Biocatalytic production of methanol from biogas

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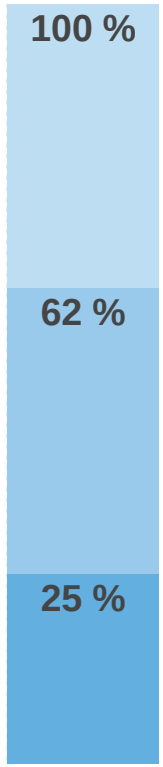
Motivation

- Biogas in Germany:
  - 8000 biogas plants
  - 4 GWel. Cogeneration (5.6 %)
- Methanol production by reforming
  - From naturel gas 2004 (€/t): 80 – 95
  - From biogas[2] 2004 (€/t): 150

The technological added value of biogas could be significantly higher!



Composition of biogas[1]
- methane 50-75 %
- CO_2 25-45 %
- H_2O 2-7 %

CO_2 remains entirely unused

Electrical efficiency of CHP
η = 38 – 43 %

[2]Bandi und Specht (2004): Expertise des Zentrums für Sonnenenergie- und Wasserstoffforschung Baden Württemberg

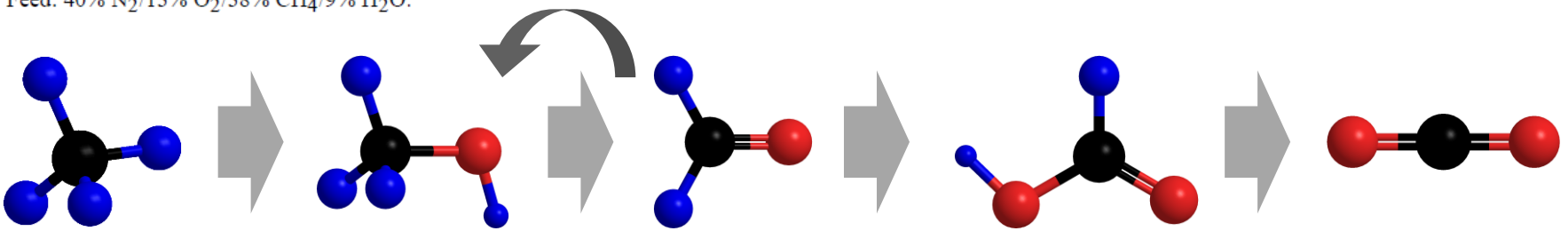
[1]Kaltschmitt, Martin, Hans Hartmann, und Hermann Hofbauer. *Energie aus Biomasse: Grundlagen, Techniken und Verfahren*. Springer Science & Business Media, 2009.

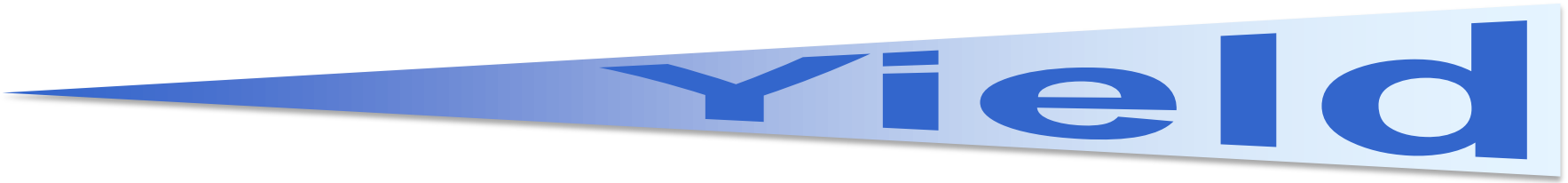
oxidation cascade of methane

Influence of contact time on the catalytic performance of the V12 catalyst at 550, 585, and 600 °C

GHSV ($L\,kg_{cat}^{-1}\,h^{-1}$)	T (°C)	Conversion (%)	Selectivity (%)				HCHO productivity ($g\,kg_{cat}^{-1}\,h^{-1}$)
			HCHO	CO	CO_2	CH_3OH	
80,000	552	2.3	82.2	14.9	0.9	2.0	801
	585	7.7	48.9	48.2	2.2	0.7	1548
185,000	549	0.9	91.9	1.4	0.7	6.0	807
	581	3.5	74.2	23.1	1.0	1.8	2435
	600	6.3	57.5	39.9	1.4	1.1	3377
545,000	552	0.2	86.1	0.0	3.2	10.7	391
	578	0.9	90.4	2.9	0.5	6.2	2389
	598	2.1	80.1	15.5	0.9	3.4	4621
740,000	550	0.1	89.3	0.0	3.7	7.0	321
	579	0.8	93.5	0.0	1.0	5.5	2834
	600	1.9	93.3	2.3	0.9	3.4	6458

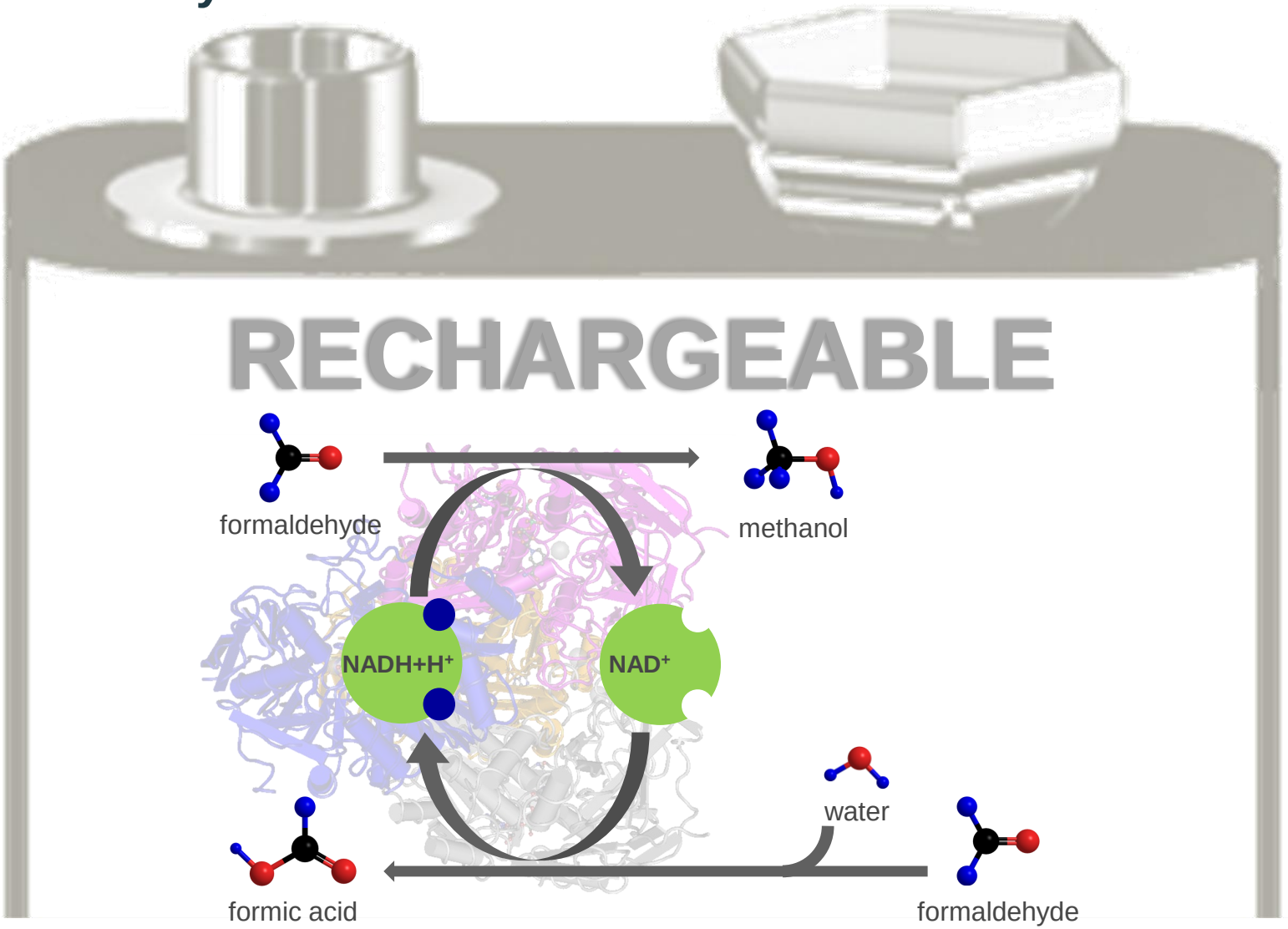
Feed: 40% N_2/13% O_2/38% CH_4/9% H_2O.





