

Reactors in Aspen Plus® MeOH -Synthesis

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Process Development – ChE459

1. General aspects on reactor models in Aspen Plus**2. MeOH synthesis reactions**

- Stoichiometric considerations
- Operating conditions

3. Tutorial in Aspen Plus

- Scaling-up: Co-electrolyzer
- Multi-stage compression (with intercooling)
- RGibb's reactor model (Equilibrium)
- Rplug reactor model (Kinetic)

4. Calculator blocks

- YIELD
- CAT-LOAD

5. Tear streams and convergence in Aspen Plus

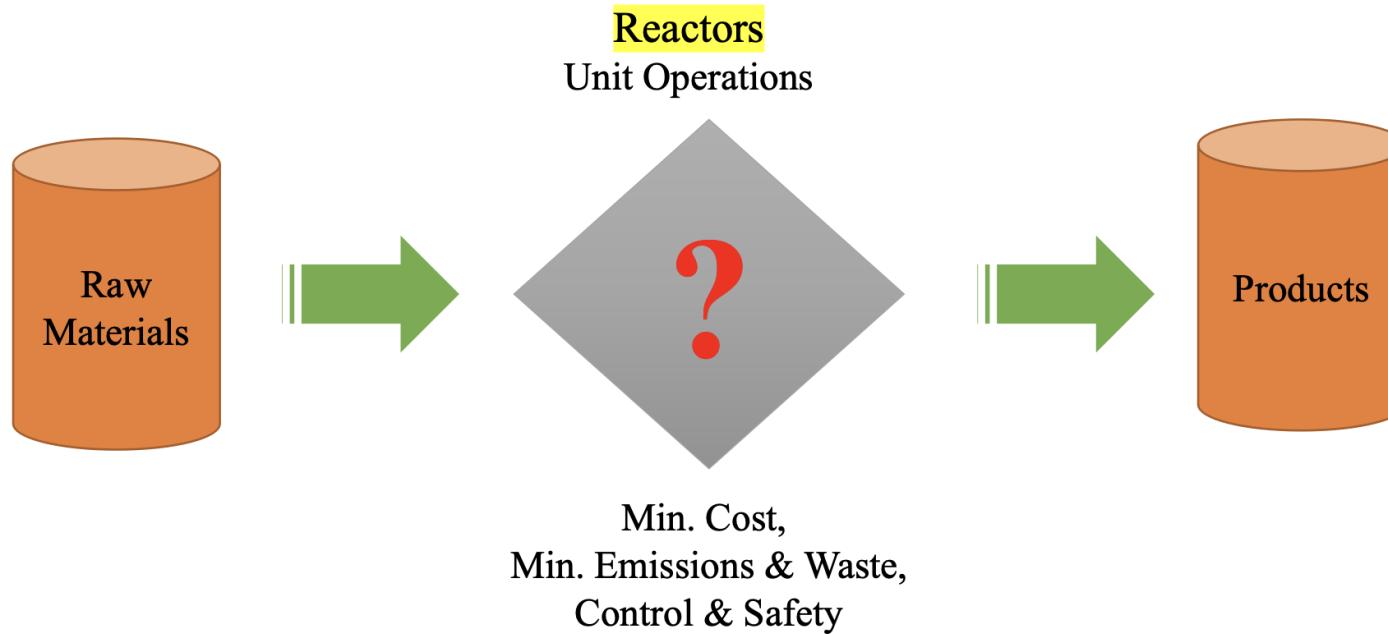
- Recycling streams to enhance MeOH yield
- Strategies to fix convergence issues

6. Sensitivity Analysis on: (in class)

- Gas hourly space velocity (GHSV)
- Visualization of results
- Pre-sizing of a reactor

