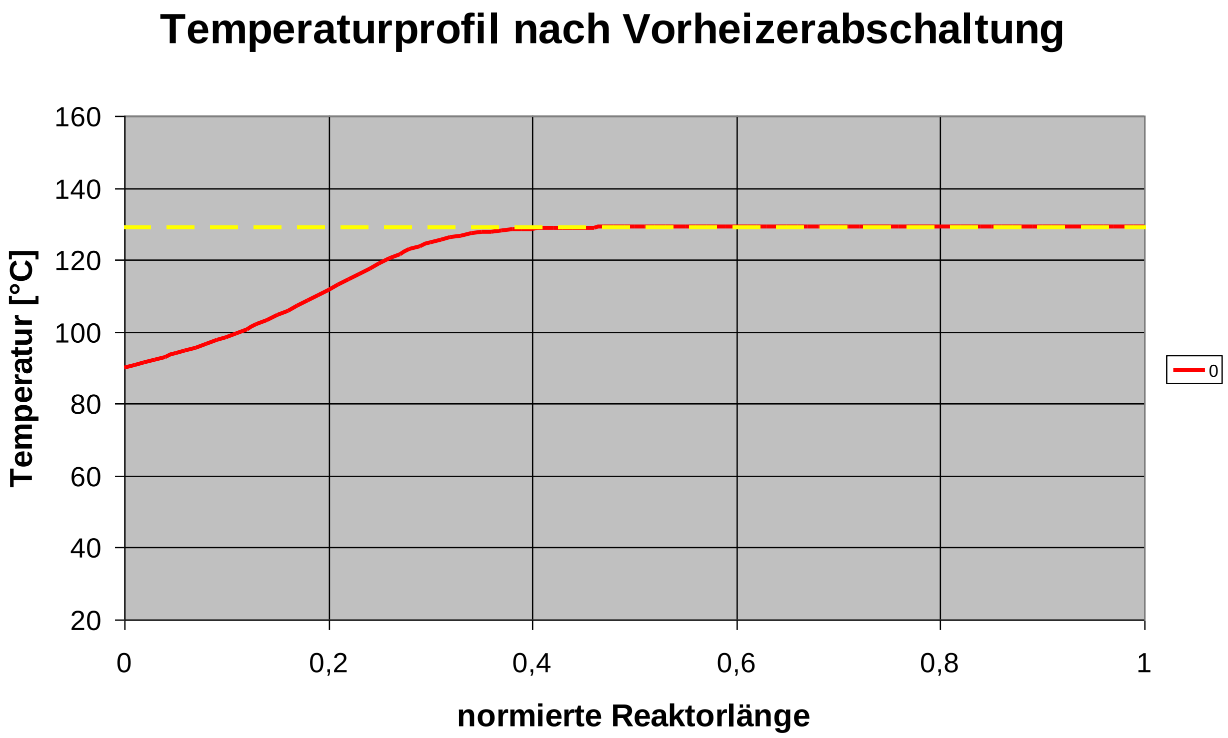

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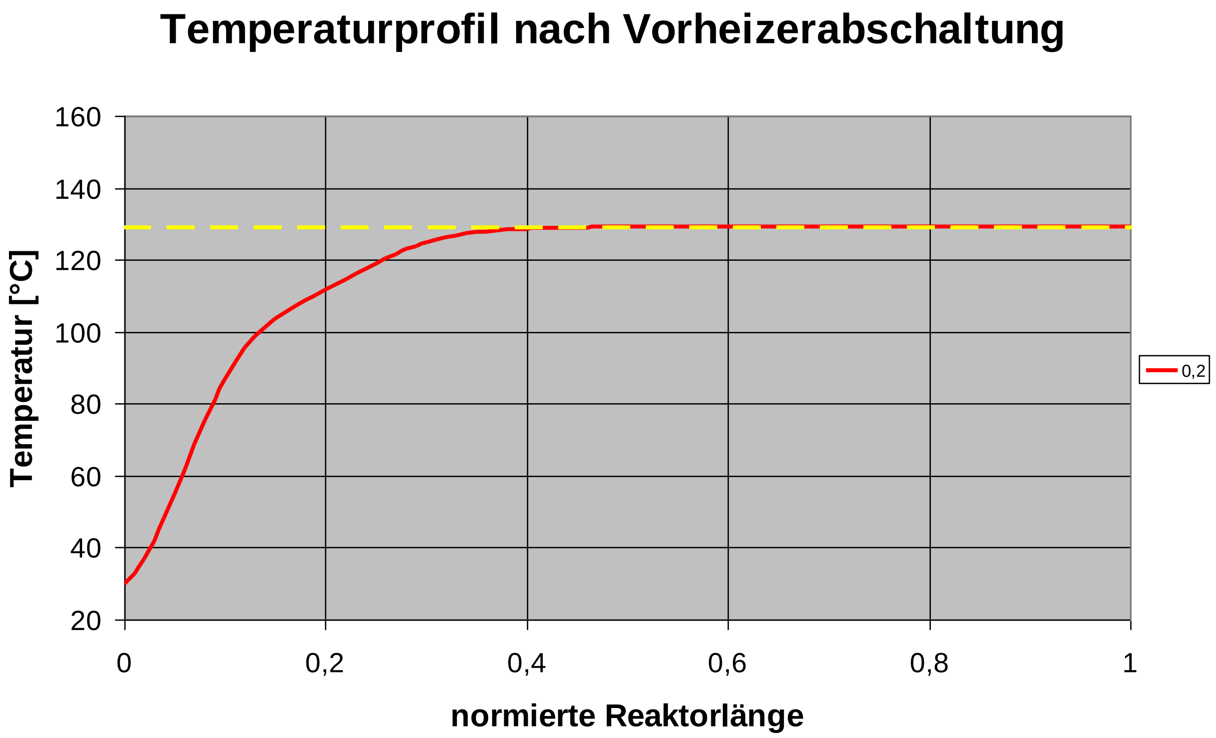

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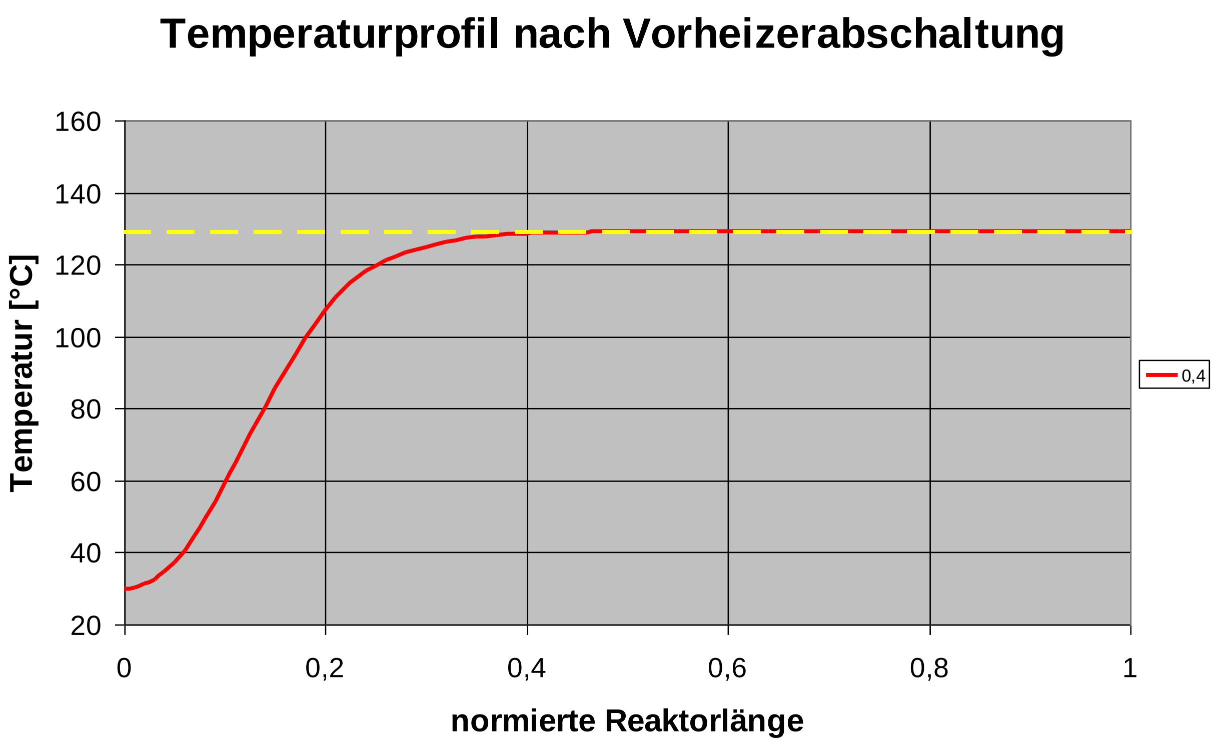

(source: D. Agar)

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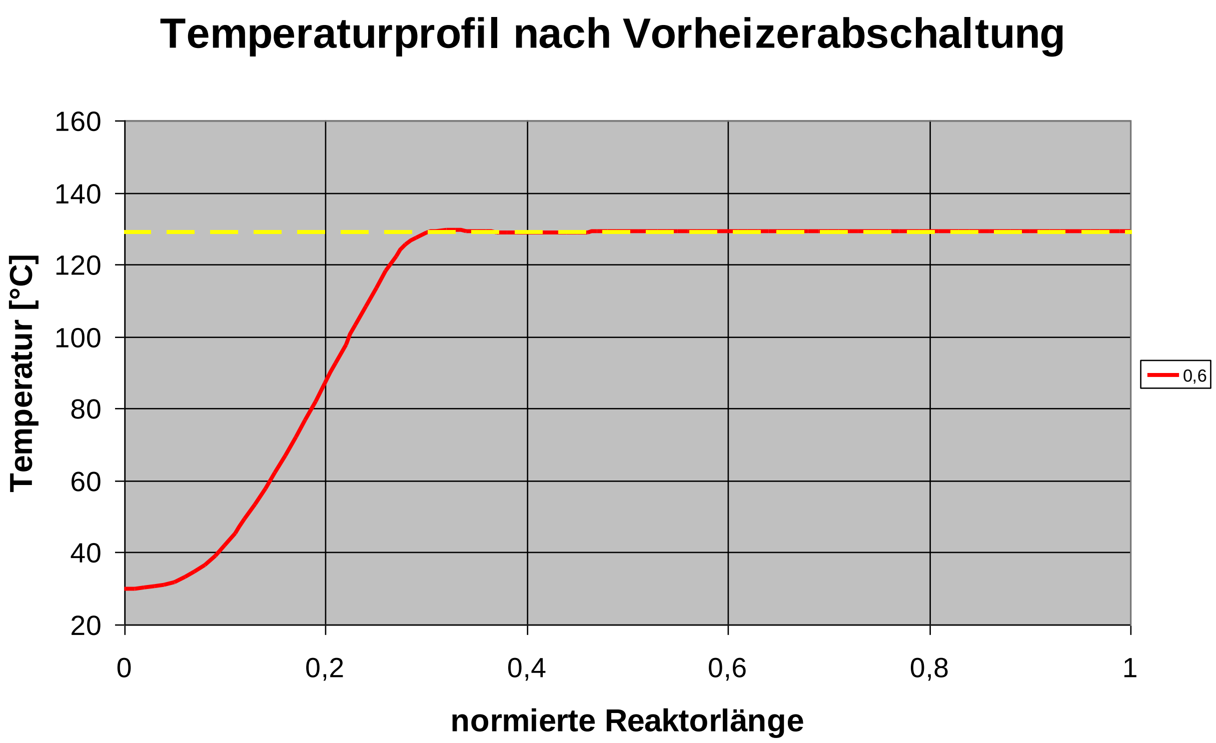

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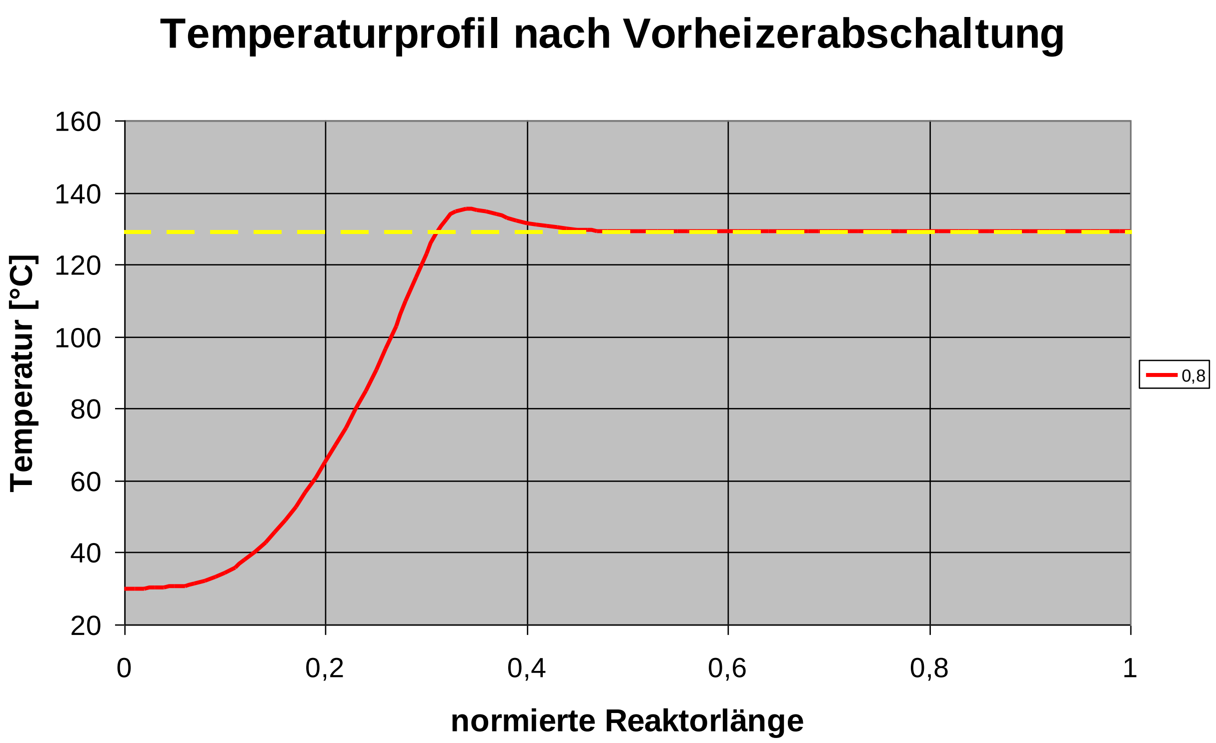

