Towards an Industrial Process for Au-Catalyzed Carbohydrate Oxidations: Evaluation of Batch- vs. Continuous Reactors

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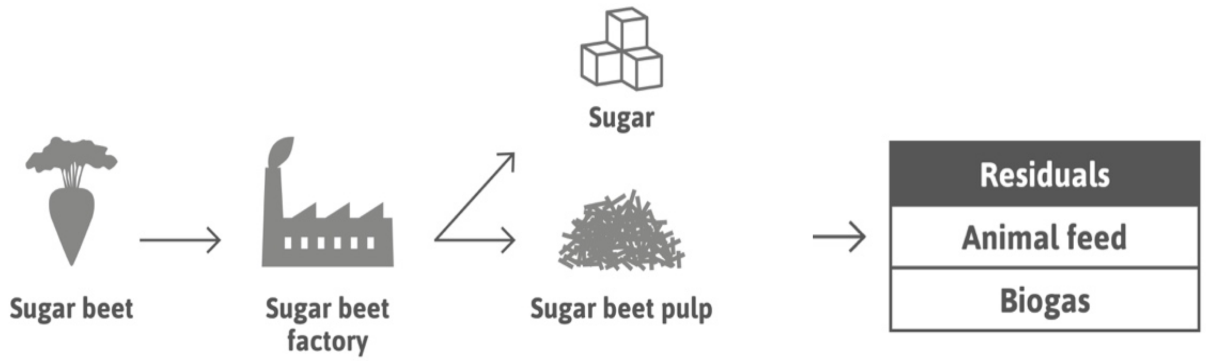
Project Background

- Sugar beet pulp is a major residual stream from the sugar beet industry

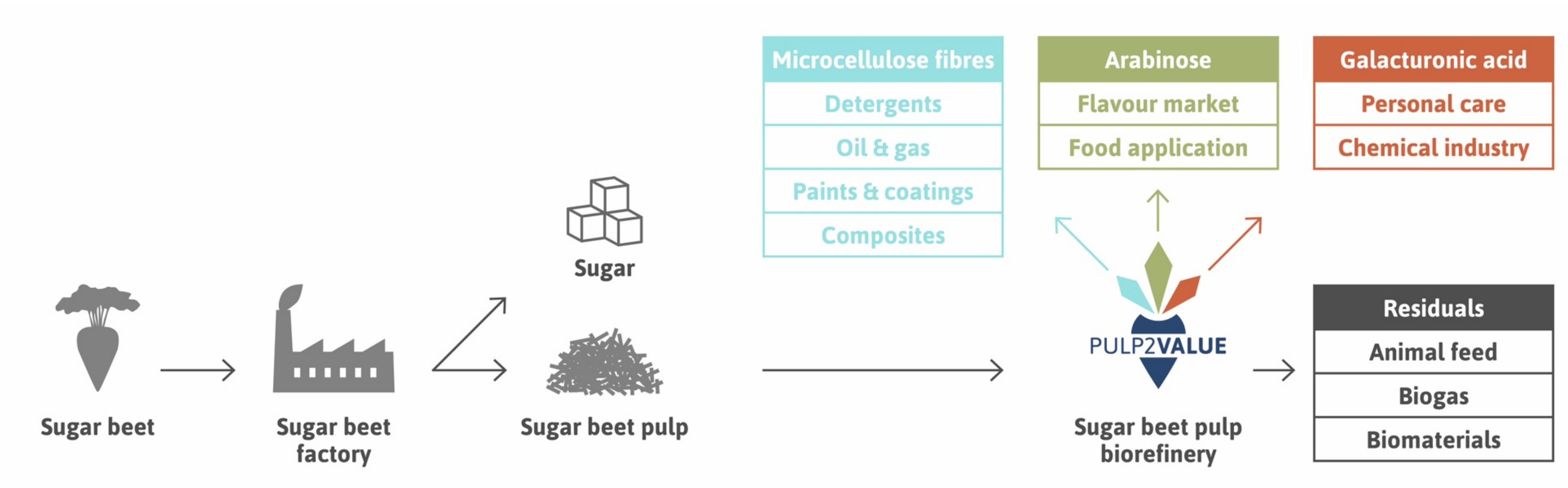
  - Sugar beets in NL: >8100 farmers & >85.000 hectares*
  - Pulp: 13 M tonnes/year in EU
  - Currently: low value feed and/or green gas



