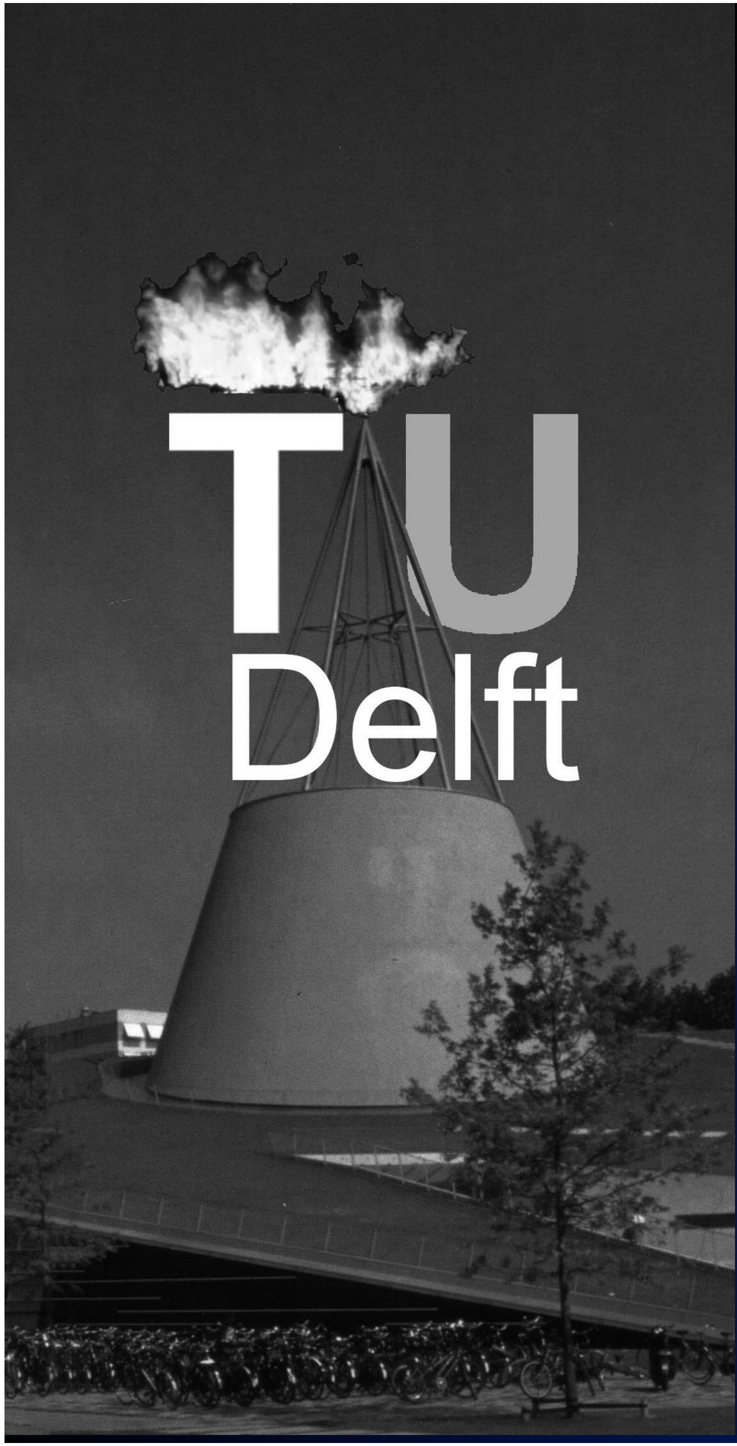


Trends in experimental techniques for kinetic studies

Freek Kapteijn

Jacob Moulijn

Industrial Catalysis

Delft University of Technology

The Netherlands

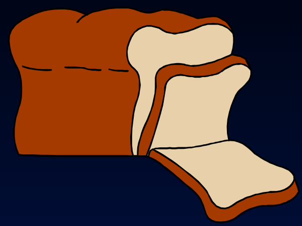
Milano, 22 September 2000

What you can expect…..

- Catalytic processes
  - Trends in development & design
- What is needed ?
  - Current developments
- Experimental methods & techniques
  - Intrinsic rates
  - Mass transport
  - Deactivation
- Other needs
- Message

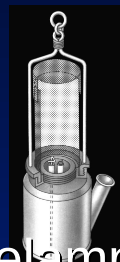
'Catalyst performance characterization'

TUDelft



b.C.

Biocatalysis



sulphuric acid (NO)

alcohol decomposition

Davy minelamp

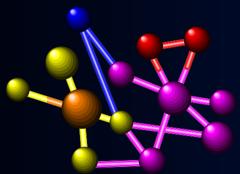
1800

Chemocatalysis

'Catalytic force'

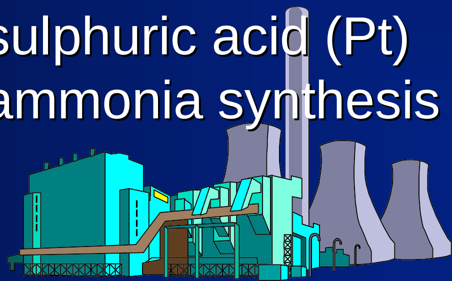
sulphuric acid (Pt)
ammonia synthesis

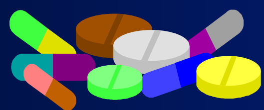
1900



Industrial Catalysis

Fine chemicals
Farmaceuticals





2000

‘Gaps & Needs & Opportunities’
in Industrial Catalysis

NICE,June 1998

- Catalysis in fine chemicals prodction
- Catalytic heterogeneous liquid phase processes
- Testing and Characterization
- Kinetics and Modelling
- Reactor concepts and chemical engineering
- New catalysis
- New feedstocks
- Catalysts recycle or disposal

- G/S, L/S, G/L/S systems
  - realistic conditions
  - in-situ activity/selectivity
  - downscaling reactors
  - parallel screening
  - accelerated deactivation
- Extrapolation models
  - reduced development time
  - reaction & reactor modelling
    - » improved monitoring
    - » process control
  - molecular level

Eurokin

TUDelft

90-ies: Increased interest catalyst performance testing

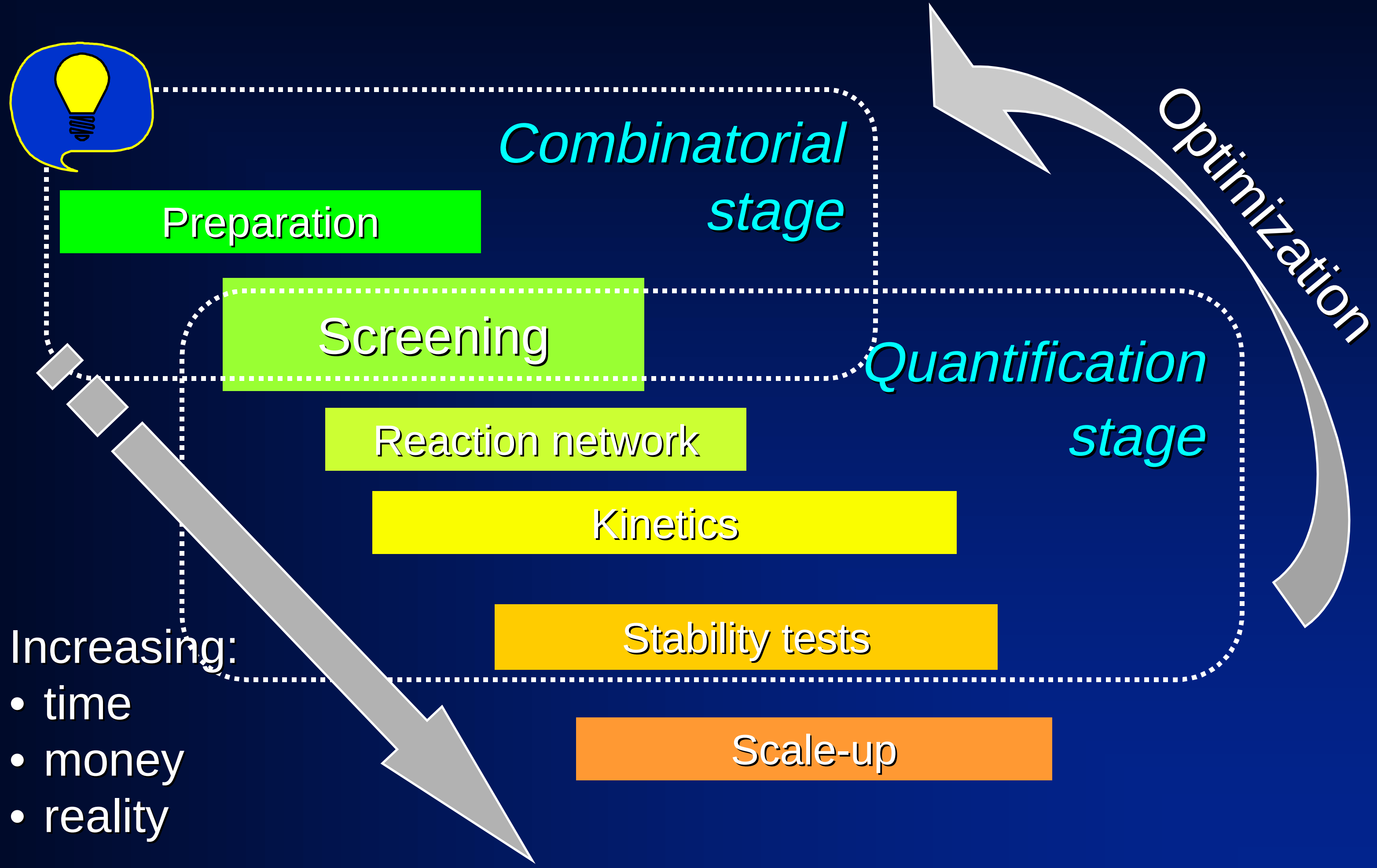
- Zeolite based processes (bulk & fine chemistry)
  - selectivity, activity, molecular transport
- Structured catalysts
  - efficiency, productivity, selectivity, energetics
- Awareness
  - poor kinetic bases many processes
- Combinatorial techniques
  - rapid new catalyst development
- Microreactor technology
  - miniaturization
- Computers

