G-L Taylor Flow reactor system
Oxidation of ethylbenzene

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ECN

Energy research Centre of the Netherlands

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ECN Mission and Units

Mission statement

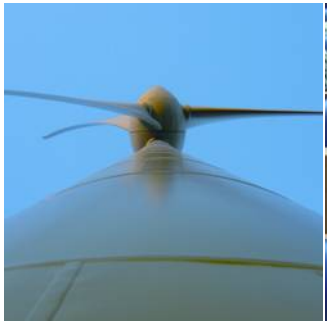
ECN develops and brings to market high-level knowledge and technology for a **sustainable energy** society

- Largest Dutch R&D institute on energy
- Independent and committed
- Link between fundamental academic research and market application

ECN Business units


Solar energy


Biomass

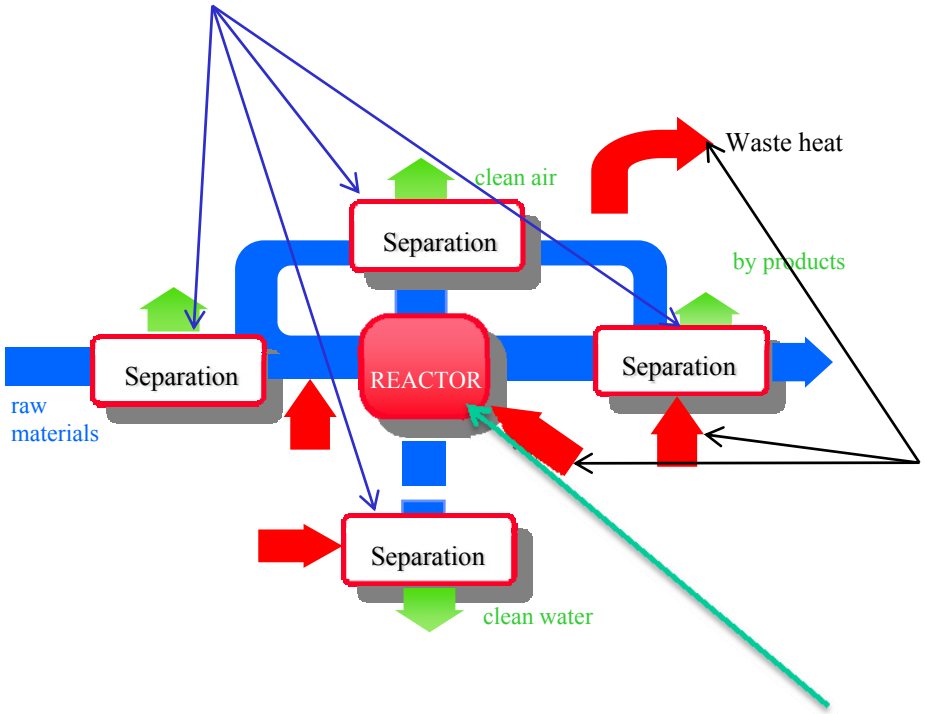

Wind energy


Policy Studies


Efficiency & Infrastructure

Research areas ECN - E&I

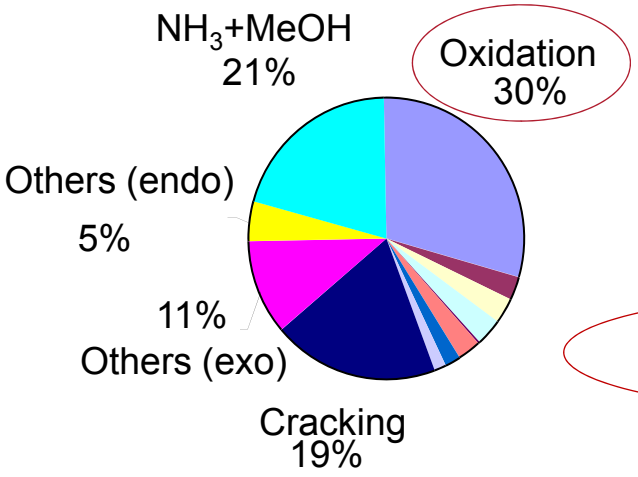
2. Molecular Separation Technology



1. Industrial waste heat

3. Process intensification/
Multifunctional reactors

Process and technology selection



