From First Principles to Pilot Scale: Kinetic Modeling of Sour gas-based CO Conversion to Methanol

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Introduction

Large amounts of CO_2 from heating and industry are emitted annually, with only ~2 Gt/year naturally sequestered and a small fraction captured technically at €70–100/ton. Less than 300 kt/year is recovered, and no complete circular CO_2 value chain exists. Refineries and petrochemical plants emit 1.24 Pt/year of CO_2 and process over 3.6 Mt/year of H_2S.

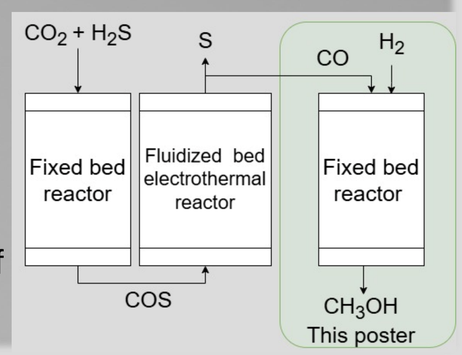
Sour gas—a CO_2 and H_2S mixture—is generated during refining, natural gas extraction, and biogas upgrading. Current treatment relies on the Claus process for sulfur recovery, which requires fuel gas for lean H_2S streams (<55%). CO_2 capture, on the other hand, needs high purity. No existing technology allows for simultaneous reduction of both CO_2 and H_2S.

The **eCODUCT** project addresses this challenge by electrifying the conversion of acid gases to valuable products (CO and sulfur) through a two-step process:

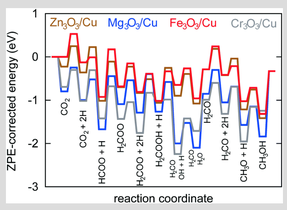
Conversion to COS: CO_2 and H_2S are converted into carbonyl sulfide (COS) in a fixed-bed reactor over a zeolite catalyst.

Decomposition to CO and S: COS is then thermally decomposed into CO and sulfur in a fluidized-bed electrothermal reactor.

The final step involves converting **CO into methanol**. A kinetic model for this reaction has been developed using a combination of first-principles calculations and regression based on experimental data.



Previous DFT study on CO_2/CO and H_2 conversion to methanol



Surface reactions

$H_2 \rightleftharpoons 2H$

$CO + H \rightleftharpoons HCO$

$HCO + H \rightleftharpoons H_2CO$

$H_2CO + H \rightleftharpoons H_3CO$

$H_3CO + H \rightleftharpoons CH_3OH$

Adsorption/Desorption

$CO + * \rightleftharpoons CO_{ads}$

$H_2 + * \rightleftharpoons H_{2\,ads}$

$CH_3OH + * \rightleftharpoons CH_3OH_{ads}$

Activation energies for the dominant reaction pathway

aspentech

Conversion and yield at **thermodynamic equilibrium**

$CO + 2\,H_2 \rightleftharpoons CH_3OH$

Microkinetic model design

Reaction rates

$$r_j^{ads} = k_j^{ads} \cdot P_j \cdot \theta_{VS} \qquad r_j^{des} = k_j^{des} \cdot \theta_j$$

$$r_i^{surf} = k_i^{surf} \cdot \theta_m \cdot \theta_n$$

$$k_i^{surf}(T) = k_i^{surf}(T_{ref}) \cdot \exp\left(\frac{Ea_i^{surf}}{R} \cdot \left(\frac{1}{T_{ref}} - \frac{1}{T}\right)\right)$$

Mass balances

$$\frac{\partial P_j}{\partial t} = -\frac{\partial}{\partial z}\left[v_z \cdot P_j - D_j^e \cdot \frac{\partial P_j}{\partial z}\right] + \left(-r_j^{ads} + r_j^{des}\right) \cdot \frac{R \cdot T \cdot n_{TS}}{V^G}$$