* Final data over 2017; www.cbs.nl

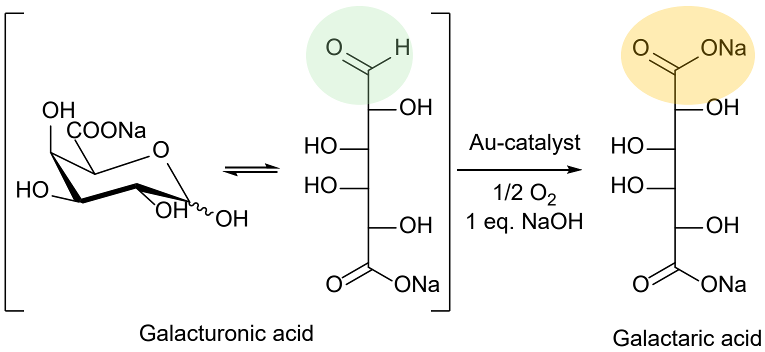
Project Background

- Desire to create added value for 3 sugar beet pulp components:
  - Microcellulose fibres
  - Arabinose
  - Galacturonic acid



Project Background

- This talk: Galacturonic acid
  - Oxidation to galactaric acid



- Product Applications:
  - Personal care, sequestering, FDCA synthesis, etc.

- Mild, green and robust batch process:*
  - Mild conditions (RT-60 °C)
  - O_2 as oxidant & water as solvent
  - Re-usable and stable Au-catalyst

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* van der Klis, *ChemSusChem*, **2013**, *6*, 1640 – 1645.

Aim

- *Oxidation currently in batch at lab scale; now bring to industrial level*

- Questions:
    - Industrial requirements?
    - Reactor choice?
    - Critical reaction parameters?

* Chemical Processing Cartoon by Jerry King

Outline

- Requirements: Evaluation of industrial performance
- Process options:
  - Batch
  - Continuous

- Comparison of

batch & continuous

*Chemical Processing Cartoon by Jerry King

Requirements: Evaluation of industrial performance

- "Industrial performance window"*
  - Selectivity : 70-100 mol%
  - Productivity : 100kg – 10 $t_{prod}/m^3/h$
  - Catalyst consumption : 1-100 t_{prod}/kg catalyst
  - Product concentration : 3-100 wt%

- Note: Economics also depend on feedstock / product price

(e.g. bulk vs specialty chemical)

* J.-P. Lange, *Catal. Sci. Technol.*, **2016**, 4759-4767.

Process Options: Batch / Continuous

- Evaluation of reactor types[1]:

Characteristic / Criteria	BSTR[2]	CSTR[2]	PFR[2]
Acid/base produced or consumed	+	+	-
Gas consumed / produced	+	+	-
Insoluble substrate / product	+	+/-	-
High selectivity	+	-	+
Low catalyst consumption	+/-	+	+
High productivity	+	+/-	++
High reliability & safety	-	+	+
	Batch	Continuous	

- BSTR & PFR chosen to investigate

[1] J. M. Woodley & M. D. Lilly, *Applied Biocatalysis*, 2nd edn, **2000**, pp 371-394.
[2] BSTR / CSTR = **B**atch / **C**ontinuous **S**tirred **T**ank **R**eactor;
PFR = **P**lug **F**low **R**eactor

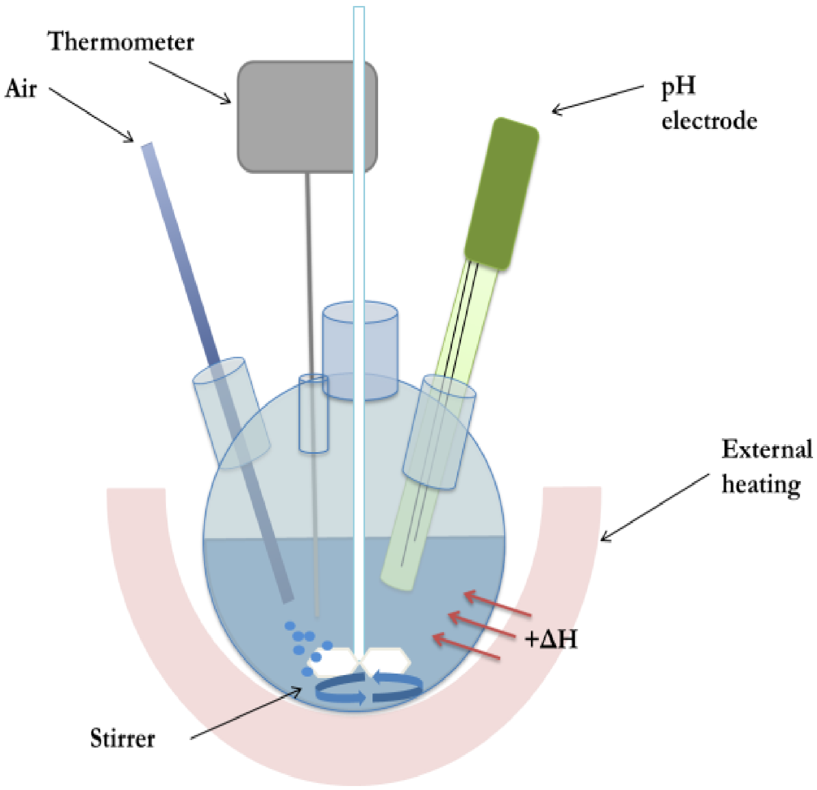
Batch results

- Evaluations based on selectivity and reaction rate (= productivity)