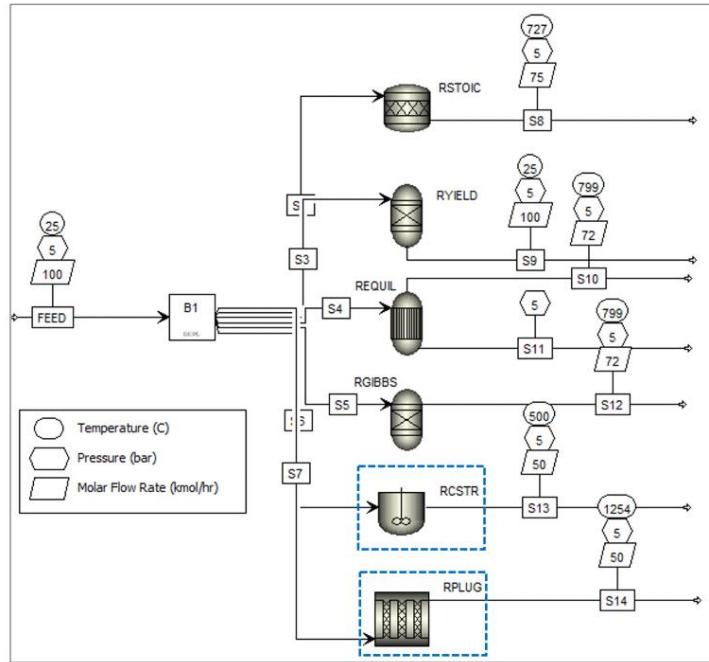
EPFL Chemical reactors to model ... chemical reactions

3

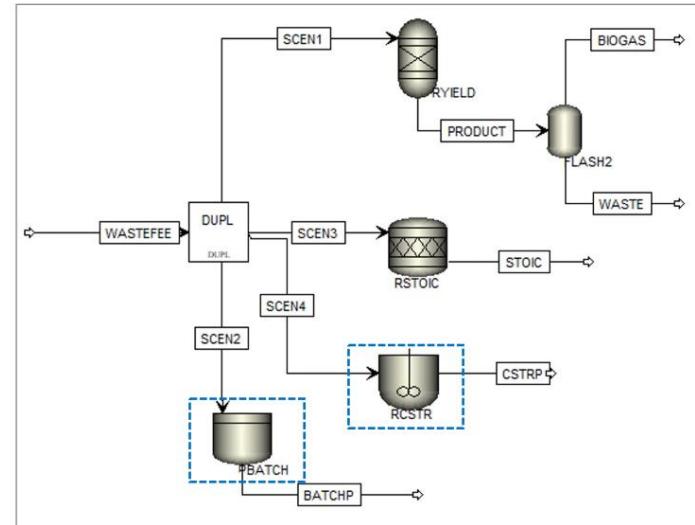


- **Decide the type of reactor**
Batch, CSTR (continuous stirrer tank), PFR (plug flow), PBR (packed bed), etc,
- **Find the information for modelling of reactor**
Reaction stoichiometry, reaction conversion, reaction yield, reaction kinetics, isothermal/adiabatic

Many different reactor models



Fermentation Process



These simulation files are available on Moodle.

➤ **Aspen Help Window** for more details on each reactor model

- Choose model based on the literature data

- 3 main chemical reactions in competition:



- The Stoichiometric number (SN) of the feed must be ≥ 2 for good conversion

$$\text{SN} = \frac{y_{\text{H}_2} - y_{\text{CO}_2}}{y_{\text{CO}} + y_{\text{CO}_2}}$$