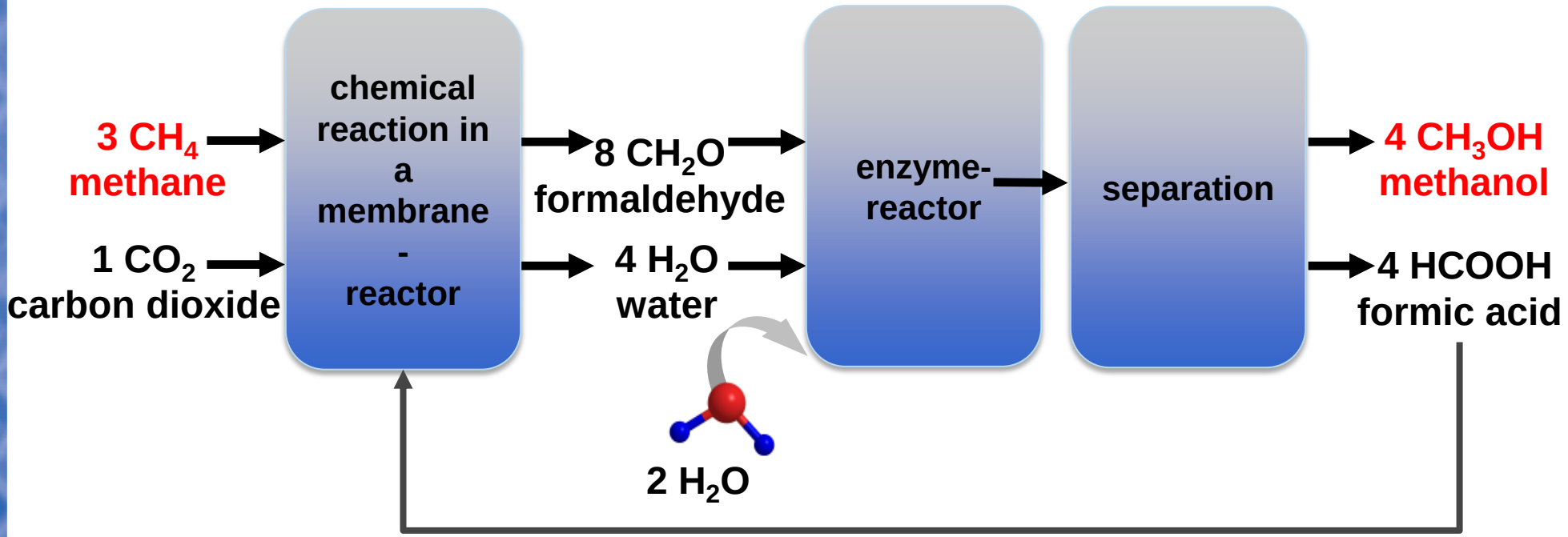
[2]Nguyen, L., Loridant, S., Launay, H., Pigamo, A., Dubois, J., Millet, J., 2006. Study of new catalysts based on vanadium oxide supported on mesoporous silica for the partial oxidation of methane to formaldehyde: Catalytic properties and reaction mechanism. Journal of Catalysis 237, 38–48. doi:10.1016/j.jcat.2005.10.016