Bos et al.
Appl.Catal. A: Gen.
160 (1997) 185

Screening & Kinetics

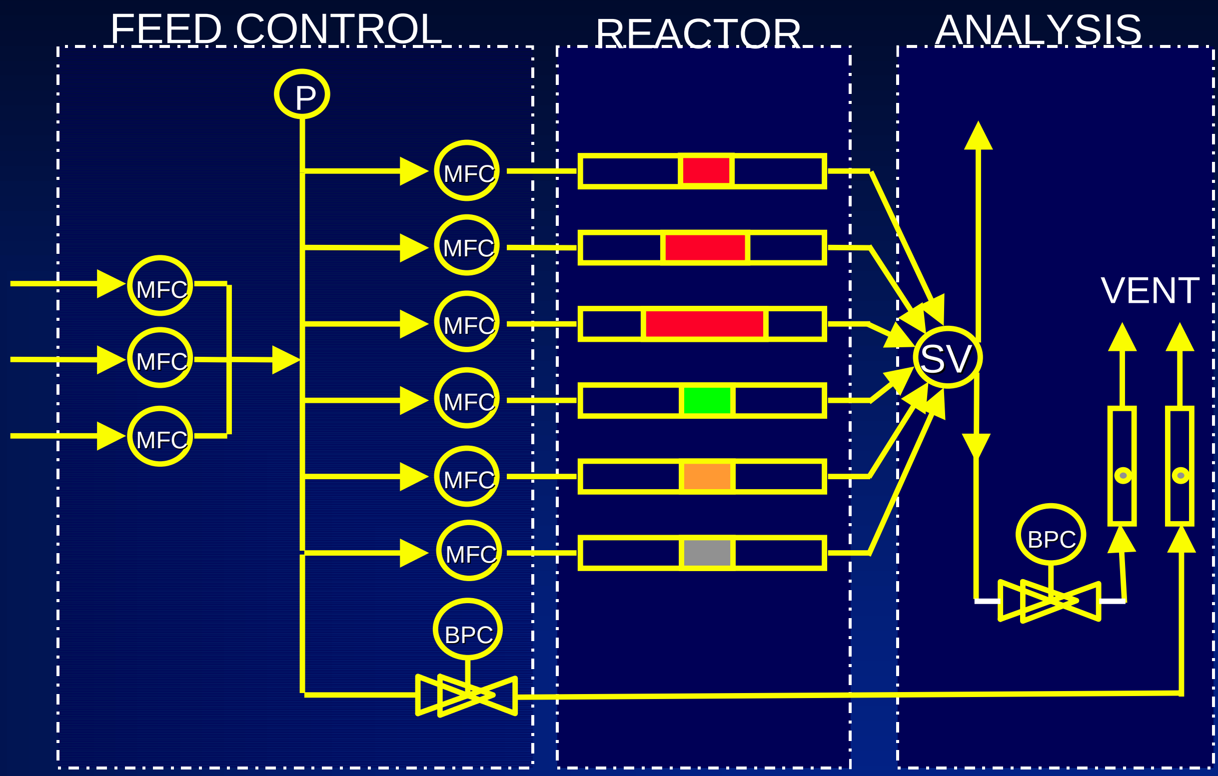
Speed
Efficiency
Quantification

Catalyst development



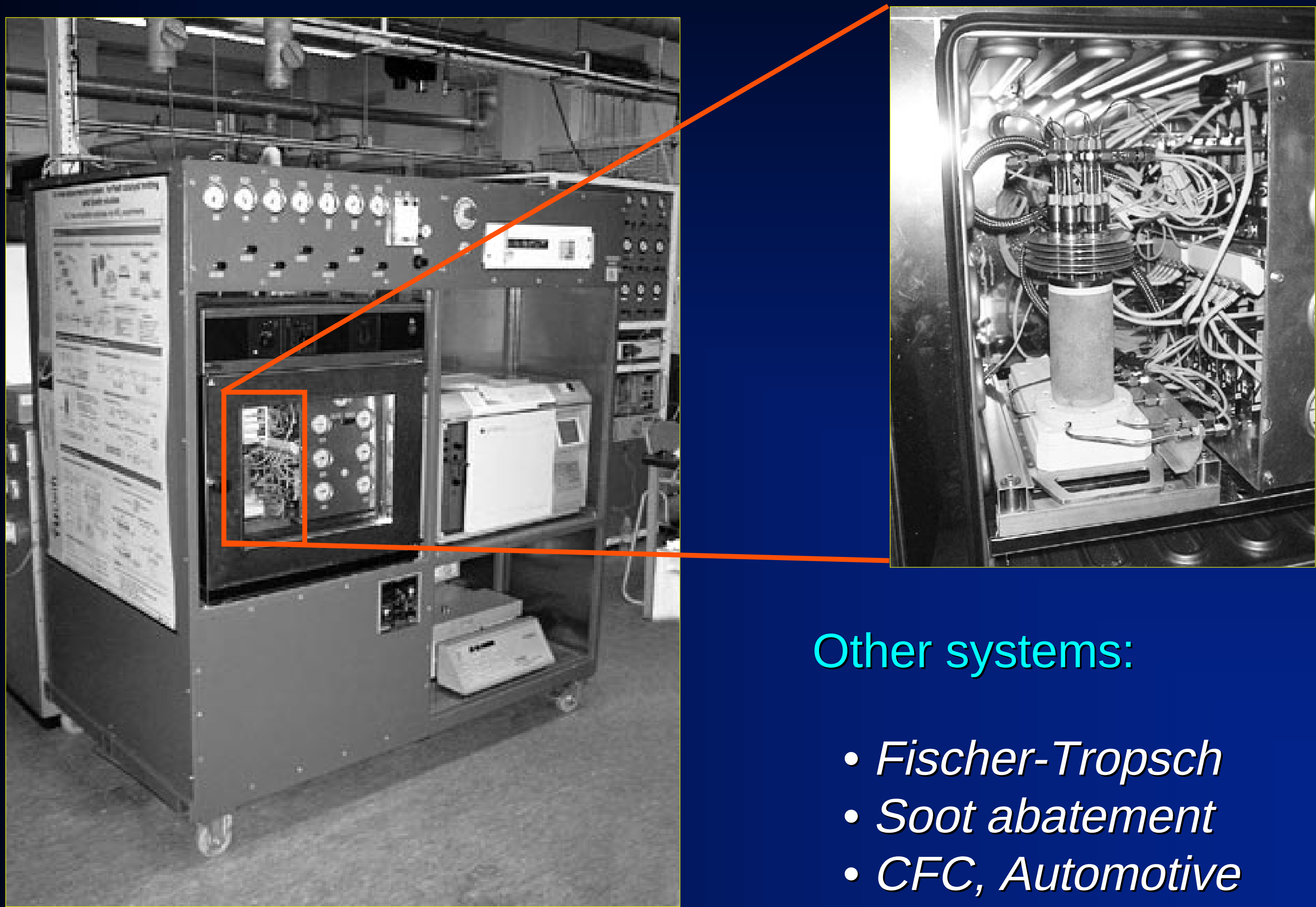
Efficient testing methods necessary

Parallelization catalyst testing sixflow set-up



Screening catalysts
Kinetic studies
Deactivation/stability
Easy handling - Quantitative

N_2O/NO_x decomposition set-up

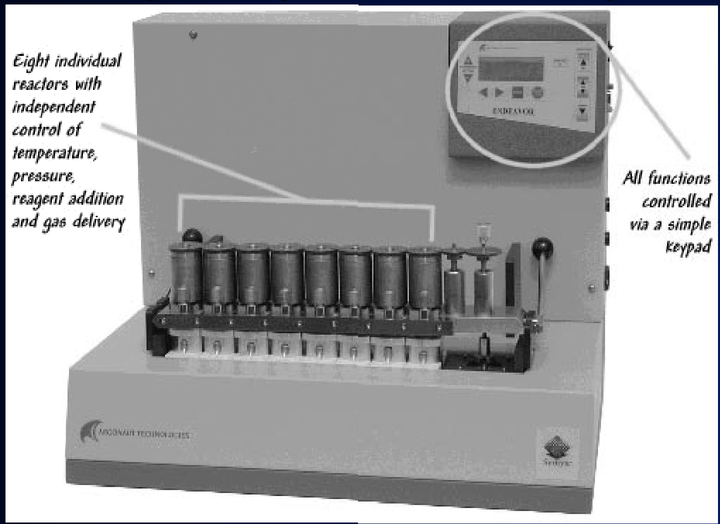


Other systems:

• *Fischer-Tropsch*	*GC*
• *Soot abatement*	*NDIR*
• *CFC, Automotive*	*GC*
• *SCR*	*MS, NOx*

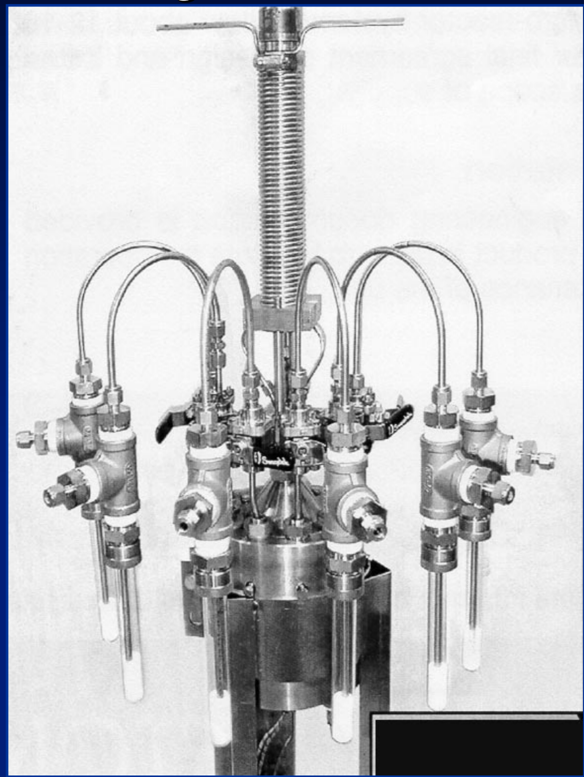
Commercial parallel experimentation rigs