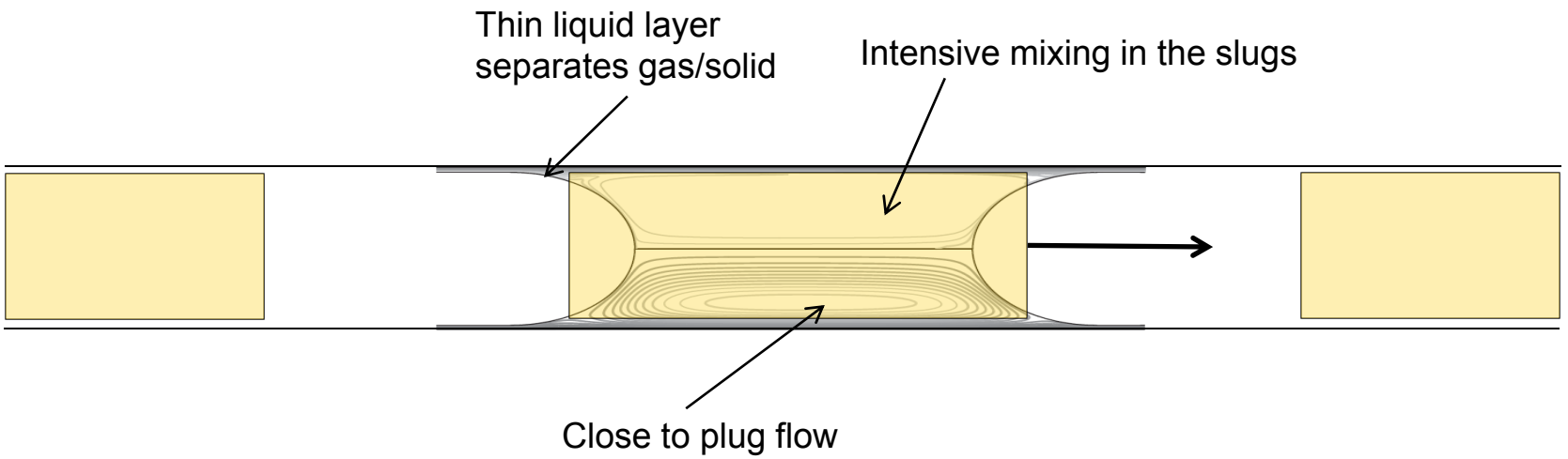
Relative energy usage NL

	Oxidation	Cracking	Ammonia	Hydrogenation	Dehydrogenation	Hydration	Dehydration	Condensation	Alkylation	Isomerization
MR / pervaporation membrane										
MR / hydrogen selective										
Catalytic membrane reactor										
HEX-reactor										
Structured (monolith) reactor										
Micro-reactor										
Short residence time reactor										
Reactive distillation										
Sorption enhanced reactor										
Supercritical reactor										
Advanced distillation										

Technologies for process intensification

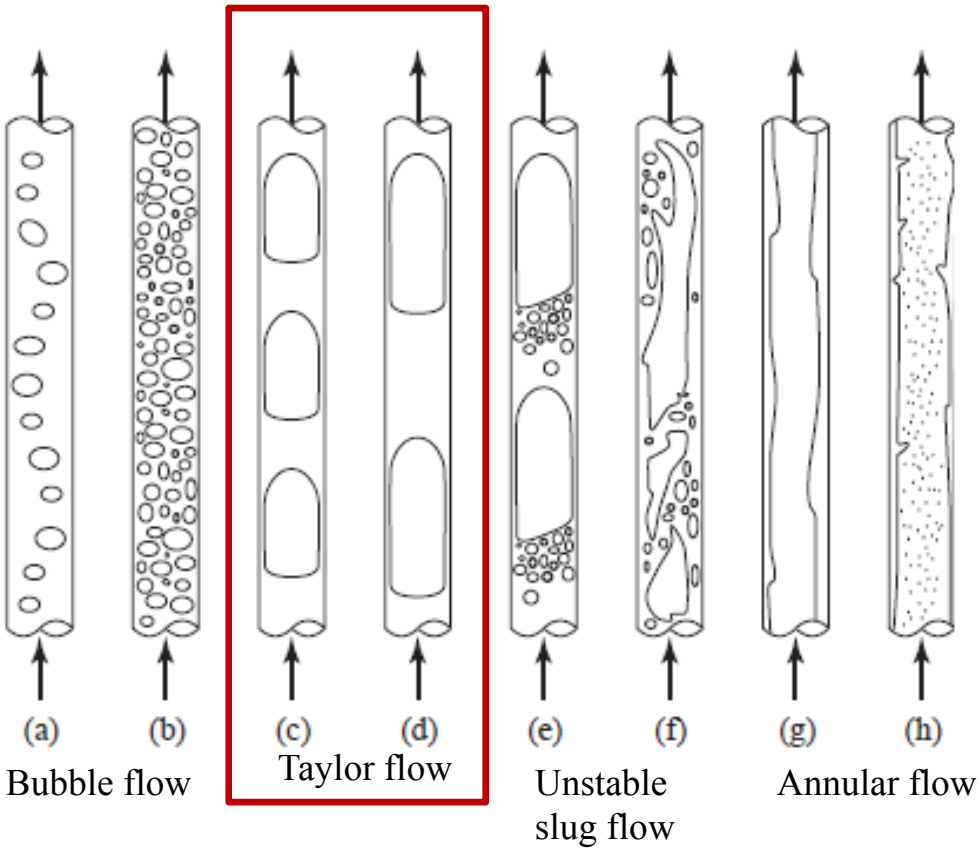
J. Hugill Monolith reactors for gas-liquid reactions: Internal ECN Report

Structured reactor and Taylor flow



- Good mass transfer
- Good mixing in the liquid slugs
- Overall plug flow
- Good heat transfer

Structured reactor - 2-phase flow pattern



Flow patterns depend on V_G ,V_L[1]