Formaldehyde Dismutase

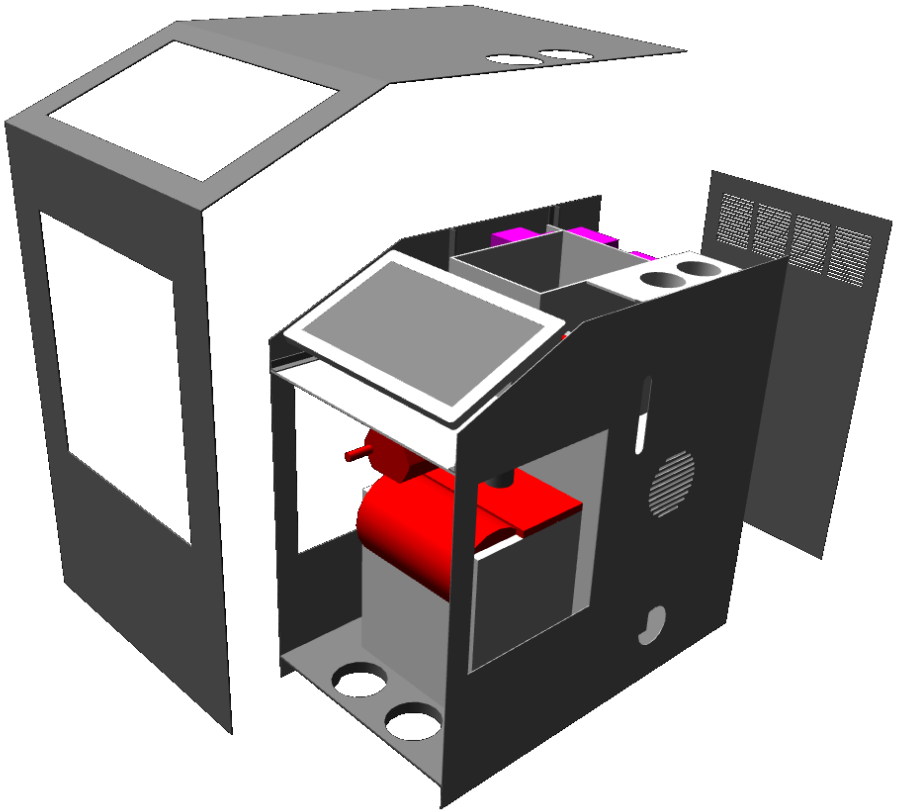


Combination of chemo- and bio- catalysis

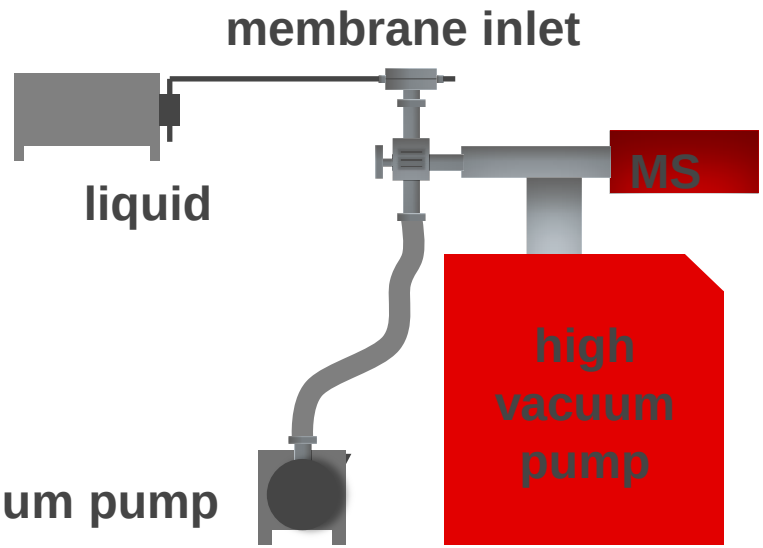
- If the produced formic acid is recycled to the catalytic process, in the whole process three moles of methane and one mole of carbon dioxide are converted to four moles methanol.
- There is no loss in the balance of energy.



Real-time process mass spectrometer

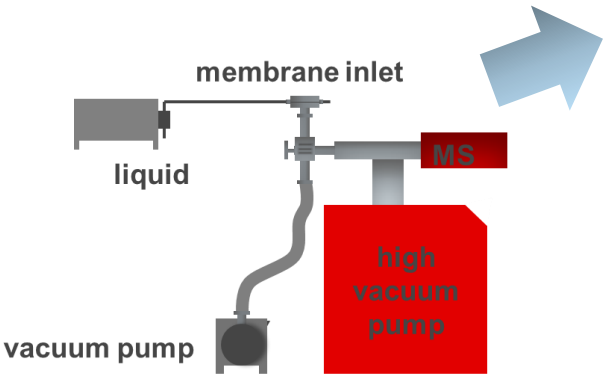


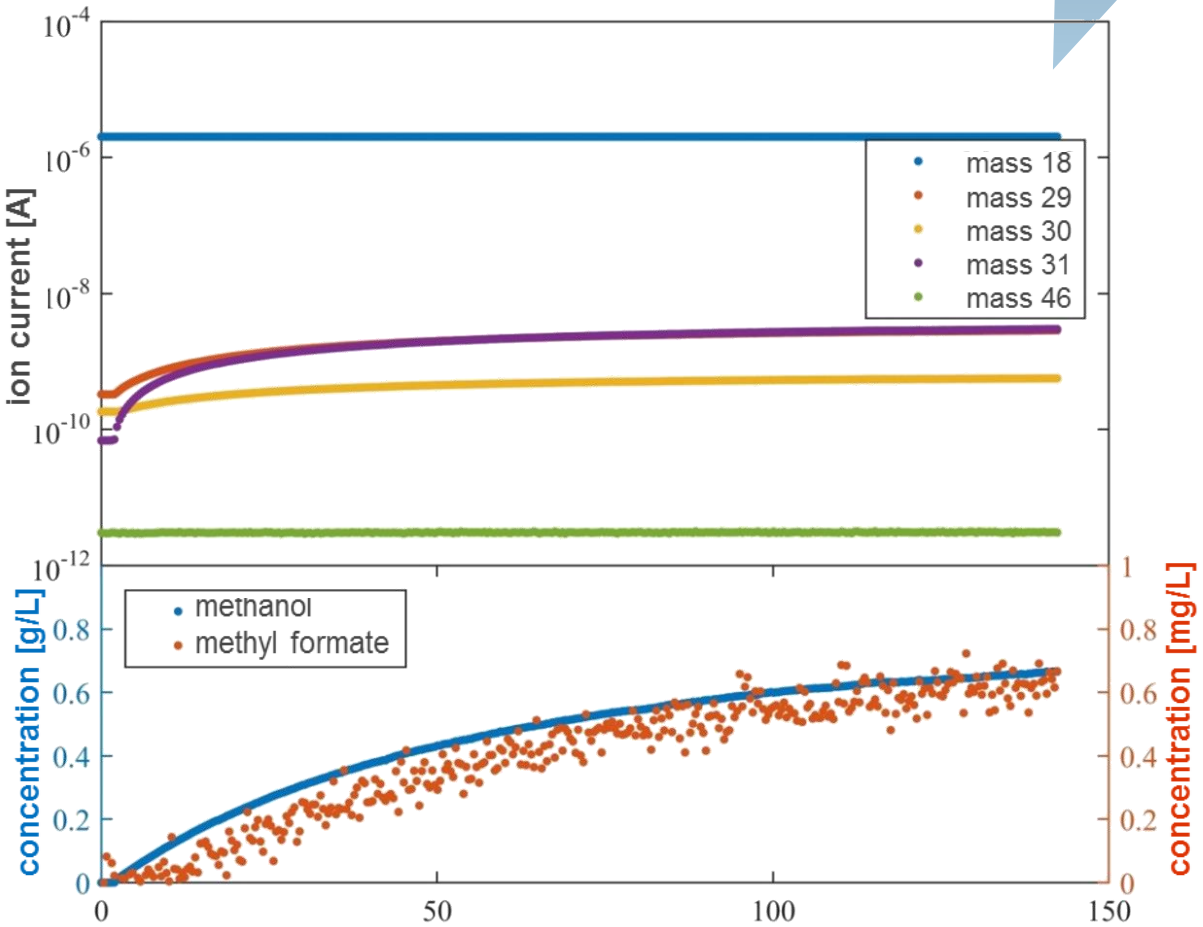
- Simultaneous measurement of the composition of a gas phase and all volatile component of a liquid.
- Measures up to 30 components simultaneously in the lower ppb range.