SN = 3 as a design specification in previous tutorial

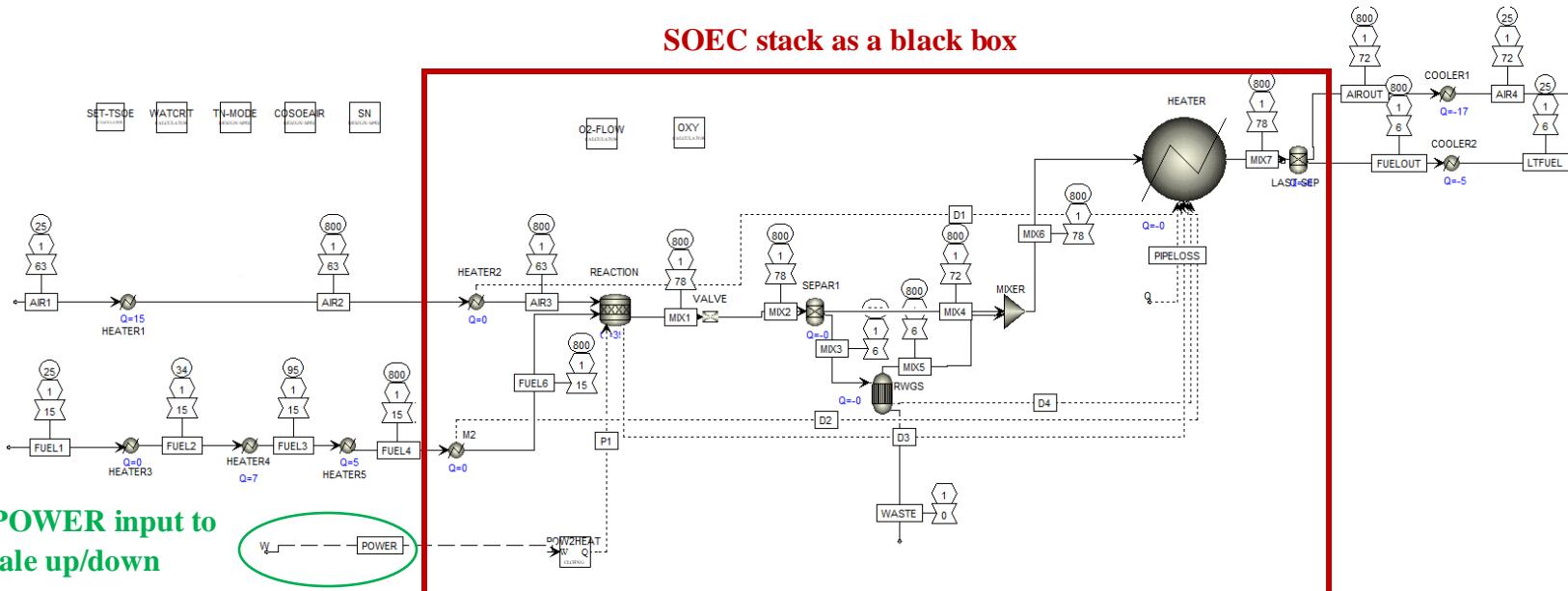
- Operating conditions:

➤ $T = [200 - 300] \text{ }^\circ\text{C}$

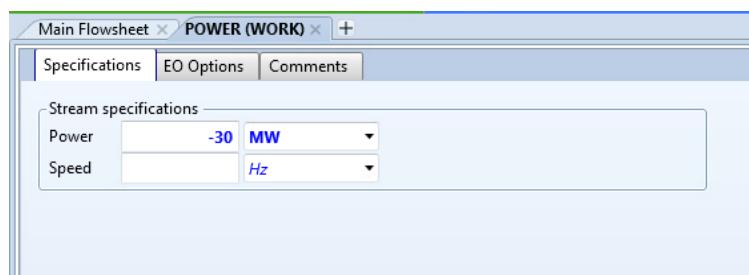
➤ $P = [50 - 100] \text{ bar}$

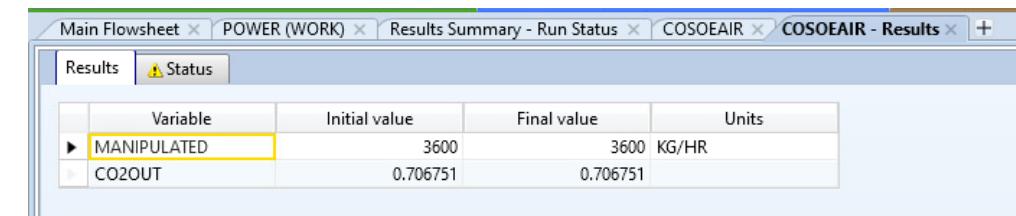
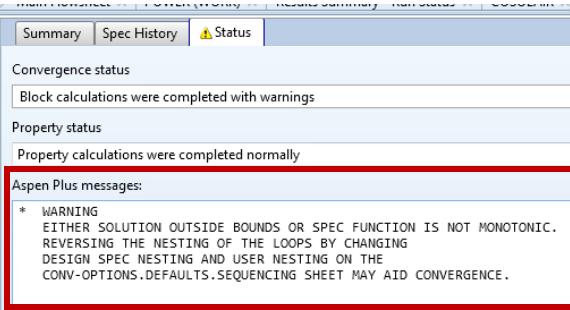
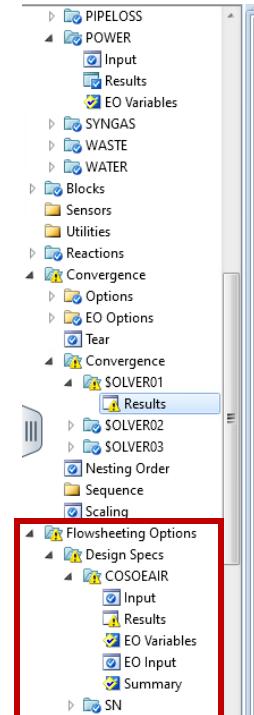
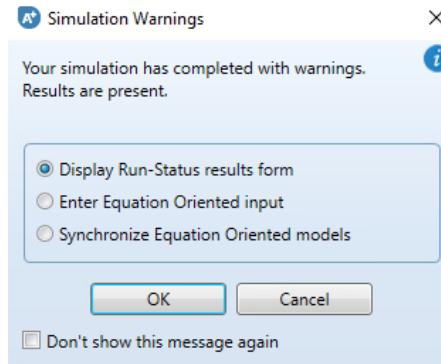
➤ $\text{SN} = 2-3$

SOEC stack as a black box



- SN design specification:
 - Get desired Syngas composition
 - varying H₂O/CO₂ ration at inlet
- POWER stream to scale Syngas flow rate output
 - FUEL1 flow rate changed automatically in OXY