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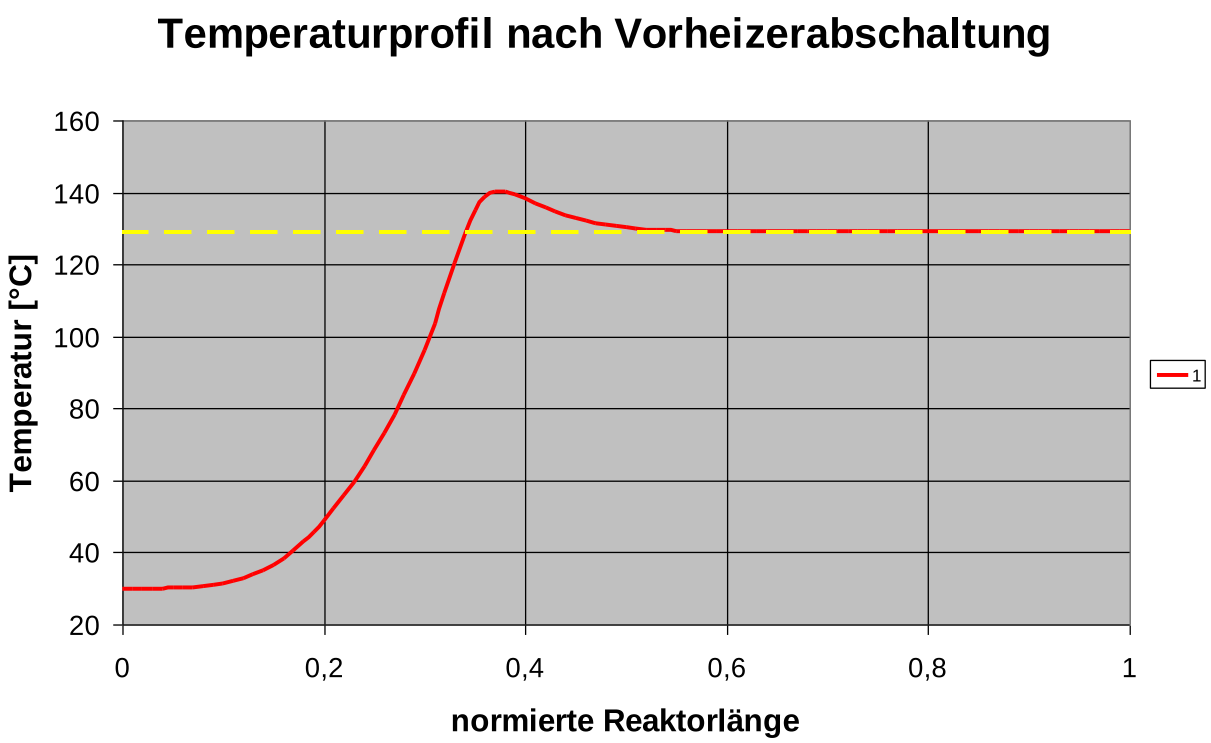

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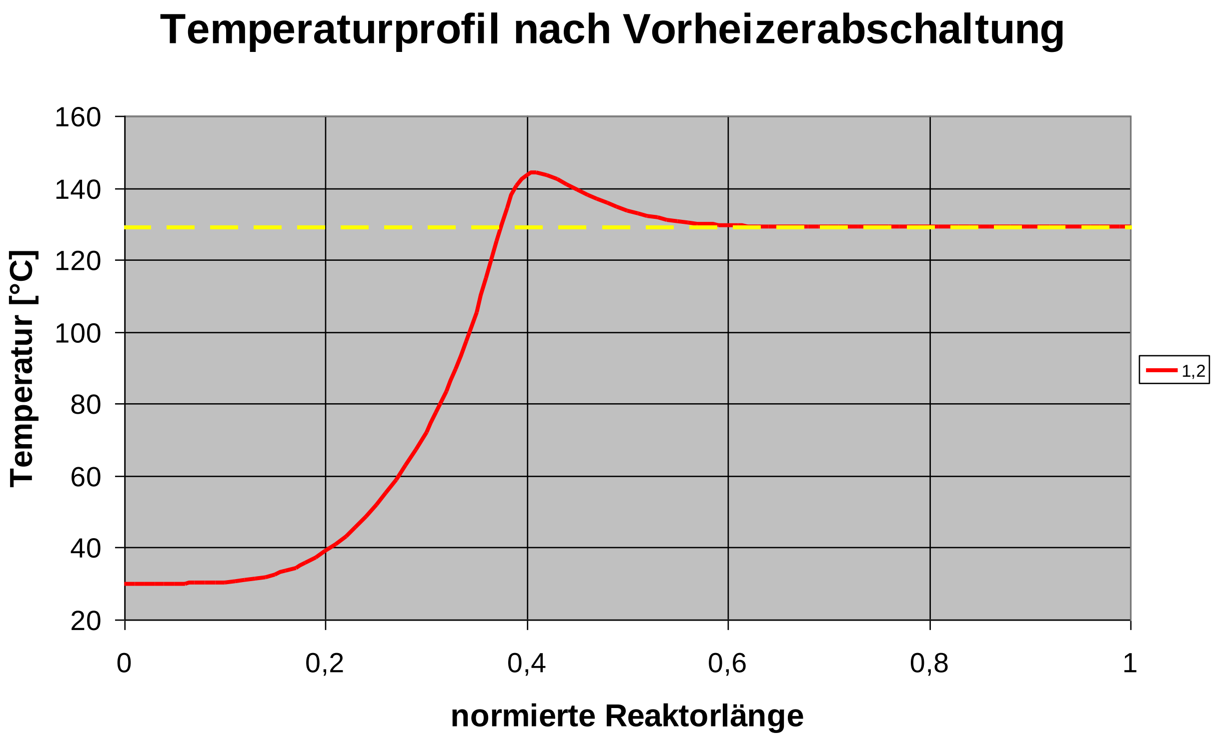

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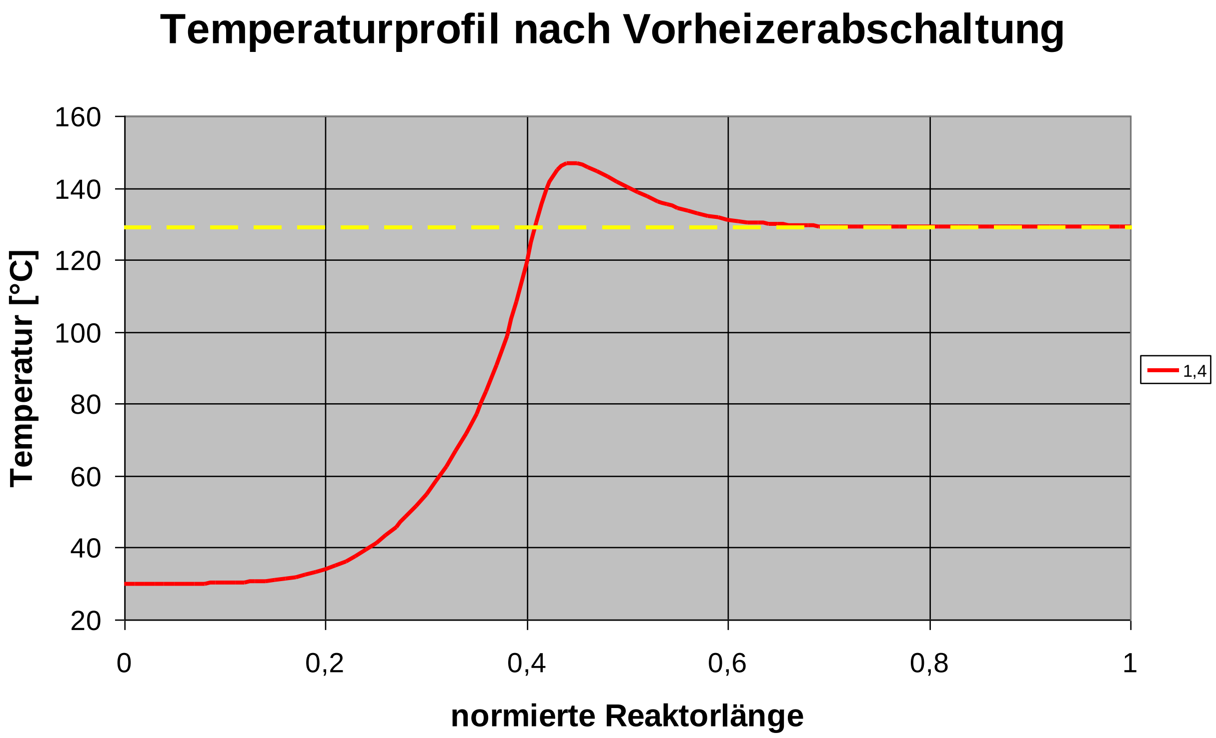

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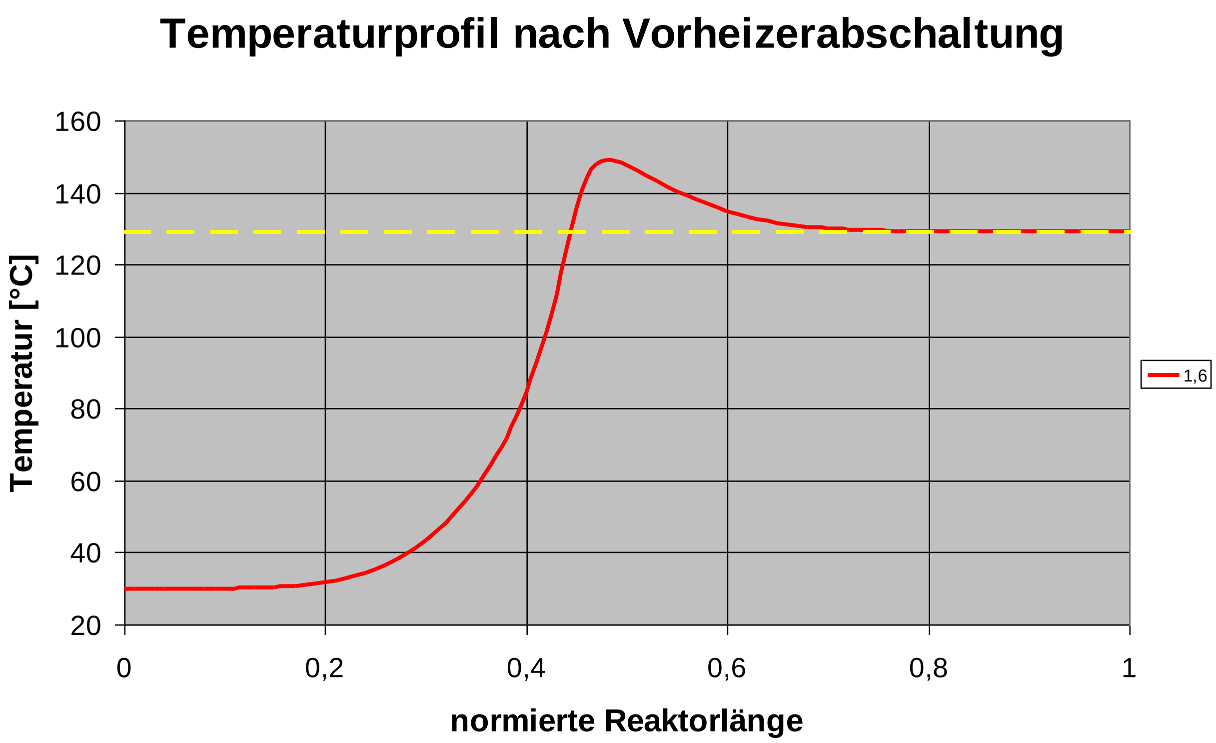

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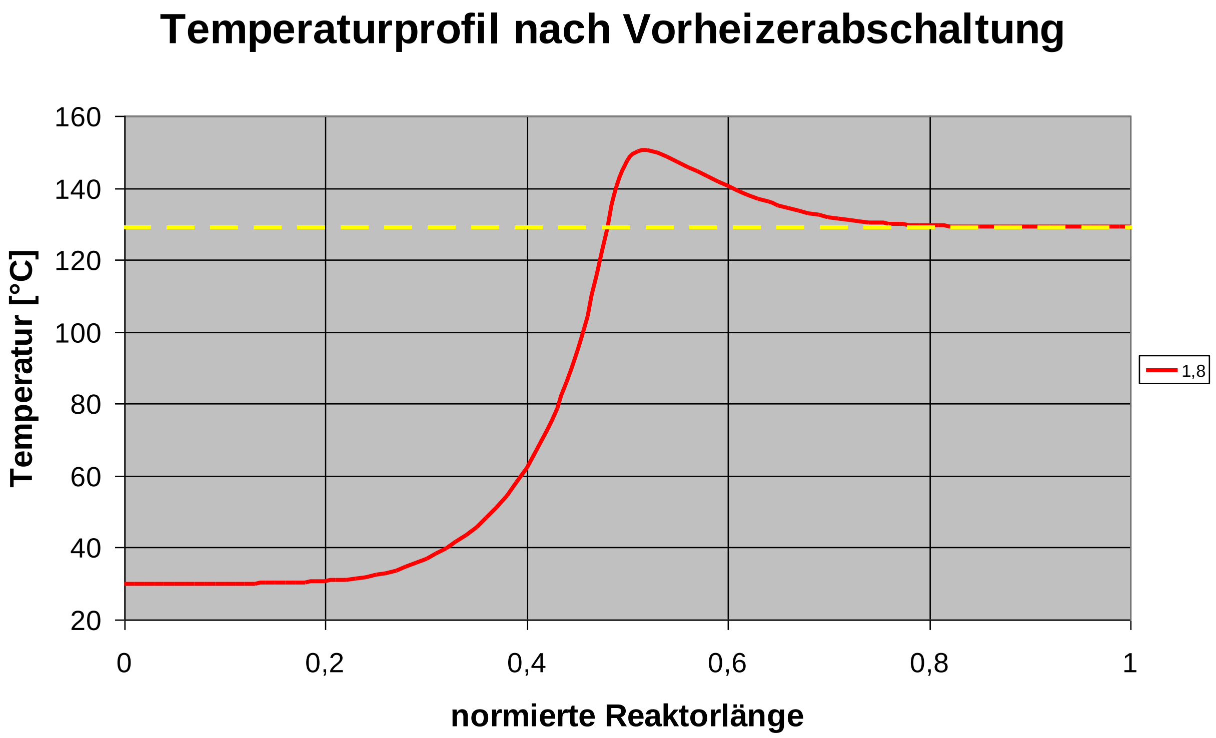