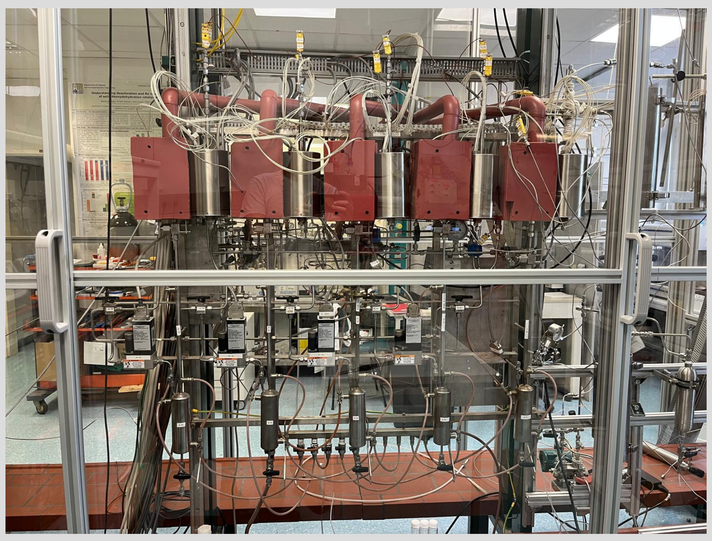
$$\frac{\partial \theta_j}{\partial t} = r_j^{ads} - r_j^{des} \sum_i \pm r_i^{surf}$$

Matlab 2025a: **ode15s** and **fminsearch**

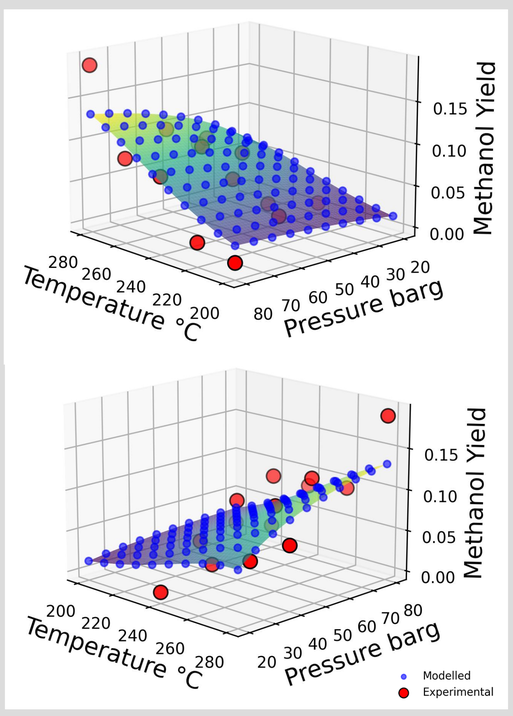
$$f\left(k_j^{ads}, k_i^{surf}, k_j^{des}\right) = \sum_j^I \left(P_j^{measured} - P_j^{calculated}\left(k_j^{ads}, k_i^{surf}, k_j^{des}\right)\right)^2$$

