UNIVERSITEIT GENT

FACULTY OF ENGINEERING AND ARCHITECTURE

Steam methane reforming unraveled by the MicroKinetic Engine, a user-friendly kinetic modeling tool

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MicroKinetic Engine

regression and simulation software

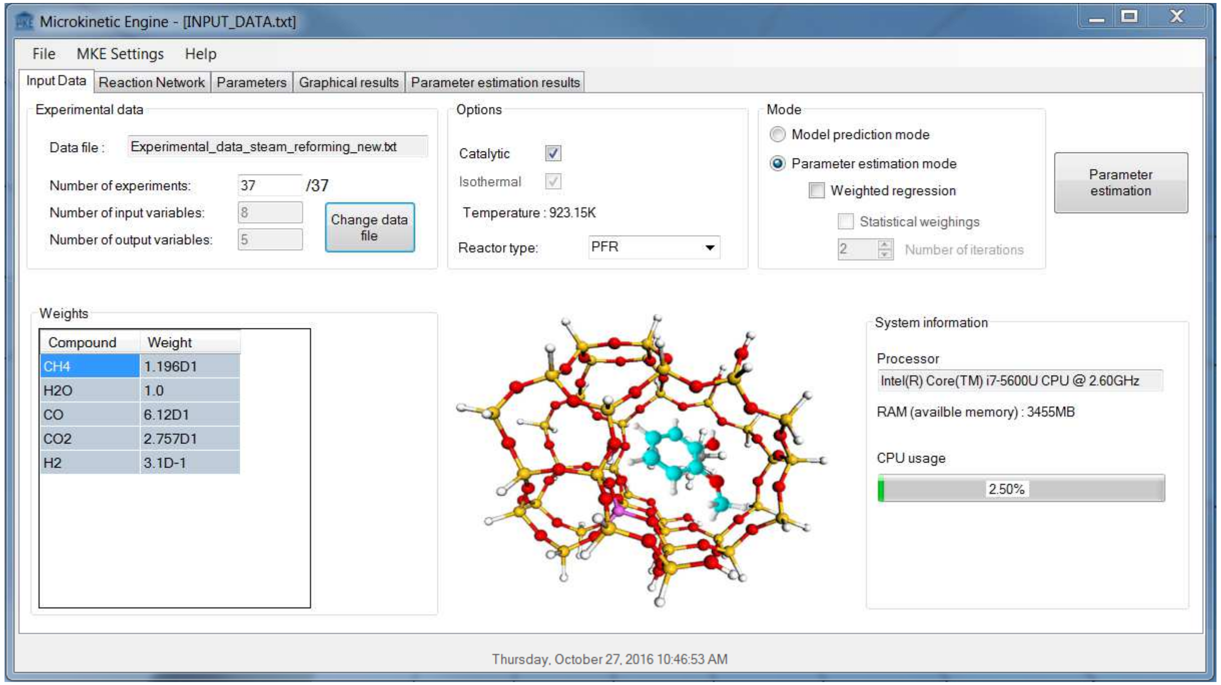
chemical and non-chemical systems

Rosenbrock & Levenberg-Marquardt

user-friendliness

visit booth 7

ShARP Engineering



K. Metaxas et al., Top. Catal., 53 (2010) 64-76.
C. Sprung et al., Appl. Catal. A-Gen., 492 (2015) 231-242.

methodology

adequate

kinetic model

?

new concept
new reaction

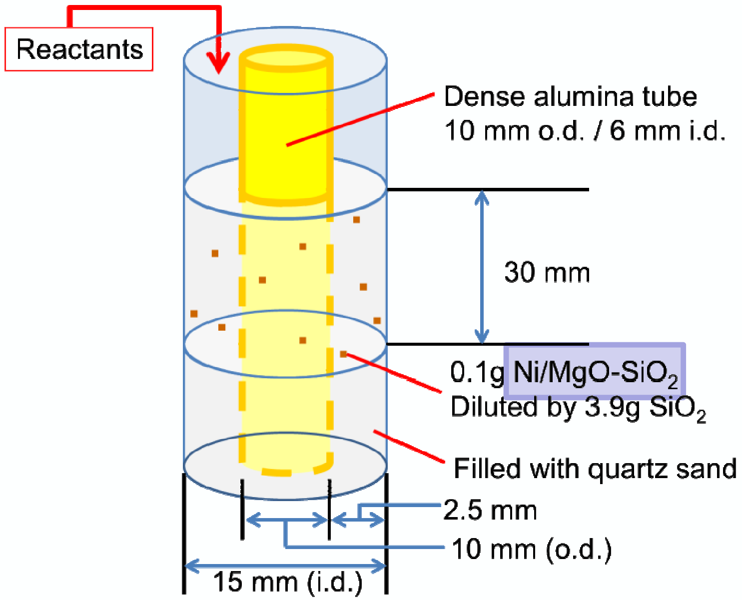
K. Toch et al., AIChE Journal, 61 (2015) 880-892.