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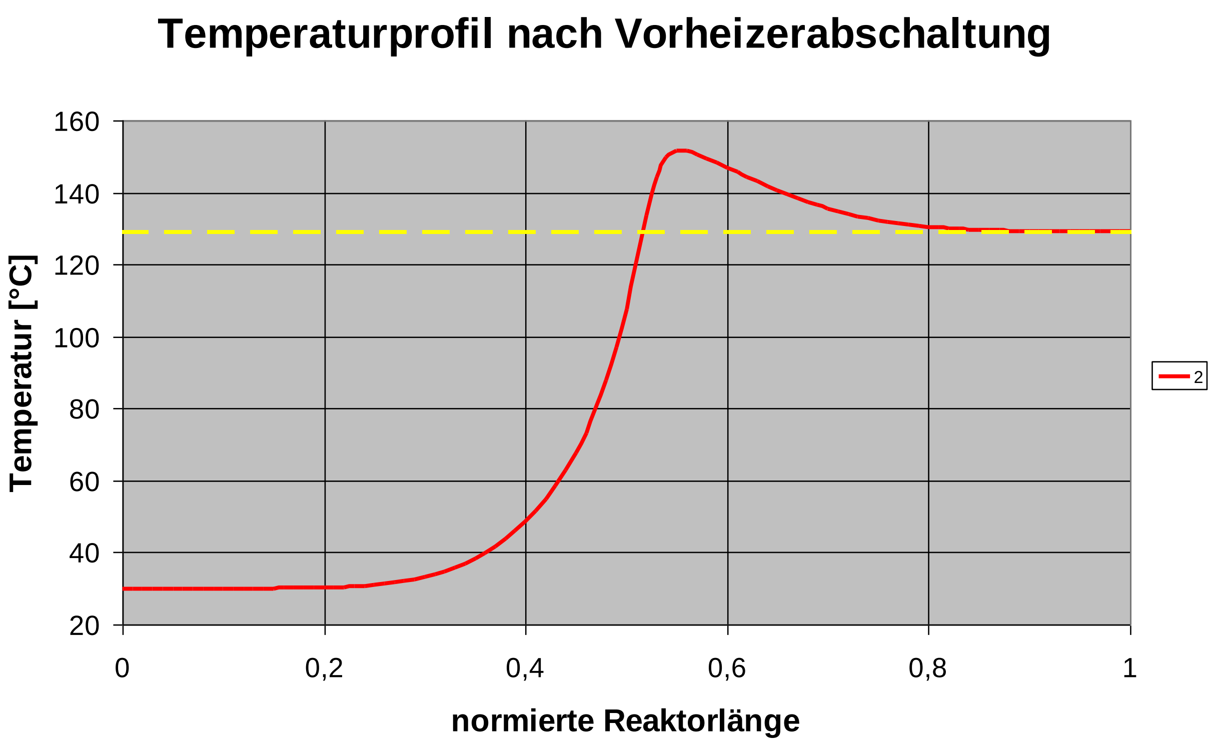

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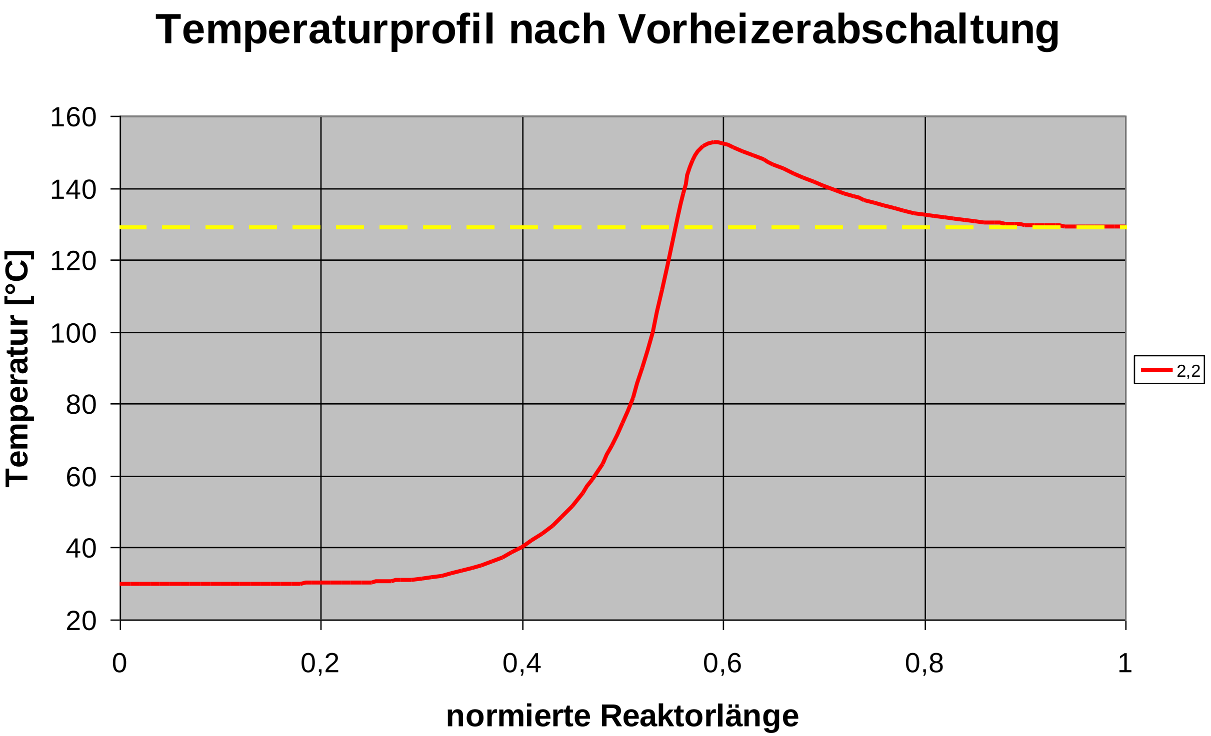

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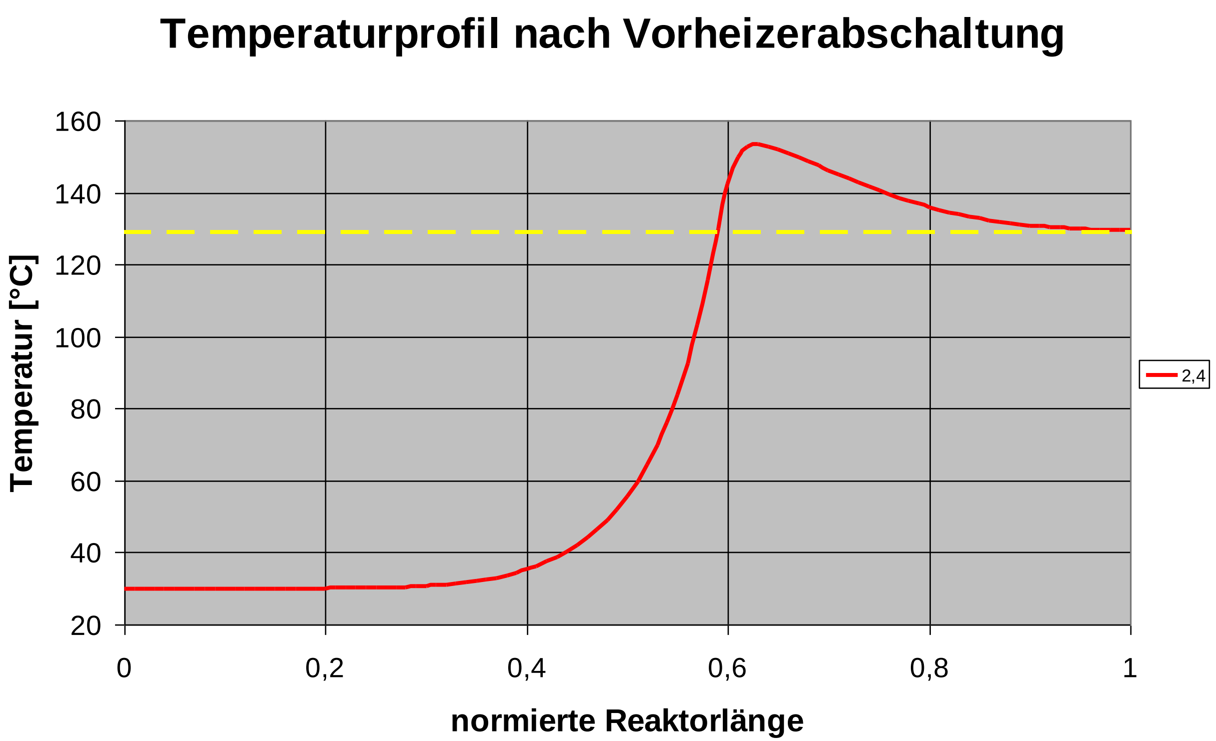

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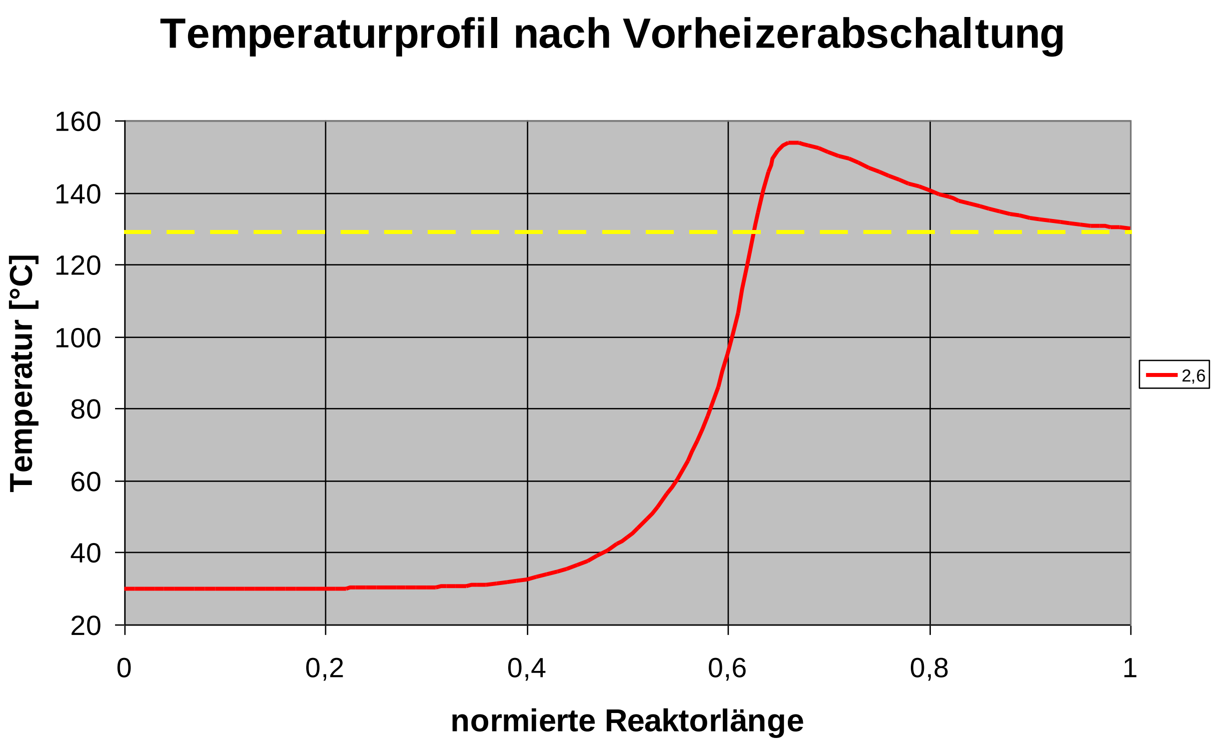

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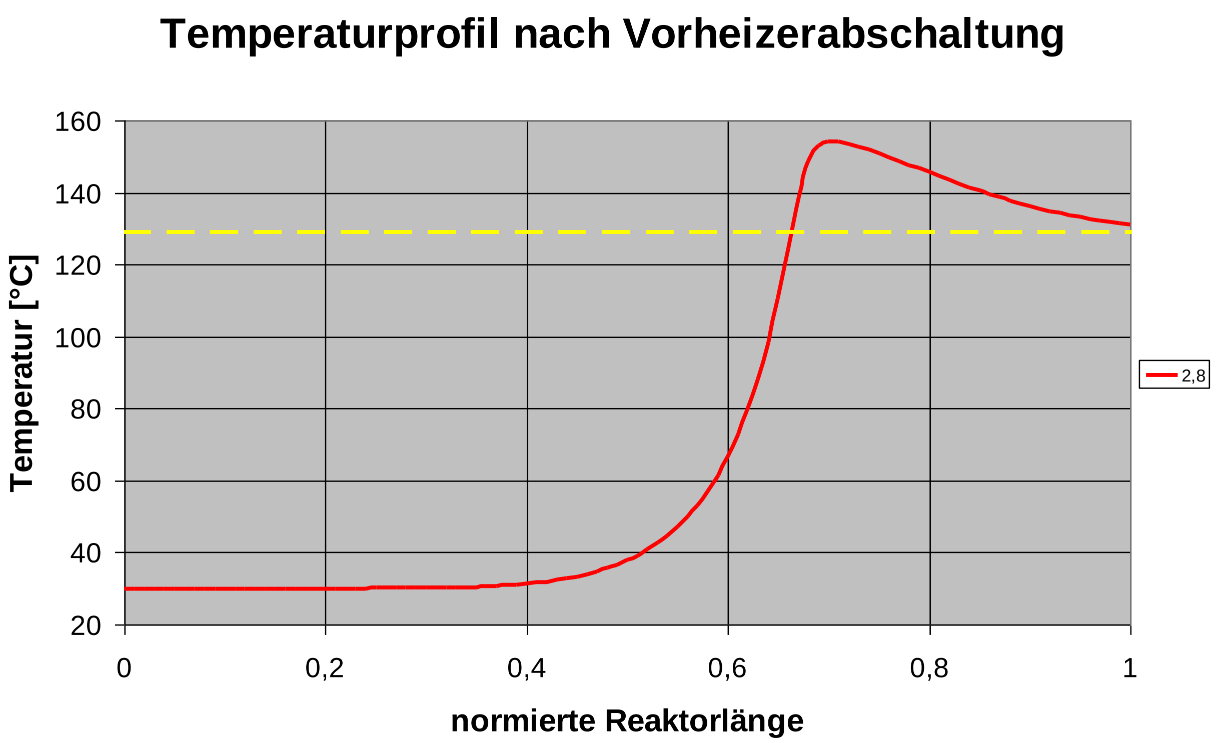