gas/liquid/solid slurry



Argonaut Technologies

gas/solid

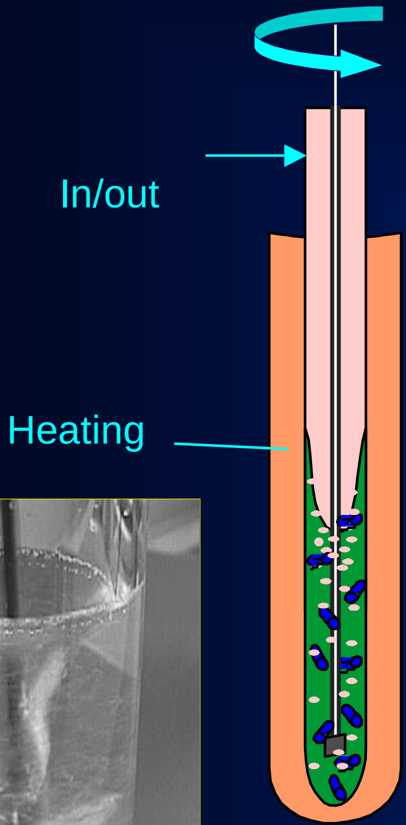


Zeton-Altamira

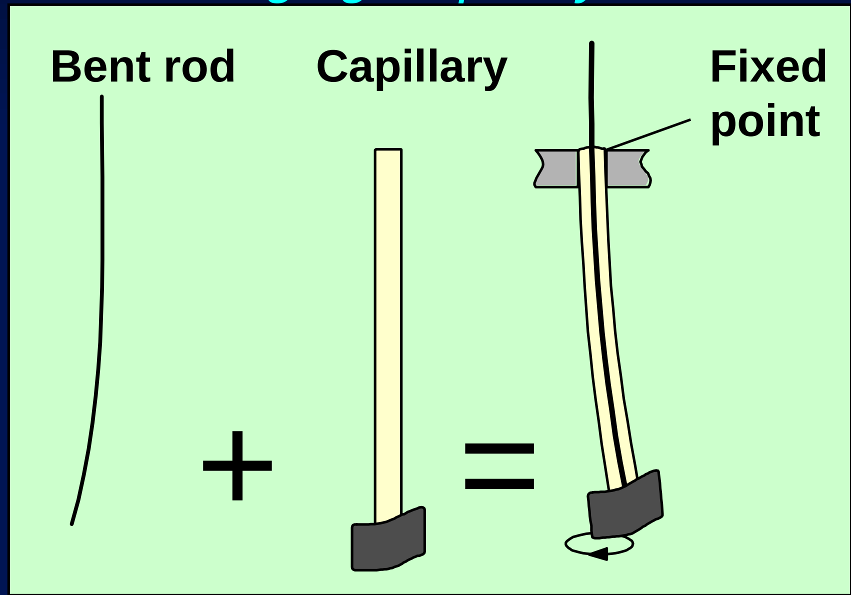
Swinging Capillary Microautoclave

S. Tajik et al. *Meas.Sci.Technol.* 1990, *1*, 815-817

Imtech Systems

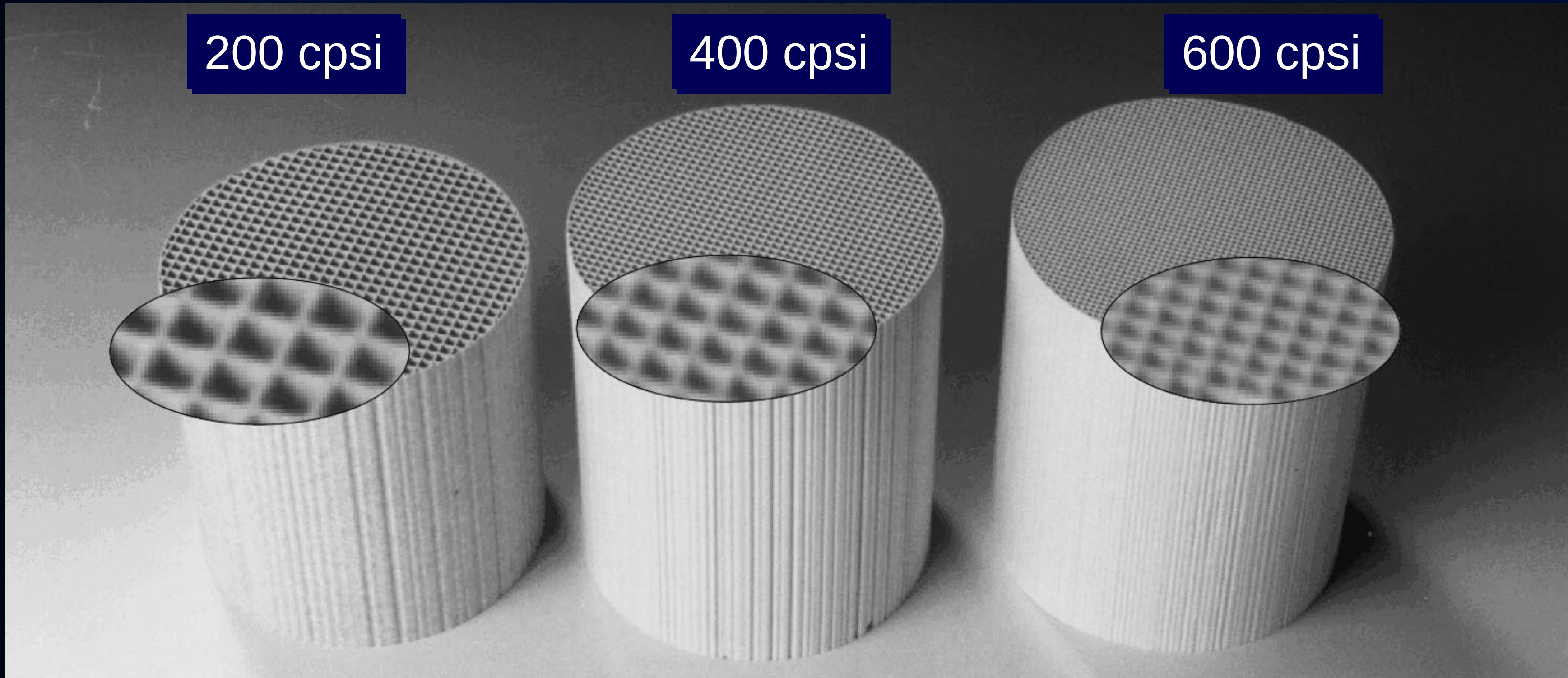


Swinging Capillary Stirrer



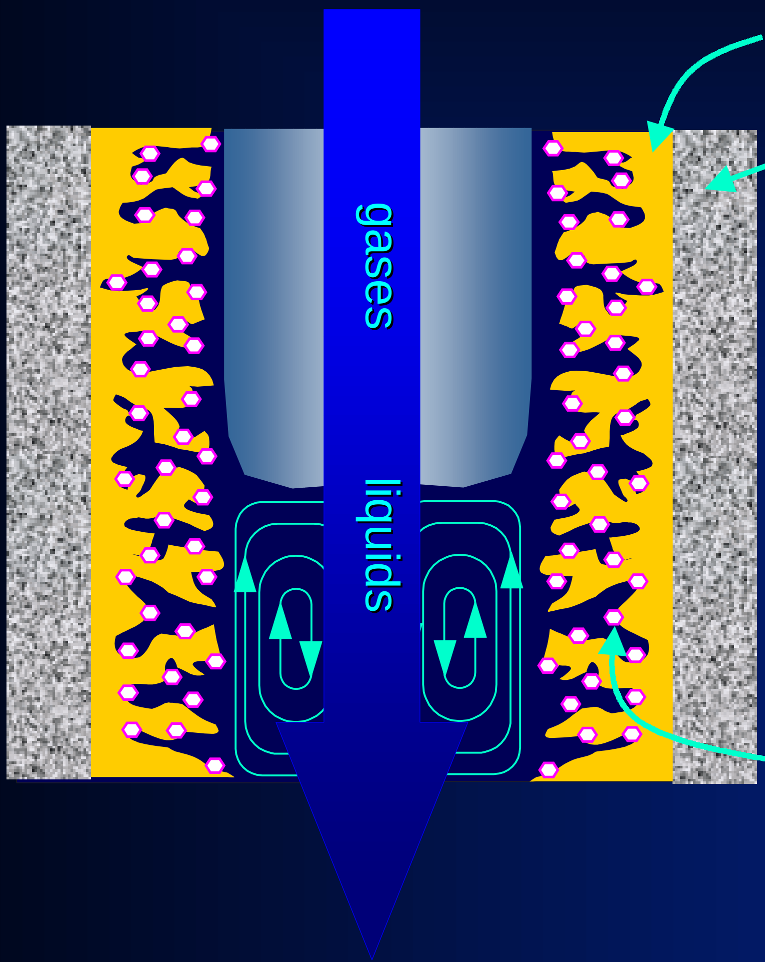
- *compact (30 ml), no dead volume*
- *no feedthrough sealing*
- *high T, high p*

Monoliths - Cell density

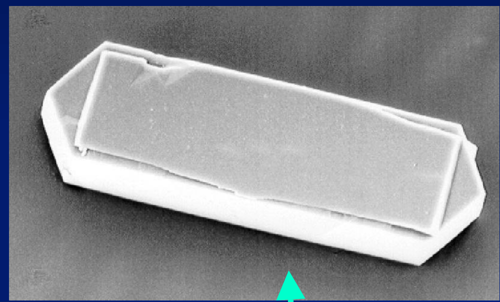


200 cpsi	400 cpsi	600 cpsi
1.80/0.27 mm	1.27/0.16 mm	1.04/0.11 mm
1890 m^2/m^3	2740 m^2/m^3	3440 m^2/m^3
$\varepsilon = 0.72$	$\varepsilon = 0.76$	$\varepsilon = 0.8$

Gas-liquid-solid system monolith



zeolite

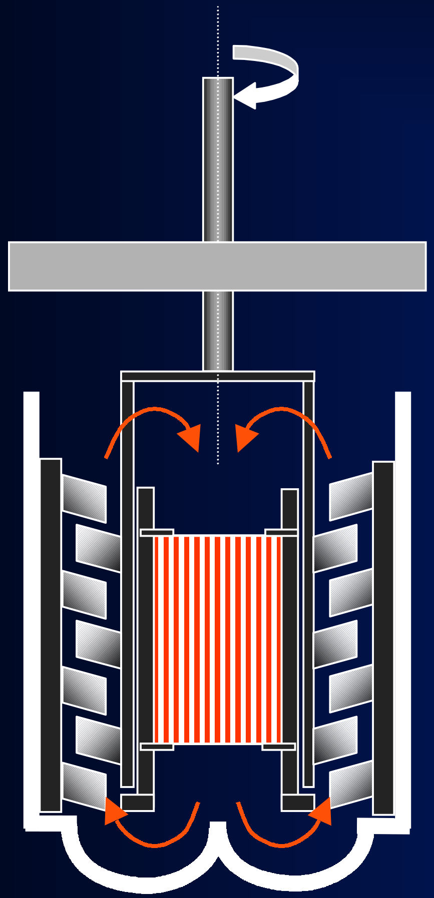


'Taylor-flow'

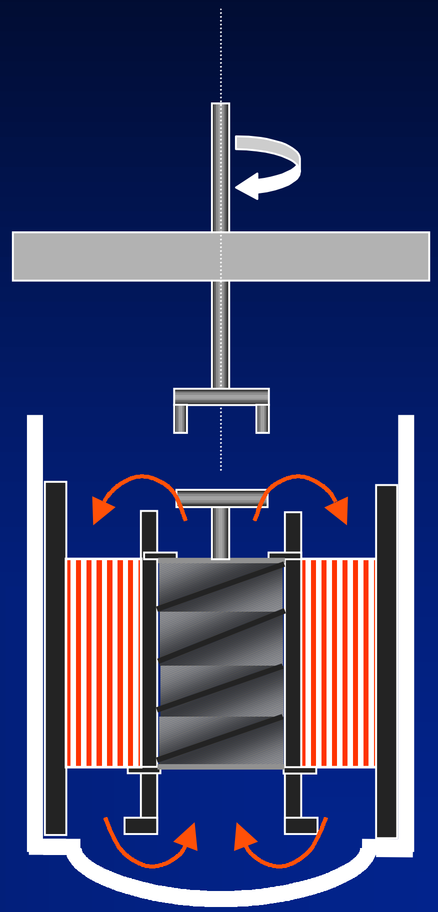
Plug flow, cocurrent
Mass transfer excellent
→ ***Intrinsic kinetics***