- Reactions performed by varying:
    - Temperature (RT – 60 °C)
    - pH (7-12)
    - Stirring speed (200-650 rpm)

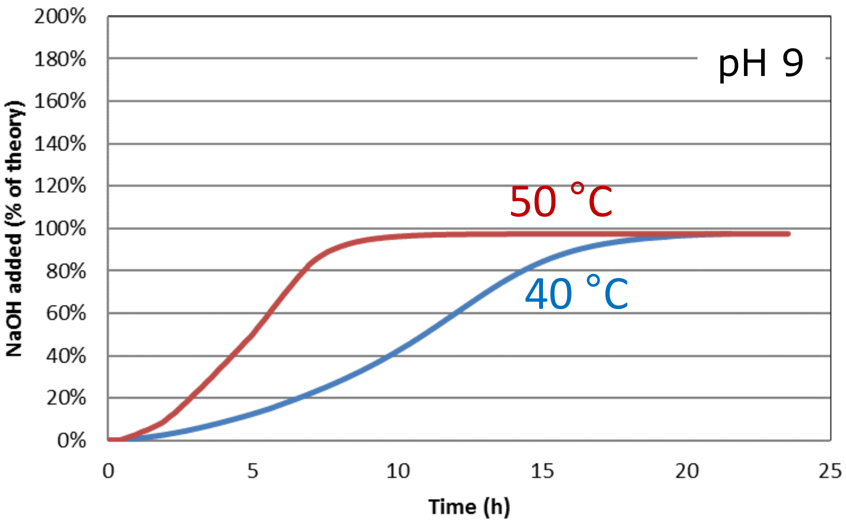
- Set-up: Glass reactor

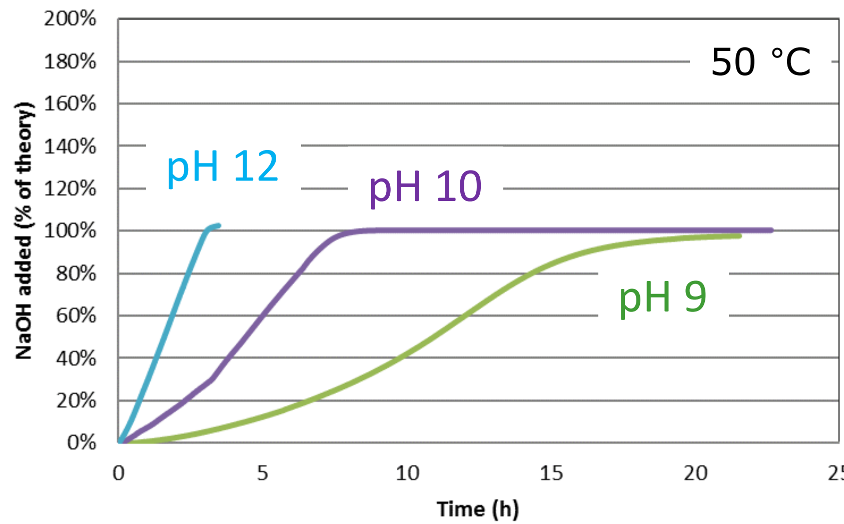
(no pH control under O_2-pressure)



Batch results: key findings

- Selectivity and rate: trade off between T and pH

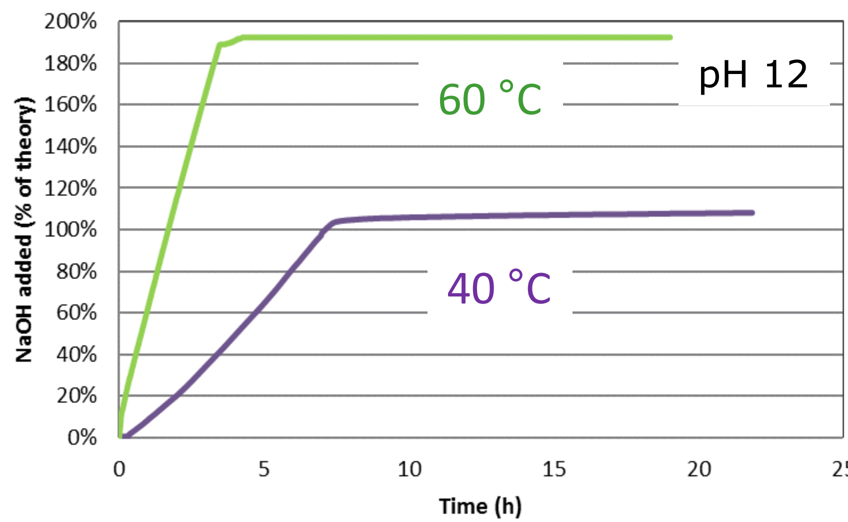




- Selectivity confirmed by HPLC

At high pH & temp:

side products are formed



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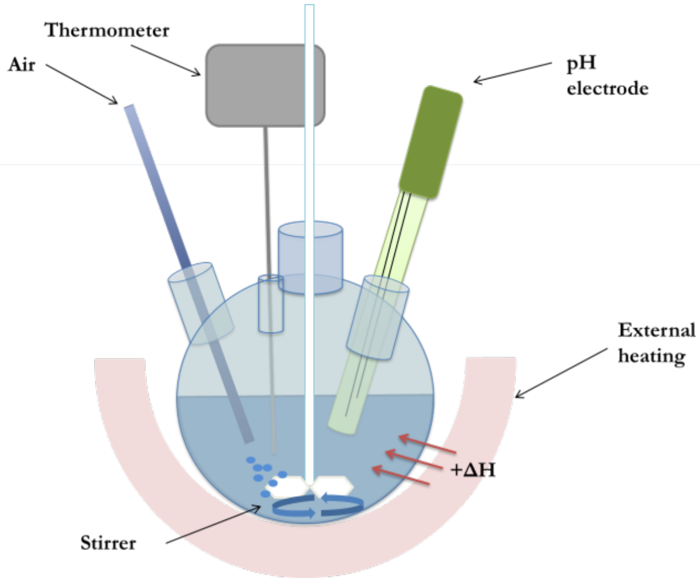
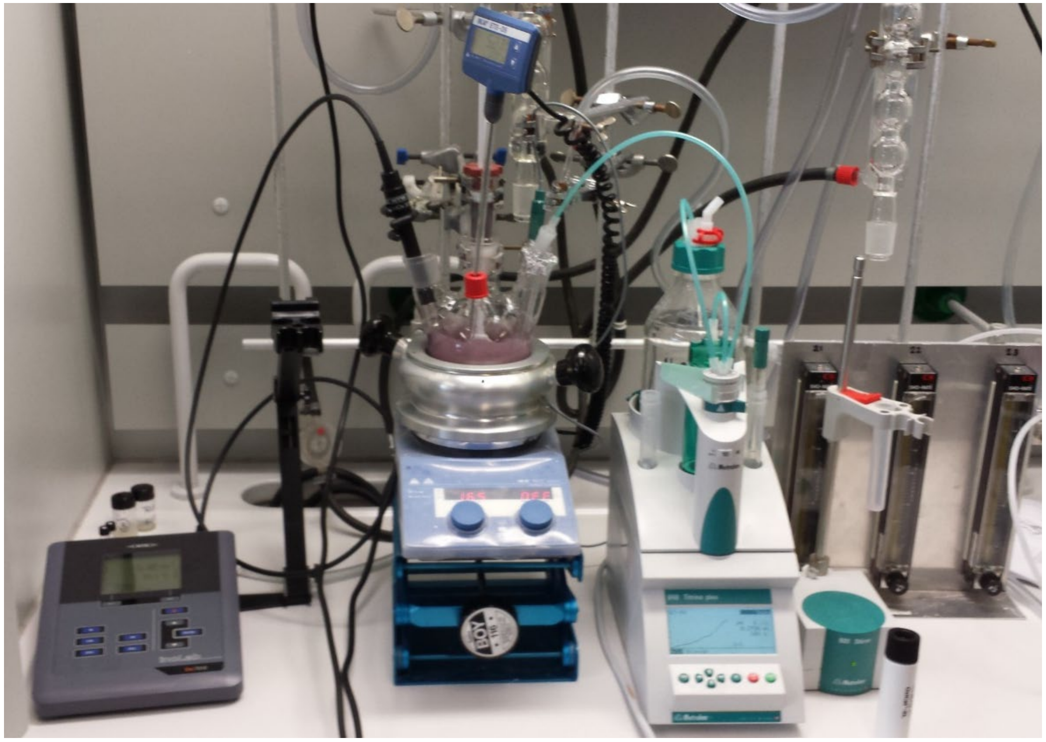
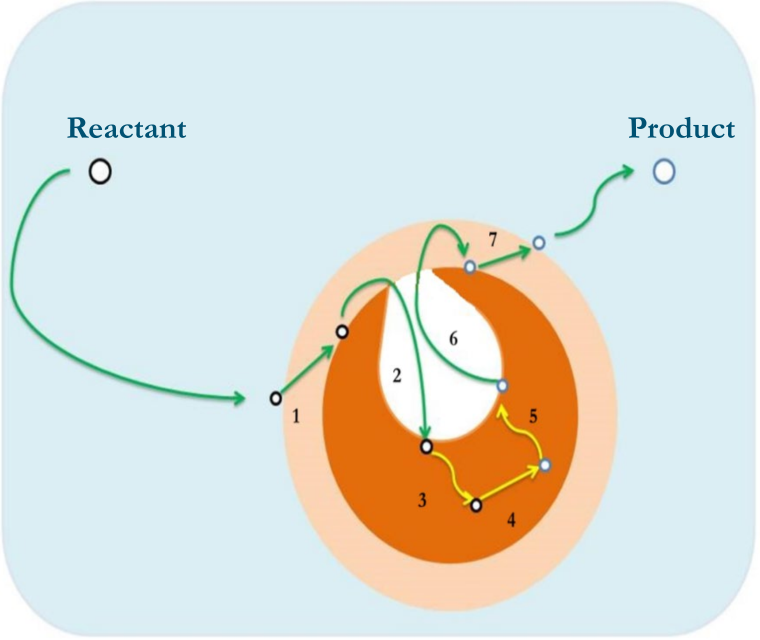
Batch results