Results

kinetics

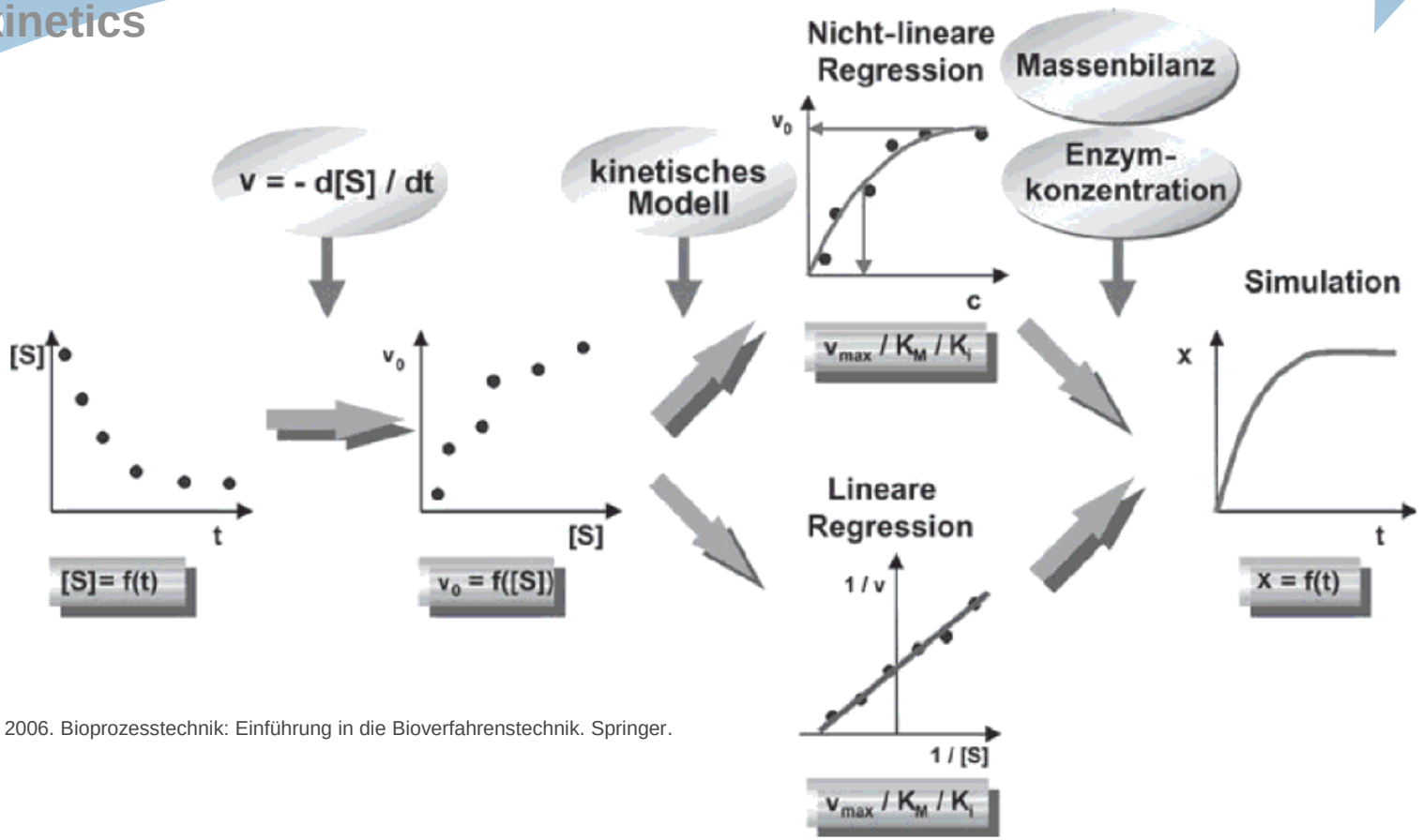




Results

model

kinetics



Horst Chmiel, 2006. Bioprozesstechnik: Einführung in die Bioverfahrenstechnik. Springer.