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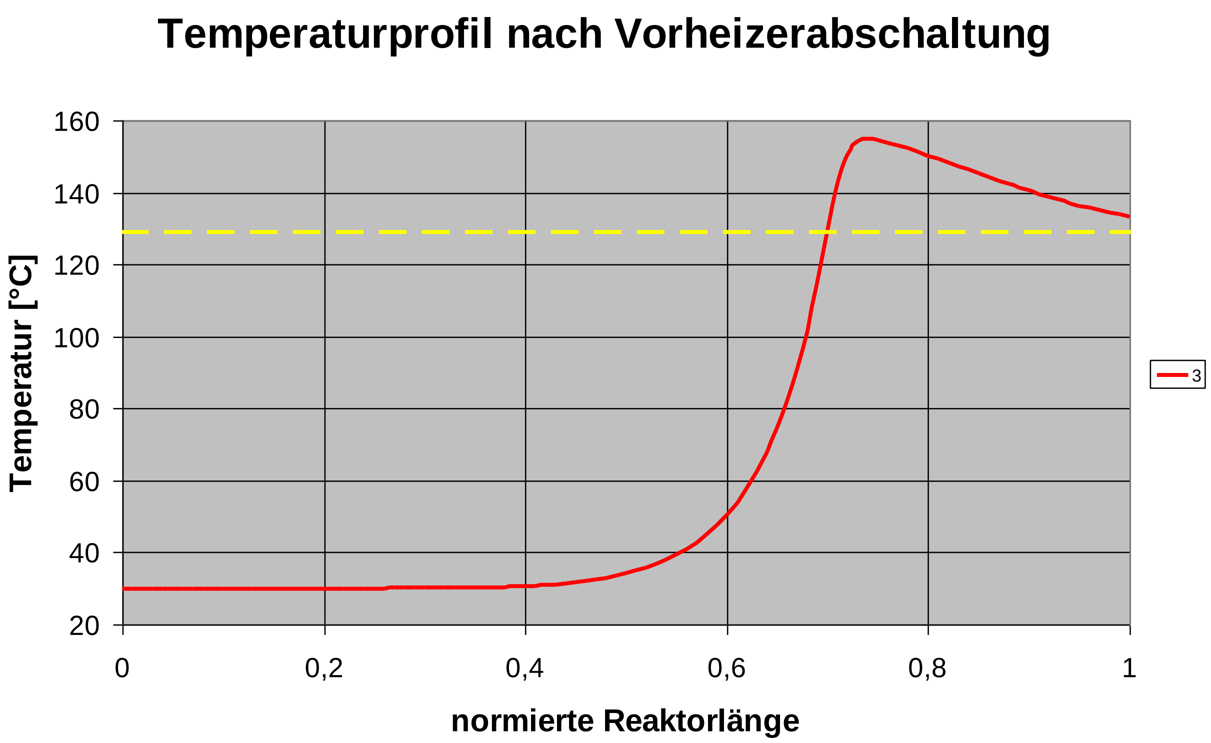

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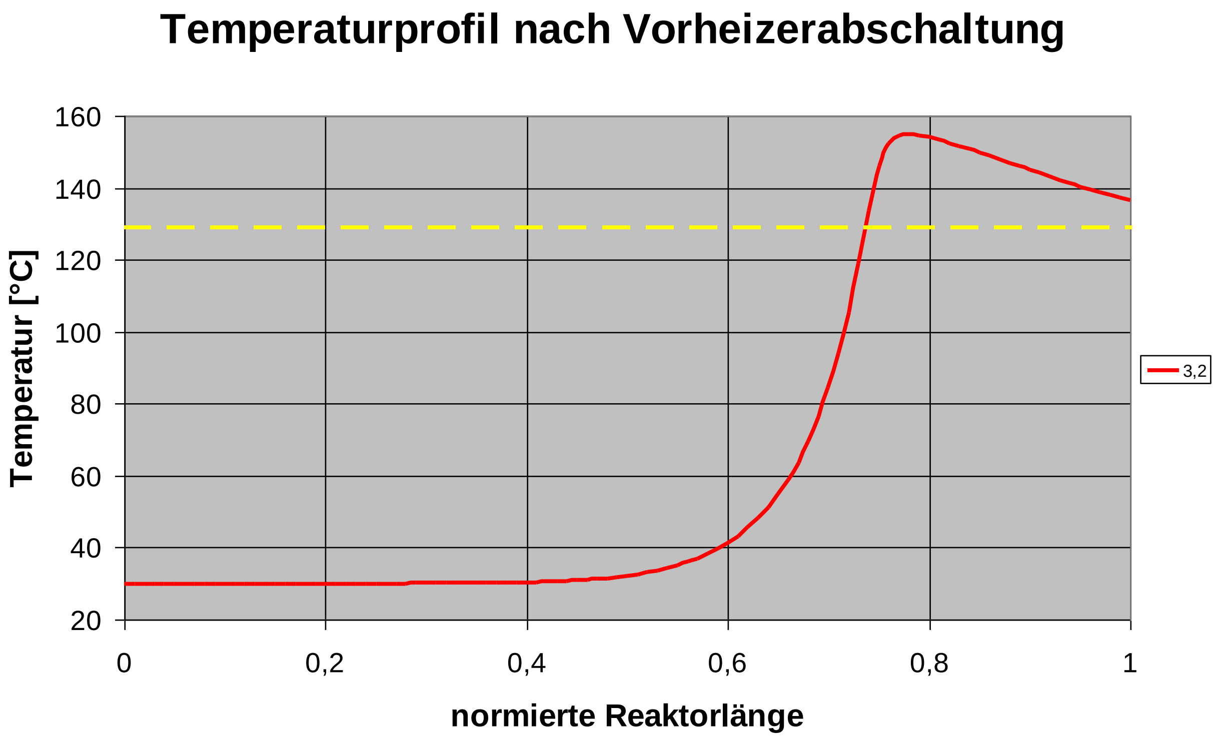

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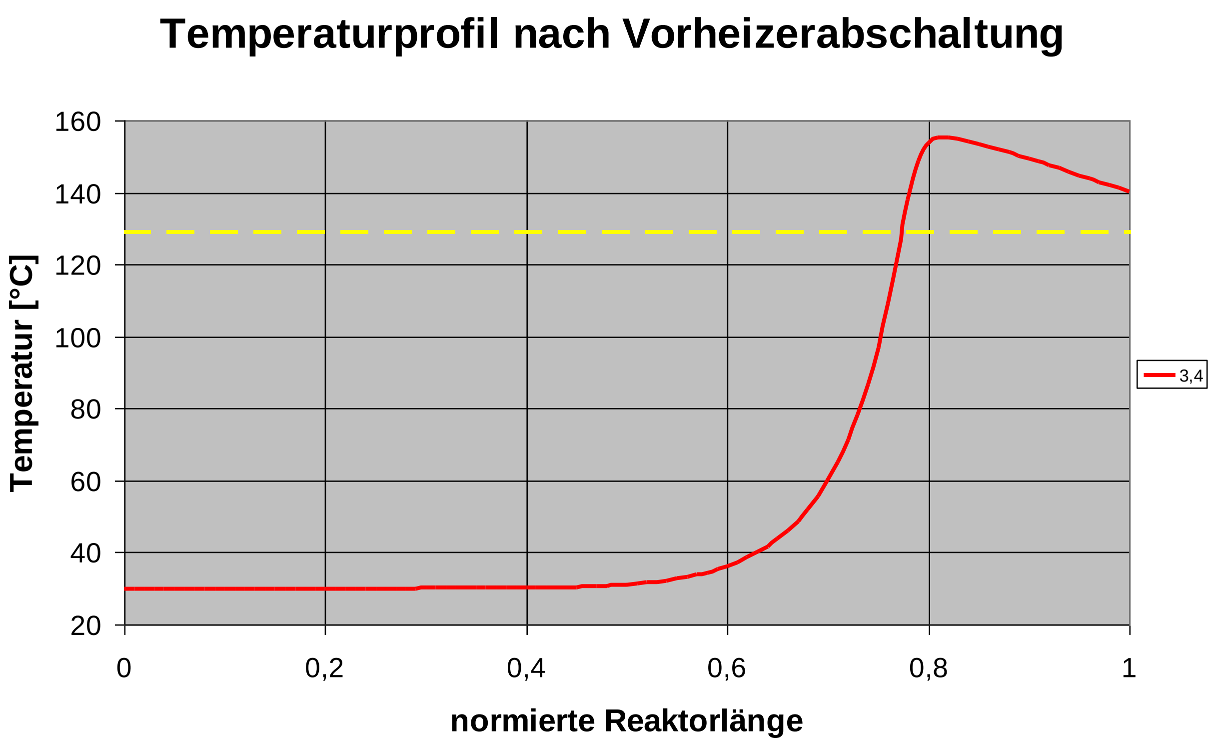

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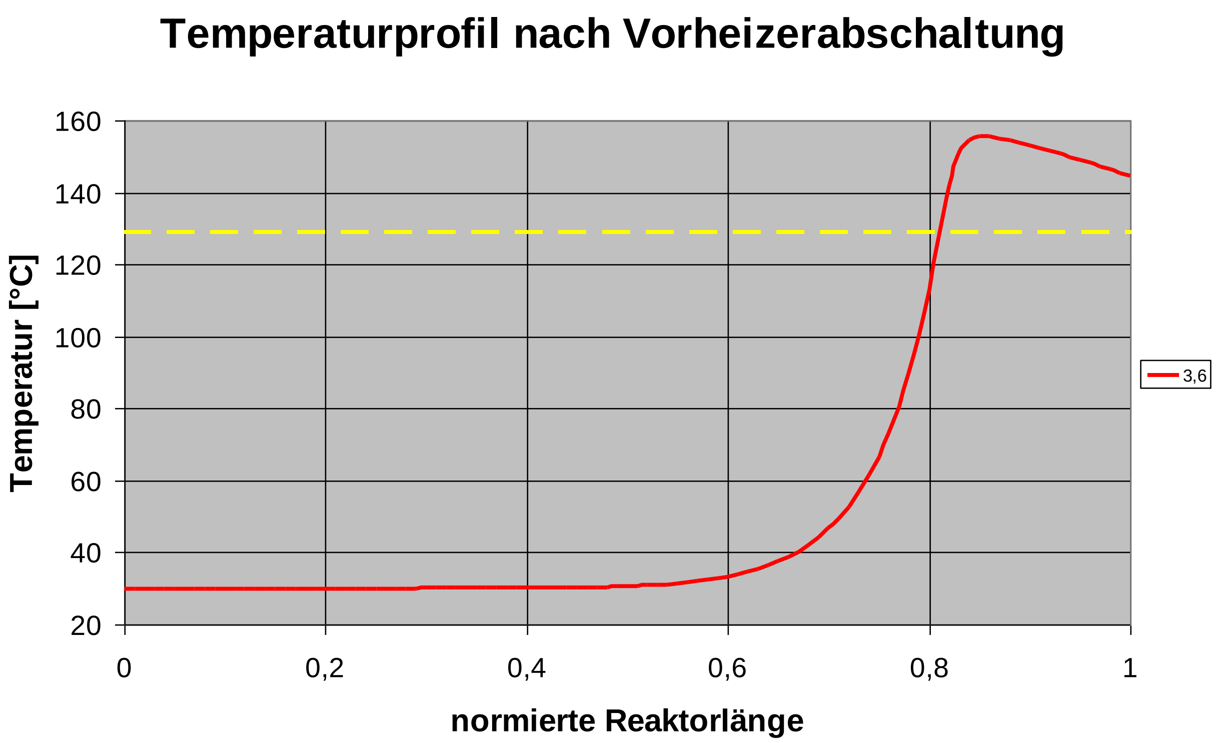

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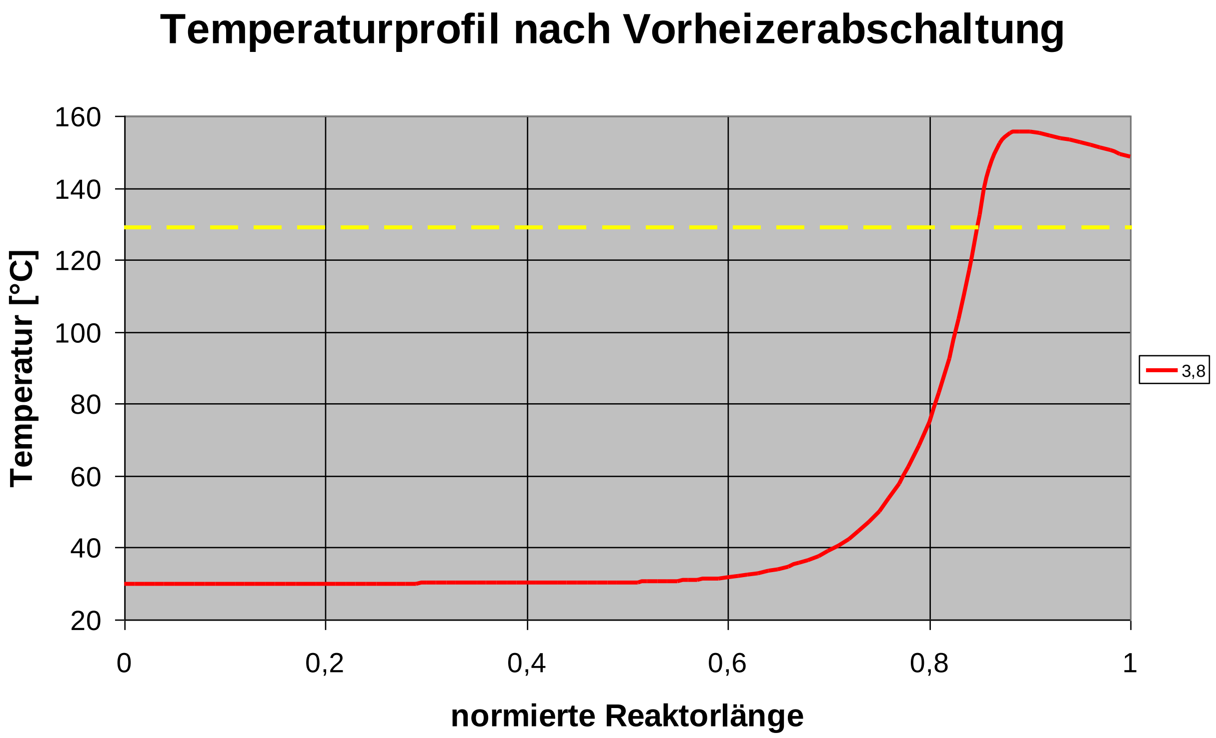

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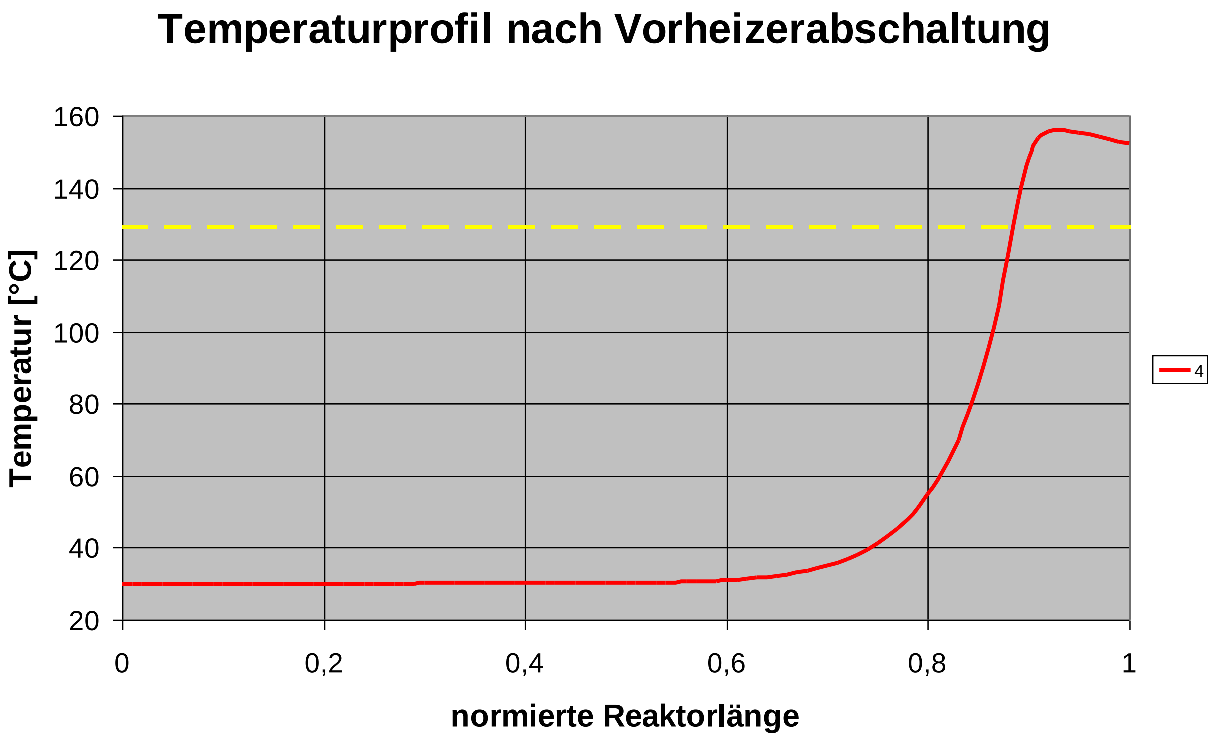