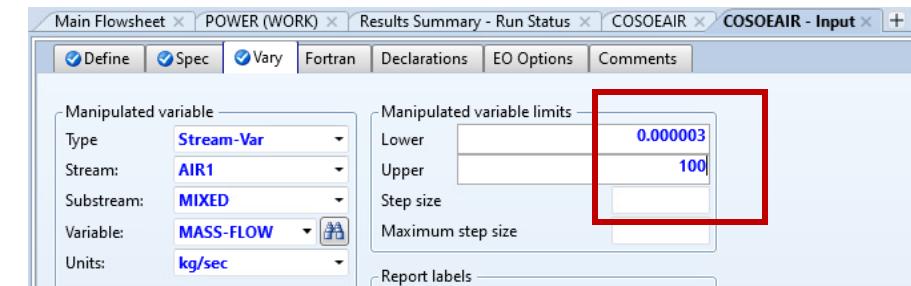


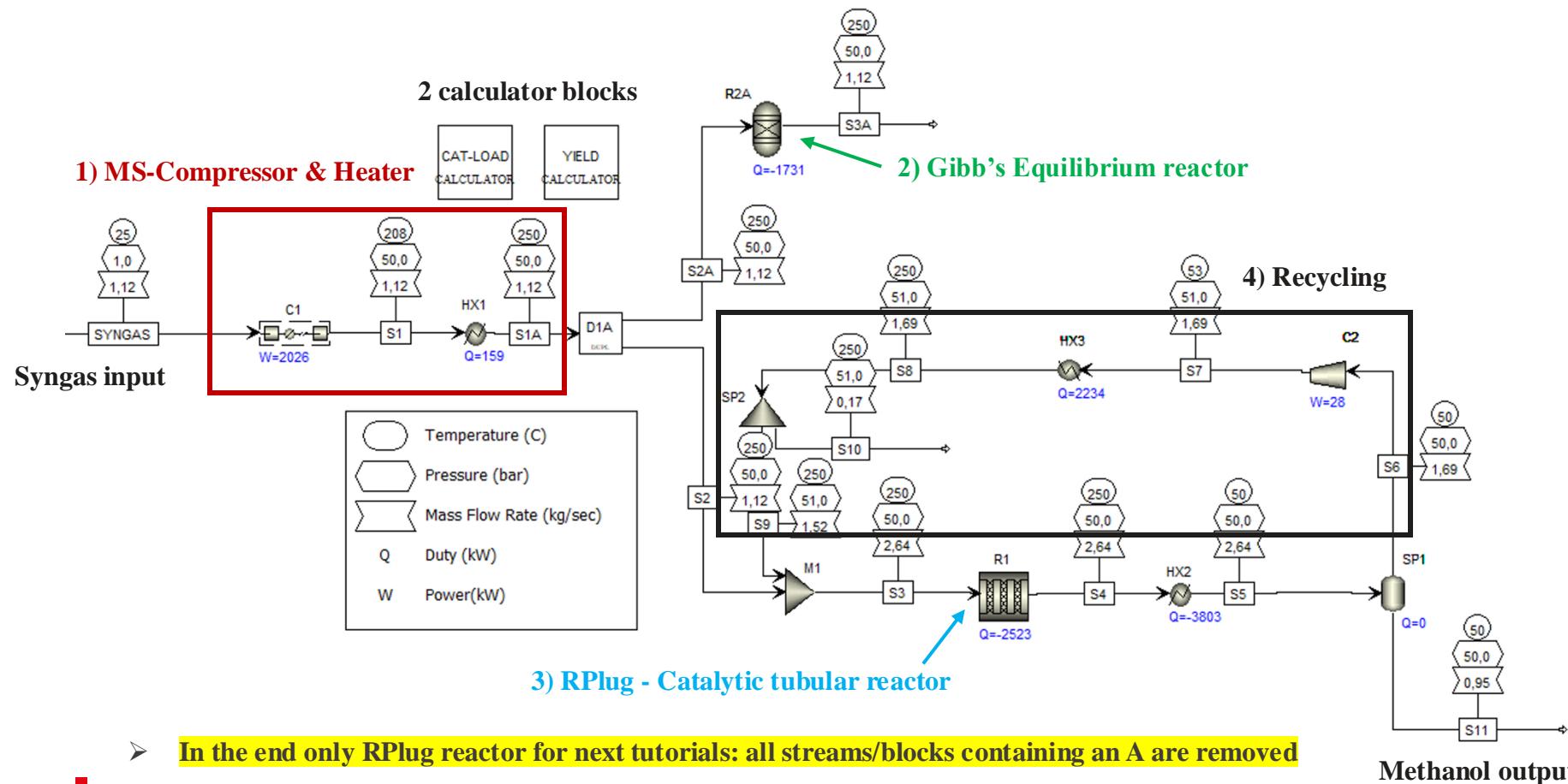
➤ Results completed with warnings ?

- Open control panel
- Read message
- Locate the error
- Try to fix it by yourself

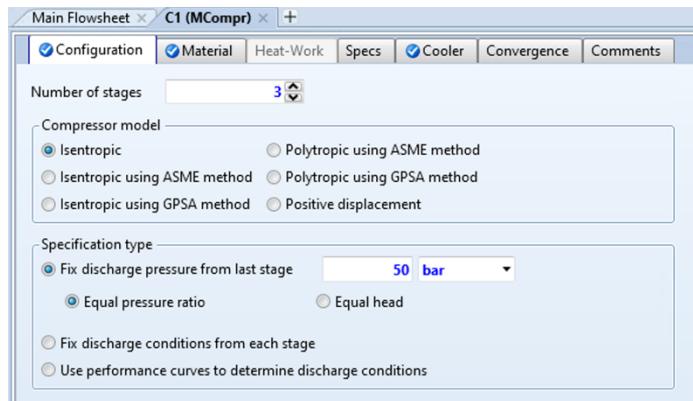
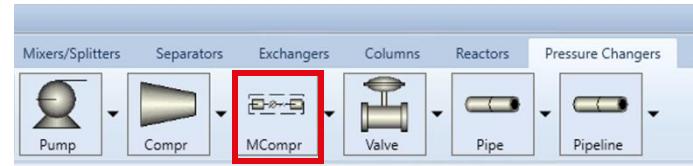
➤ Always analyse results when computed with warnings

➤ Final value is at upper bound
→ Increase bound to 100 kg/s, RESET, RE-RUN





- In the end only RPlug reactor for next tutorials: all streams/blocks containing an A are removed