steam methane reforming

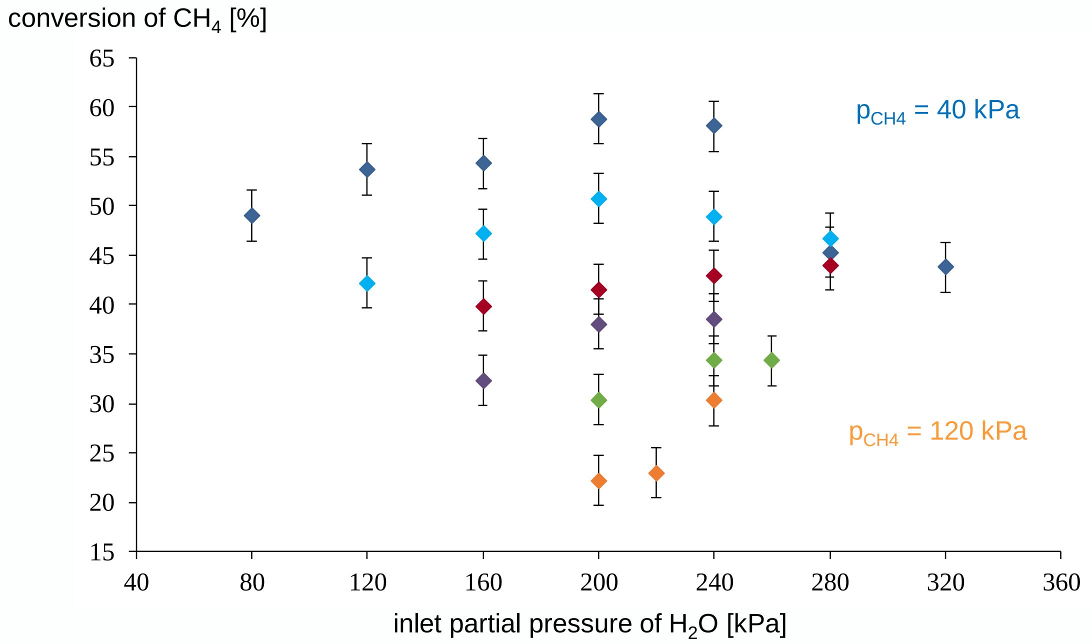
$$CH_4 + H_2O \rightleftharpoons CO + 3H_2 \qquad \Delta H_r^0 = 224\ \mathrm{kJ\ mol^{-1}}$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad \Delta H_r^0 = -36\ \mathrm{kJ\ mol^{-1}}$$

- 923.15 K
- 4 bar
- CH_4/H_2O: 1/1.4 – 1/8
- 1.12 - 6.72 $kg_{cat}\ s\ mol^{-1}$
- N_2 diluent
- 37 experiments