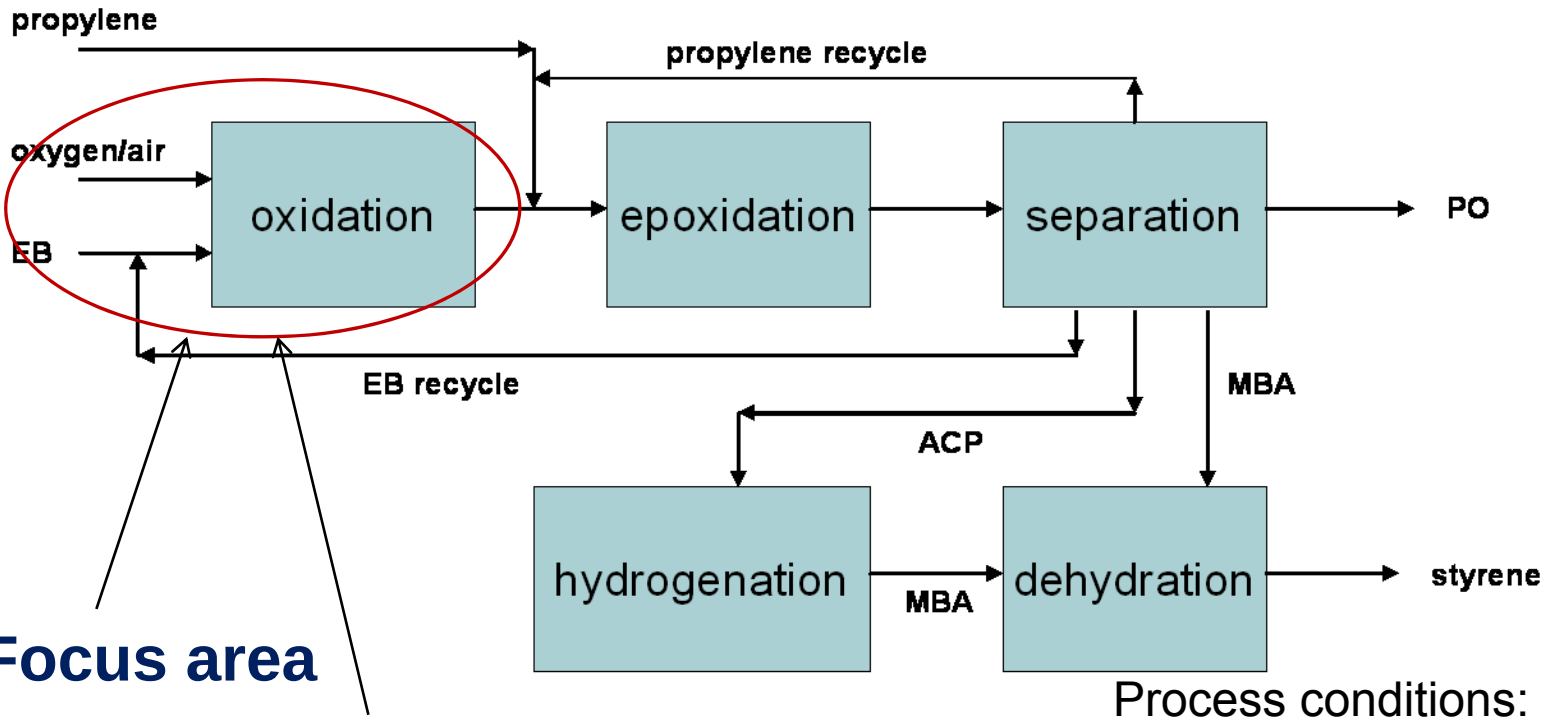
Best operating condition for the reaction in the channels is Taylor flow (PF).

[1] Kreutzer et al (2001), Chem. Engg. Sci. 56 (2001) p.p.:6015-6023

Process selection for energy savings in NL [1]

- Inventory of oxidation processes in the NL
- Selection of top 5 oxidation processes in NL based on energy usage
- Selection of one process based on
  - -Total production capacity in the NL
  - -Reaction heat
  - -Temperature
  - -Pressure
  - -Catalyst
- Result : Styrene - Propylene oxide process

Styrene process



Focus area

EB oxidation to EBHP

Process conditions:

P = 2 bar

T = 140 °C

Conversion = 10 wt%

Selectivity = 90 %

Residence time = 1 hr

Realization prototype reactor

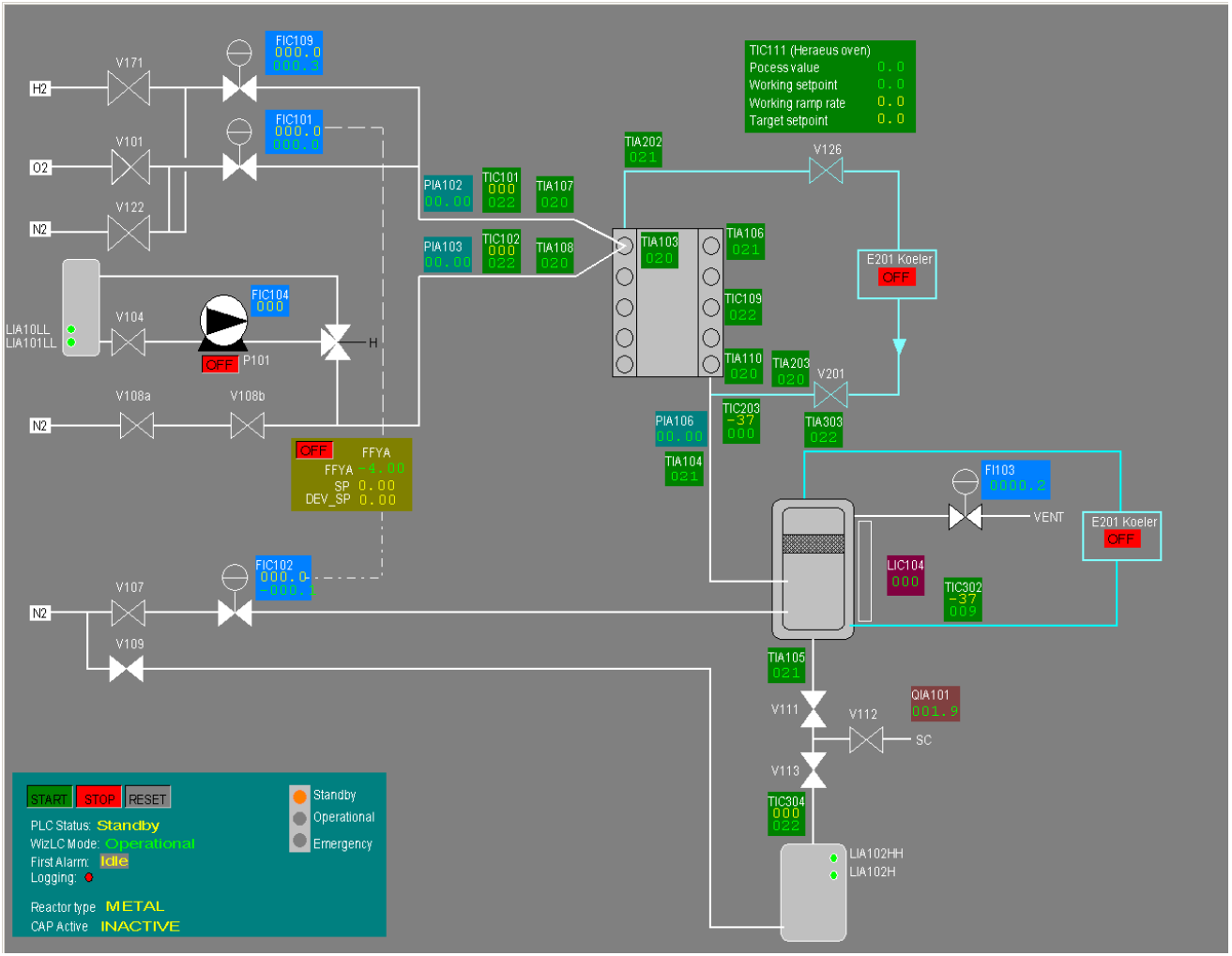
- G/L oxidation reactions are highy exothermic in nature
- Formation of explosive gas mixtures
- Demanding high safely operating equipment

Procedure for realization prototype reactor:

- Chemical and physical hazards
- Conceptual design of installation
- Critical operation hazards and required safety measures
- Detailed design of installation
- Prototype - computer controlled