Monolithic catalyst investigations

Reactor types



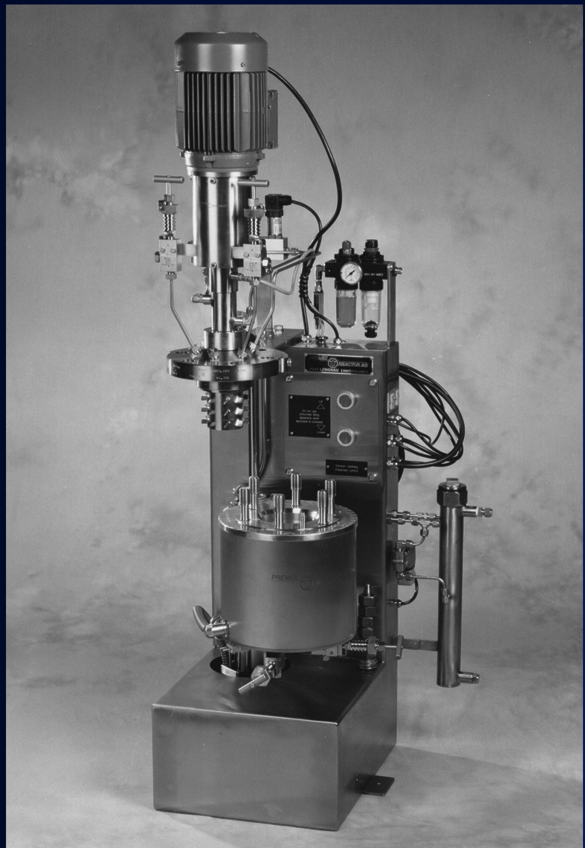
Turbine reactor



Screw impeller stirred reactor

Batch/semi-batch/continuous
Monoliths, packed beds

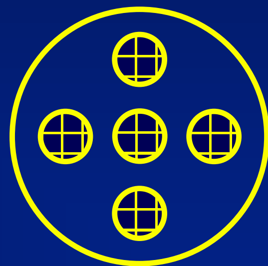
Turbine reactor - Monolithic catalyst studies



Recirculation type

300 ml

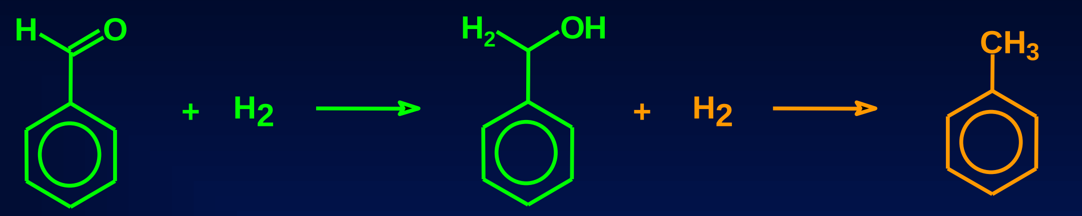
- *Commercial system (Premex)*
- *Inserts for monoliths 10-45 mm Ø*



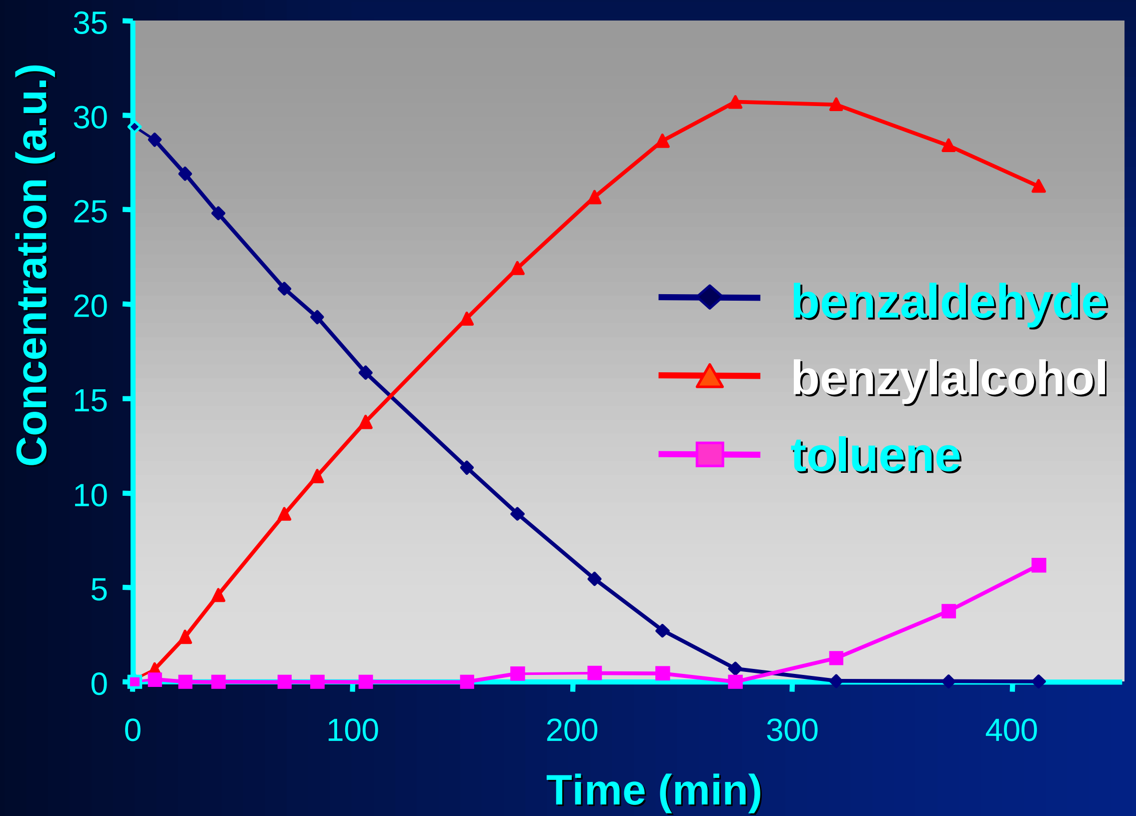
SISR – Screw Impeller Stirred Reactor

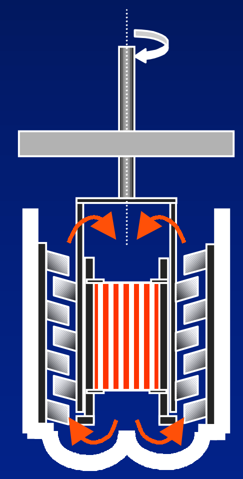
- *Standard autoclave*
- *Dedicated insert for monoliths*

Batch reactor - monolith, turbine



Ni/γ-Al_2O_3
410 K
15 bar





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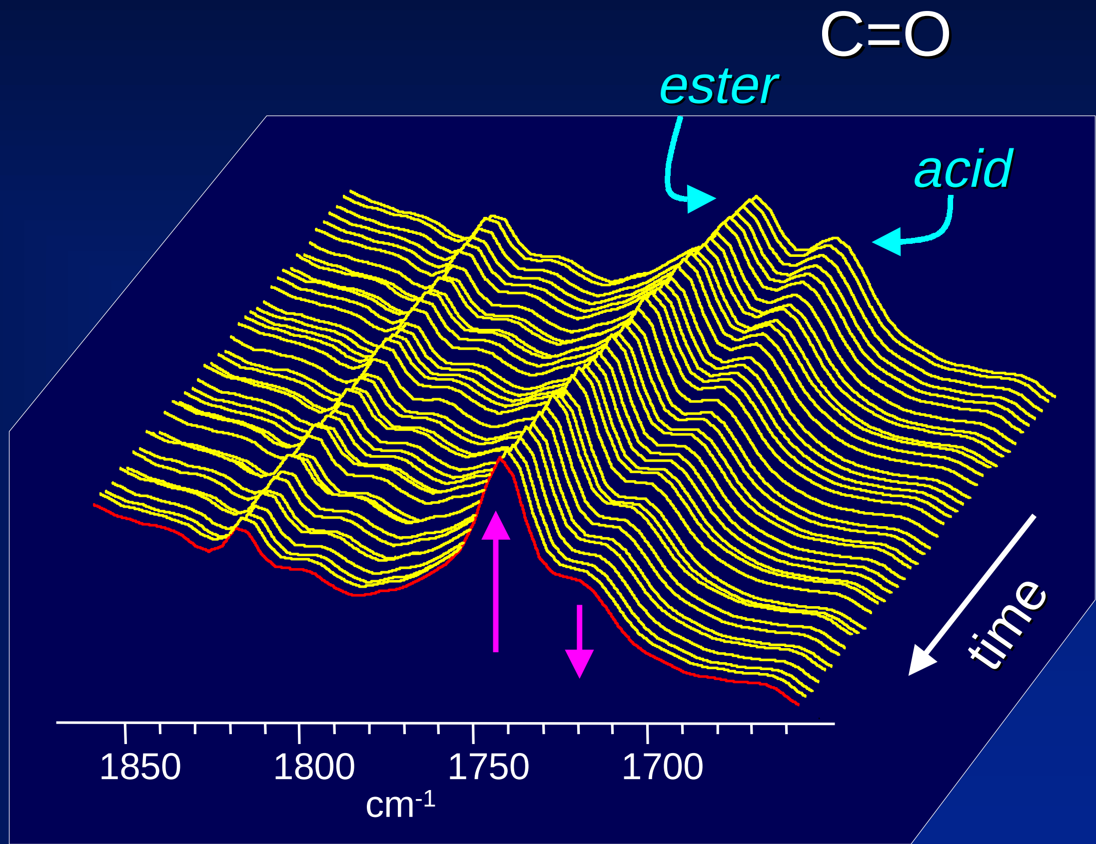
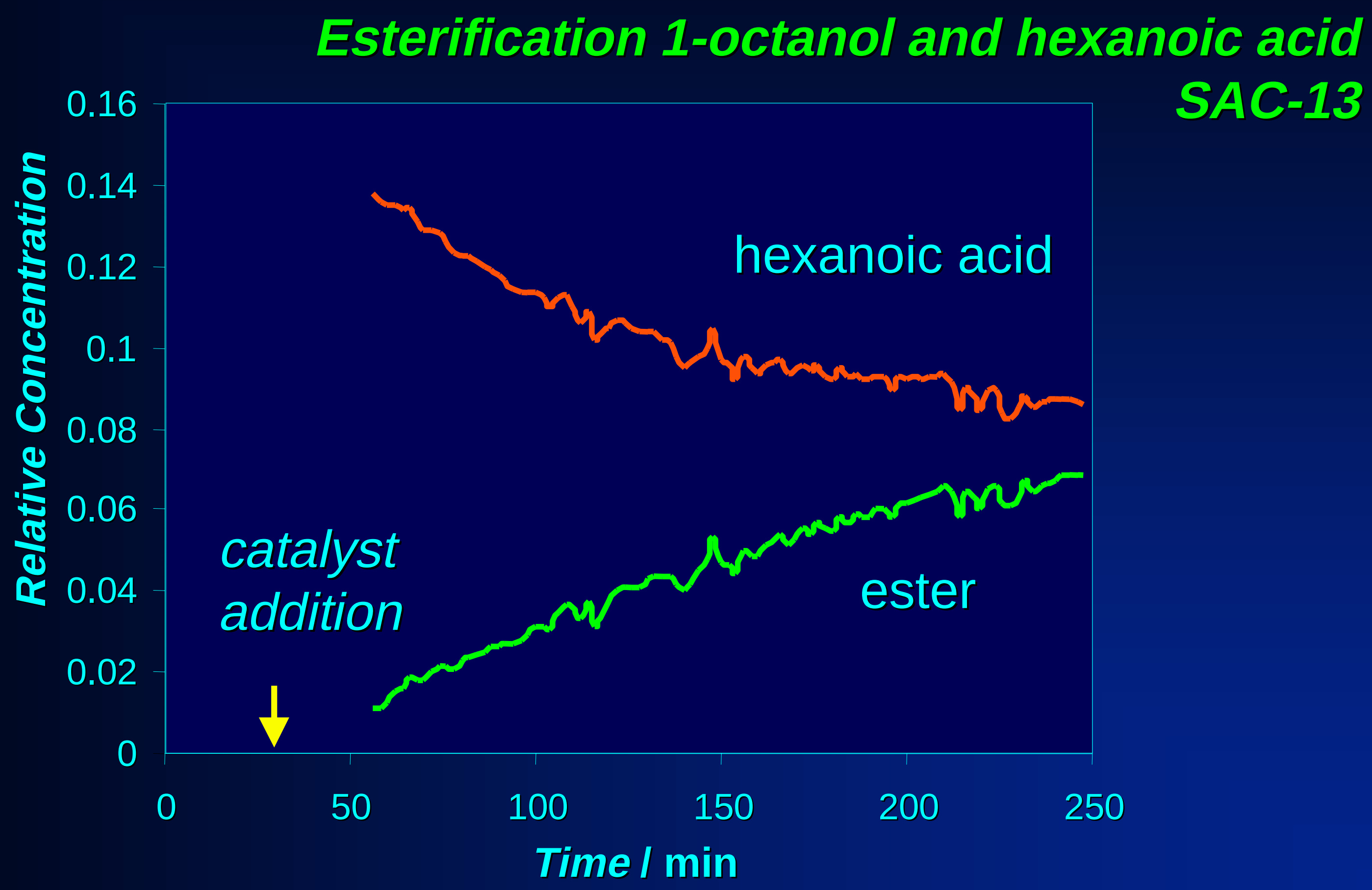
In-situ real-time monitoring – IR probe