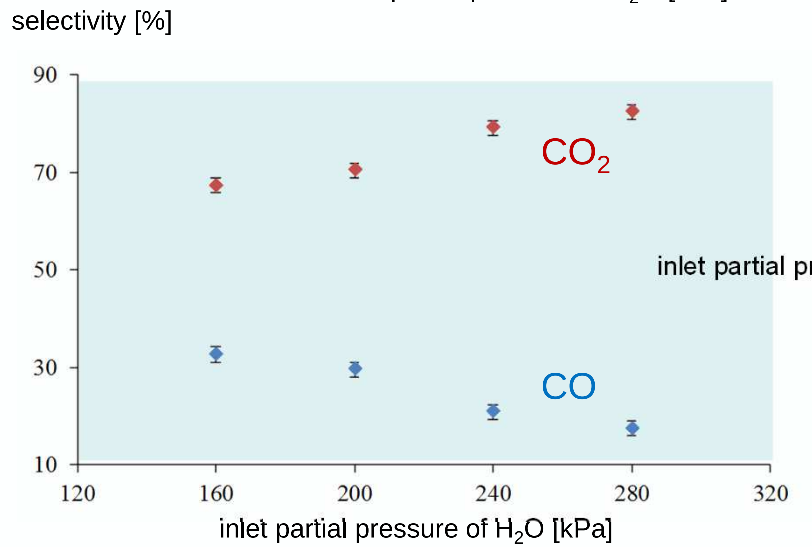
experimental data

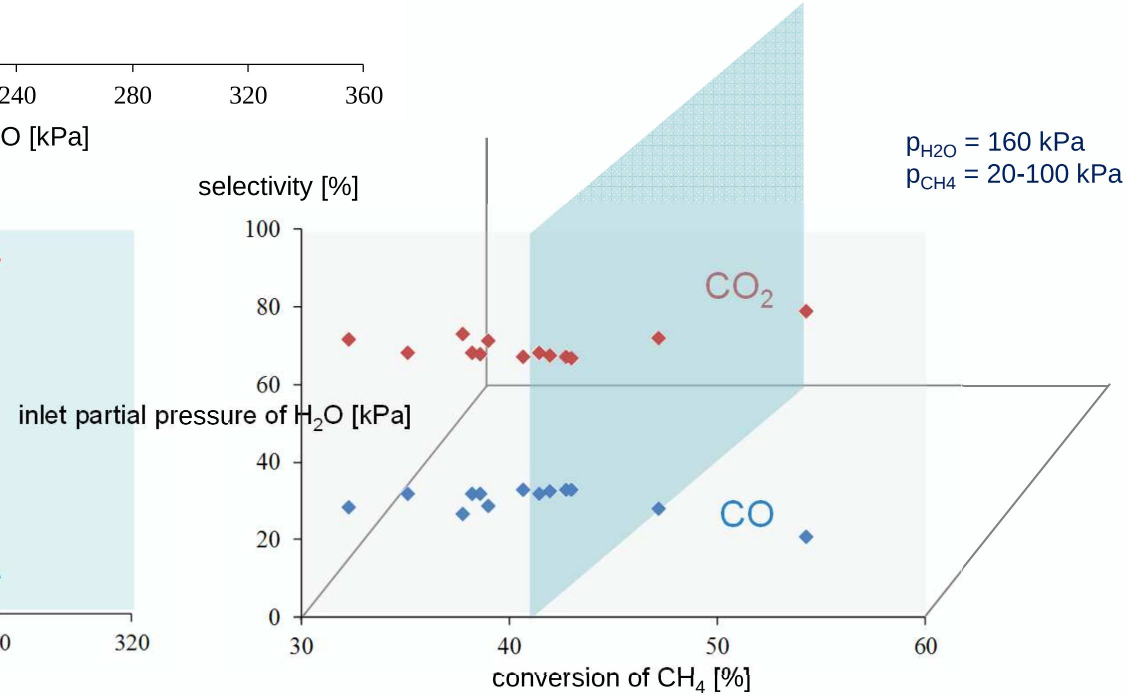


affinity at reactor end:

reforming A > 10 000 J

WGS |A| < 10 000 J





power law model

$$CH_4 + H_2O \xrightarrow{k_1} CO + 3H_2$$

$$CO + H_2O \xrightarrow{k_2} CO_2 + H_2$$

$$r_1 = k_1 p_{CH_4}^{a} p_{H_2O}^{b}$$

$$r_2 = k_2 p_{CO}^{c} p_{H_2O}^{d}$$

$$k_1 = (1.76 \pm 0.34) \cdot 10^{-3} \frac{\text{mol}}{\text{s kg}_{\text{cat}}\text{Pa}^{0.44}}$$

$$k_2 = (1.89 \pm 1.34) \cdot 10^{-5} \frac{\text{mol}}{\text{s kg}_{\text{cat}}\text{Pa}^{0.91}}$$

