Process Modelling: An End-User's Perspective Using COCO

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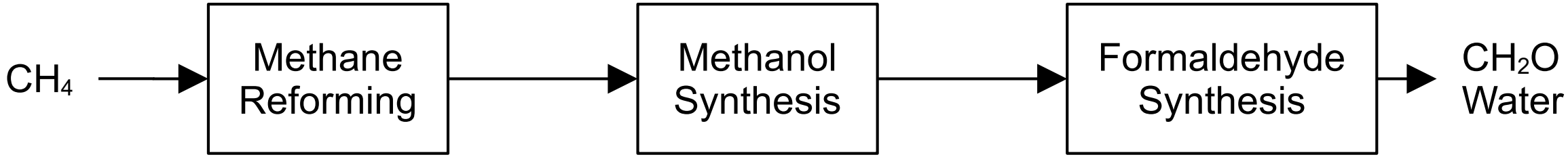
Presentation Outline

- Project Background:
  - MSc Title: **Process Modelling and Optimisation of the Direct Methane-to-Formaldehyde Process**
- Conventional Modelling with COCO
- Complex Modelling with COCO
- Final Thoughts

Project Background
Conventional Process



$$CH_4 + H_2O \leftrightharpoons 3H_2 + CO$$

- High temperatures
- Endothermic – requires significant amount of fuel

$$CO + 2H_2 \leftrightharpoons CH_3OH$$

- High pressures
- (together with reforming step): ca. 895 kJ / mol MeOH [1]

$$CH_3OH + O_2 \rightarrow CH_2O + H_2O$$
$$CH_3OH \leftrightharpoons CH_2O + H_2$$

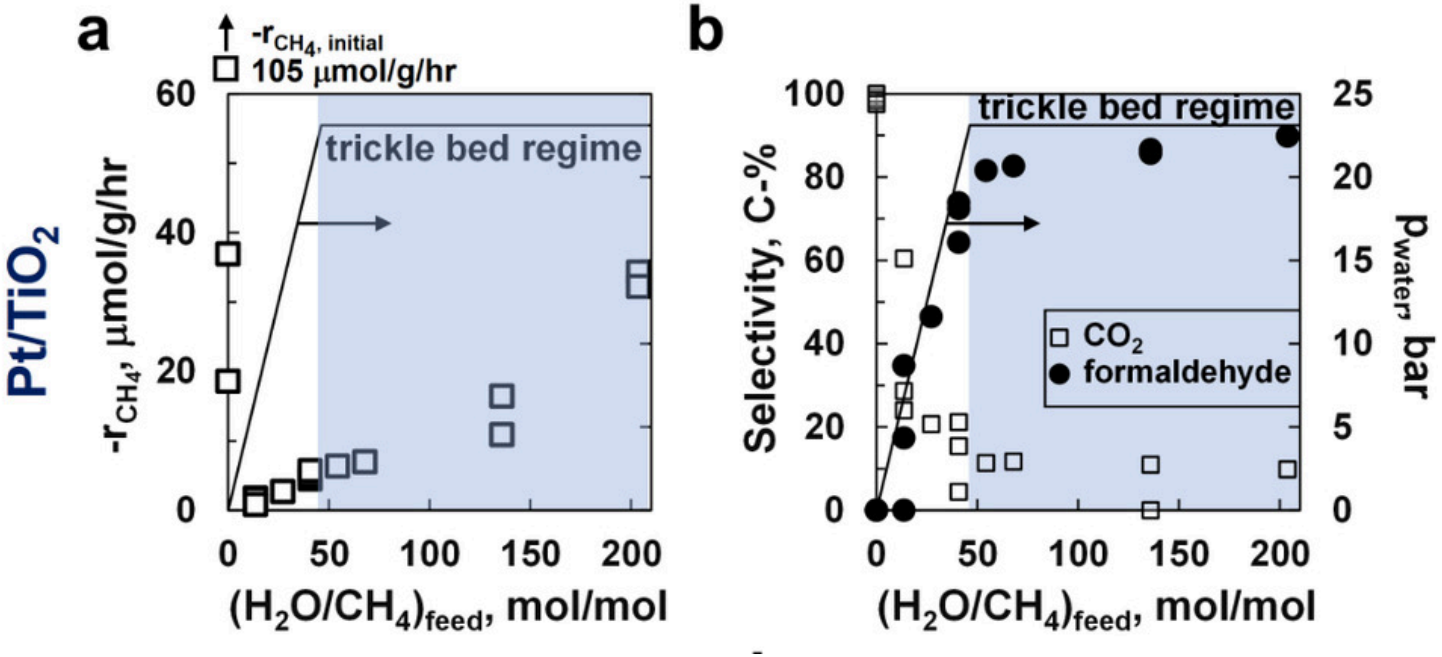
- Low energy requirements

Overall exergetic efficiency: **43.2%** [2]