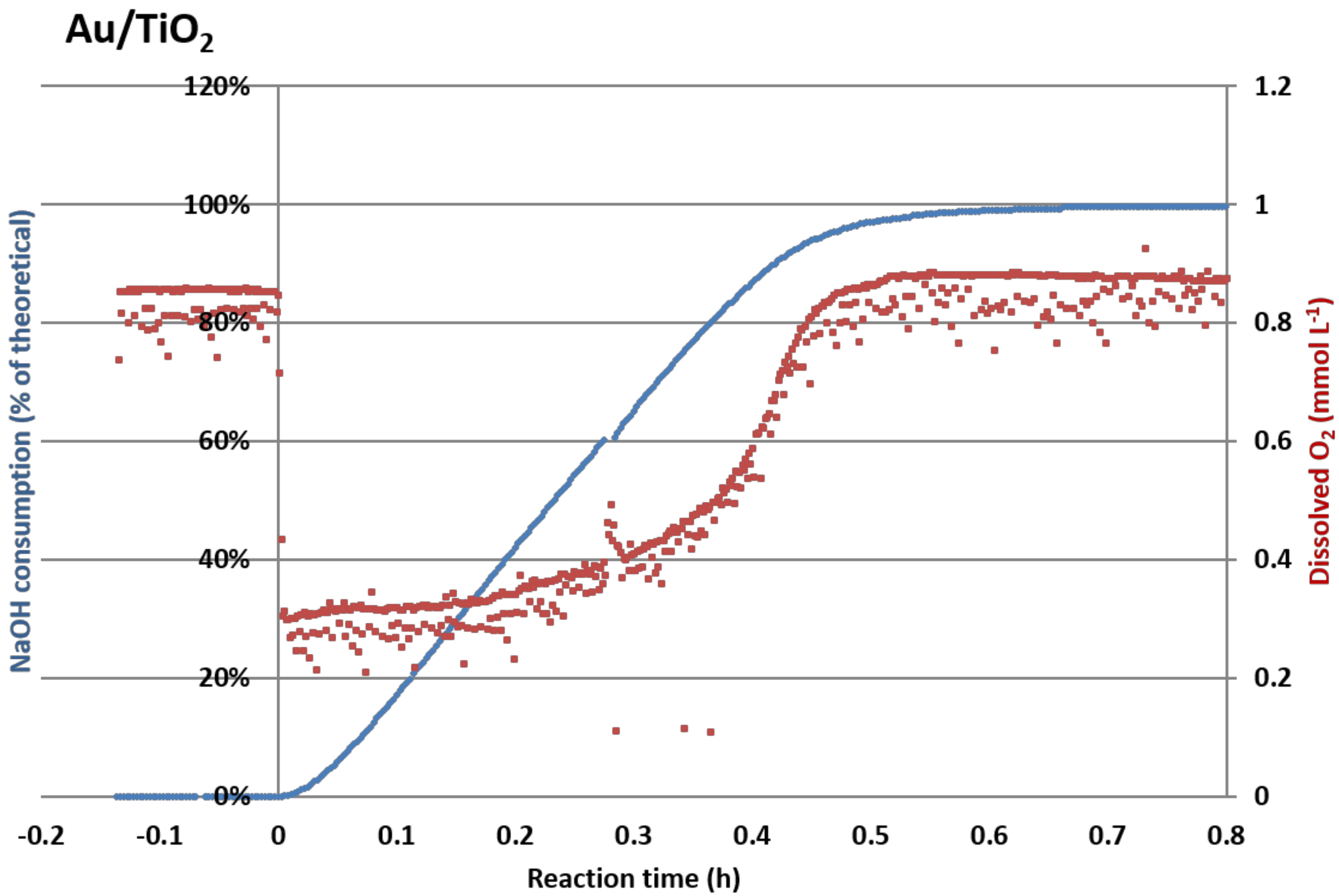
- Stirring speed
  - Increasing stirring speed shows increasing reaction rate => mass transfer limitations!
- Oxygen supply was monitored as well