- Compression ratio < 4 to limit Costs & Temperature issues
- Use 3-stage compression to reach 50 bars

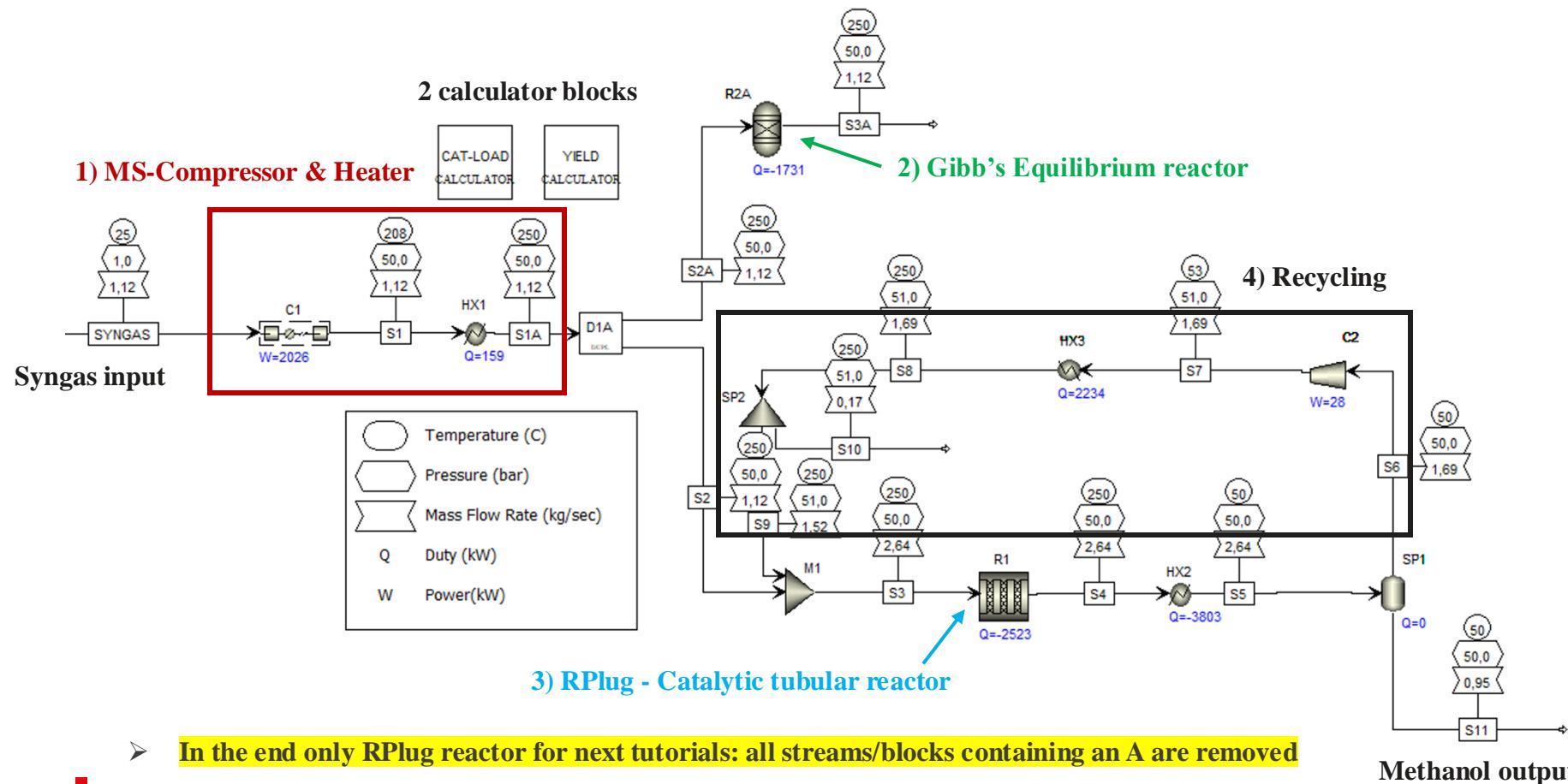
Stage	1	2	3
Specification	Outlet Temp	Outlet Temp	Duty
Value	25	25	0
Units	C	C	kW
Pressure drop	bar	0	0
Utility			