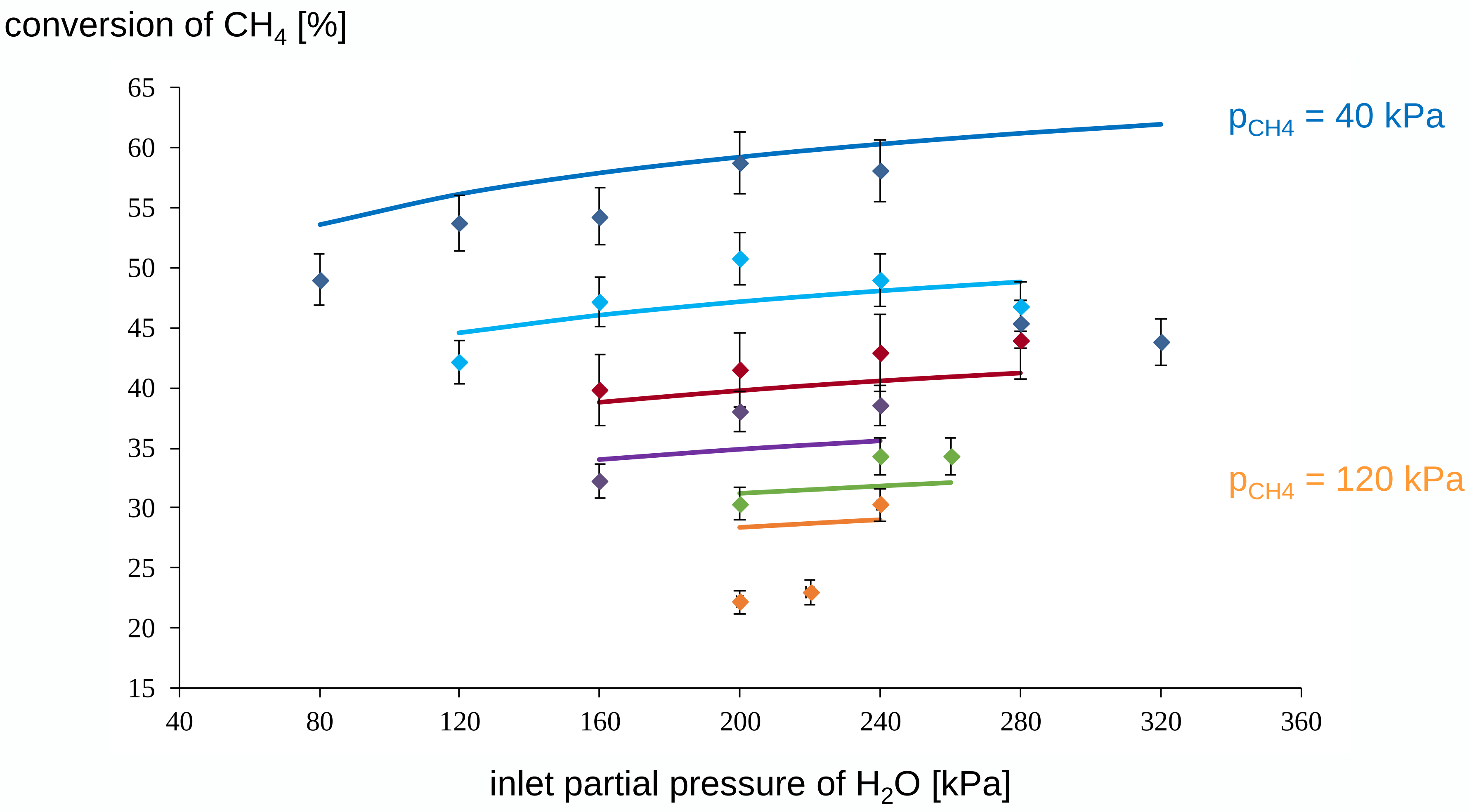
$$a = 0.36 \pm 0.05$$

$$b = 0.081 \pm 0.078$$

$$c = 0.50 \pm 0.13$$

$$d = 0.41 \pm 0.10$$

power law model



model with adsorption reactants

$$CH_4 + * \underset{k_{1-}}{\overset{k_{1+}}{\rightleftharpoons}} CH_4^*$$

$$H_2O + * \underset{k_{2-}}{\overset{k_{2+}}{\rightleftharpoons}} H_2O^*$$

$$CH_4^* + H_2O^* \xrightarrow{k_3} CO + 3H_2 + 2*$$

$$CO + H_2O^* \underset{k_{4-}}{\overset{k_{4+}}{\rightleftharpoons}} CO_2 + H_2 + *$$

$$r_3 = \frac{k'_3 K_1 K_2 p_{CH_4} p_{H_2O}}{\left(1 + K_1 p_{CH_4} + K_2 p_{H_2O}\right)^2} \qquad r_4 = \frac{k'_{4+} K_2 \left(p_{CO} p_{H_2O} - \frac{p_{CO_2} p_{H_2}}{K_{WGS}}\right)}{1 + K_1 p_{CH_4} + K_2 p_{H_2O}}$$

model with adsorption reactants

$$r_3 = \frac{k'_3 K_1 K_2 p_{CH_4} p_{H_2O}}{\left(1 + K_1 p_{CH_4} + K_2 p_{H_2O}\right)^2}$$

$$r_4 = \frac{k'_{4+} K_2 \left(p_{CO} p_{H_2O} - \frac{p_{CO_2} p_{H_2}}{K_{WGS}}\right)}{1 + K_1 p_{CH_4} + K_2 p_{H_2O}}$$