Esterification 1-octanol and hexanoic acid
SAC-13



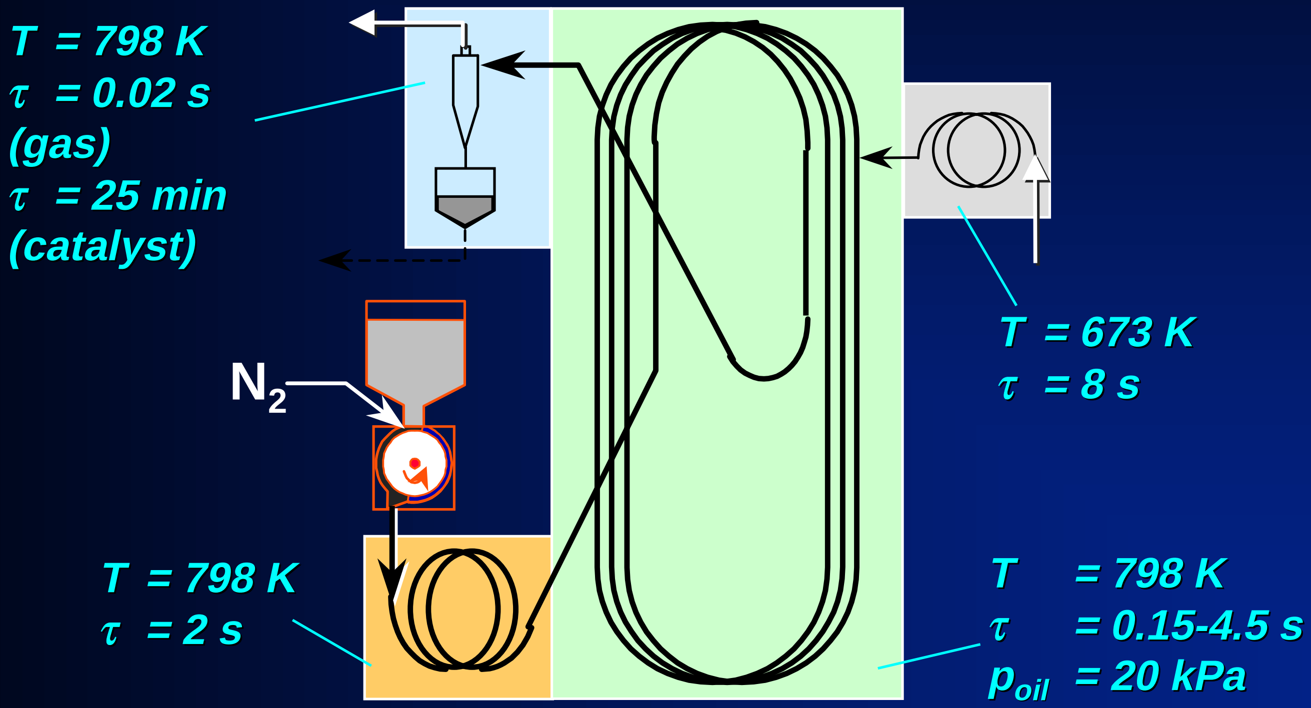
Reaction profiles



- *real-time analysis*
- *no sample losses*

Labscale Riser reactor - FCC

M. P. Helmsing et al. *Chem.Engng.Sci.* 1996, *51*, 3039-3044



well-defined residence time
meaningful catalyst performance

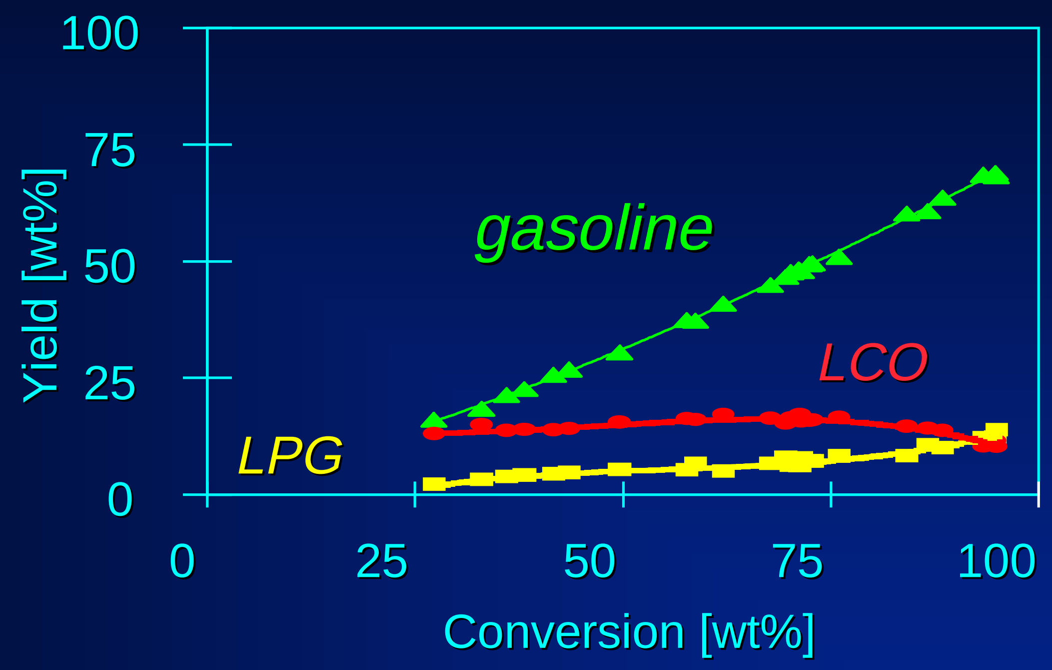
Labscale Riser reactor – Real look

Catalyst feeder

Labscale riser unit

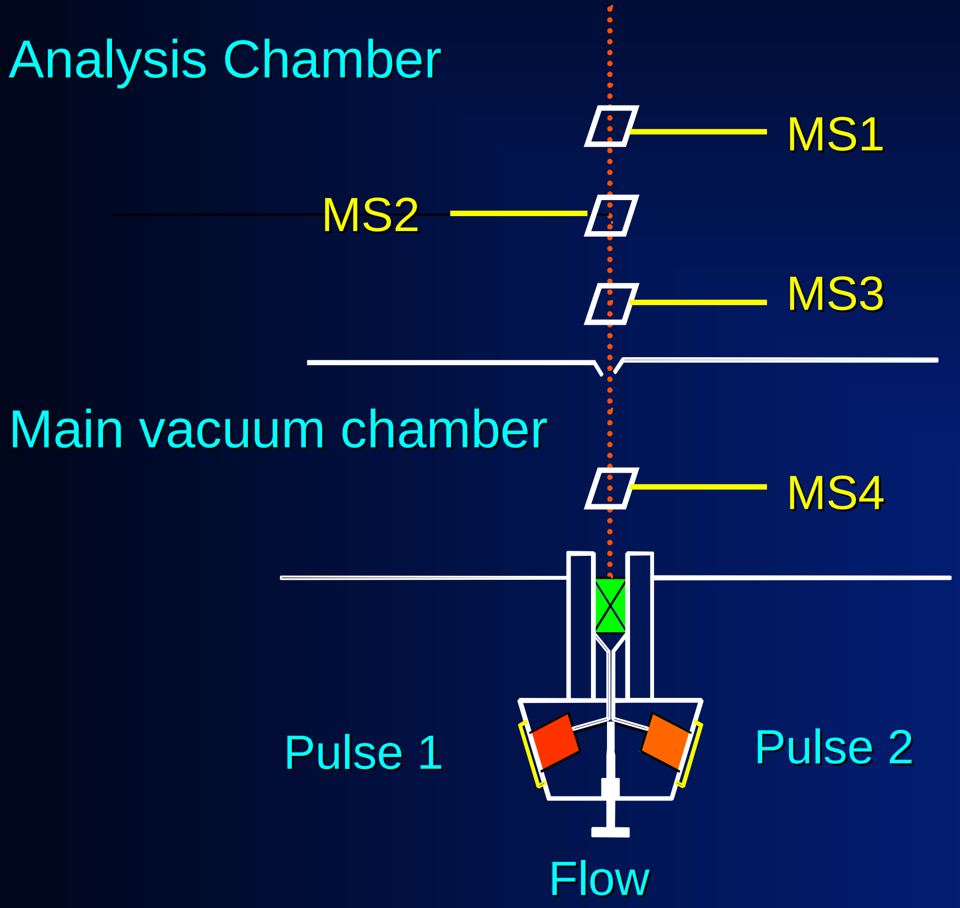
Labscale microriser performance

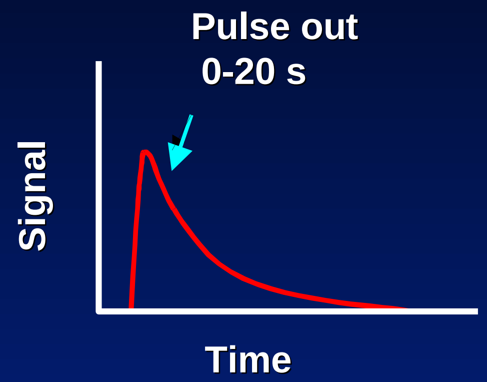
HCO cracking

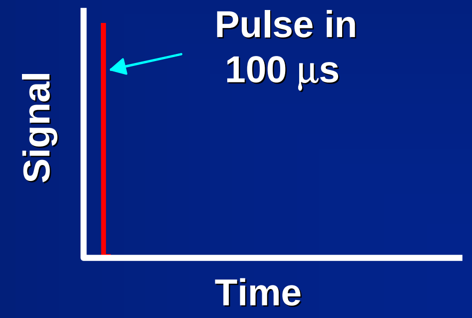


- *Gasoline yield proportional to conversion up to 95 wt%*
- *Performance catalyst representative for practical application*