Prototype Taylor flow reactor

Prototype Taylor flow reactor - control unit



Prototype Taylor flow reactor

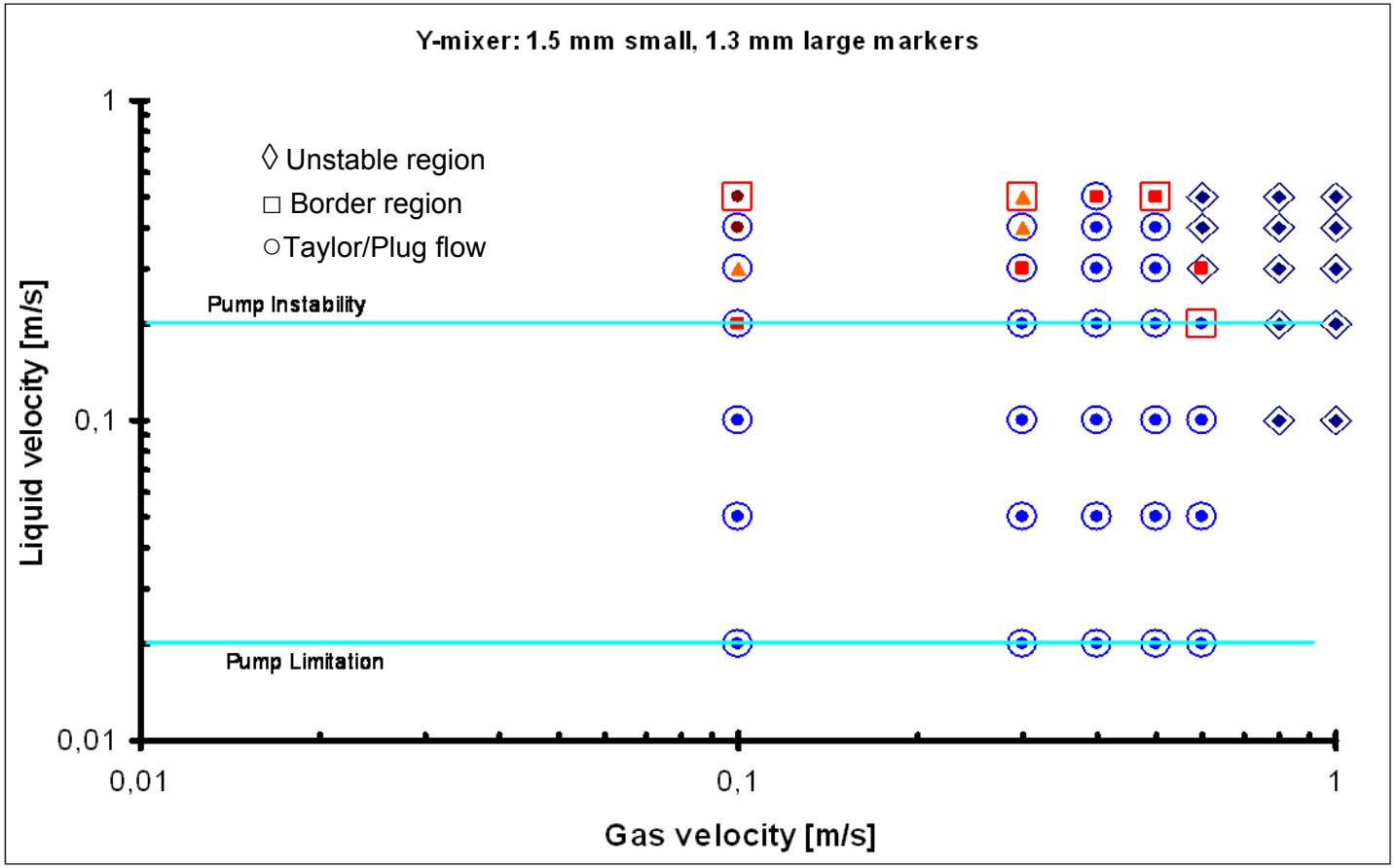
Preliminary oxidation study

Demonstrating that in TF mode oxidation can be performed with improved yield.

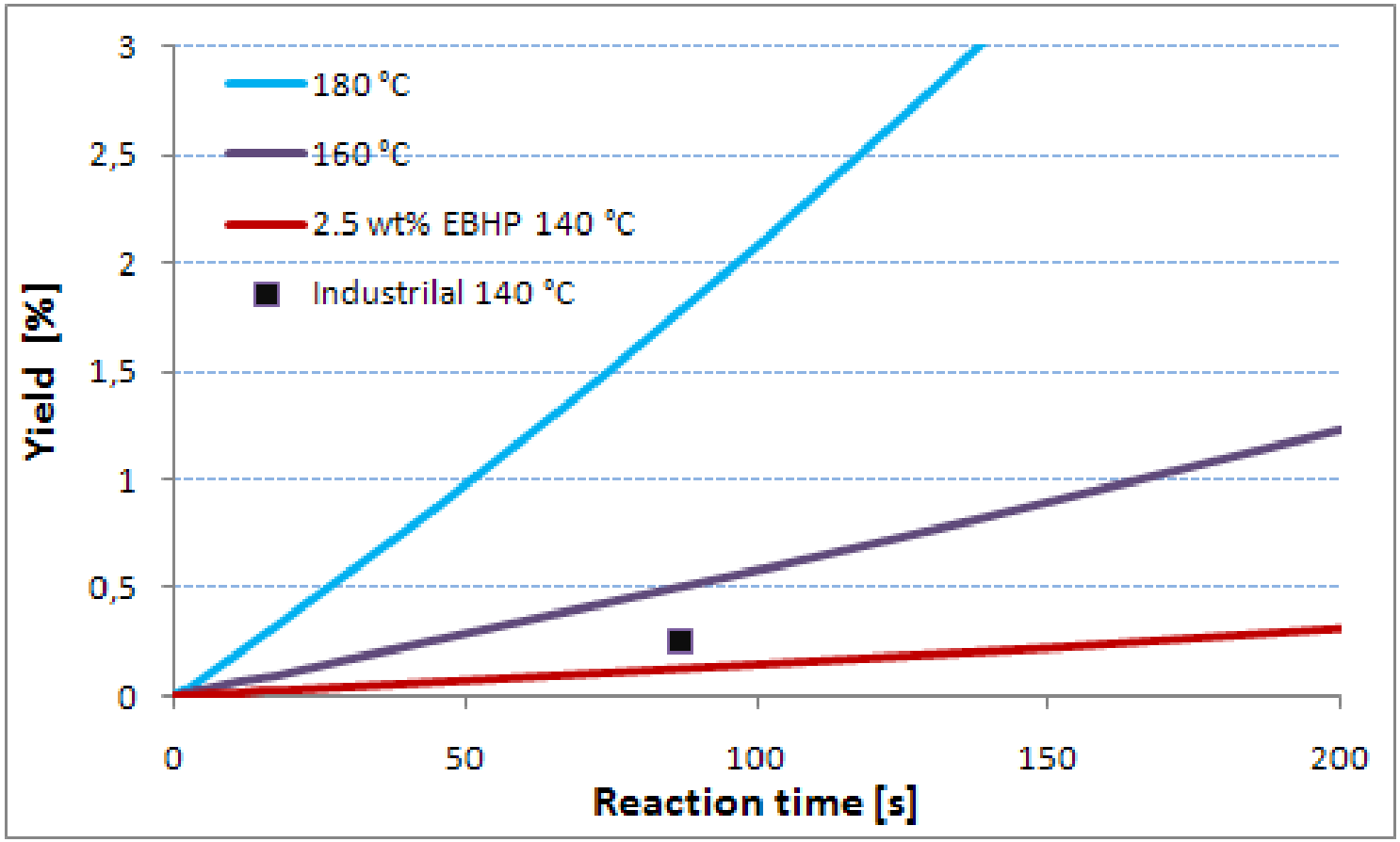
Defining process window

- Verification of flow pattern with water/N_2 and different P and T.
- Development of a kinetic model for EB oxidation