Batch results

- Dissolved oxygen measurements: Big drop = oxygen limited



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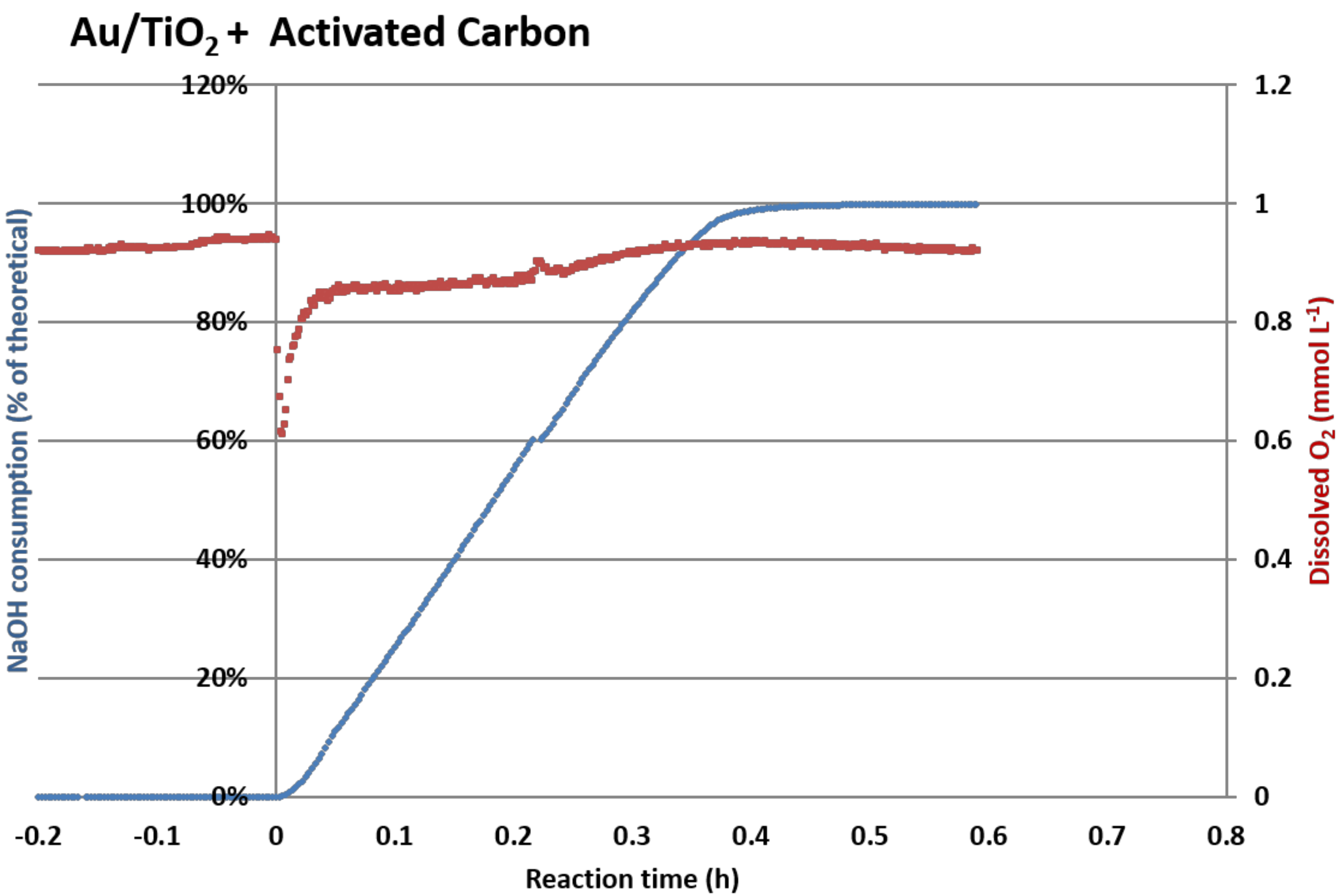
* F. van der Klis, *React. Chem. Eng.*, **2018**, 540-549.

Batch results

- Addition of carbon: Low drop = not limited in O_2



* F. van der Klis, *React. Chem. Eng.*, **2018**, 540-549.