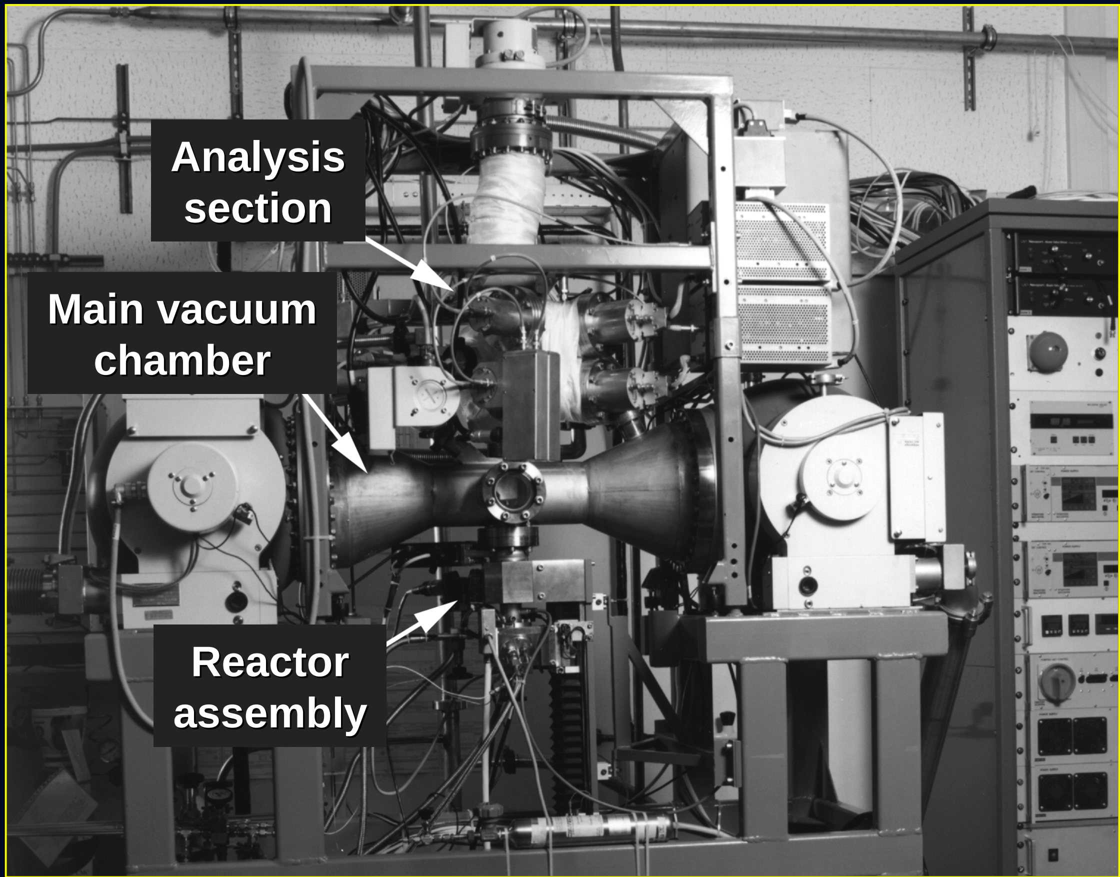
Multitrack - TAP Transient kinetics







Multitrack equipment



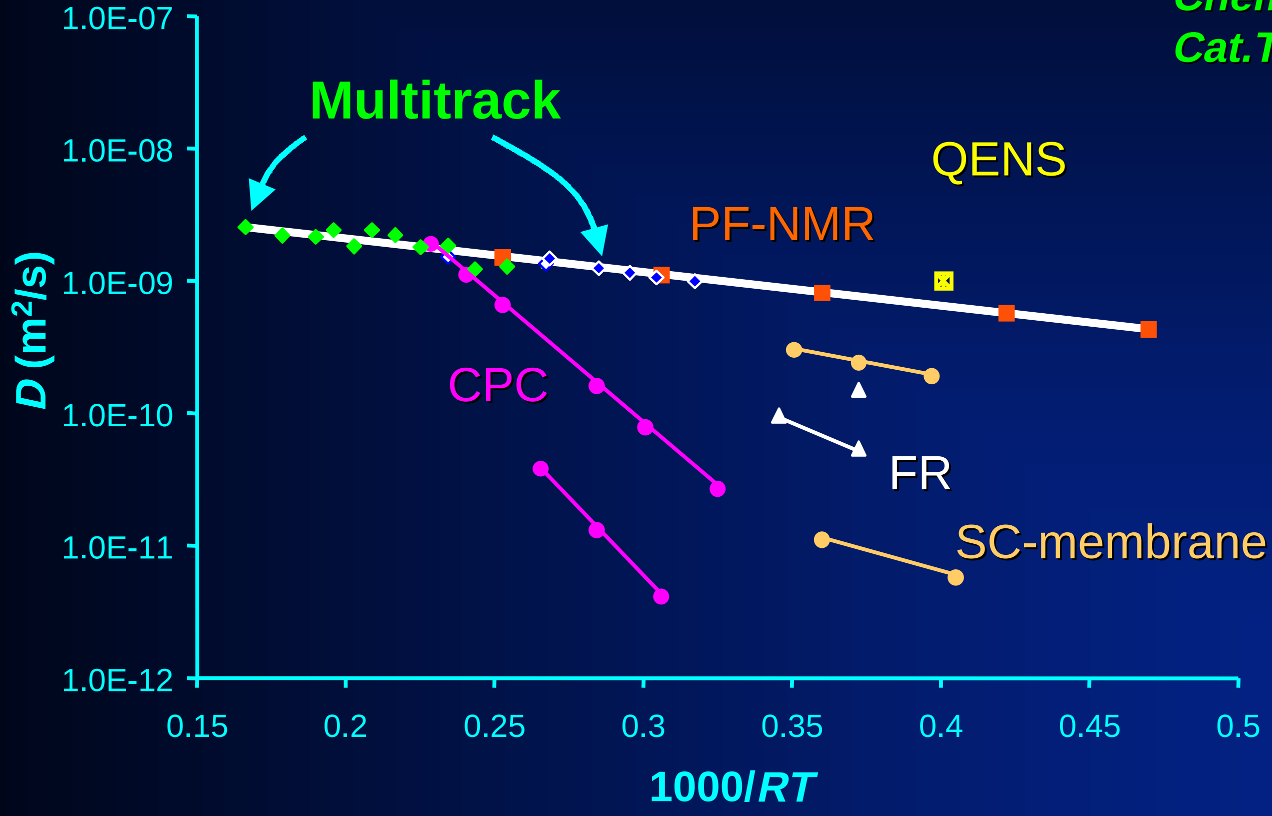
fast
minute amounts

- ***Diffusion***
- ***Adsorption***
- ***Catalysis***

Comparison of Diffusivities

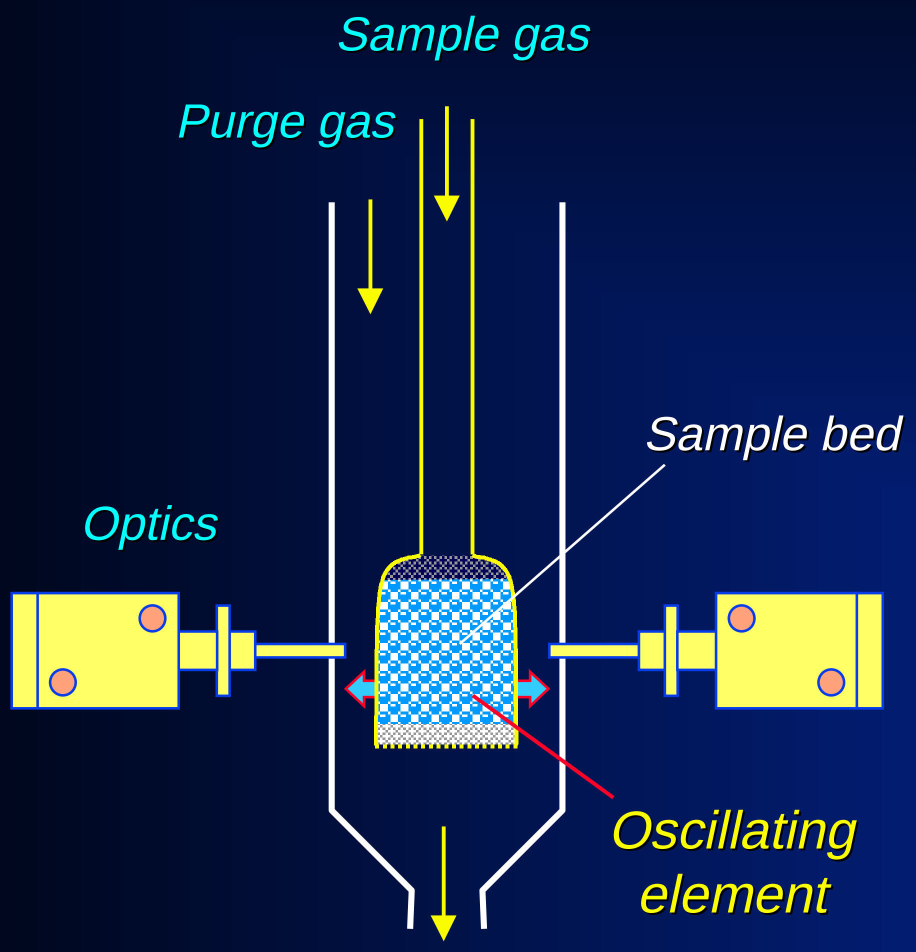
n-butane in silicalite-1

T.A. Nijhuis et al.,
Chem.Eng.Sci. 54 (1999) 4423
Cat.Today 53 (1999) 189



Similar as microscopic techniques

Tapered Element Oscillating Microbalance
TEOM



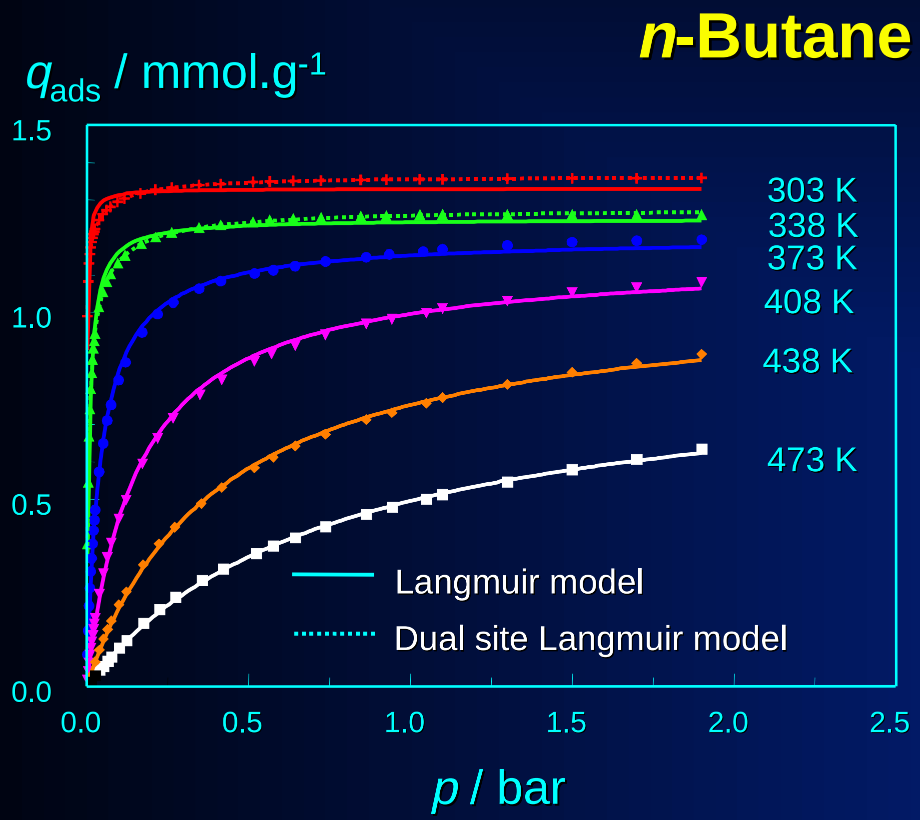
Operating principle

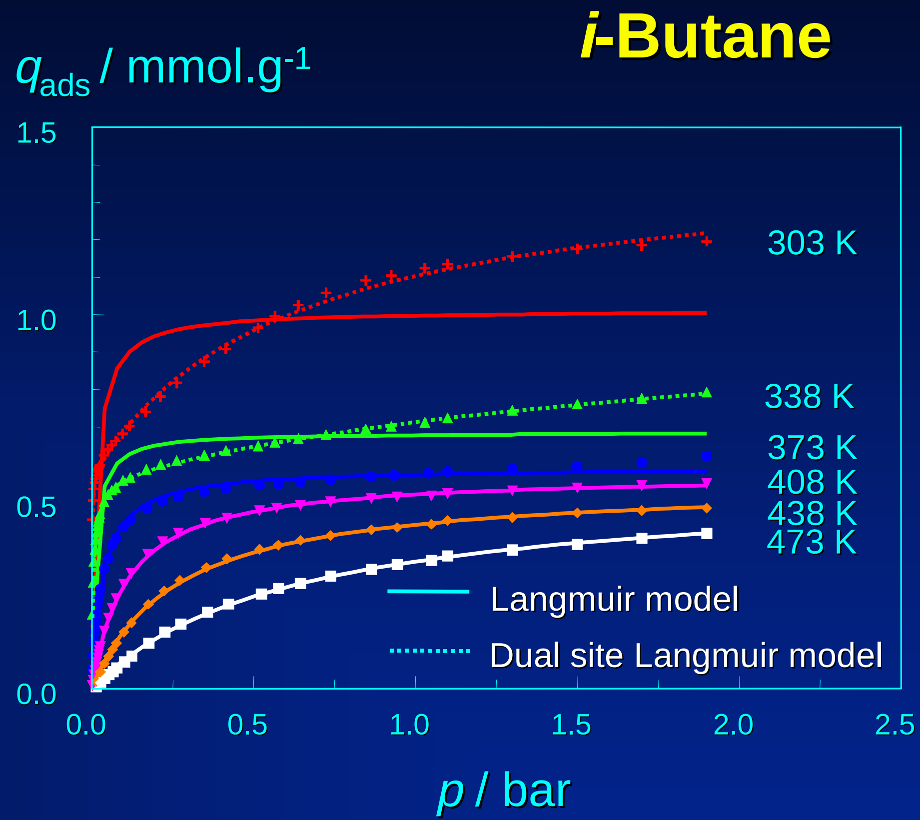
$$\Delta M = K_0 \cdot \left[\frac{1}{f_2^2} - \frac{1}{f_1^2}\right]$$

Mass changes
T: 300-823 K
p: 0-10 bar
sensitivity 1 µg

- ***Conditions relevant practice***
- ***Deactivation***
- ***Adsorption/Diffusion***

Adsorption isotherms - Alkanes in silicalite-1





$$q_{ads} = \frac{q_{sat1} K_1 p}{1 + K_1 p} + \frac{q_{sat2} K_2 p}{1 + K_2 p}$$

TUDelft

Trends in catalyst testing equipment

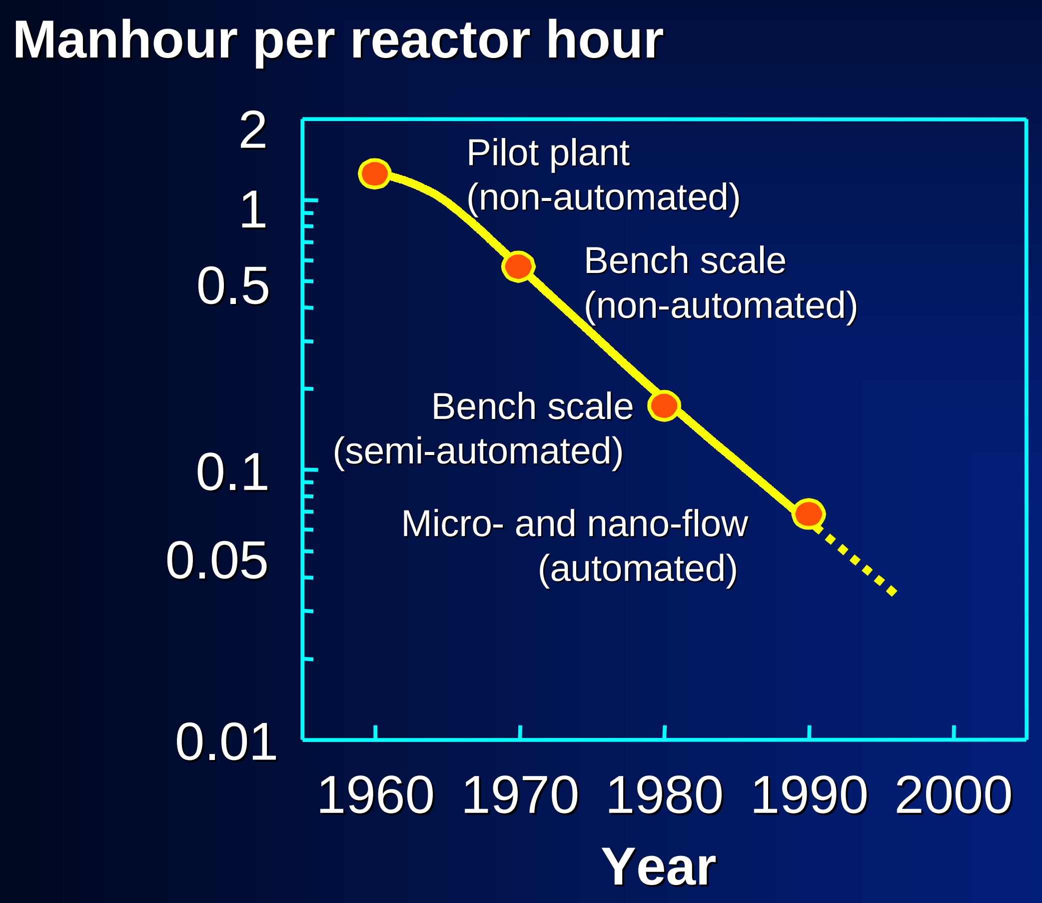
- Parallellization
  - Multiflow: black & white or quantitative
- Automization – PC control
  - Running overnight, unattended
  - Ramping experimental conditions (TSR)
- Reactors