Operating window - fluid flow



Prediction of Temp. window by Kinetic model



[1] A.Yurdakul "Reactor Modelling of GL Reactions in Small Channels Intermediate Report" ECN-ei-2009-265

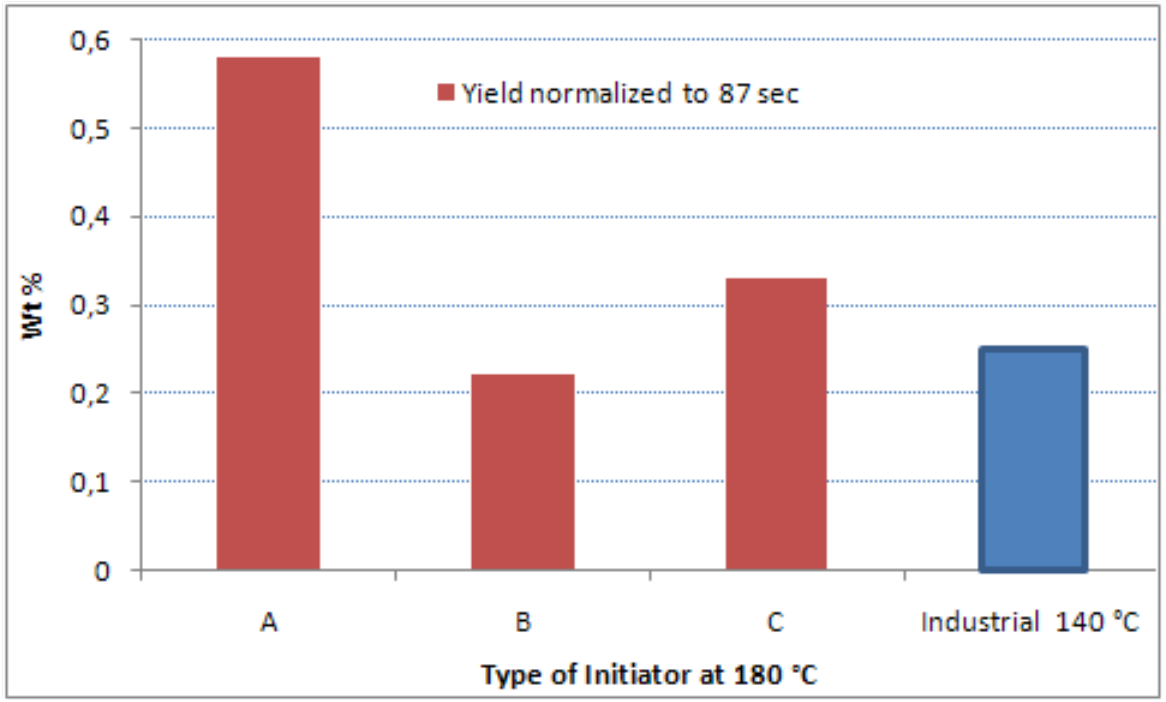
Experimental Program (1)
Reaction steps in oxidation of Ethylbenzene

Autocatalytic reaction
- **Initiation (Low residence time → improve initiation rate)**
- Propagation
- Termination

Competing reactions for byproducts
- **Decomposition of Ethylbenzene hydroperoxide**

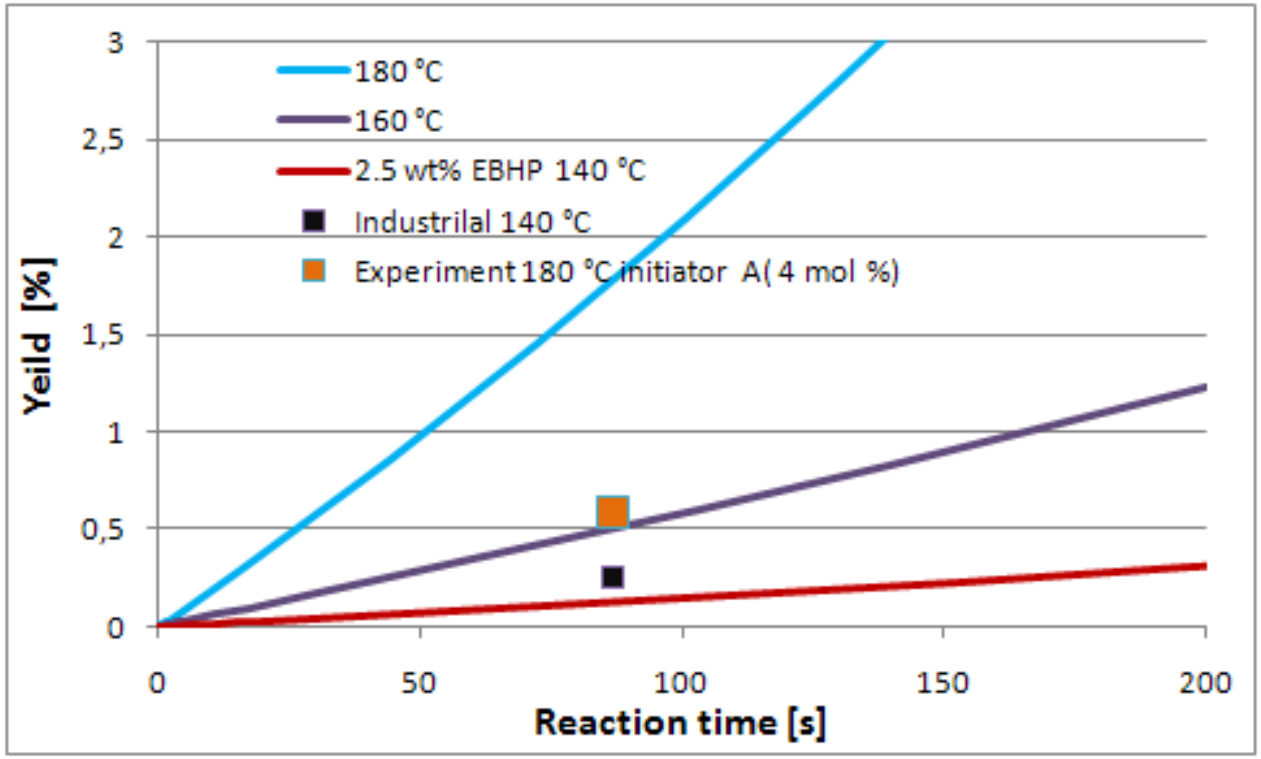
L.A. Tavadyan et al., Kinetics and Catalysis, 44, 91-100, 2003