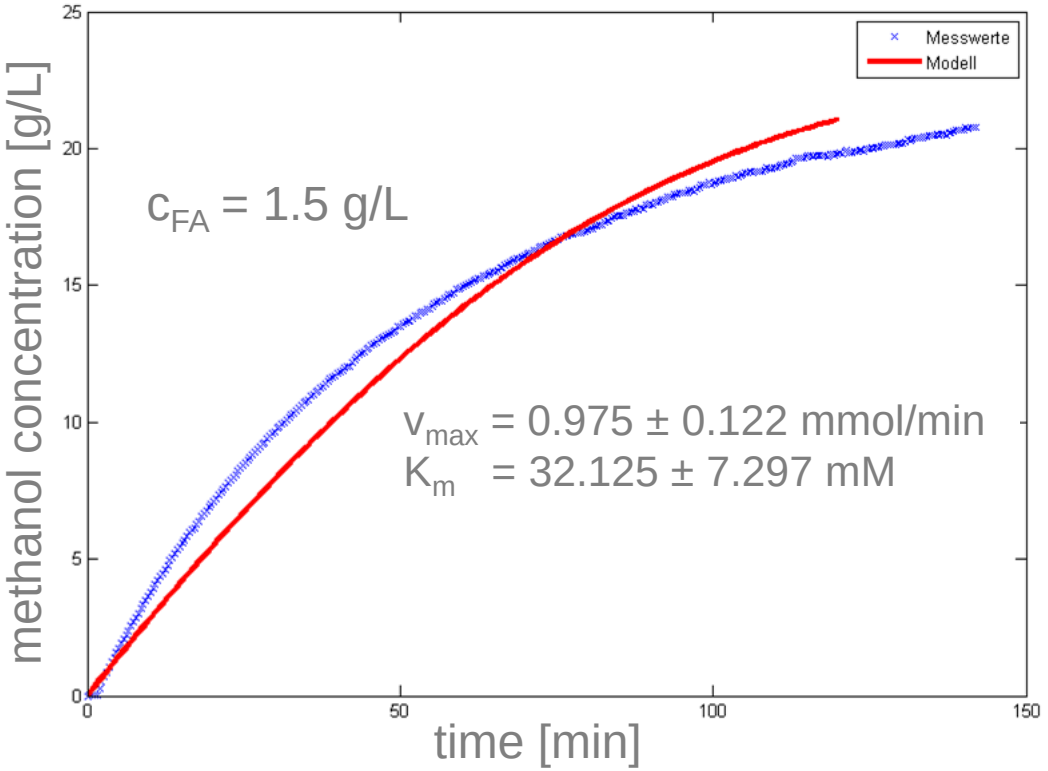
Results

model

kinetics

Michaelis-Menten-Equation

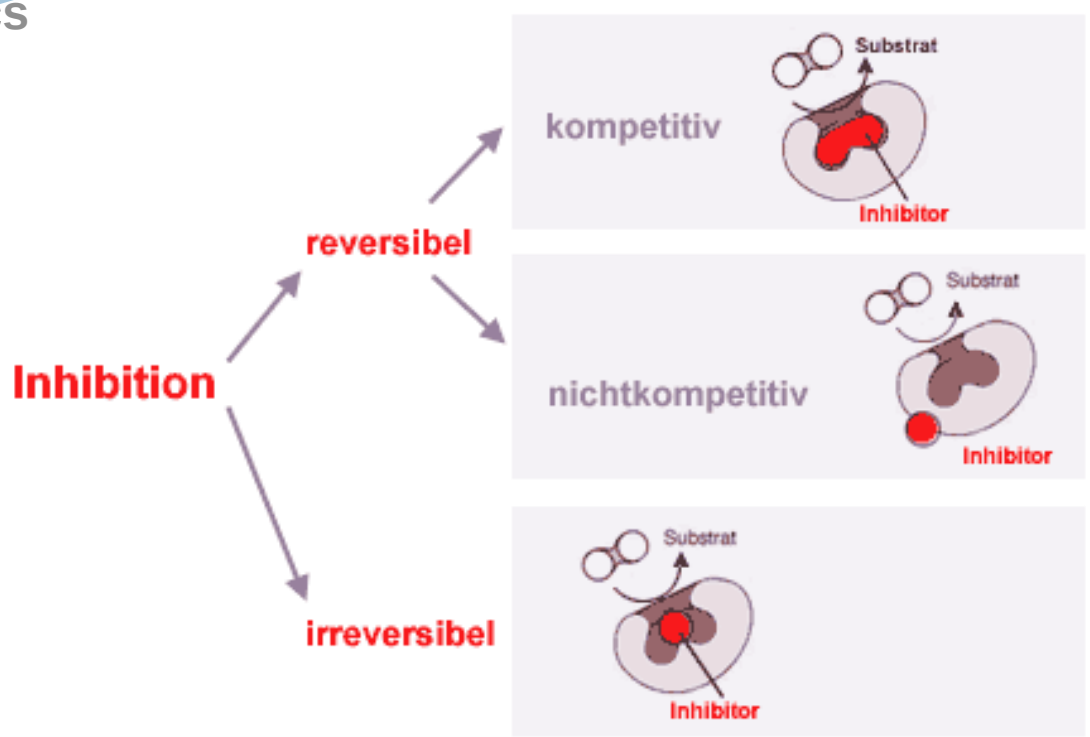
$$v = \frac{v_{max} \cdot c_{FA}}{c_{FA} + K_m}$$



Results

model

kinetics



http://www.biokurs.de/skripten/bs11-15.htm

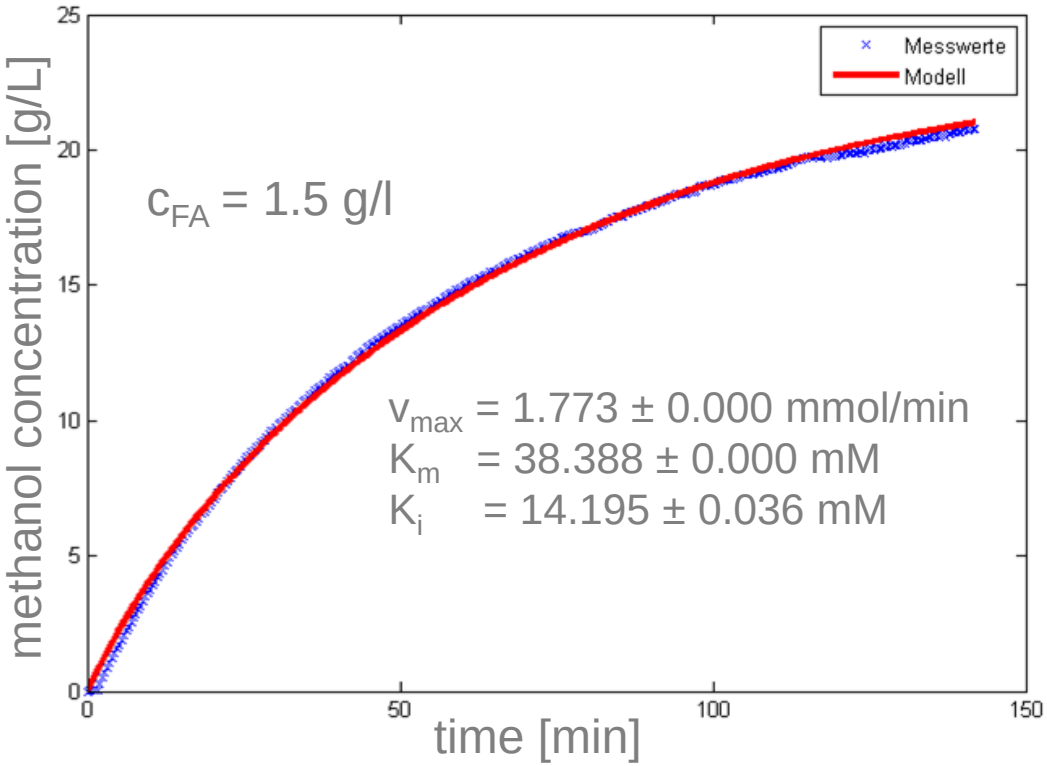
Ergebnisse

model

kinetics

Michaelis-Menten-Equation
Non-competitive inhibition

$$v = \frac{v_{max} \cdot c_{FA}}{c_{FA} + K_m} \cdot \frac{K_i}{[\mathrm{I}] + K_i}$$



Ergebnisse

model

kinetics

$$FDM(NAD(H)) + FA \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} FDM(NAD(H))FA \xrightarrow{k_2} FDM(NAD(H)) + [P] \underset{k_{-i}}{\overset{k_i}{\rightleftarrows}} FDM\big(NAD(H)\big)[P]$$

$$v = \frac{v_{max} \cdot c_{FA}}{c_{FA} + K_m \cdot \left(1 + \frac{c_{MeOH}}{K_i}\right)}$$

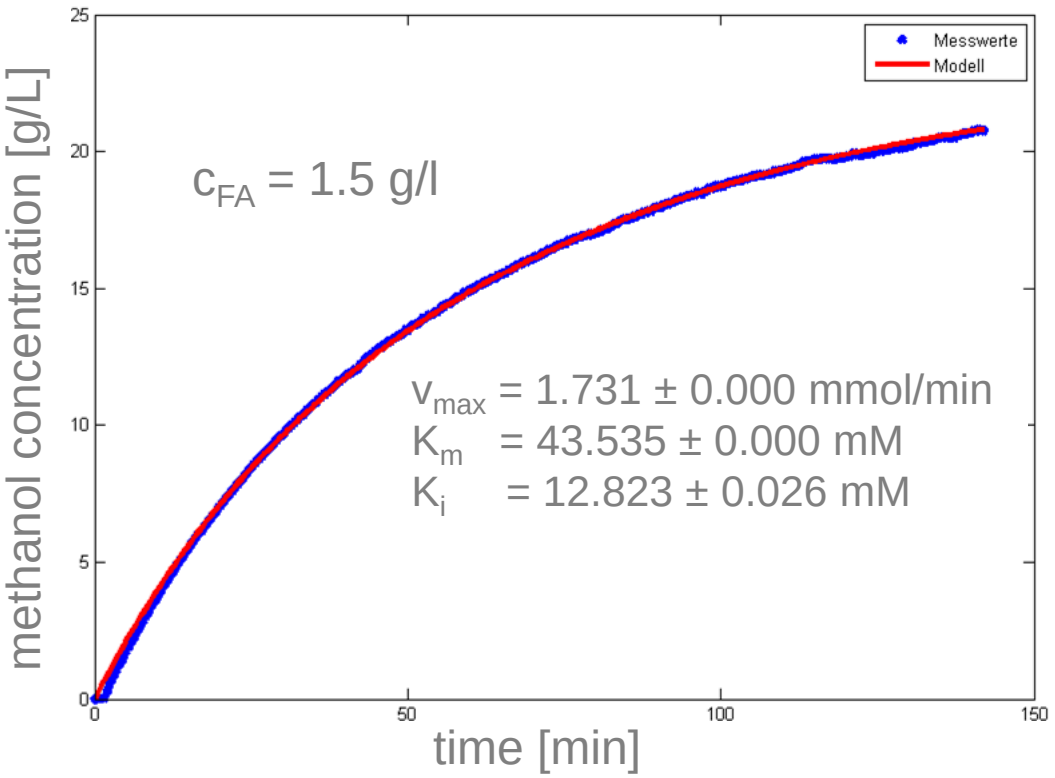
Results

model

kinetics

Michaelis-Menten-Equation
competitive inhibition

$$v = \frac{v_{max} \cdot c_{FA}}{c_{FA} + K_m \cdot \left(1 + \frac{c_{MeOH}}{K_i}\right)}$$