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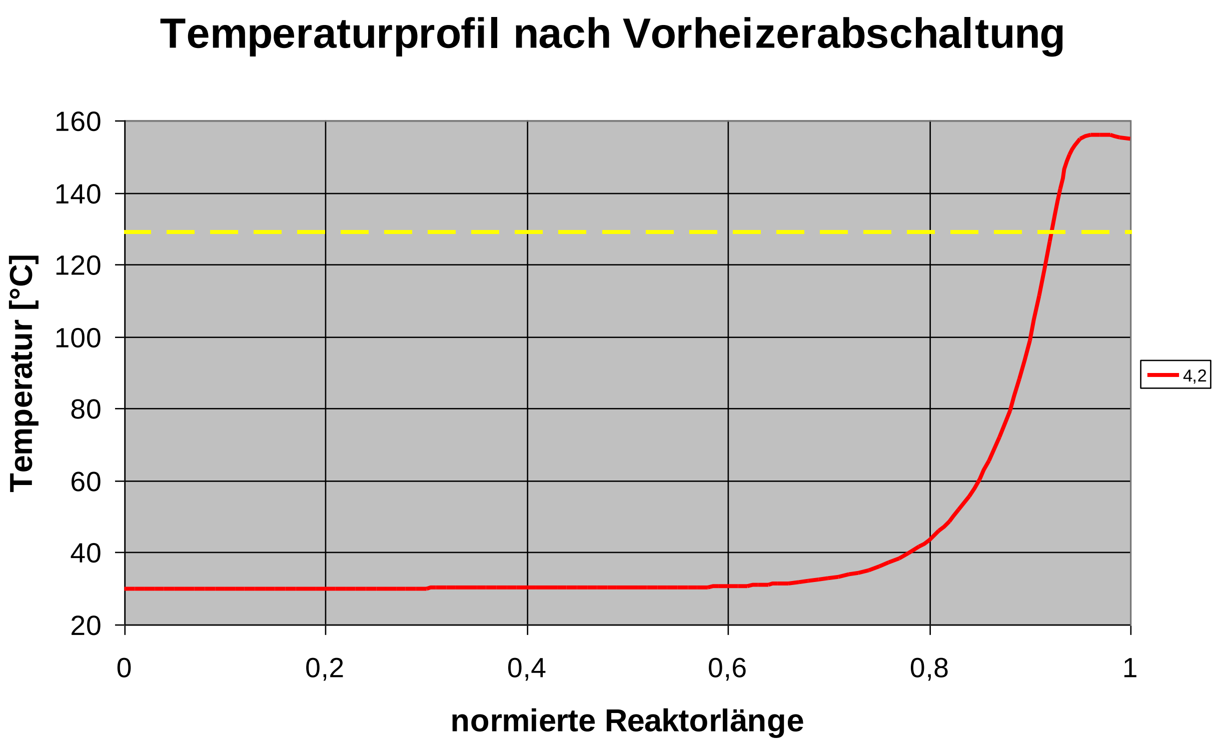

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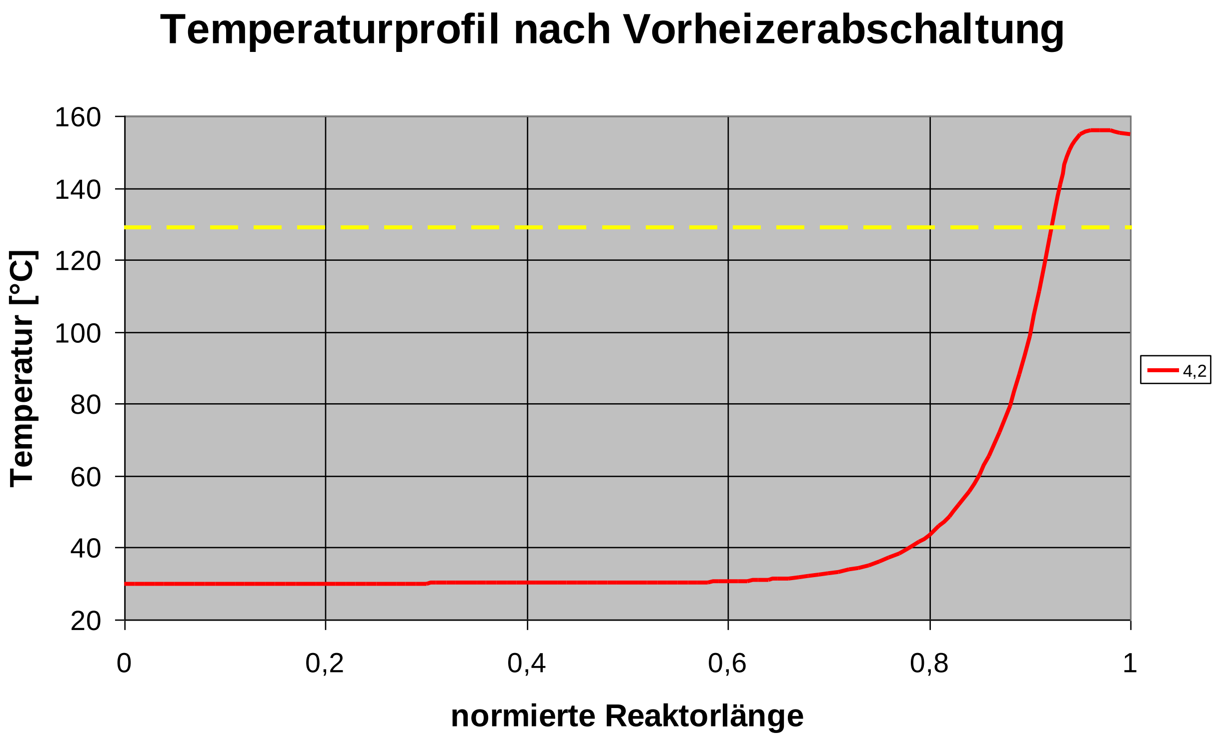
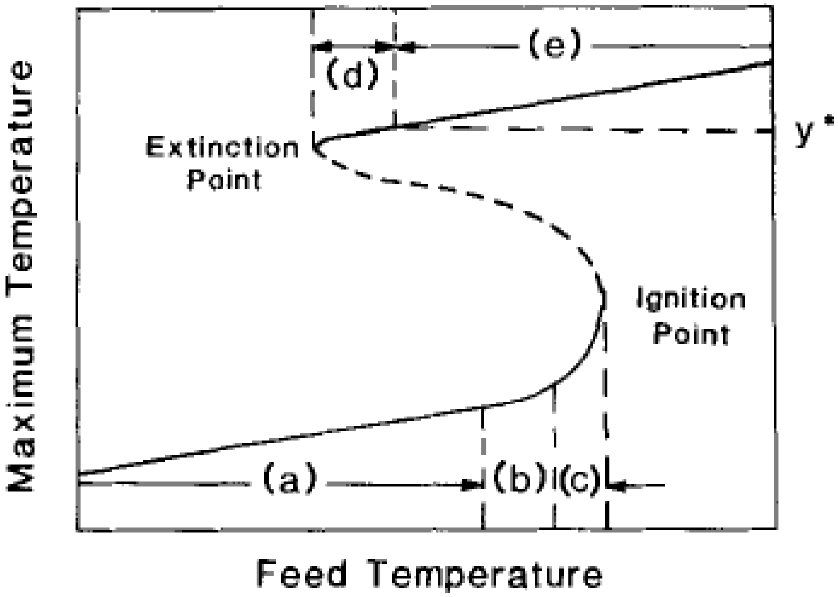


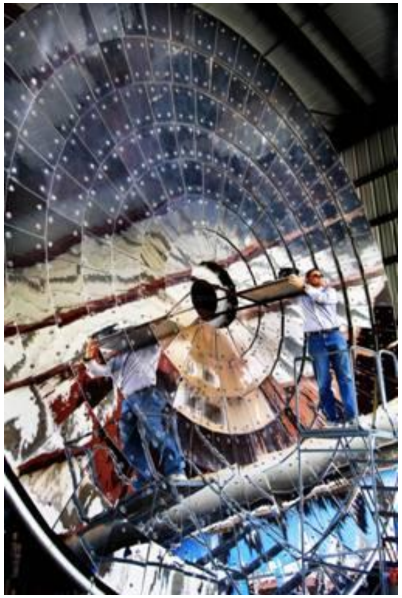
(source: D. Agar)

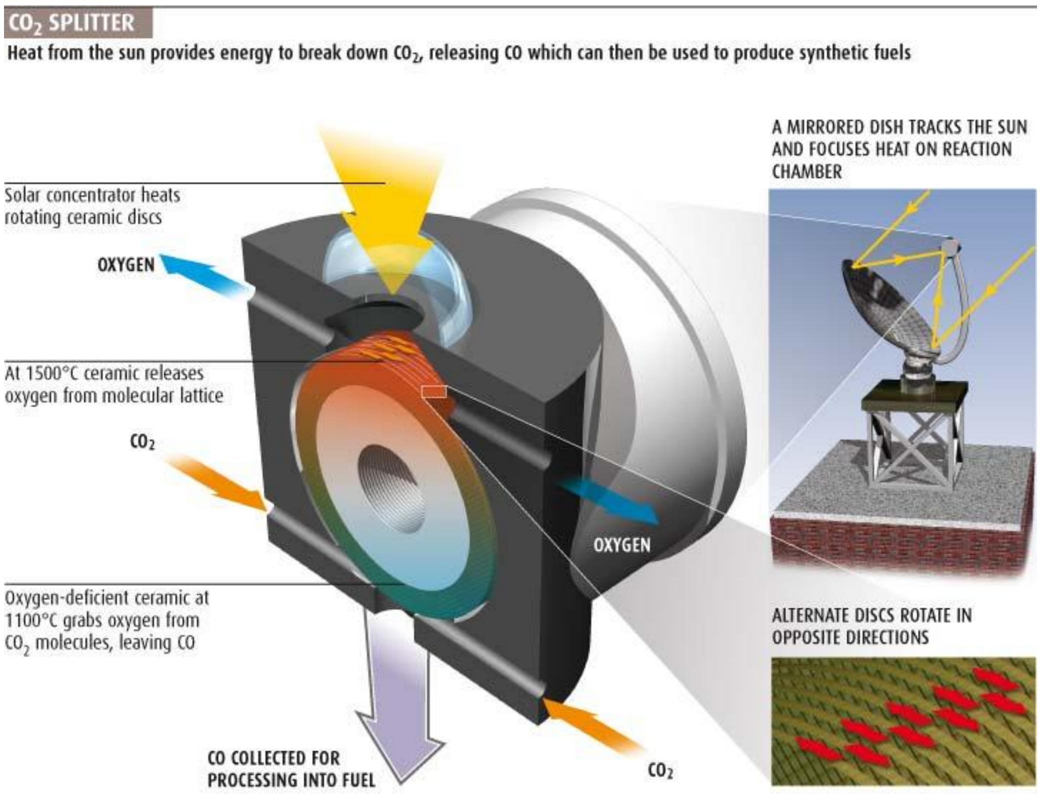
Wrong-way behavior

- May be detrimental for the catalyst and product selectivity
- The system may “jump” to an undesired steady-state if multiplicity of steady-state occurs



Regenerative process: thermochemical CO2 splitting

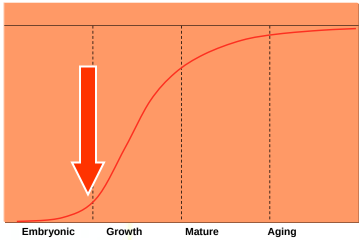


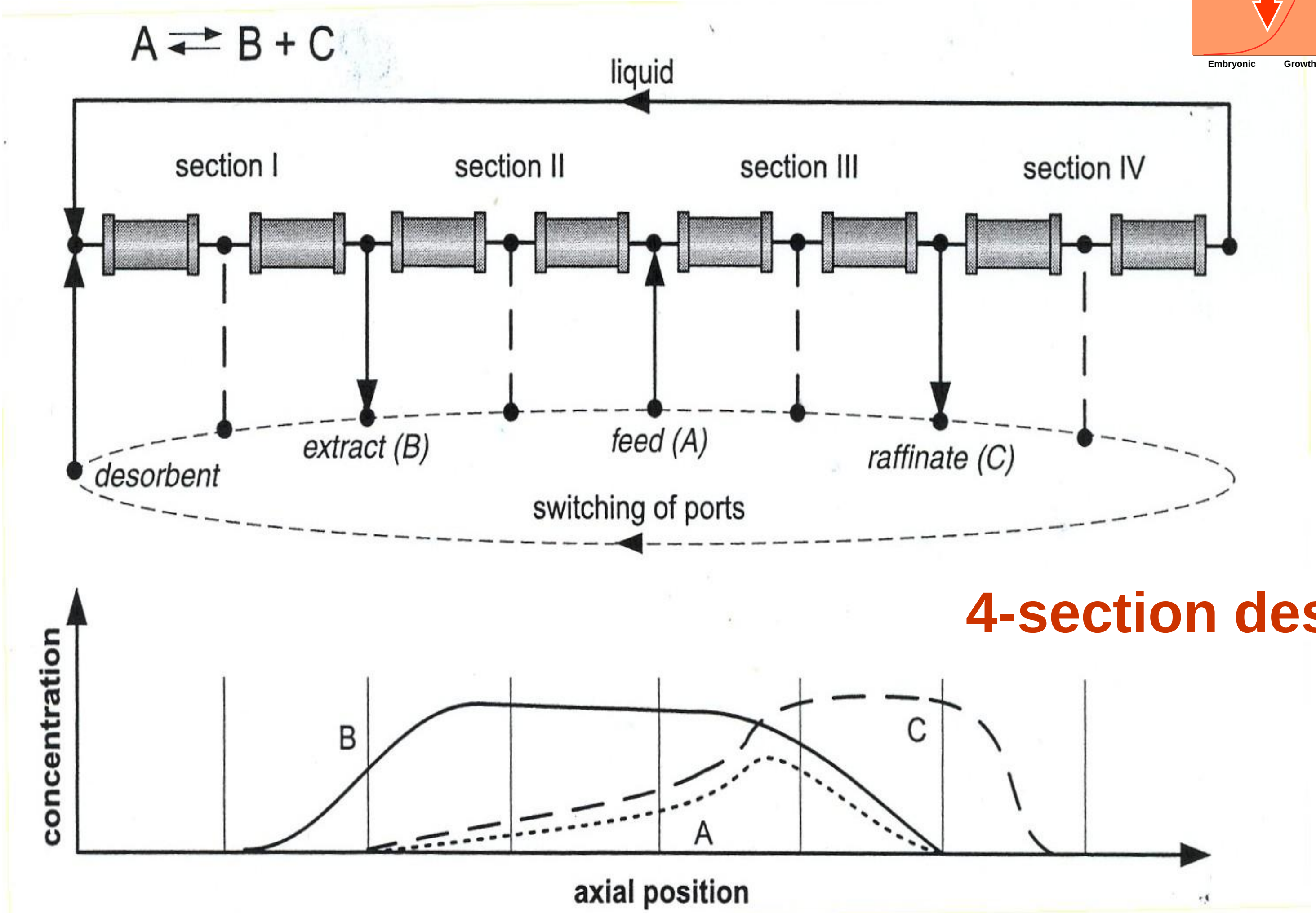


(Courtesy of Sandia National Laboratory)