Preliminary results
Different commercial initiators: A, B, C (4 mol%)



Initiator A shows highest Yield

Experiment vs Kinetic model



- Industrial yield is in agreement with the model at 140 °C
- Experimental yield is lower than the model at 180 °C
- By-product formation in our reactor at 180 °C is higher than predicted

Summary

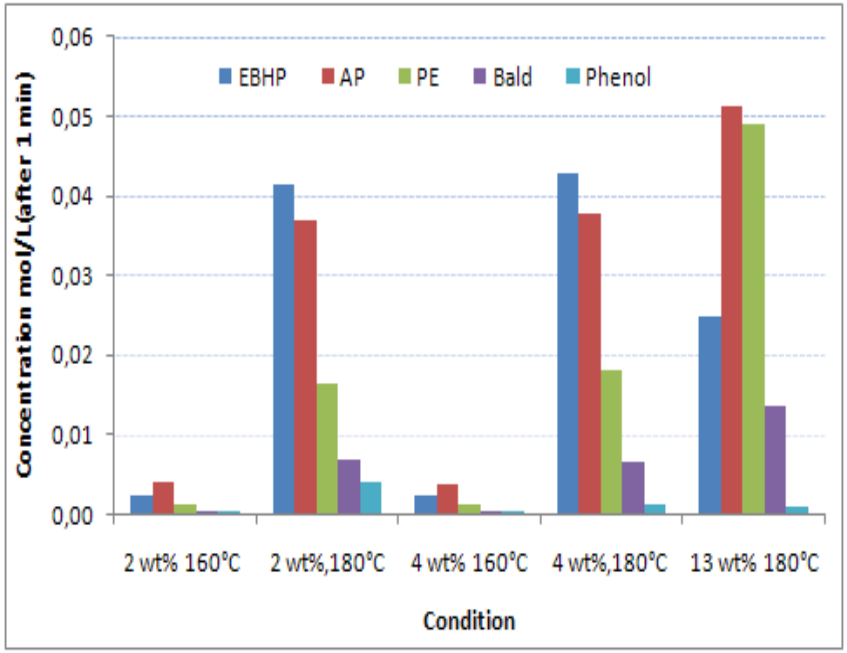
- Prototype CRS can handle dangerous reactions without reaching explosive situations.
- Oxidation in TF mode is demonstrated.
- In the prototype CRS EBHP yield is lower than expected.
- Hydrodynamic results are in agreement with the literature.
- Yield highly depends on initiator type.

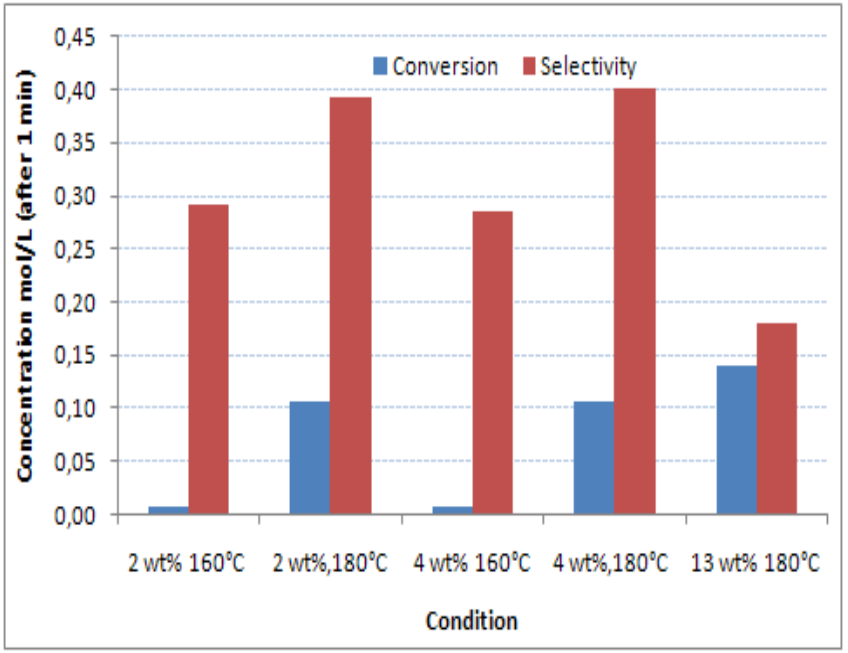
Plans for future

- Experimental kinetic studies (increasing yield)
  - Reactor geometry
  - Process conditions
- Other oxidation reactions