Results

model

kinetics

Michaelis-Menten-Equation
competitive inhibition

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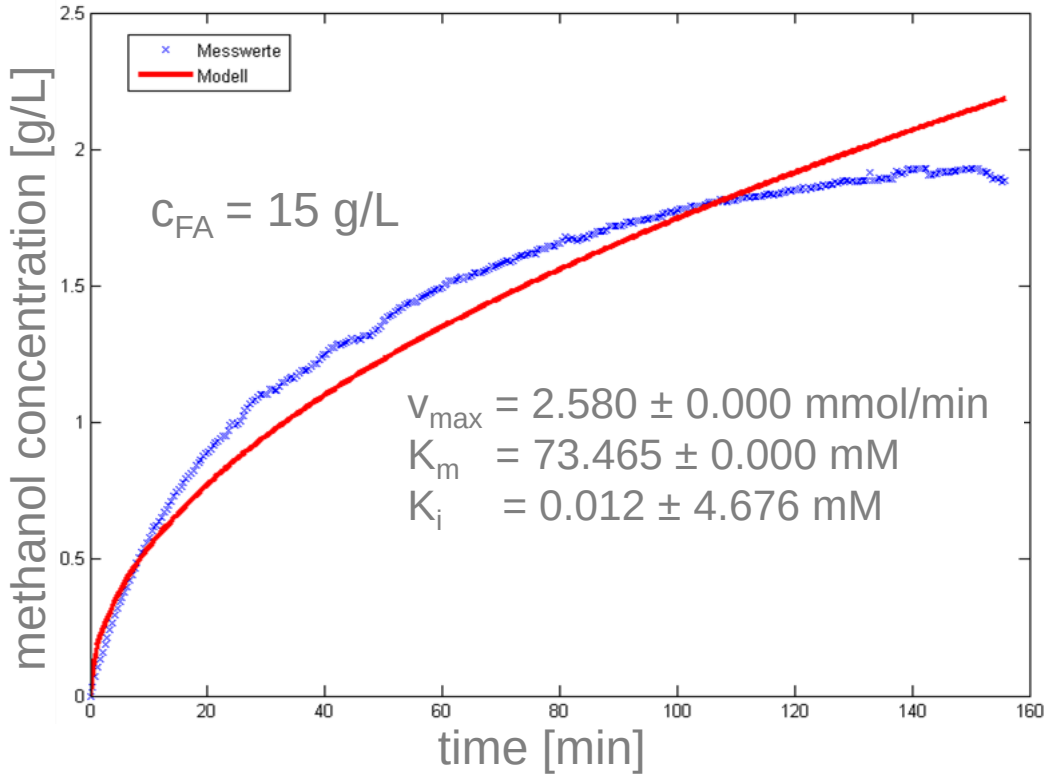
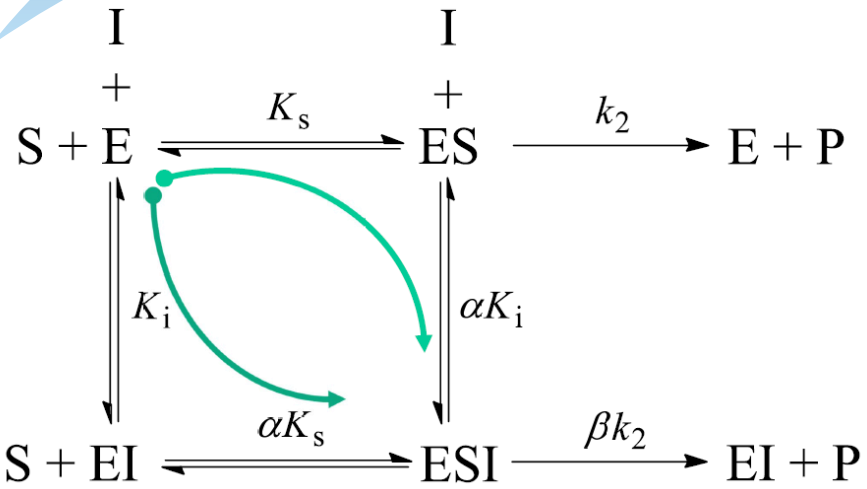


Results

model

kinetics



$$v = v_{max} \cdot \frac{\frac{c_{FA}}{K_m}\left(1 + \beta \frac{c_{MeOH}}{aK_i}\right)}{1 + \frac{c_{MeOH}}{K_i} + \frac{c_{FA}}{K_m}\left(1 + \frac{c_{MeOH}}{\alpha K_i}\right)}$$

a	b	Type of inhibition
$0 < \alpha < \infty$	$\beta = 1$	competitive
$0 < \alpha < 1$	$0 < \beta < 1, \alpha = \beta$	Non-competitive
$1 \leq \alpha < \infty$	$0 < \beta < 1$	mixed