Experimental conversions and yields

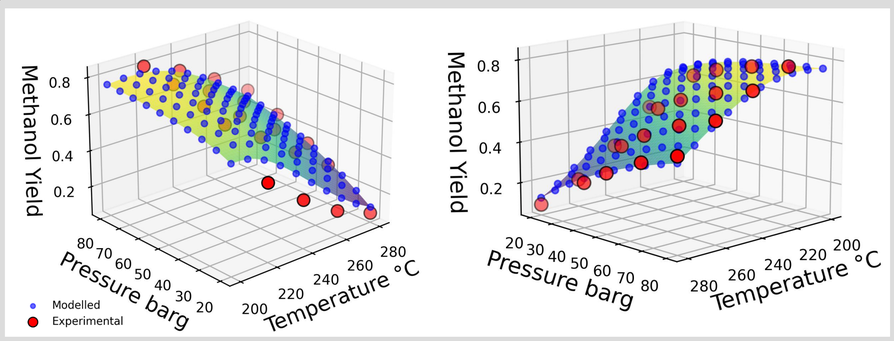
Lab scale experiments



Lab to pilot

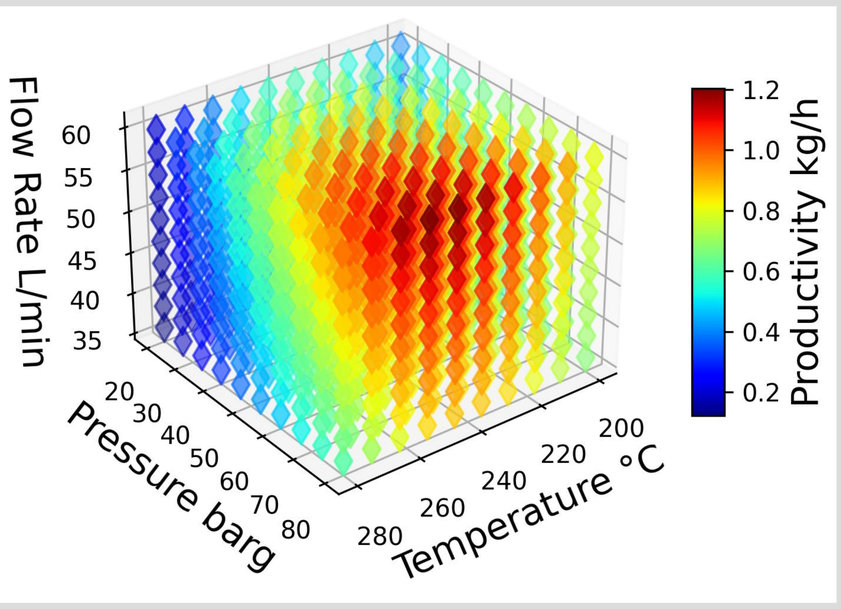


Lab scale experiments data and prediction by the kinetic model



Aspen equilibrium data and prediction by the kinetic model

Process parameter **prediction** for **optimal operation** on the pilot scale, based on the dimensions of the reactor



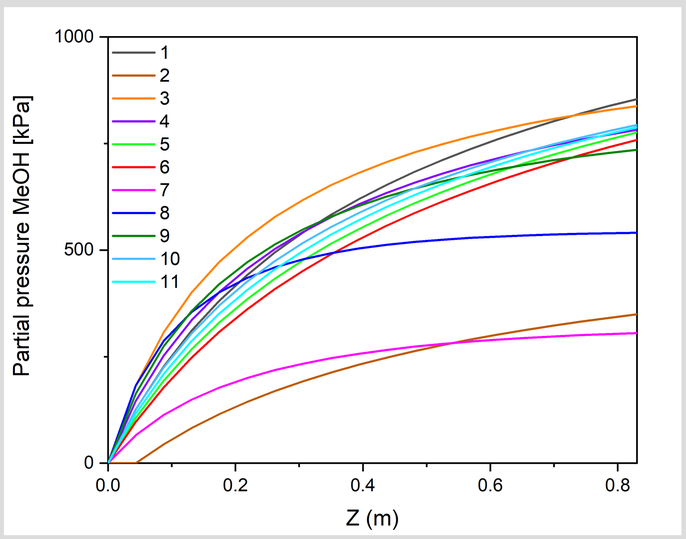


Table 1 Predicted data for our pilot scale for **L** = 0.86m, **ID** = 0.065 m and $\mathbf{m_{catalyst}}$=4.24 kg

#	Temperature °C	Pressure tot barg	Flow rate L/min	Productivity kg/h
1	225	50	36	0.7158
2	225	25	36	0.5107
3	250	50	36	0.6925
4	250	50	50	0.8757
5	230	50	50	0.8699
6	225	50	50	0.8447
7	250	25	36	0.4213
8	280	50	50	0.5464
9	260	50	50	0.8053
10	240	50	50	0.8946
11	235	50	50	0.887

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