  - Ease of handling, speed, size
- Analysis techniques
  - micro GC
  - MS
  - Spectroscopy (FT techniques)
  - sensors/probes
- Miniaturization

transient operation

in-situ analysis

Manpower needed in catalyst development

Sie, AIChE J. 42 (1996) 3498



- ***Downscaling***
- ***Reduced cost***
- ***Safety***

- ***Confidence data***
- ***Reliable models***
- ***Scale-up***

What can be concluded?

- Rapid equipment development
  - reactors
  - analysis
  - downscaling

→ *Fast determination catalyst performance*

Enabling:

- Kinetics studies / quantitative data
- Deactivation / catalyst stability
- Kinetics & Deactivation

What else can be tackled?

- 'Irreducible' kinetics
- Downscaling L/S and G/L/S reactors
- Photocatalytic reactors
  - well-controlled energy introduction
- Deactivation

- Data mining
- Sequential experimental design
- Direct linking to practical realization
  - What are the reactor sizes?
  - How does the reactor look like
  - Which reactor is optimal?

Techniques
Hardware
Software

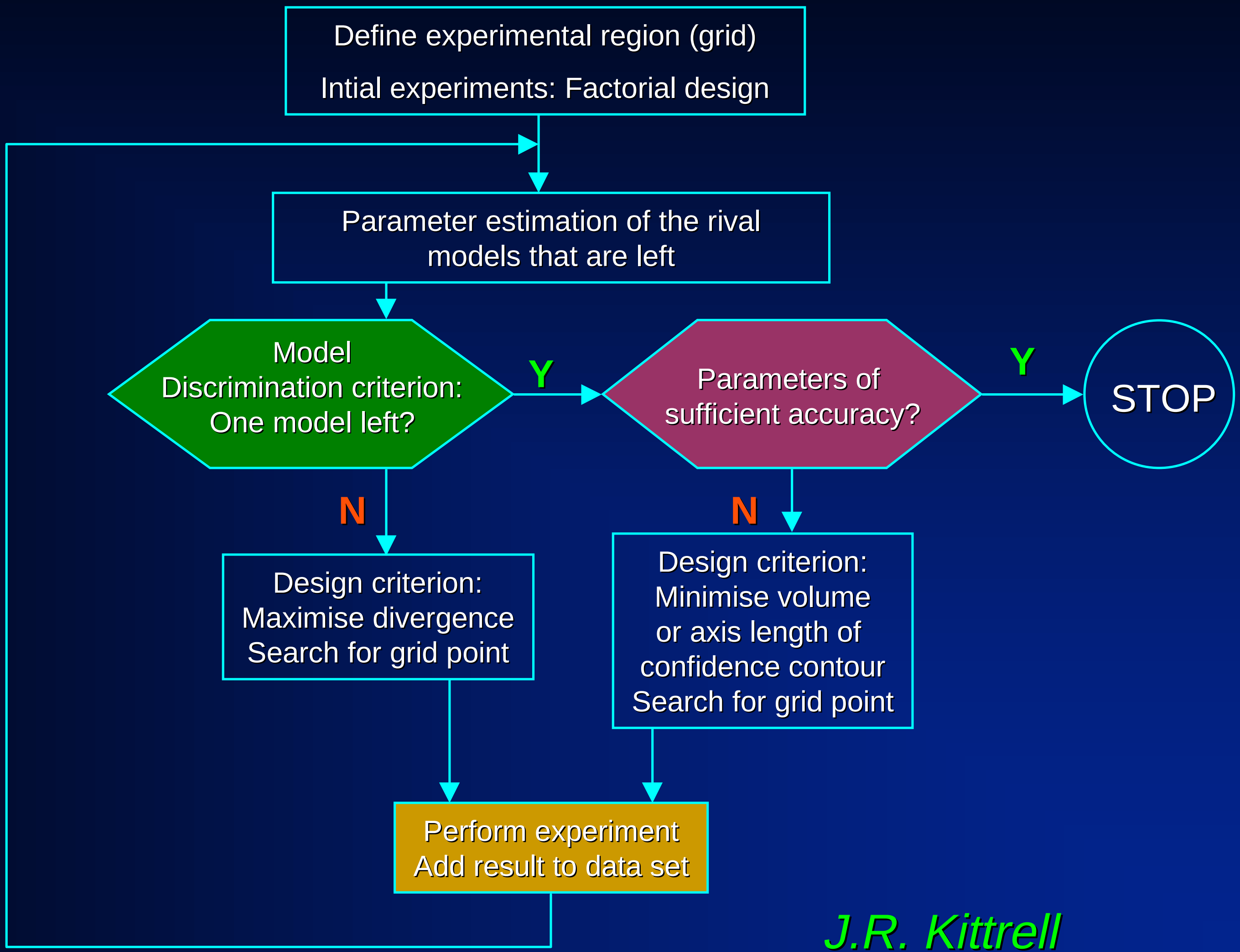
Many thanks to…

- Xander Nijhuis
- Guido Mul / Annemarie Beers
- Saeed Tajik
- Javier Pérez / Ronald de Deugd
- Edwin Crezee
- Marion den Hollander