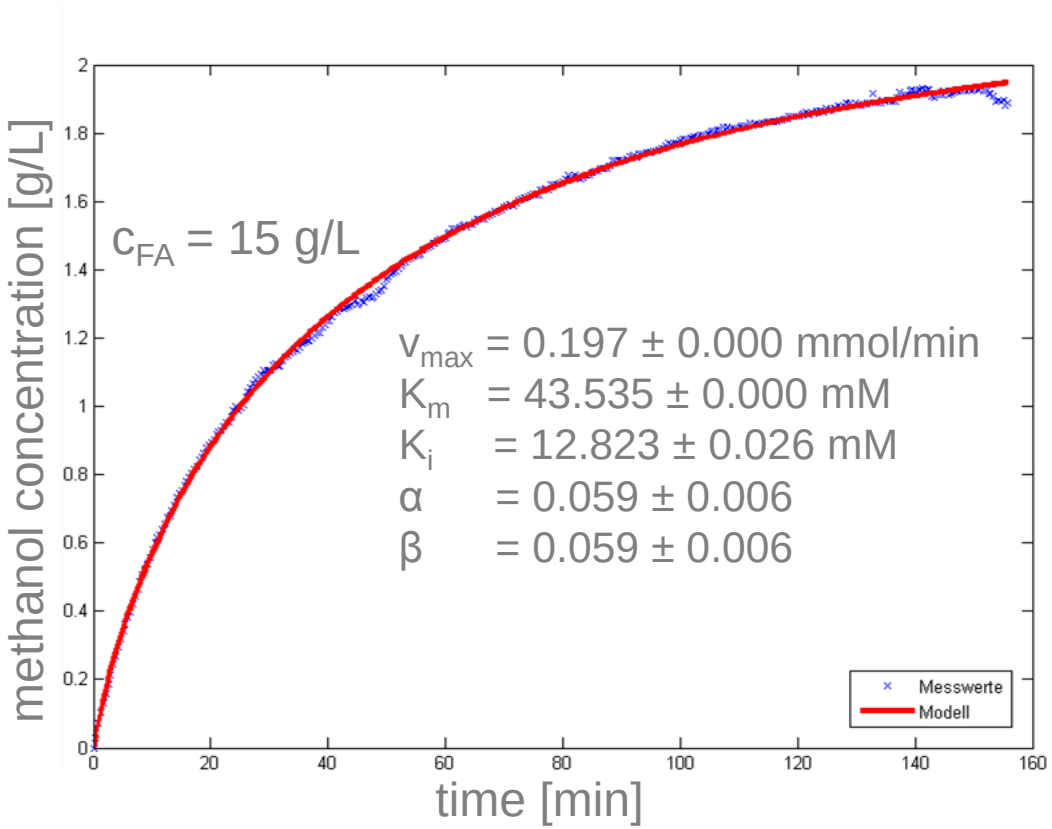
Results

model

kinetics

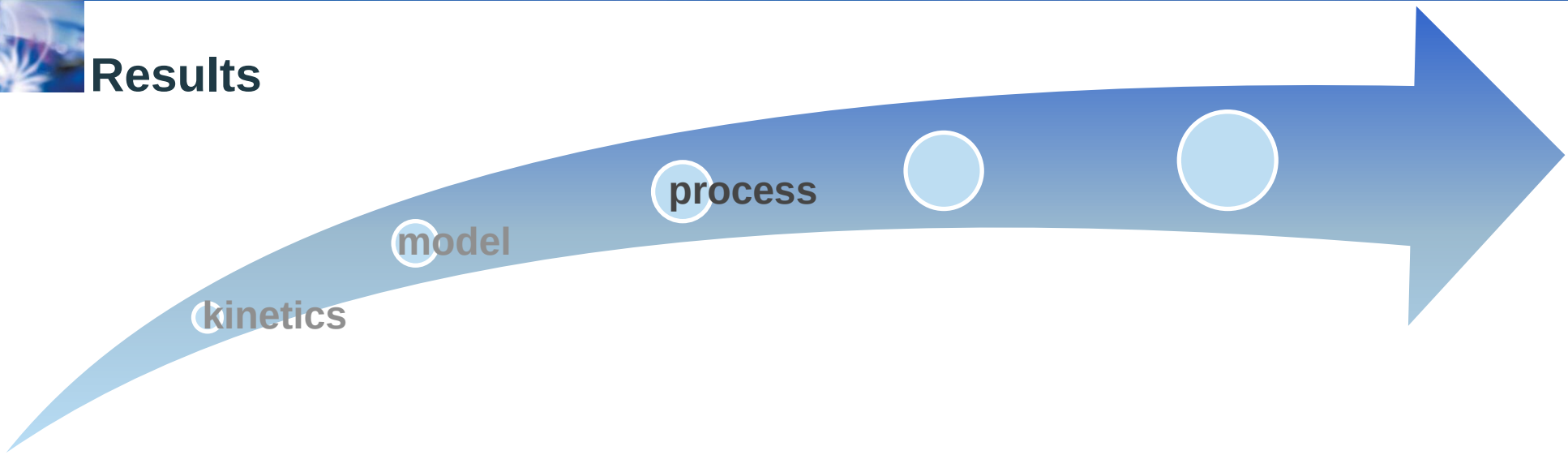
Hyperbolic equation

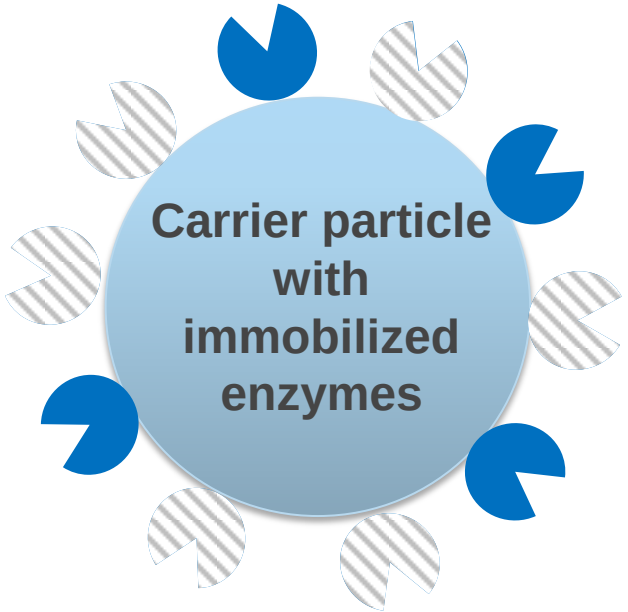
$$v = v_{max} \cdot \frac{\frac{c_{FA}}{K_m}\left(1 + \beta \frac{c_{MeOH}}{\alpha K_i}\right)}{1 + \frac{c_{MeOH}}{K_i} + \frac{c_{FA}}{K_m}\left(1 + \frac{c_{MeOH}}{\alpha K_i}\right)}$$



$0 < \alpha < 1$	$0 < \beta < 1, \alpha = \beta$	Non-competitive

Results



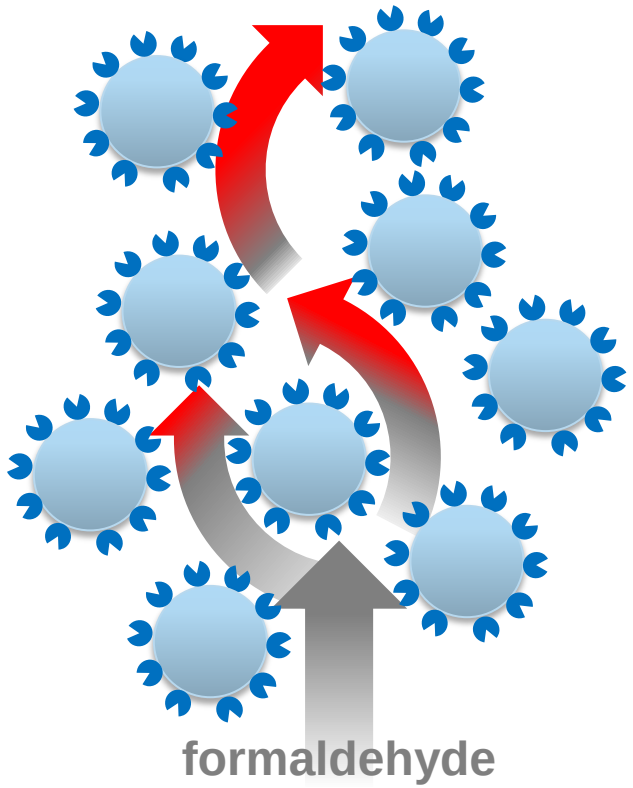


- The carrier particles showed after 440 days 40 % of the primary catalytic activity.