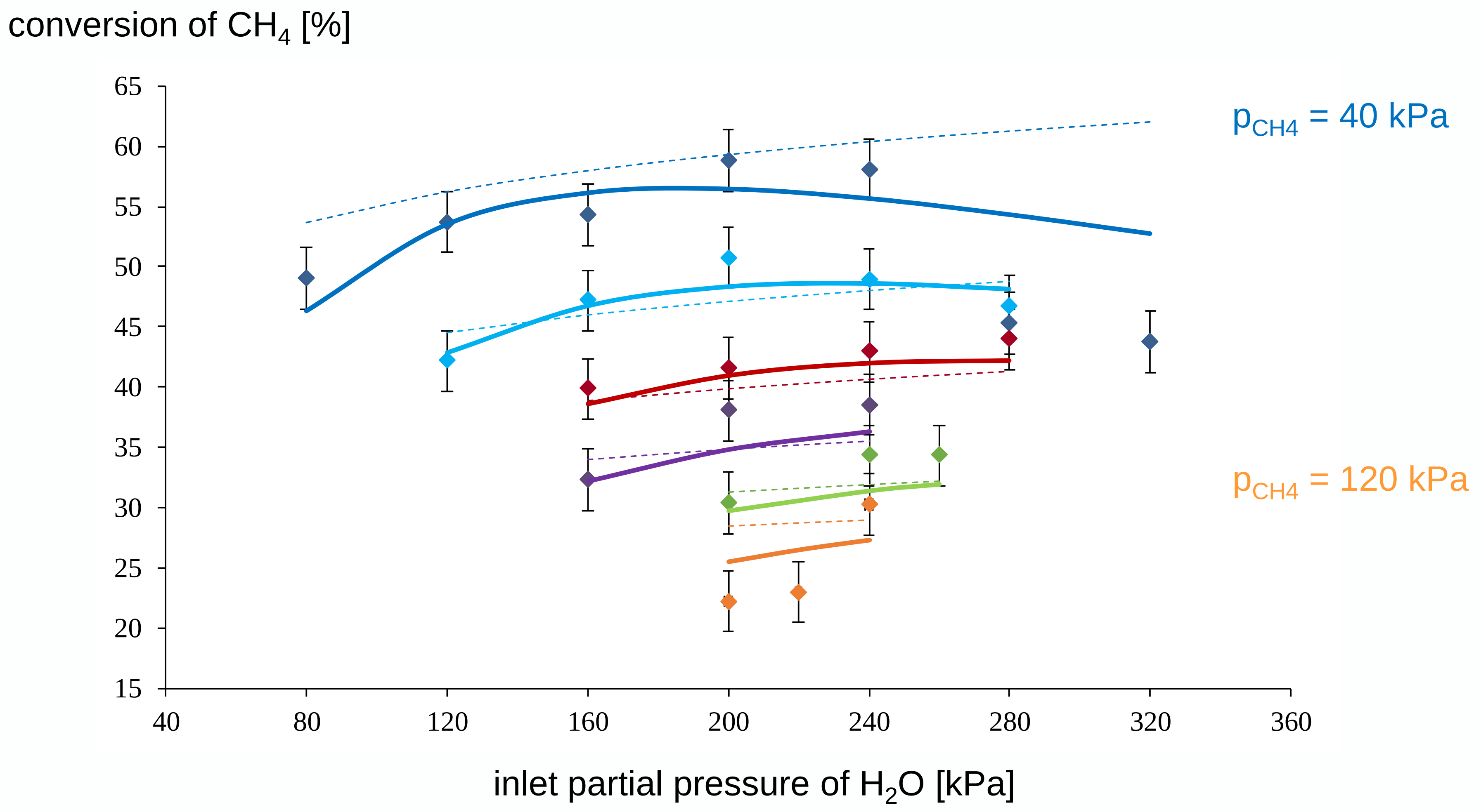
$$K_1 = 28.8 \pm 4.8 \text{ MPa}^{-1}$$

$$K_2 = 12.5 \pm 2.3 \text{ MPa}^{-1}$$

$$k'_3 = 1.63 \pm 0.12 \text{ mol s kg}_{cat}^{-1}$$

$$k'_{4+} = (1.11 \pm 0.03) \cdot 10^{10} \text{ mol s kg}_{cat}^{-1} \text{ MPa}^{-1}$$

model with adsorption reactants



Langmuir-Hinshelwood

$$CH_4 + [\ ] \underset{k_{1-}}{\overset{k_{1+}}{\rightleftharpoons}} [CH_4]$$

$$H_2O + [\ ] \underset{k_{2-}}{\overset{k_{2+}}{\rightleftharpoons}} [H_2O]$$

$$[CH_4] + [H_2O] + 2[\ ] \underset{k_{3-}}{\overset{k_{3+}}{\rightleftharpoons}} [CO] + 3[H_2]$$

$$[CO] + [H_2O] \underset{k_{4-}}{\overset{k_{4+}}{\rightleftharpoons}} [CO_2] + [H_2]$$

$$[CO] \underset{k_{5+}}{\overset{k_{5-}}{\rightleftharpoons}} CO + [\ ]$$

$$[CO_2] \underset{k_{6+}}{\overset{k_{6-}}{\rightleftharpoons}} CO_2 + [\ ]$$

$$[H_2] \underset{k_{7+}}{\overset{k_{7-}}{\rightleftharpoons}} H_2 + [\ ]$$

Langmuir-Hinshelwood

$$r_3 = \frac{k'_{3+}K_1K_2p_{CH_4}p_{H_2O} - \frac{k'_{3+}K_1K_2}{K_R}p_{CO}p_{H_2}^{3}}{\left(1 + K_1p_{CH_4} + K_2p_{H_2O} + K_5p_{CO} + K_6p_{CO_2} + K_7p_{H_2}\right)^{4}}$$

$$r_4 = \frac{k'_{4+}K_2K_5p_{CO}p_{H_2O} - \frac{k'_{4+}K_2K_5}{K_{WGS}}p_{CO_2}p_{H_2}}{\left(1 + K_1p_{CH_4} + K_2p_{H_2O} + K_5p_{CO} + K_6p_{CO_2} + K_7p_{H_2}\right)^{2}}$$