- Workshop IC-TUDelft

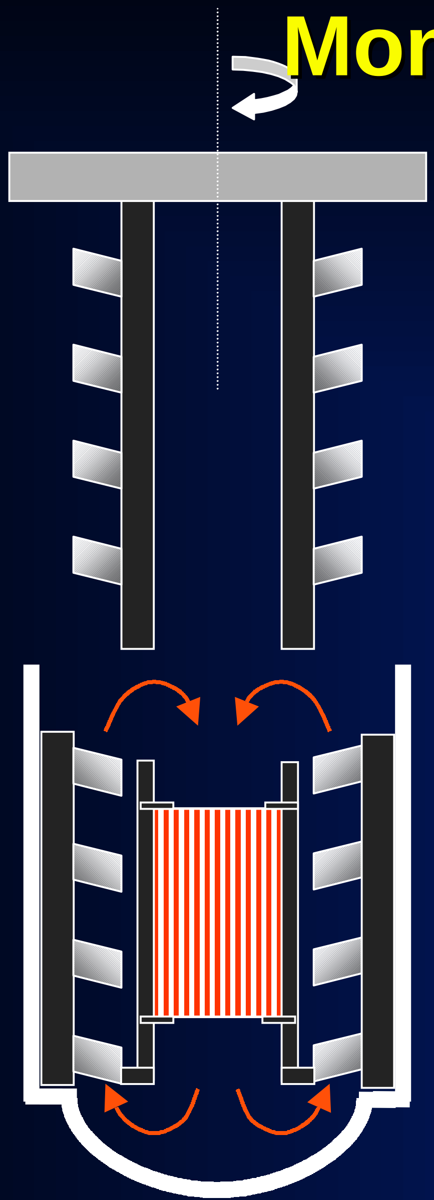
and others………….

Sequential experimental design

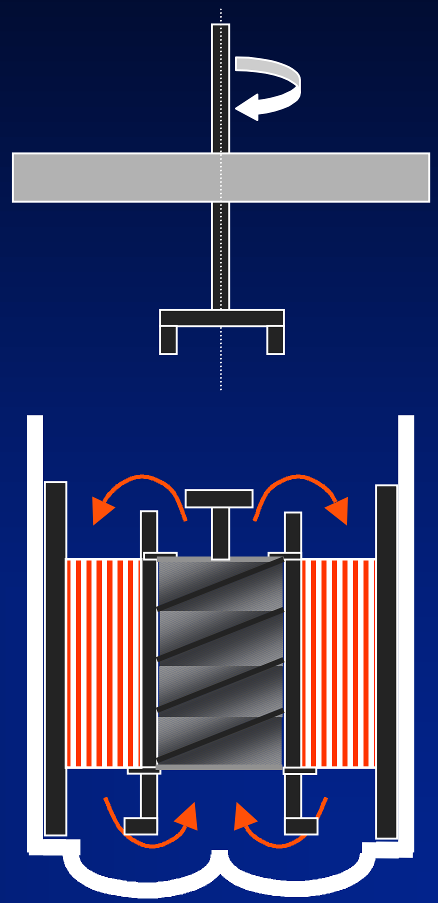


J.R. Kittrell
G.F. Froment, L.H. Hosten

Monolithic catalyst investigations
Reactor types

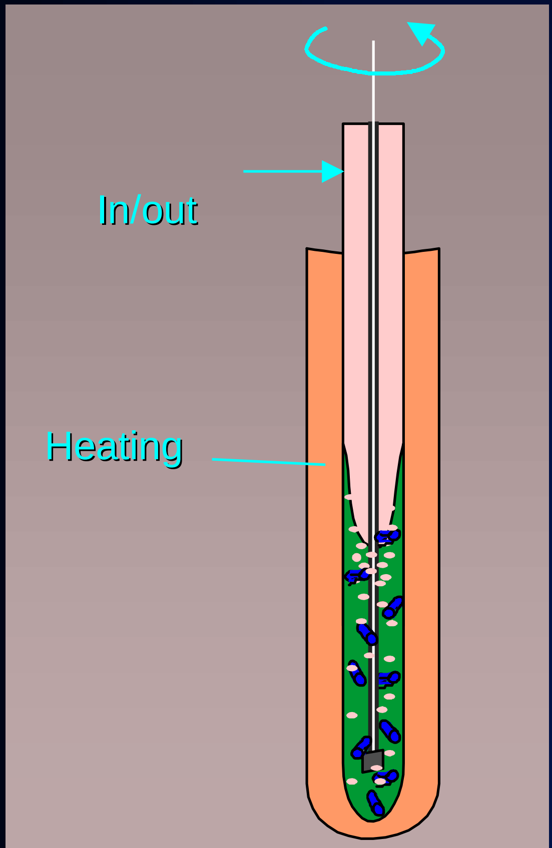


Turbine reactor



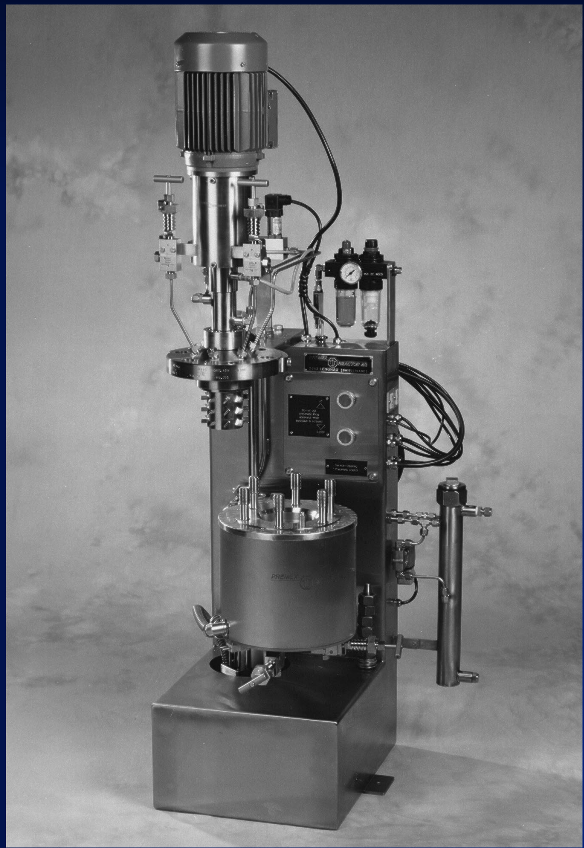
Screw impeller stirred reactor

Monolithic catalysts: test reactors



Swinging capillary

10 ml



Recirculation type

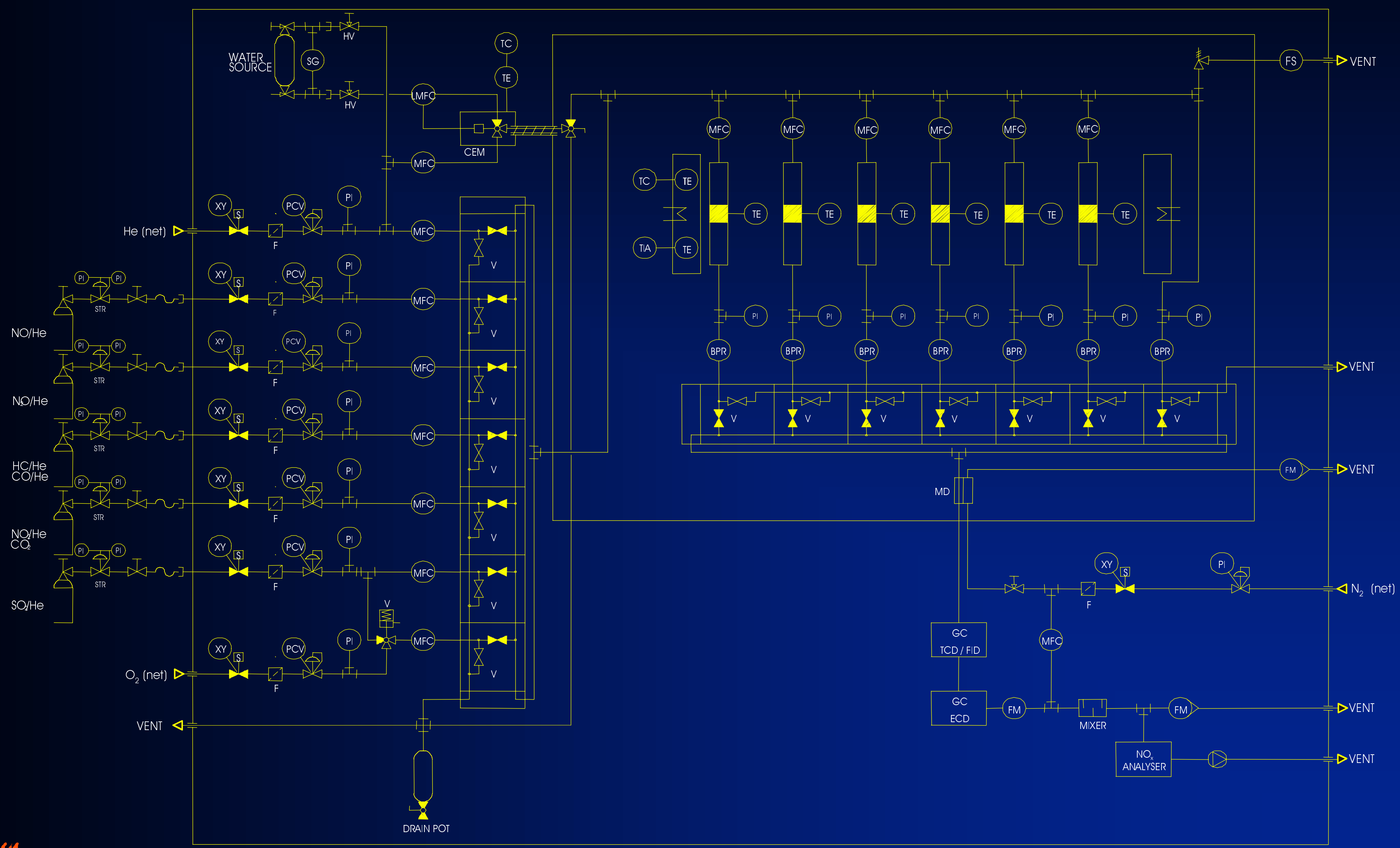
300 ml

Pilot reactor

40 l

TUDelft

Sixflow equipment lay-out



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