Challenge: to convert CO_2 and H_2O to useful fuels using solar energy

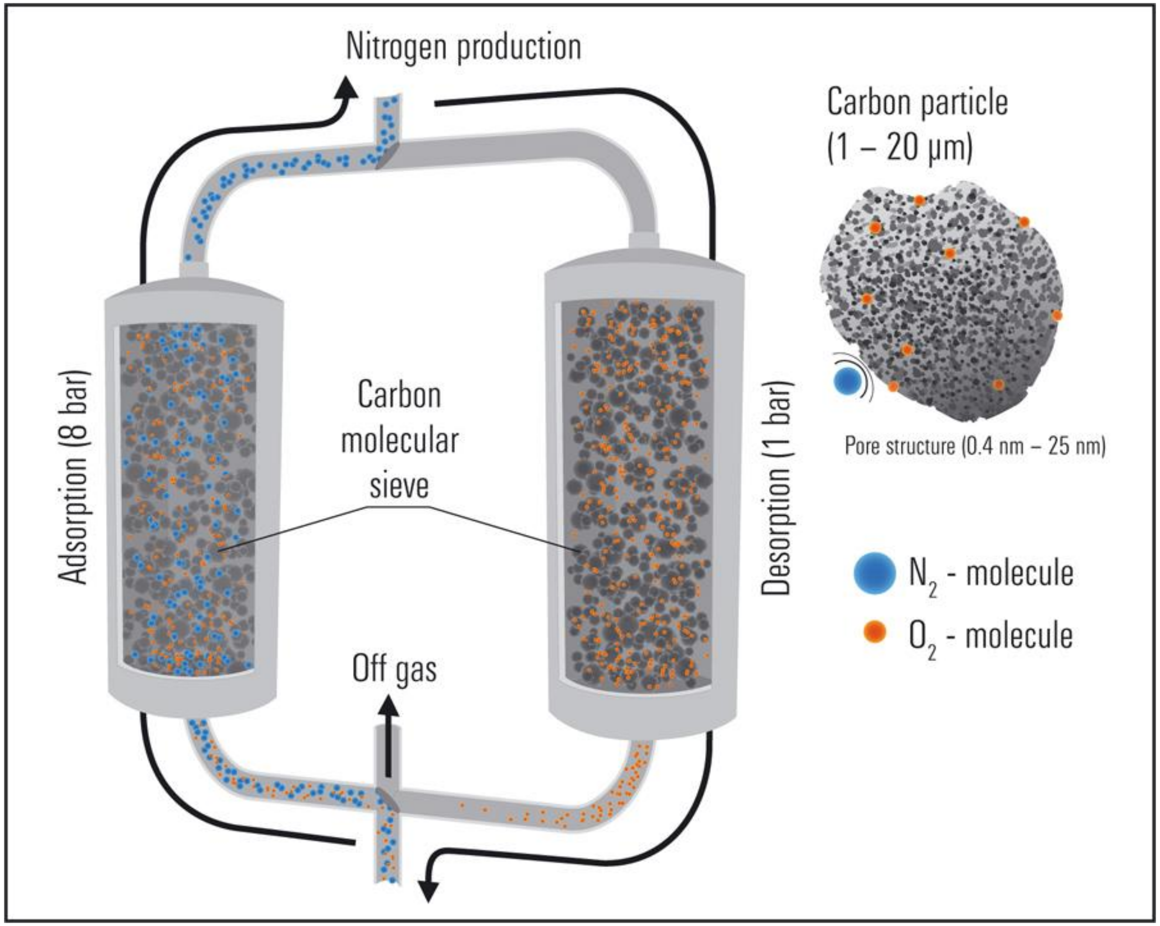
Regenerative process: Simulated Moving Bed (SMB) reactor





4-section design

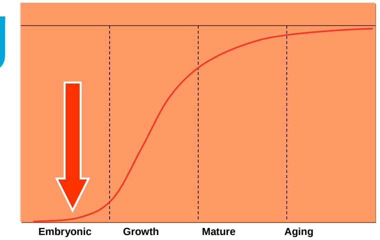
Regenerative process: Pressure Swing Adsorption

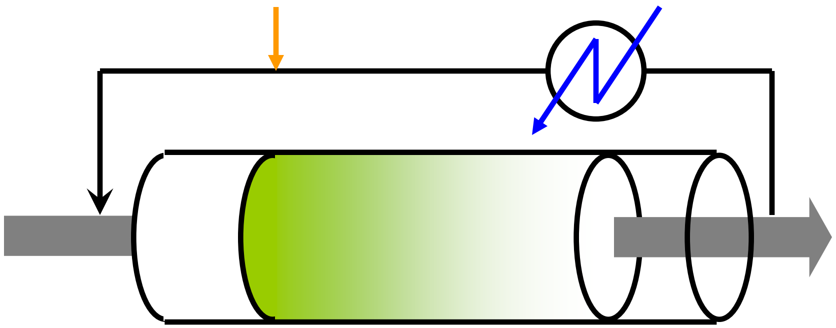


- **Two major steps: a production step, in which high-pressure vapour is introduced into the column for adsorption, and a regeneration step, in which the pressure is drastically reduced for desorption**

- **The use of two columns with alternating production and regeneration steps enables a continuous adsorption process.**

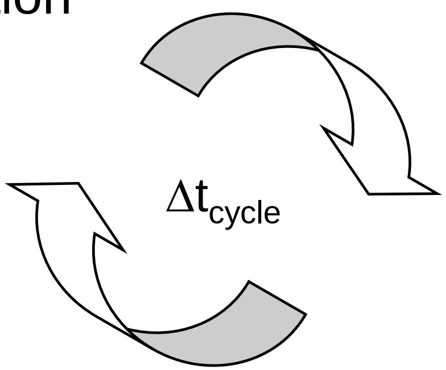
Regenerative process: desorptive cooling





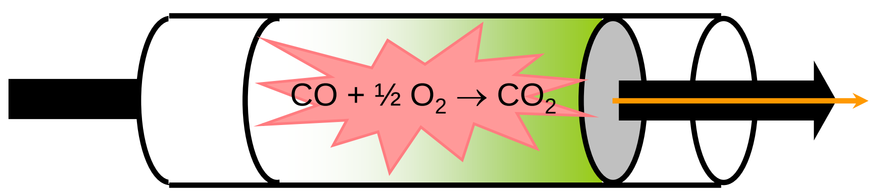
Adsorption

Principle: enhanced, 'active' regenerative heat removal



- Heat of reaction consumed by desorption of inert (●) from loaded adsorbent in mixed catalyst + adsorbent fixed-bed
- Adiabatic cyclic reactor operation

M. Franke (2001) Diploma thesis, University of Dortmund



Reaction + Desorption

(source: D. Agar, in: *Re-Engineering the Chemical Processing Plant*, Marcel Dekker, 2003)

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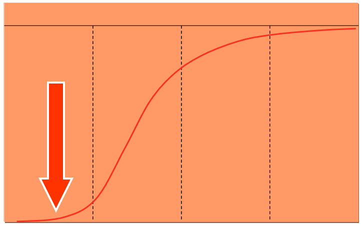
Desorptive cooling



Pros and Cons:

+ high intensity cooling system
+ no heat exchange surface in reactor
+ self-regulating heat uptake process
+ customised heat removal *via* adsorbent distribution
– unsteady-state operation
– low space time yields
– compatibility of adsorption & reaction systems

(source: D. Agar, in: *Re-Engineering the Chemical Processing Plant*, Marcel Dekker, 2003)

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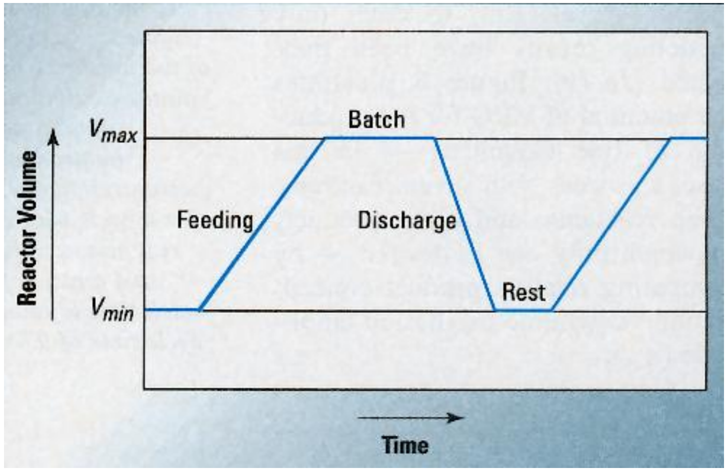
Forced Dynamic Operation of Chemical Reactors

Purposeful dynamic operation to increase reactor productivity by changing its mixing characteristics

e.g. Variable-Volume-Operation of stirred-tank reactors: basically continuous process with batch-process characteristics



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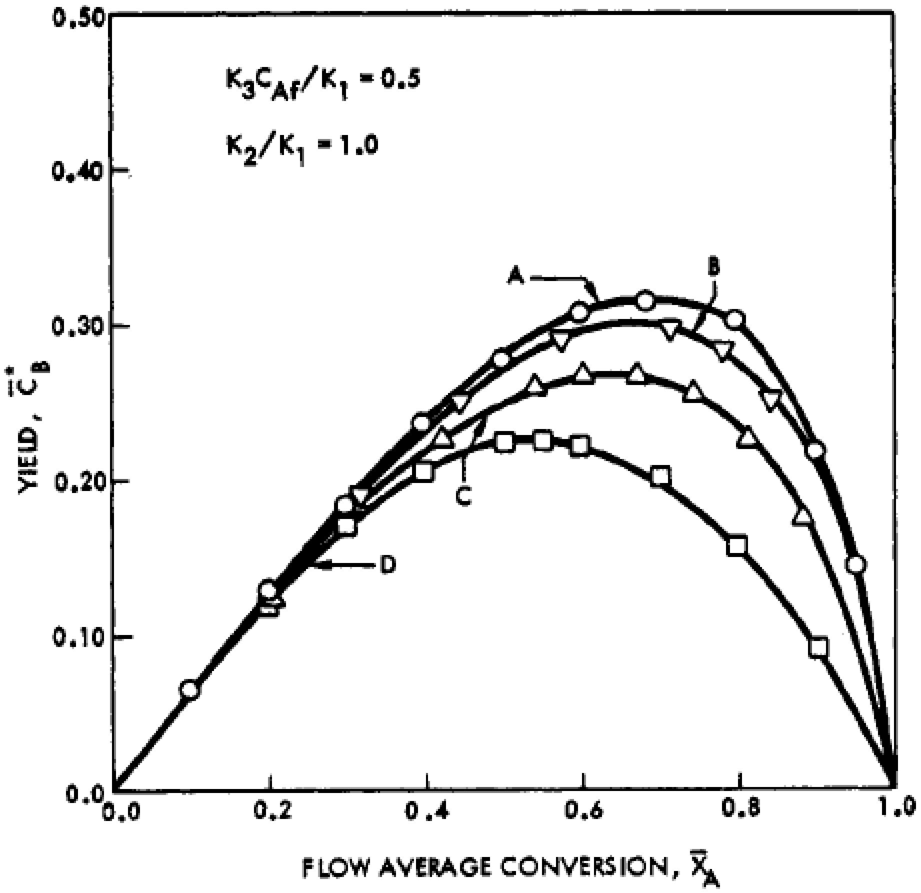
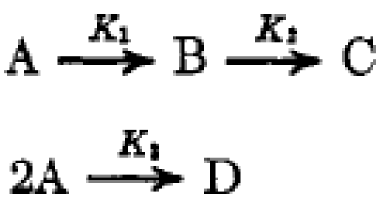
Forced Dynamic Operation of Chemical Reactors

Variable Volume Operation



Van de Vusse



A – plug-flow reactor
B, C – variable volume operation of a stirred-tank reactor
D – continuous stirred-tank reactor

- Highest yield of B in PFR
- Semibatch performance between PFR and CSTR

(source: M.M. Lund and R.C. Seagrave, 1971)

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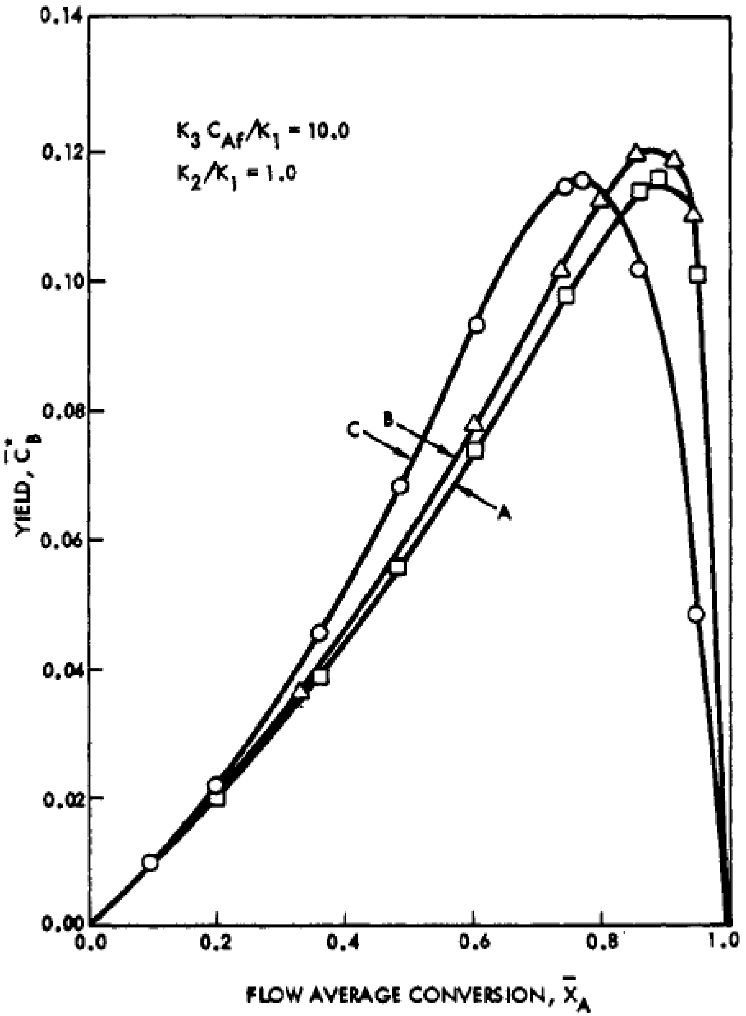
Forced Dynamic Operation of Chemical Reactors