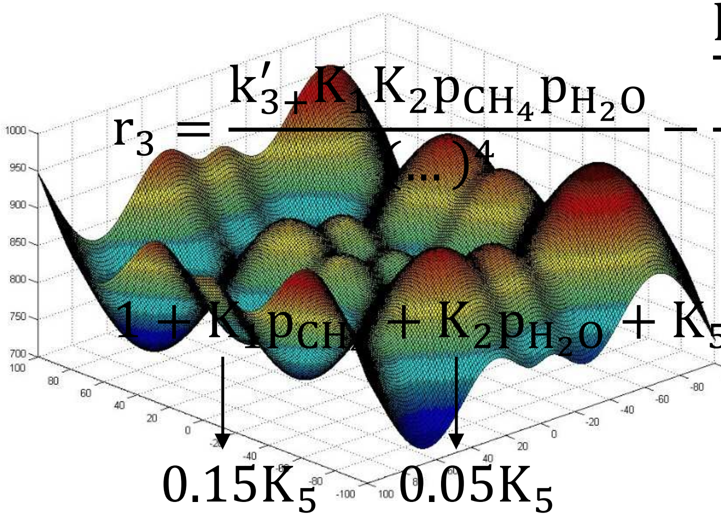
step 1

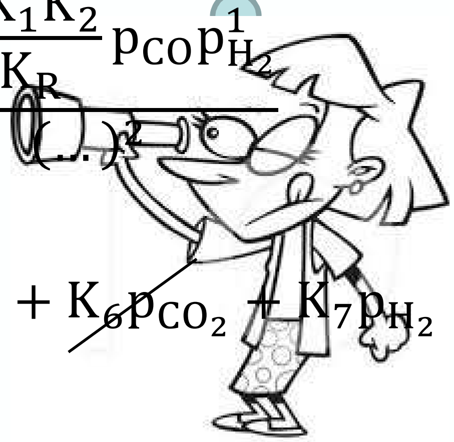
$$r_3 = \frac{k'_{3+}K_1K_2p_{CH_4}p_{H_2O}}{(\dots)^4} - \frac{\frac{k'_{3+}K_1K_2}{K_7^2K_R}p_{CO}p_{H_2}^{1}}{(\dots)^2}$$

step 2

$$1 + K_1p_{CH_4} + K_2p_{H_2O} + K_5p_{CO} + K_6p_{CO_2} + K_7p_{H_2}$$

$0.15K_5$ $0.05K_5$





Langmuir-Hinshelwood

$$r_3 = \frac{0.0075k'_{3+}K_5^2 p_{CH_4} p_{H_2O}}{(\dots)^4} - \frac{\frac{0.0075k'_{3+}K_5^2}{K_7^2 K_R} p_{CO} p_{H_2}}{(\dots)^2}$$

$$r_4 = \frac{0.05k'_{4+}K_5^2 p_{CO} p_{H_2O} - \frac{0.05k'_{4+}K_5^2}{K_{WGS}} p_{CO_2} p_{H_2}}{(\dots)^2}$$

$$\dots = 1 + 0.15K_5 p_{CH_4} + 0.05K_5 p_{H_2O} + K_5 p_{CO} + K_7 p_{H_2}$$

$K_1 = 0.15K_5$

$K_2 = 0.05K_5$

$K_6 = 0$

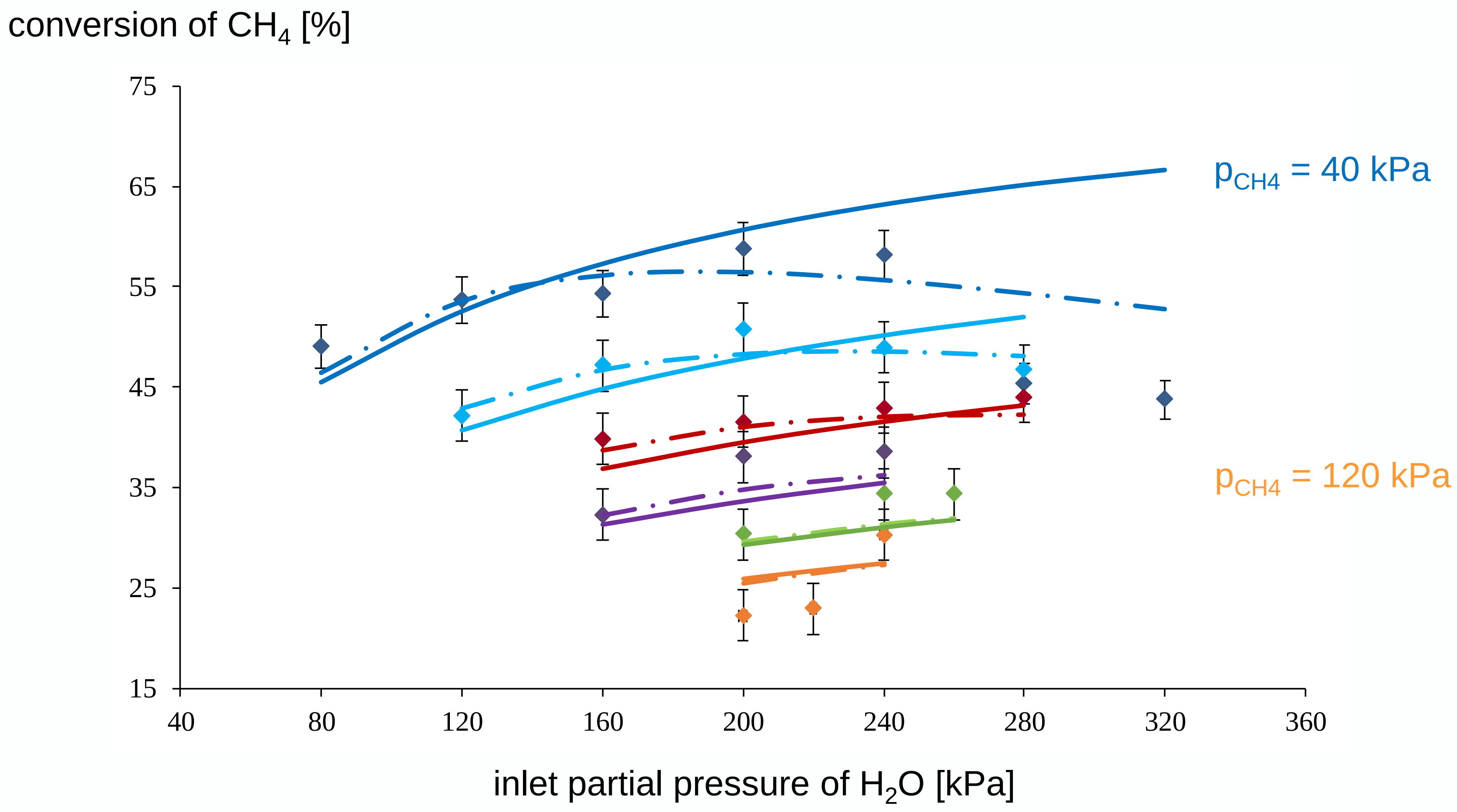
$k'_{3+} = 267 \pm 238 \text{ mol s kg}_{cat}^{-1}$