[1] C.A. del Pozo, S. Cloete, Á.J. Álvaro, *Energy Conv. Manag.* **266**:115785 (2022)
[2] A.M. Bahmanpour, A. Hoadley, A. Tanksale, *Reviews in Chemical Engineering.* **30**(6):583-604 (2014)

Project Background
Direct Methane-to-Formaldehyde (DMTF)

$$CH_4 + O_2 \leftrightharpoons CH_2O + H_2O$$



High selectivity: ~90%
Moderate conditions: 493 K, 30 bar

BUT

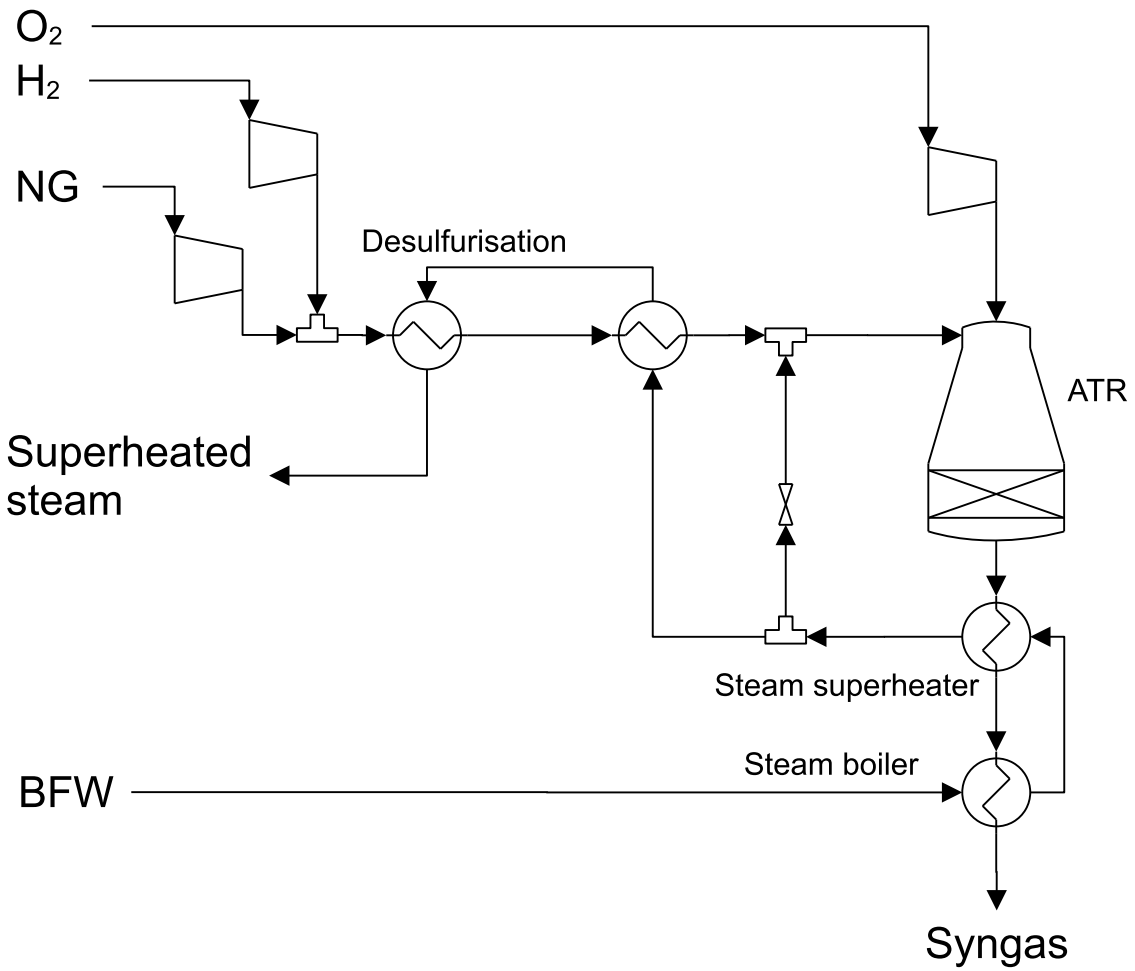
Low conversion: ~3%
High water ratios: 200