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Batch results: Summary

+ Very selective reaction (>99%)

+ Easy to control and monitor reaction progress

+/- Productivity: Increased up to 60 kg/ m^3/h

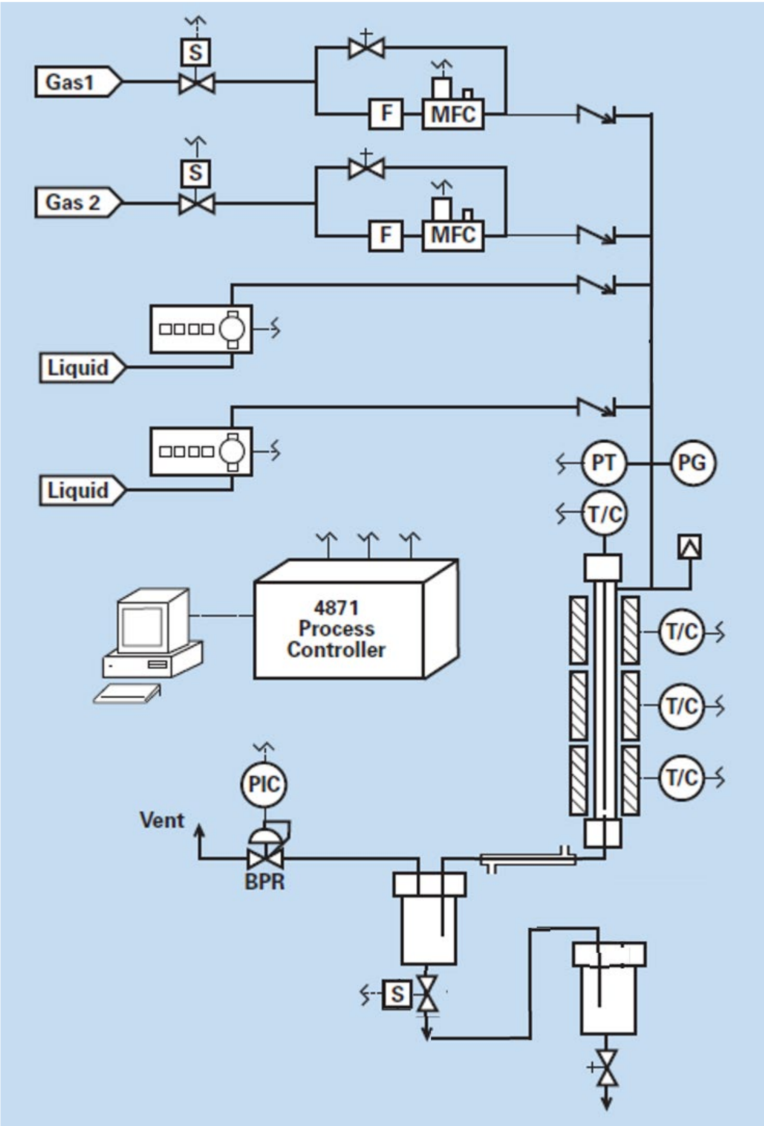
+/- Very high catalyst activity, but at low catalyst loading

- Increasing the catalyst loading will not increase the productivity (mass transfer limitations)

- Dissolving enough oxygen is main issue (selecting right catalyst support might help)

Continuous reactor (PFR)

- Set-up:



Continuous reactor (PFR)

- Reactions performed by varying:
  - Temperature (40 – 100 °C)
  - Oxygen flow / pressure (10-20 bar)

- HPLC to determine selectivity and conversion

  (= reaction rate & productivity)

- Main differences with batch: Stationary catalyst bed (relatively high catalyst loading but very short contact time of reactants ~ 1.3 min) and no pH control

Continuous reactor

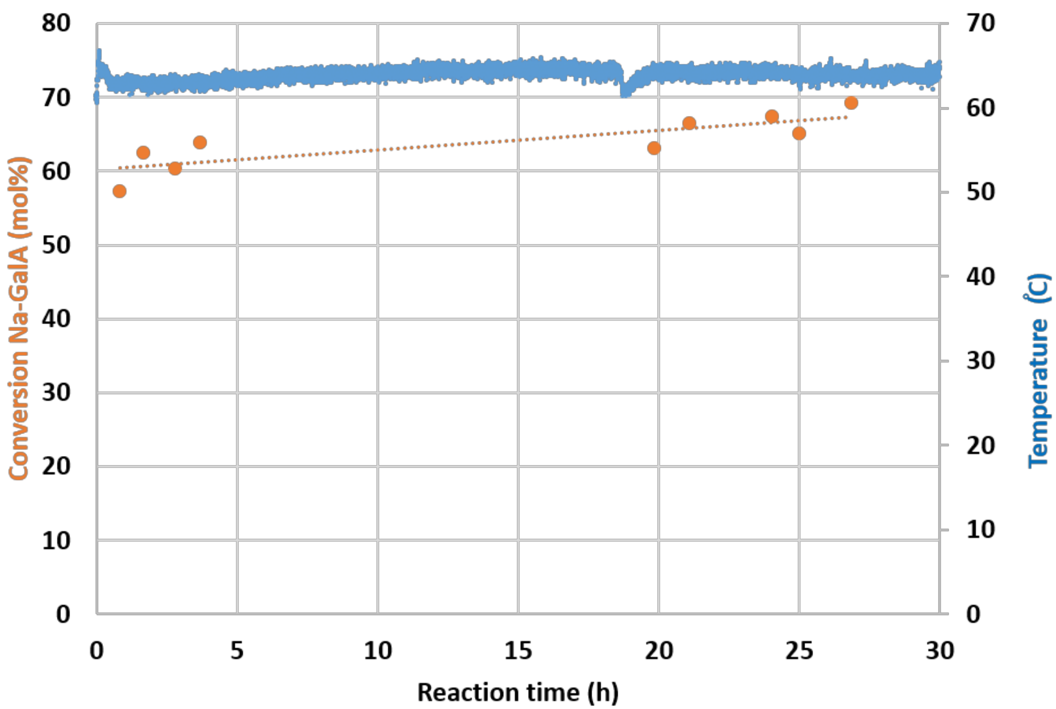
- Results
  - Conversion increases with increasing temperature, but selectivity drops
  - 0.1M @ 60 °C: Conversion 97%, selectivity 94%
  - Activity / g catalyst is lower compared to batch, due to high catalyst loading overall productivity is higher