$k'_{4+} = (1.39 \pm 0.34) \cdot 10^{10} \text{ mol s kg}_{cat}^{-1}$

$K_5 = 23.2 \pm 19.6 \text{ MPa}^{-1}$

$K_7 = 14.7 \pm 11.6 \text{ MPa}^{-1}$

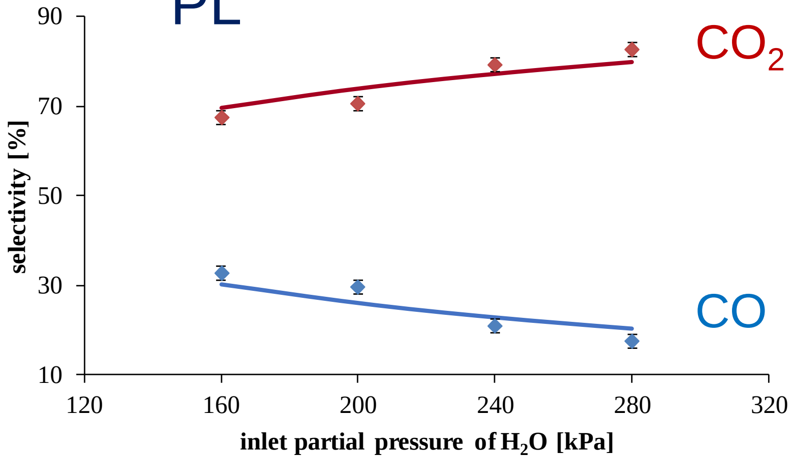
Langmuir-Hinshelwood



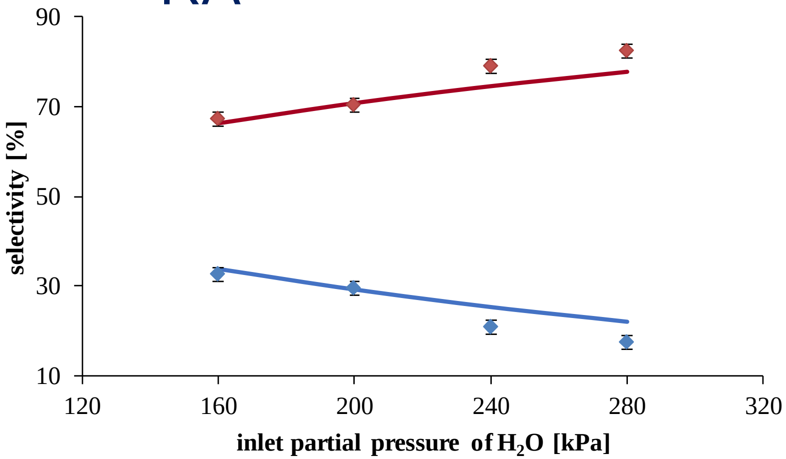
model performance

1.44 kg_{cat} s mol^{-1} and X ϵ [40, 44]