S.V.L. Mahlaba, N.H.L. Mahomed, A. Govender, J. Guo, G.M. Leteba, P.L. Cilliers, E. van Steen, *Angew. Chem. Int. Ed.* **61**(38):e202206841 (2022)

Conventional Modelling
Autothermal Reforming

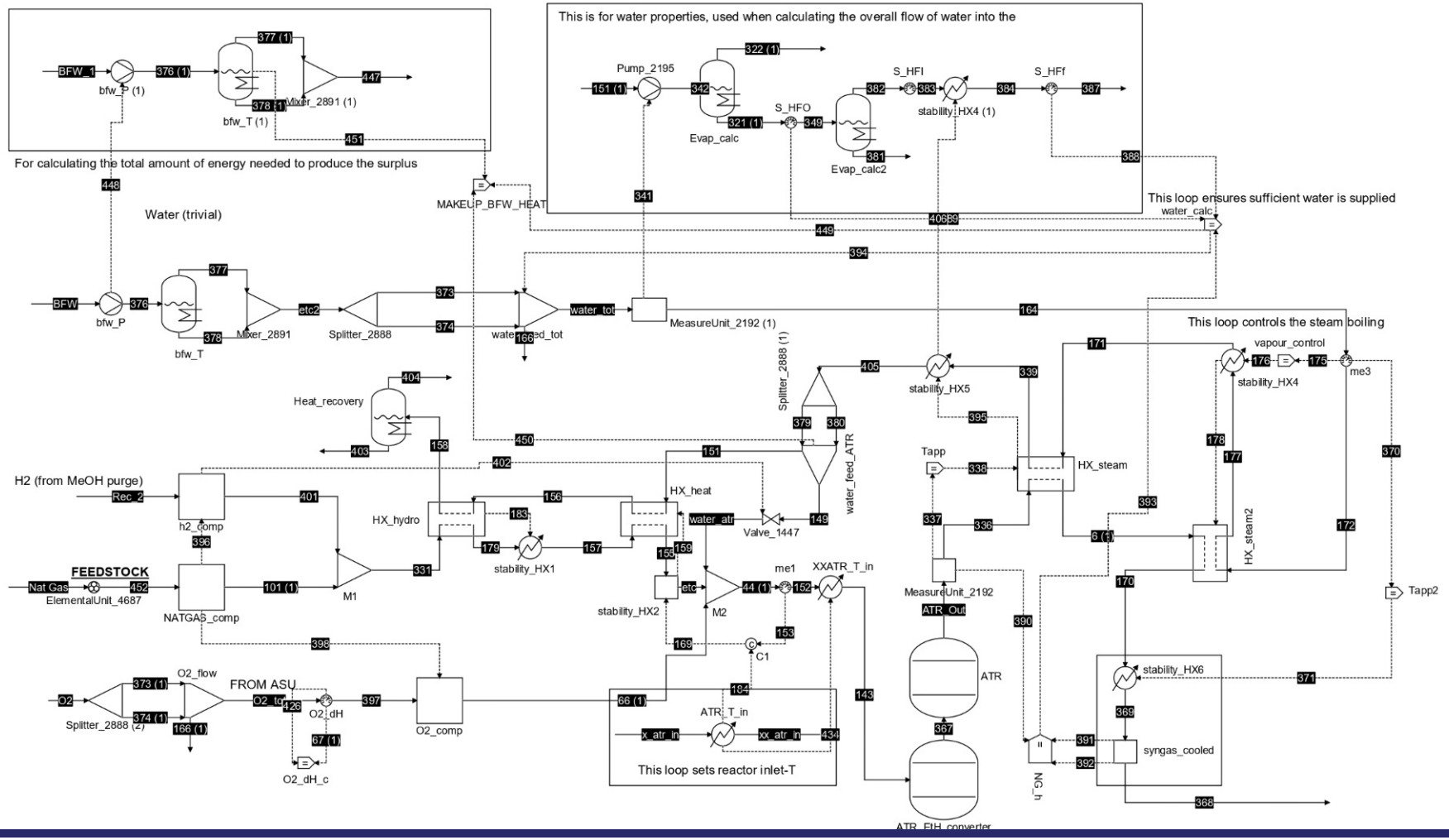
$$CH_4 + \frac{1}{2}O_2 \leftrightharpoons CO + 2H_2$$
$$CH_4 + H_2O \leftrightharpoons CO + 2H_2$$
$$CO + H_2O \leftrightharpoons CO_2 + H_2$$