Results

kinetics
model
process
reaction

methanol
formic acid

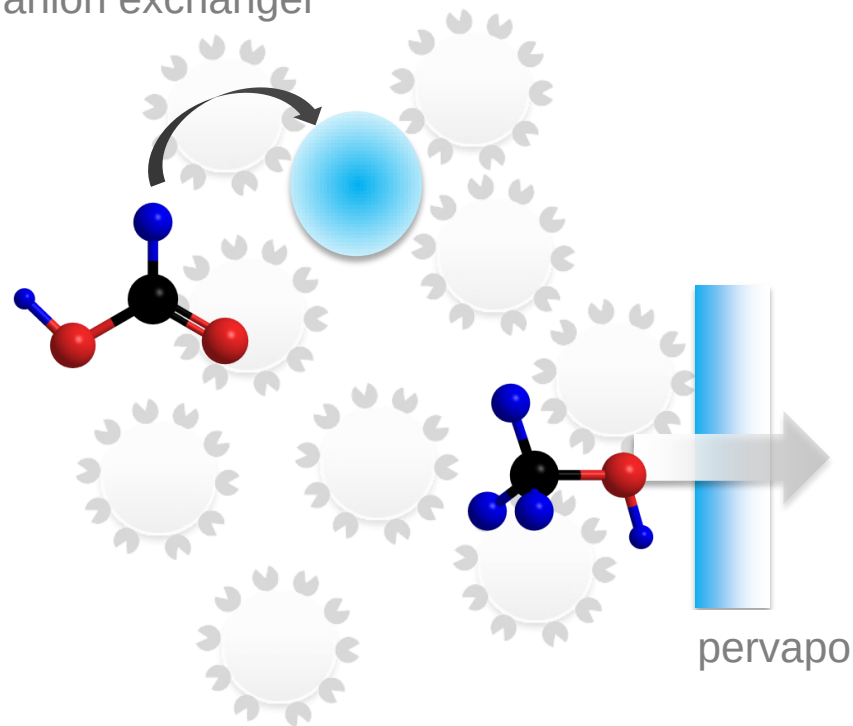


- 200 mL fixed bed reactor
- 10 mL/min flow
- 15 g/L formaldehyde conc.
- 91 % yield

Results

kinetics
model
process
reaction
separation

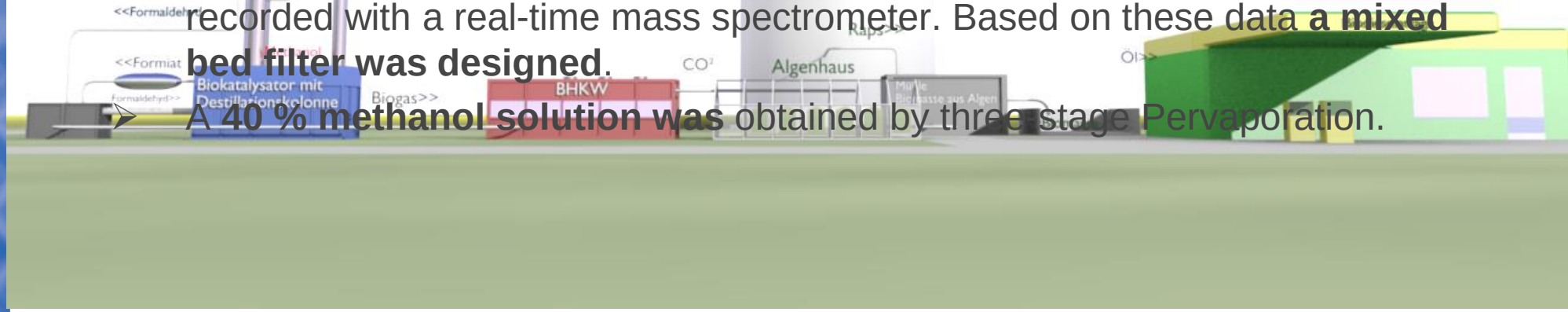
anion exchanger



pervaporationmembrane

Conclusions

- The greatest activity of the formaldehyde dismutase is at **pH 6 to pH 8 and 37 °C**.
- Several kinetics were **recorded by real-time mass spectrometry** and **mapped by a model**.
- The enzymes were bound to carrier particles and **showed 40 % of the primary catalytic activity after 440 days**.
- In a 200 mL fixed-bed reactor, a 15 g/L formaldehyde solution was reacted continuously with a flow rate of 10 mL/min and a **turnover of 91 %**.
- The kinetics of adsorption of formic acid to an anion exchanger was recorded with a real-time mass spectrometer. Based on these data **a mixed bed filter was designed**.
- A **40 % methanol solution was** obtained by three-stage Pervaporation.



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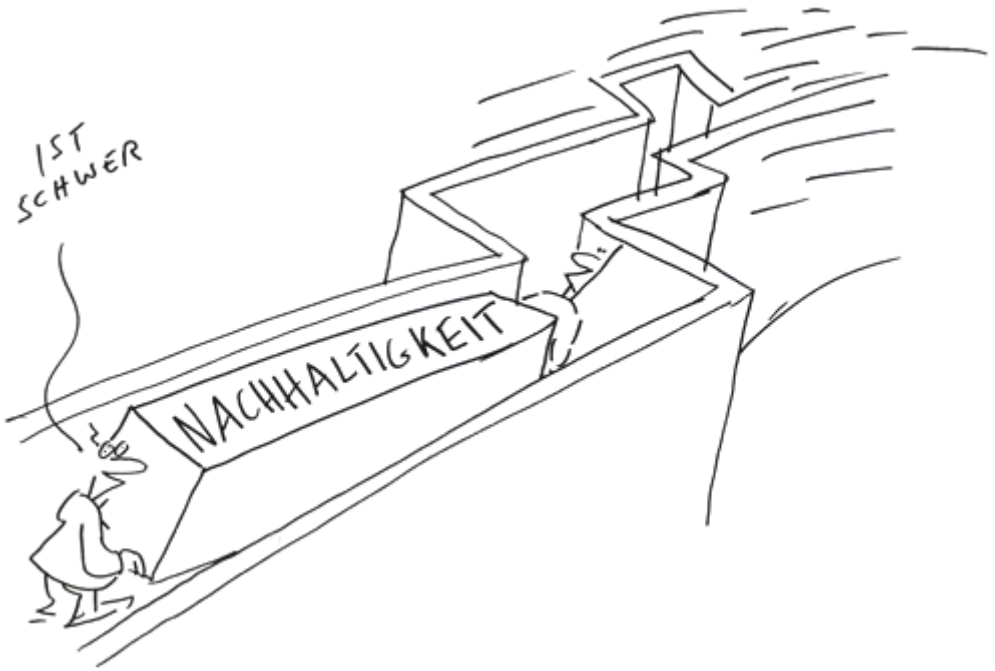

Thank you for your attention!