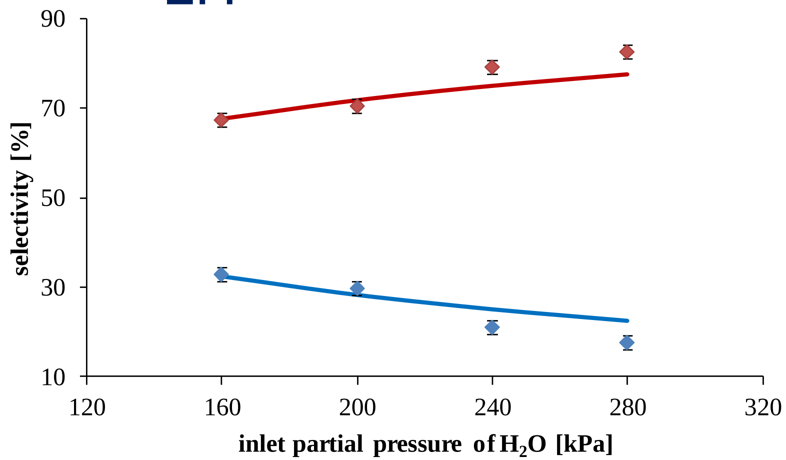
PL



RA



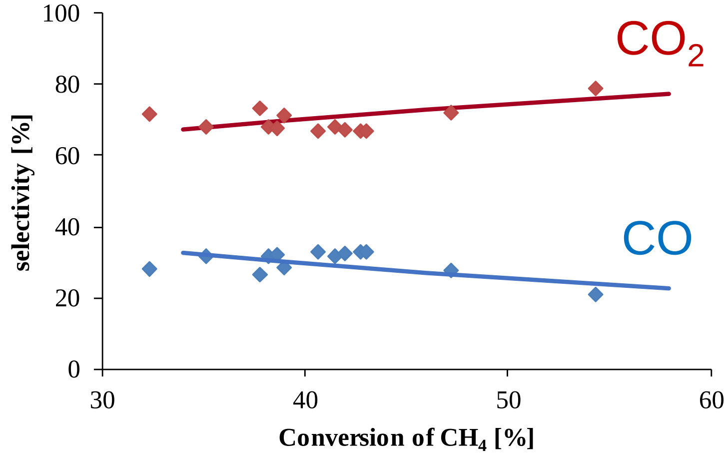
LH



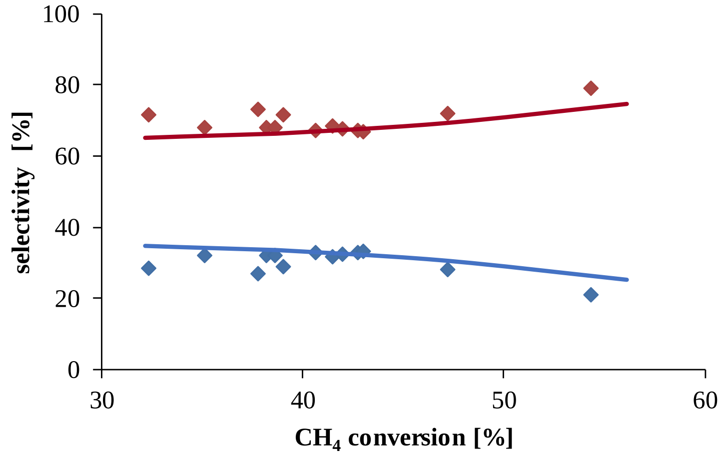
model performance

p_{H2O} = 160 kPa and p_{CH4} = 20-100 kPa

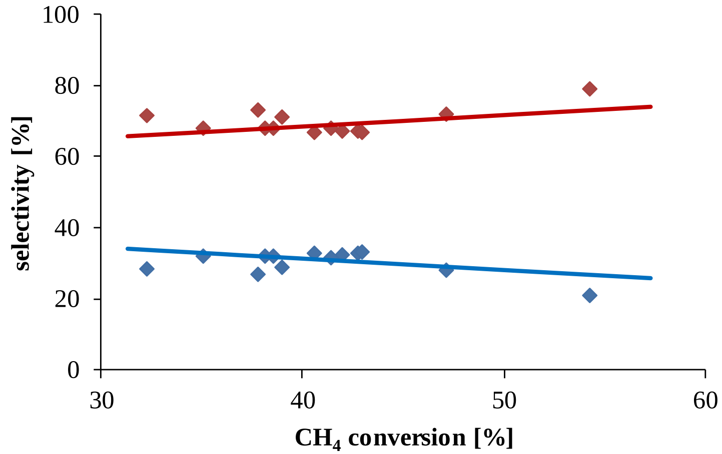
PL



RA



LH



conclusions

- most important phenomena to describe data:
  - adsorption of reactants
  - reversibility of water-gas shift reaction
- Langmuir-Hinshelwood model
  - overparametrized
  - local minimum
- more fundamental within LH: no improvement
- next step: true microkinetic model
- the MicroKinetic Engine as a user-friendly tool for kinetic modeling

acknowledgements

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Methusalem programma

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questions