- Oxygen leaves very little residual methane
- Enables higher pressure operation
- Requires no fuel input – partial combustion of feedstock



T. Blumberg, MSc: Technischen Universität Berlin (2018)

Conventional Modelling
Autothermal Reforming



Conventional Modelling
Autothermal Reforming

- Other facets of the flowsheet:
  - Multistage compressor
  - Minimum approach temperature in heat exchangers
- Optimisation and Parametric studies
  - Whole study fails when one condition fails, even if the solutions in other areas are progressing fine
  - Freezing in solving makes it difficult to assess if the study is solving or crashing
  - Lack of study progress indicators

Complex Modelling
Water-Formaldehyde VLE

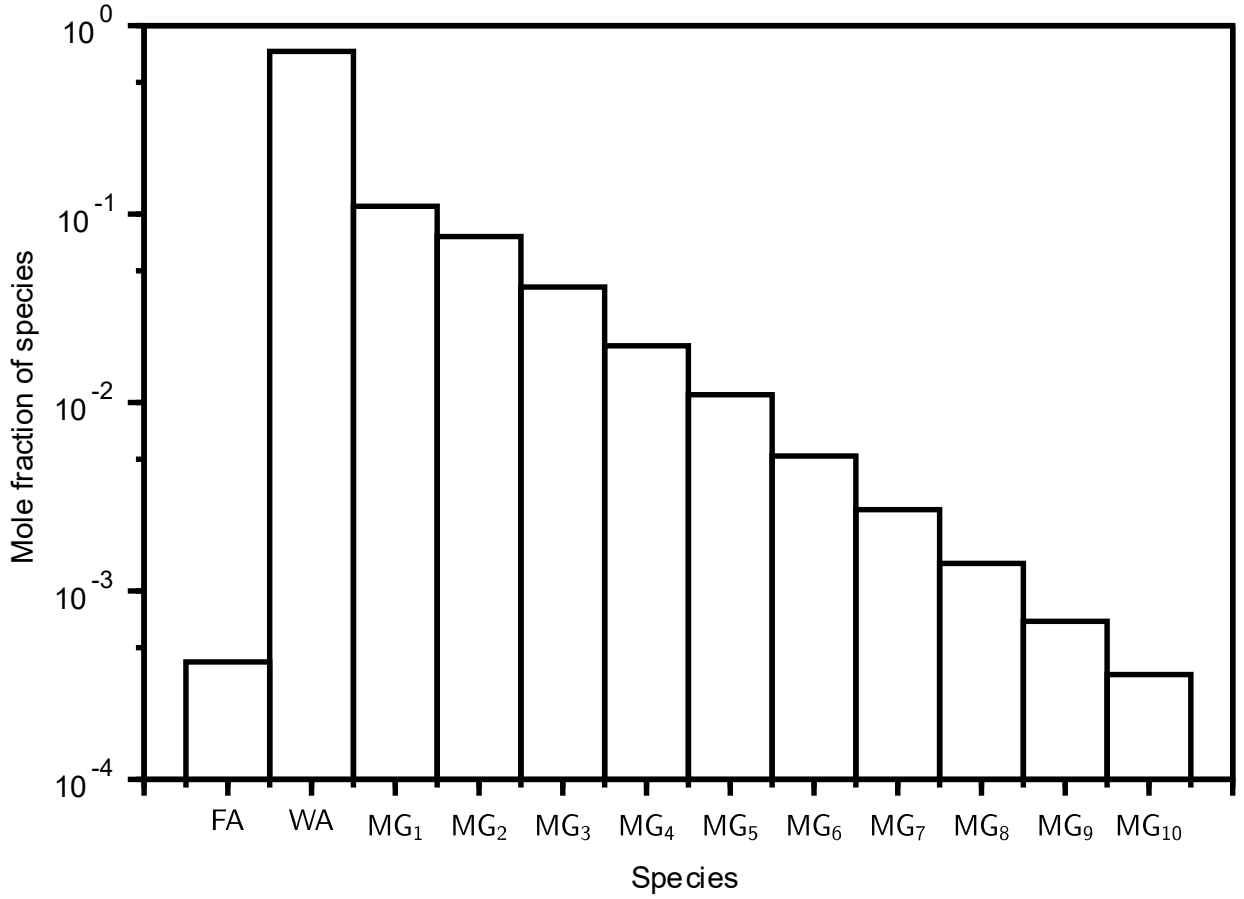
Formaldehyde:
- Volatile, boiling point of 254 K