Van de Vusse

$$A \xrightarrow{K_1} B \xrightarrow{K_2} C$$

$$2A \xrightarrow{K_3} D$$

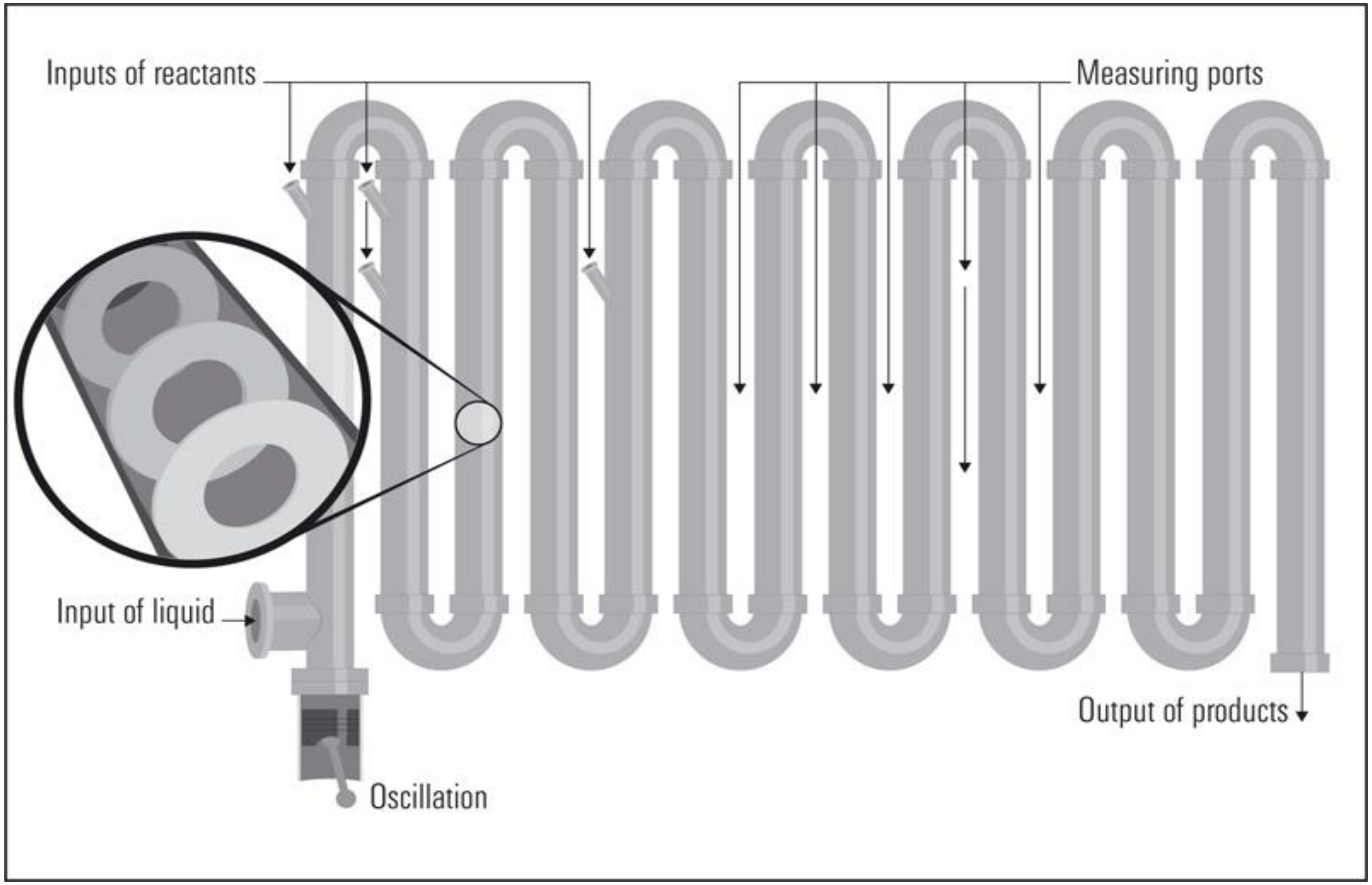
A – plug-flow reactor
B – variable volume operation of a stirred-tank reactor
C – continuous stirred-tank reactor

Highest yield of B in semibatch operation for flow average conversions > 0.75

(source: M.M. Lund and R.C. Seagrave, 1971)

Forced Dynamic Operation of Chemical Reactors

Oscillatory Flow Reactor



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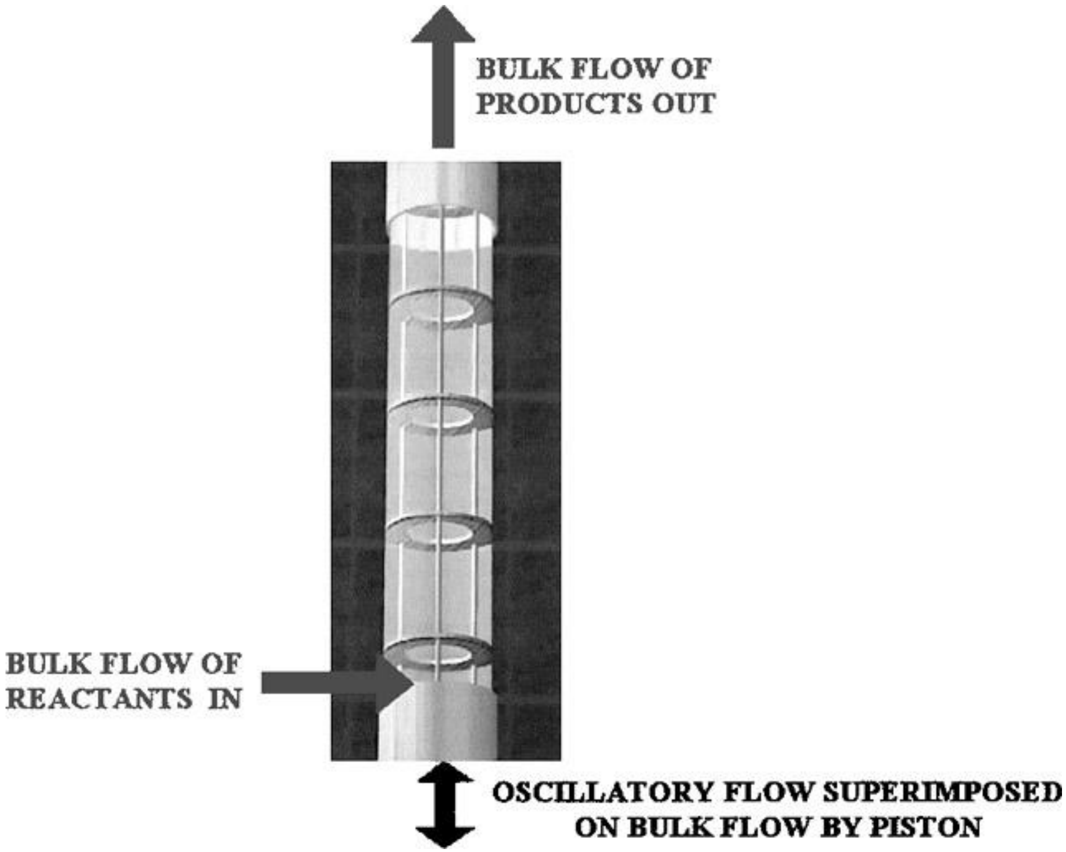
Forced Dynamic Operation of Chemical Reactors

Oscillatory Flow Reactor

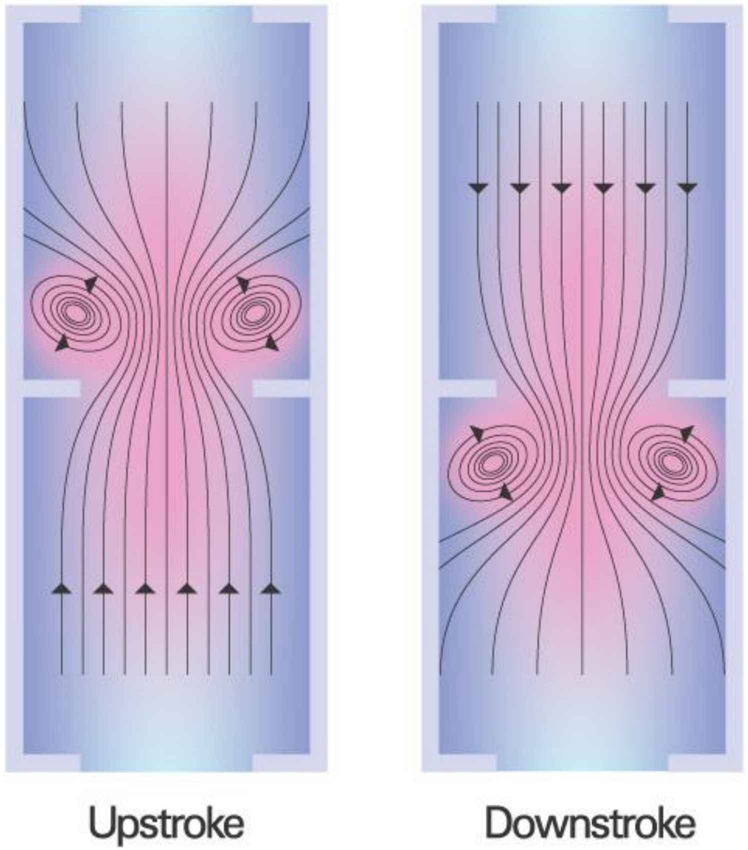


- **Tubular reactor with orifice baffles**
- **Oscillatory motion is superimposed upon the net fluid by piston**
- **Controlled degree of mixing mainly dependent on the oscillation rather than on the net flow**
- **Suitable for multiphase systems**
- **Linear scale-up**

(A.P. Harvey, et al., J. Chem. Technol. Biotechnol., 78, 338 (2003))

Forced Dynamic Operation of Chemical Reactors

Oscillatory Flow Reactor



- Periodic toroidal vortices between the baffles
- **Enhanced mixing/mass transfer/heat transfer**
- PFR behavior at laminar conditions (CSTRs in series)
- **"Slow" reactions in PFR reactors with small length to diameter ratio**
- Smaller footprint; increased product quality compared to stirred-tank reactors

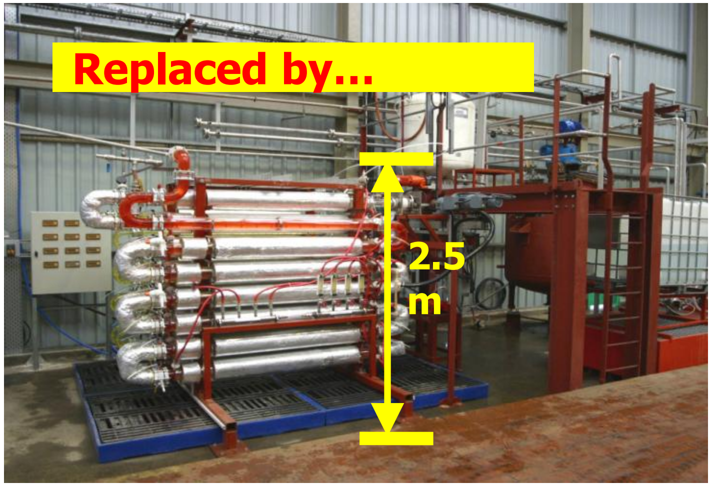
(A.P. Harvey, et al., J. Chem. Technol. Biotechnol., 78, 338 (2003))

Forced Dynamic Operation of Chemical Reactors

James Bond at James Robinson, or SHAKEN, NOT STIRRED…

Oscillatory Baffle Flow Reactor (NiTech Solutions) implemented at James Robinson

27 m



Reduction in:
Space (20x)
Process time (20x)
Capital cost (2x)
Energy and waste (many times)
Quality defects

Oscillatory Flow Reactor

Biodiesel synthesis (13 l/min)

Nitech Solutions

Oscillatory Flow Reactor

Biodiesel synthesis (13 l/min)

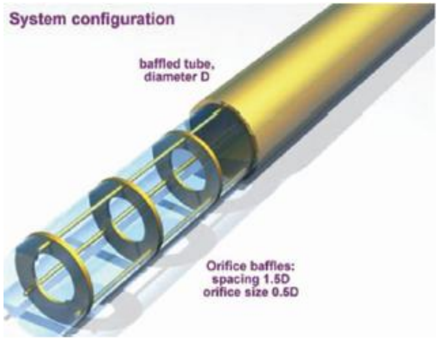
- Reaction time < 40 min
- Conversion > 99.5 %
- Oil:Methanol = 4:1 (Industry standard 6:1)
- Temperature 50-55^{o}C
- Ambient pressure

Oscillatory Flow Reactor

Other applications-Benefit

Table 1: Comparison of overall reaction times		
Process	**Batch STR**	**COBR™**
A fine chemical	6 hrs	30 mins
A polymer	8 hrs	45 mins
A speciality chemical	12 hrs	40 mins
One stage reaction of an API	10 hrs	20 mins
A sugar based product	30 mins	15 mins
Coagulation	1 hr	10 secs