Questions

Commercial Initiators:A



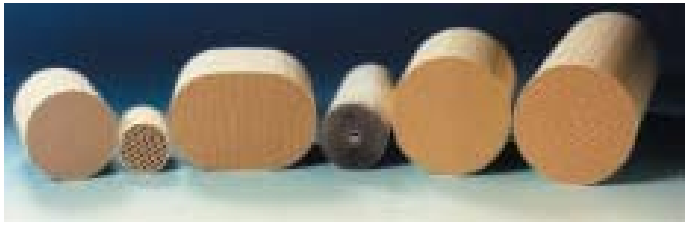


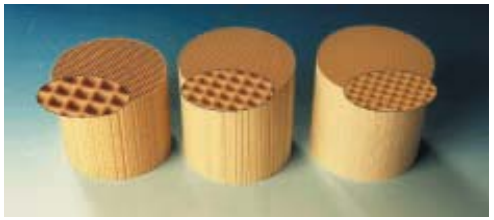
- Increase of temperature increases conversion and selectivity
- wt% increase in concentration has negative effect on selectivity
- 180 °C is promising for selection

Structured reactor in 2-phase flow (1)

- Small channels
- Small fluid mixture hold-up: safe operation of explosive mixtures

- Increased mass and heat transfer
- Heat transfer: Large surface-area/volume ratio
- Improved temperature control
- Mass transfer: Large contact area of the phases.
- Improved mixing in Taylor flow (TF) operation





[1] F.Kaptein et al ,CATTECH, Vol 3(1999), No.1,24-41

Hydrodynamics – Flow window

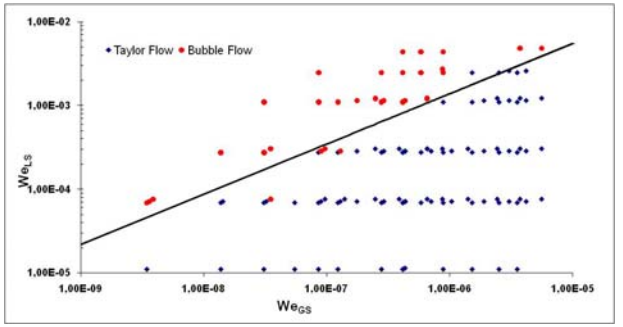
Experimental vs literature

$$We = \frac{\rho v^2 l}{\sigma}$$

Taylor flow boundary [1]

- Dimensionless number, *We*, flow pattern map for all experimental conditions, p and t shows a sharp border between Taylor and bubble flow:

$$We_{LS} = 5.5 We_{GS}^{0.6}$$



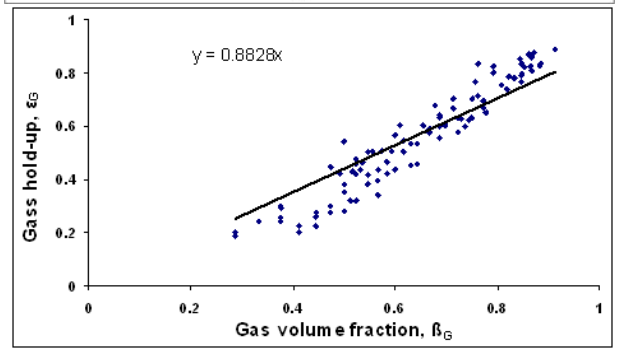
Gas hold-up [1]

- Armand correlations relates gas hold-up to the gas volume fraction

$$\varepsilon_G = 0.833\ \beta_G$$

$$\beta_G = \frac{V_G}{V_G + V_L} \qquad \varepsilon_G = \frac{G_S}{G_S + L_S} + \left(\frac{\pi}{6} - 1\right)\frac{W}{G_S + L_S}$$

- Found Armand correlation is: **0.88**.

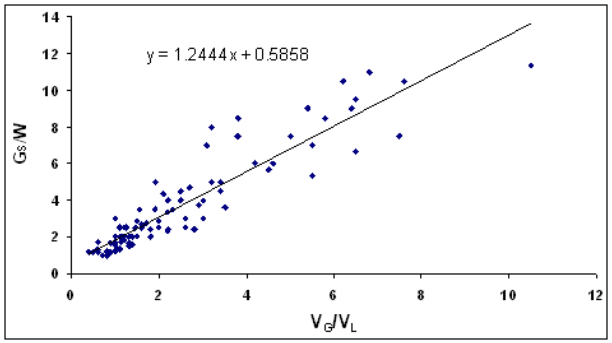


Gas slug length (G_S) [1]

- The gas slug length scales linearly with the ratio V_G/V_L .

$$\frac{Gs}{W} = \alpha_1 + \alpha_2 \frac{V_G}{V_L}$$

- For our system, α_1=1.24 and α_2=0.59 **(**α_1=1.0 and α_2=1.0 [2]**)**



[1] Jun, Y., et al, Chem. Engineering Science, 63, pp. 4189-4202, 2008
[2] van Steijn, V. (2010): *Formation and Transport of Bubbles in Micro-Fluidic Systems*. pp. 136, Delft, 2010.