Methylene glycol (MG_1)

$$CH_2O + H_2O \rightleftharpoons CH_2(OH)_2$$

Polyoxymethylene glycols (MG_n):

$$CH_2(OH)_2 + H[-OCH_2-]_nOH \rightleftharpoons H[-OCH_2-]_{n+1}OH + H_2O$$



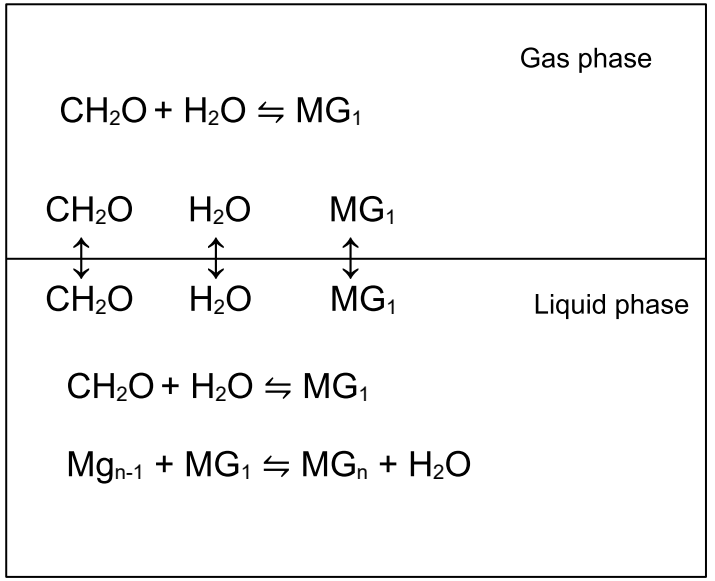
J.G.M. Winkelman, H. Sijbring, & A.A.C.M Beenackers, Chemical Engineering Science **47**(13/14):3785–3792 (1992)

Complex Modelling
Reactive VLE

Using the model developed by Hasse/Maurer at Kaiserslautern:

- UNIQUAC Functional-group Activity Coefficient (UNIFAC) model

Chemical	Formula	Groups
MeO	CH_2O	1 CH_2O
Water	H_2O	1 H_2O
MG_1	$HOCH_2OH$	1 $HOCH_2OH$
MG_n	$HO[CH_2O]_{n-1}CH_2OH$	1 CH_2, 2 OH, n-1 CH_2O (10>n>1)



- Only Water, MeO, and MG_1 present in gas phase
- Extended Raoult's Law, Ideal Gas for vapour phase

$$\gamma_i x_i P_i^{sat} = P_i$$

M. Albert, B.C. Garcia, C. Kreiter, G. Maurer, *Thermodynamics.* **45**(9):2024-2033 (1999)

Complex Modelling
Reactive VLE

Using the model developed by Hasse/Maurer at Kaiserslautern:

Group	*i* *j*	1	2	3	4	5
CH_2O	1	0.0	774.81*	189.21*	237.7	83.36
H_2O	2	−142.35*	0.0	189.52*	−229.1	300.0
$HO(CH_2O)H$	3	59.20*	−191.82*	0.0	−229.1	300.0
OH	4	28.06	353.5	353.5	0.0	156.4
CH_2	5	251.5	1,318.0	1,318.0	986.5	0.0

+ Compound property estimation for MG_2-MG_5 using PCD manager.