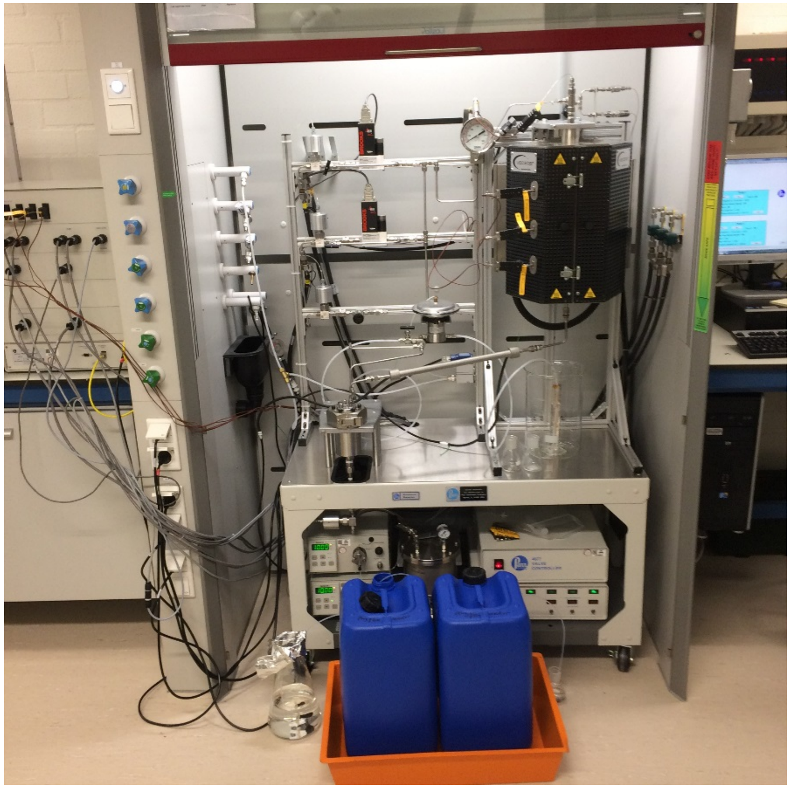
- Productivity increases at higher substrate concentrations:
  - 0.5 M @ 60 °C: Conversion 94%, selectivity 94%

- However; product solubility is low, resulting in clogging at high concentrations

Continuous reactor

- Time on stream (27h) experiment
  - No deactivation or drop in selectivity! (HPLC)





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Continuous results: Summary

+ Reasonably selective reaction (>94%)

+/- Process control: pH (-), oxygen (+)

+ Productivity: Increased >500 kg/ m^3/h

+ Oxygen supply sufficient

- Clogging of reactor at high product conc.

Comparison of batch & continuous reactor

Criteria	Industrial window	Batch	Cont.
Selectivity	70-100 wt%	>99%	>80-94%
Productivity	0.1-10 $t_{prod.}$ m^{-3} h^{-1}	0.06	0.5-2.2
Cat. consumption	1-100 $t_{prod.}$ kg_{cat}^{-1}	~ 4200[a]	~ 78[b]
Prod. conc.	3-100 wt%	~ 2-3.3	~ 2 - <10

[a]Consumption of active metal, estimation based on literature
[b]Consumption of active metal, based on measurement of gold loading spent catalyst

- A continuous reactor seems to be the best option for this process!
    - Batch however most selective

Take-home message

Considering different “reactor designs” is a useful exercise, helping to understand your reaction and catalyst performance

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