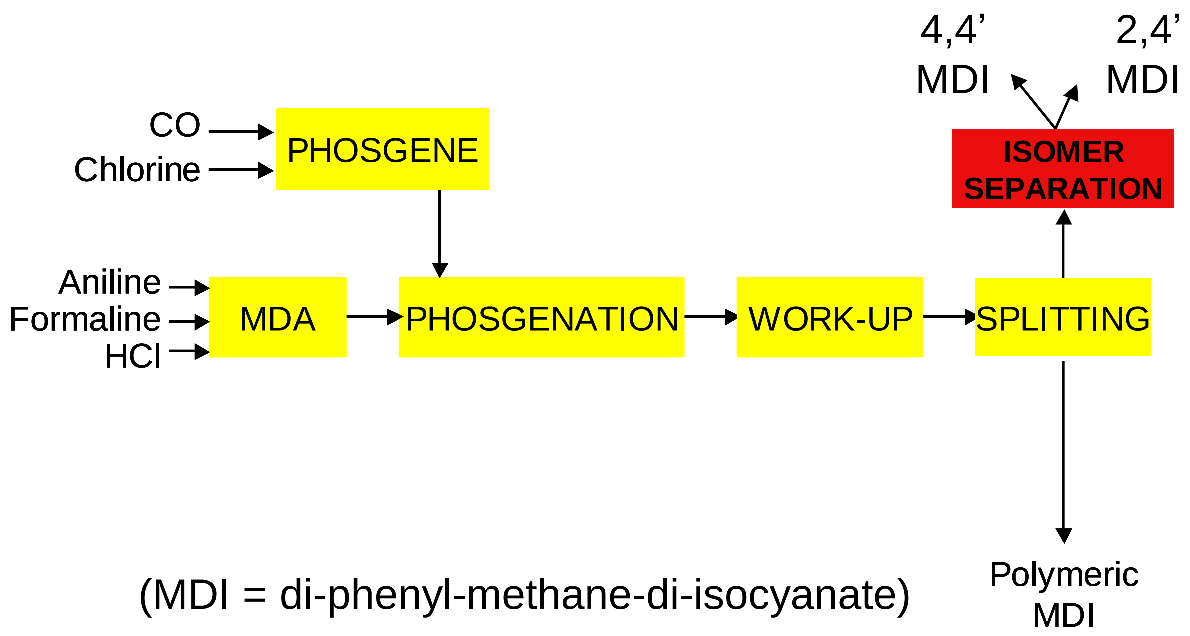
Nitech Solutions



Drastic decrease in the overall process time due to removal of mass/heat gradients

Combination of continuous and oscillatory processing in S-L system

Continuous suspension crystallization



(MDI = di-phenyl-methane-di-isocyanate)

Conventional isomer separation technology:

- distillation
- layer growth crystallization

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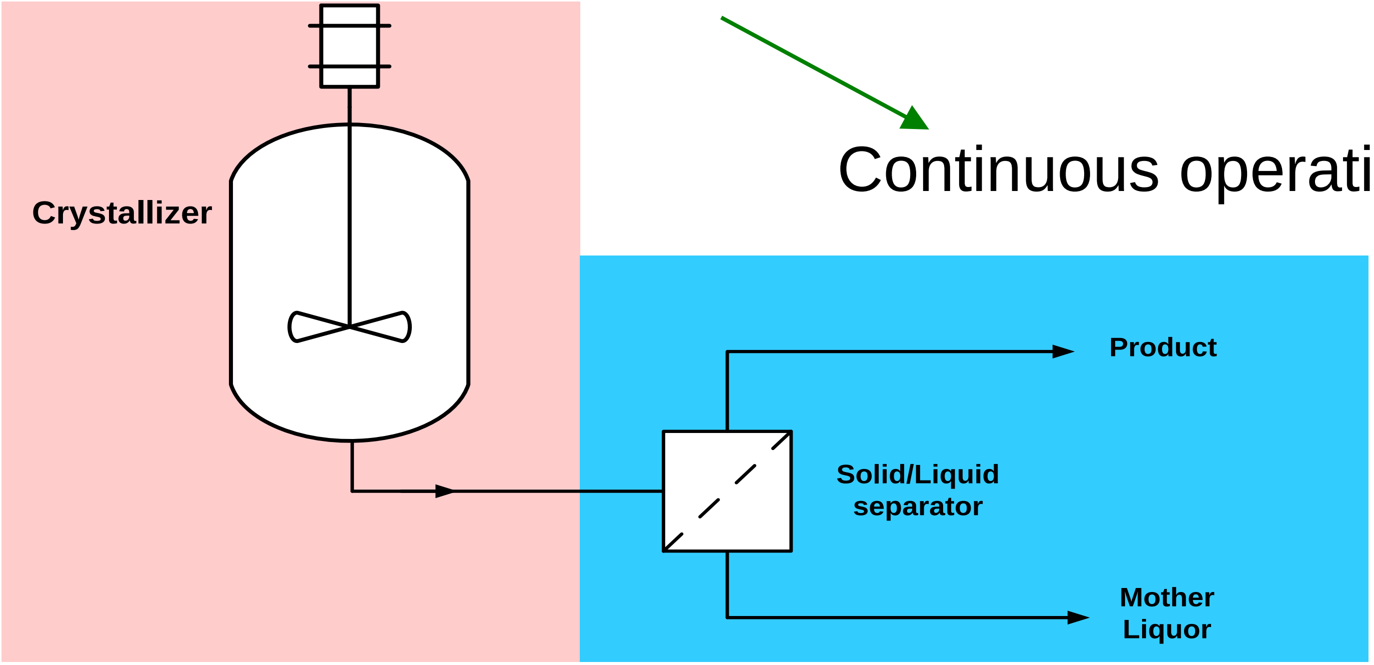
Combination of continuous and oscillatory processing in S-L system

Suspension Growth Crystallization

"Crystals are freely suspended & transportable"

Continuous operation



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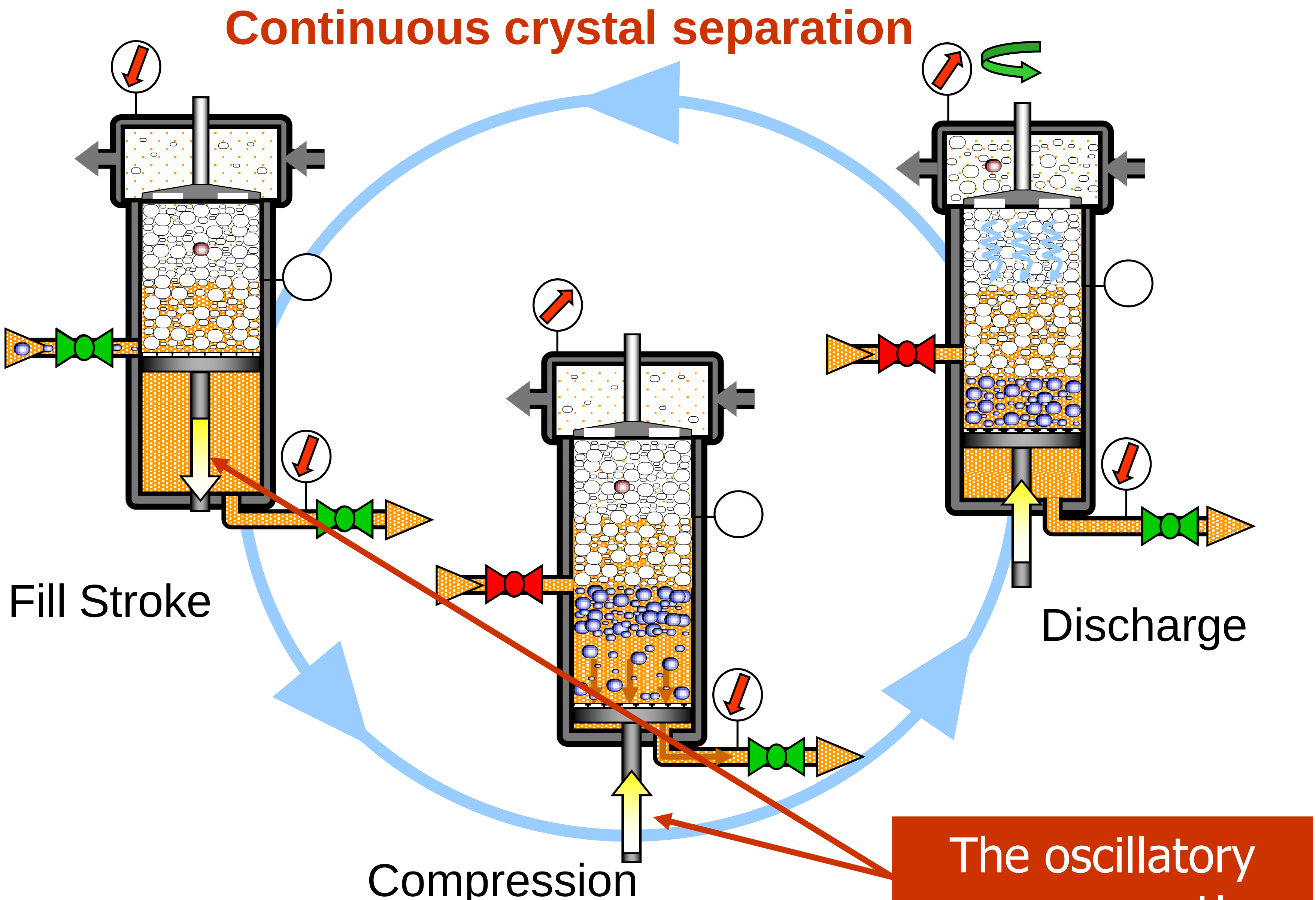
Niro Wash Column Technology



Combination of continuous and oscillatory processing in S-L system

	Distillation	Layer Crystallization	Suspension Crystallization
Operation	Continuous	Batch	Continuous
Energy	High Low α High Temp.	Medium Peak loads	Low (depends on MP) Low Temperature Use waste energy
Capital	High	High	Lower
Maintenance	High (fouling)	Low	High (moving parts)
Economy of scale	Good	Bad	Good
Selectivity	Bad	Poor (99)	Superior (99.99)

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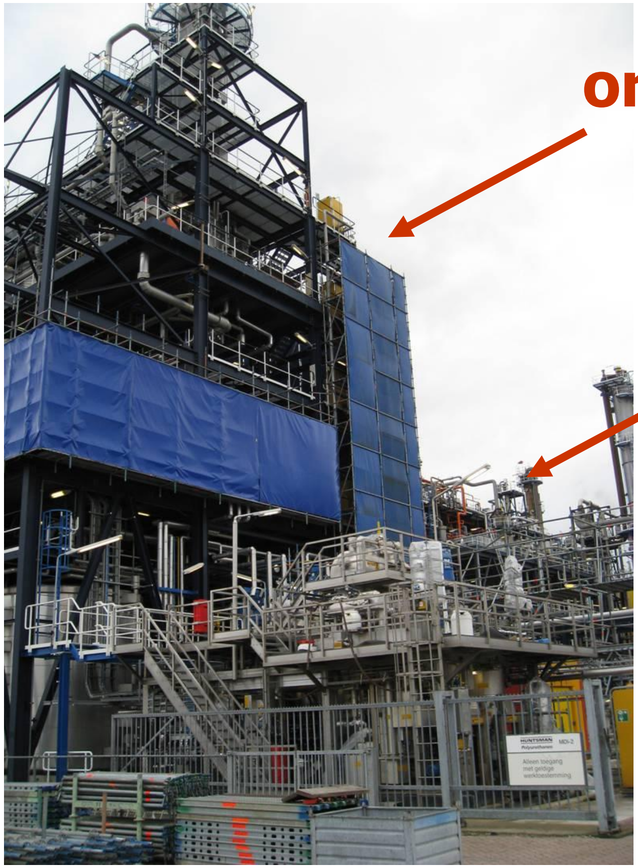
Combination of continuous and oscillatory processing in S-L system

<u>1 Sulzer dynamic crystallizer:</u>

floor area:	300	m^2
height:	19	m
capacity:	3	t/hr

<u>1 Freeze Tec SCU:</u>

floor area:	100	m^2
height:	6	m
capacity:	2	t/hr



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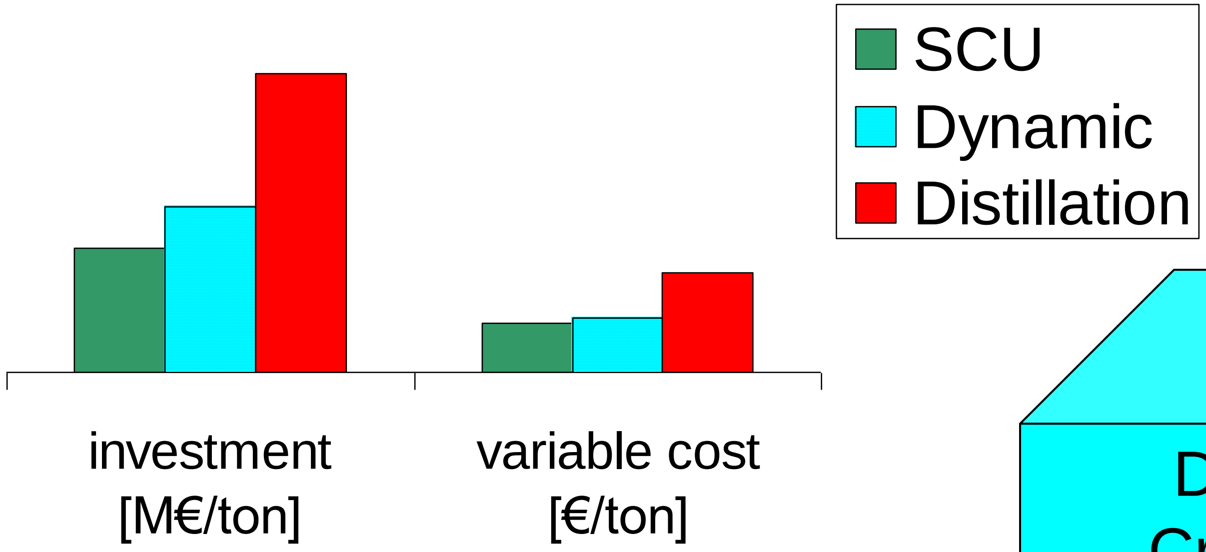
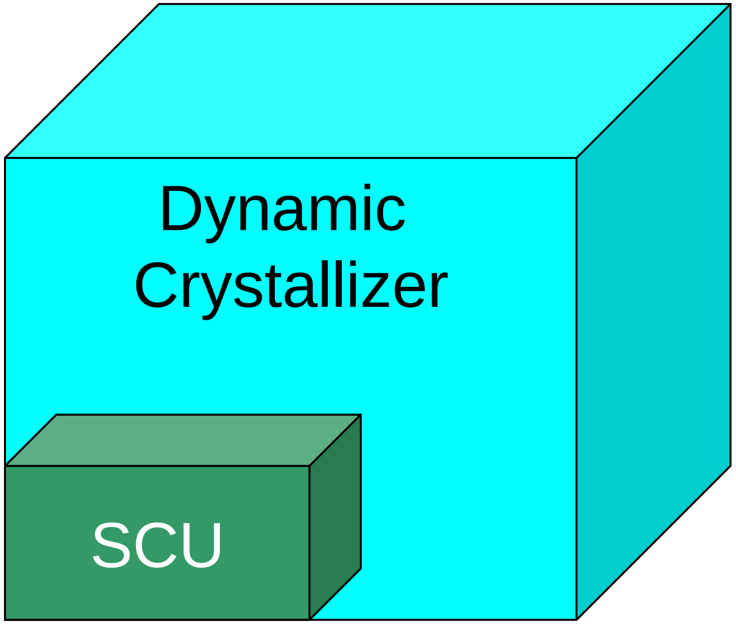
Combination of continuous and oscillatory processing in S-L system





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Forced Dynamic Operation of Chemical Reactors

Barriers:

- **Reliable models**
- **Costs of instrumentation/control systems**
- **Interactions with the stationary part of the plant – damping buffers may be needed**