UNIFAC-VL groups:

Parameter: interaction

Group	OH	CH2	CH2O	H2O	HOCH2OH
OH	N/A	156.4	28.06	353.5	353.5
CH2	986.5	N/A	251.5	1318	1318
CH2O	237.7	83.36	N/A	774.81	189.21
H2O	-229.1	300	-142.35	N/A	189.52
HOCH2OH	-229.1	300	59.2	-191.82	N/A

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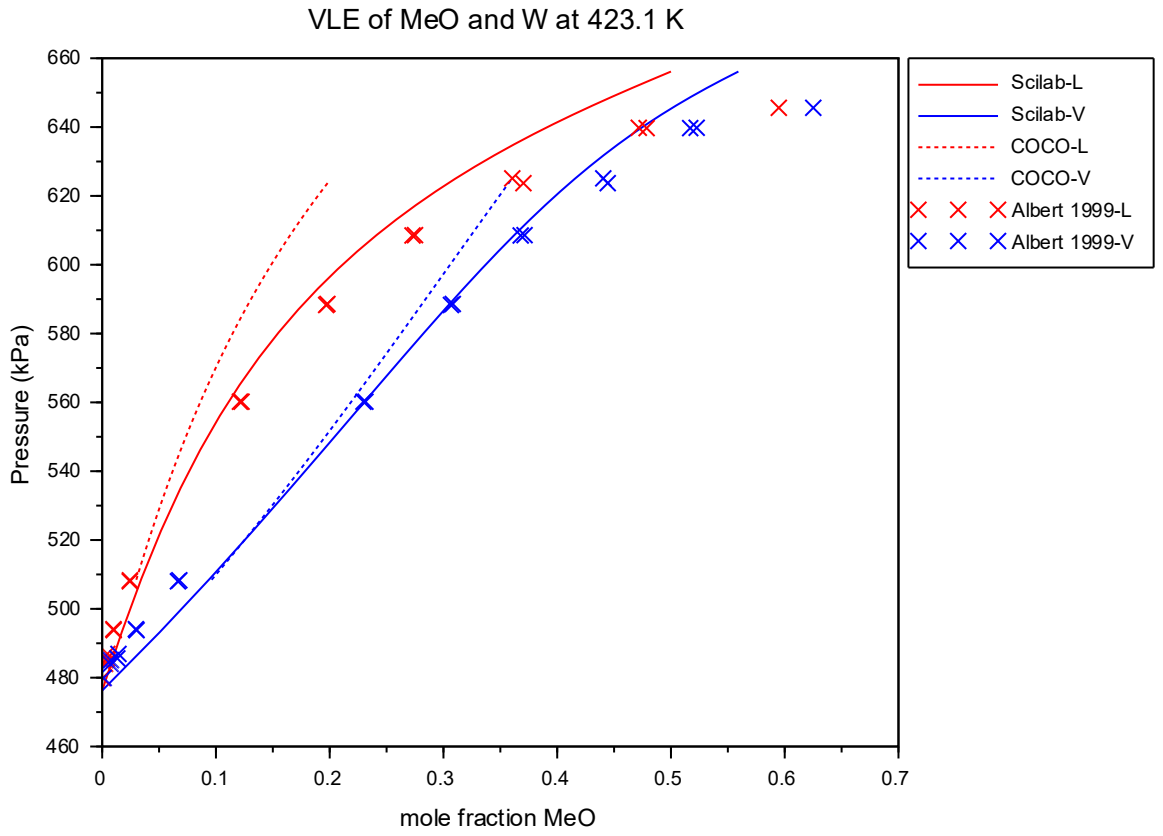
Complex Modelling
Comparison with external VLE Model

- Scilab code vs COCO
  - Failure for smaller values of formaldehyde (ca. <0.03 mole fraction): Preconditioning failure / Line search failure.
  - Also fails at higher formaldehyde fractions (ca. >0.2 mole fraction)
  - Unable to get to work at lower pressures → likely due to smaller MeO fractions present
- Needs improvement
- Slightly awkward to carry out in COCO; but ChemSep's reactive flash and equilibrium reaction do not currently work



M. Albert, B.C. Garcia, C. Kreiter, G. Maurer, *Thermodynamics.* **45**(9):2024-2033 (1999)

Final Thoughts

- Performs well as a conventional process modelling software
- Generally user-friendly, low-intensity
- Allows for complex process modelling, albeit with restrictions
- Lacking several quality-of-life functionalities
  - However, many of these “quality of life” issues can be circumvented by custom units / effective use of information streams and calculators

- Overall, COCO is effective as a Flowsheet Simulator

Acknowledgement

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