- Intercooling back to 25°C to save electrical power
- No post-compression cooling as high T is desired

Heater

- Add Heater (HX1) to bring Syngas at 250°C
- Pressure of 0 bar means no pressure drop

Flash Type	Temperature	Pressure
Temperature	250	C
Temperature change		C
Degrees of superheating		C
Degrees of subcooling		C
Pressure	0	bar
Duty		kW
Vapor fraction		
Pressure drop correlation parameter		
<input type="checkbox"/> Always calculate pressure drop correlation parameter		
Valid phases	Vapor-Liquid	



RGibb's equilibrium reactor

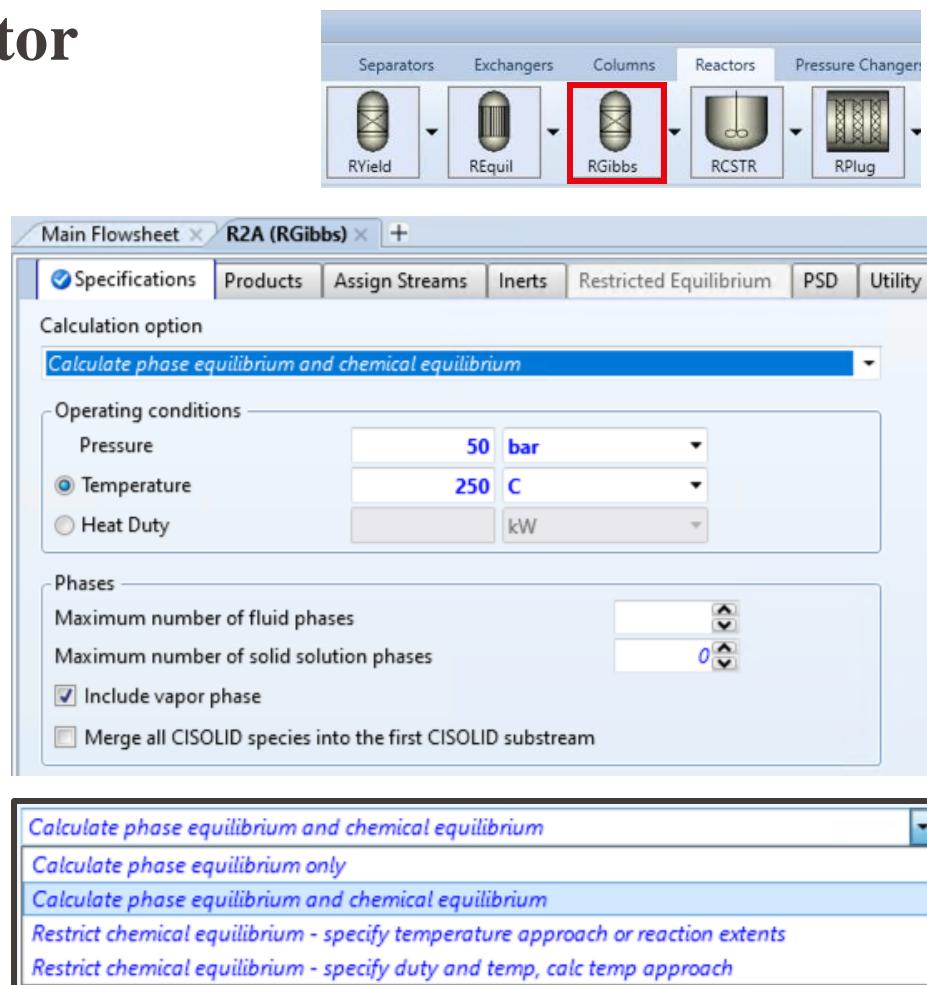
- Add Duplicator block (D1A)
- Add RGibbs reactor model

RGibbs models reactions at equilibrium

- Minimizes the Gibb's free energy of the mixture
- Often over-estimates the production of products for finite reaction time
- Mimics perfect catalyst when “Restrict chemical equilibrium” is selected and products are specified

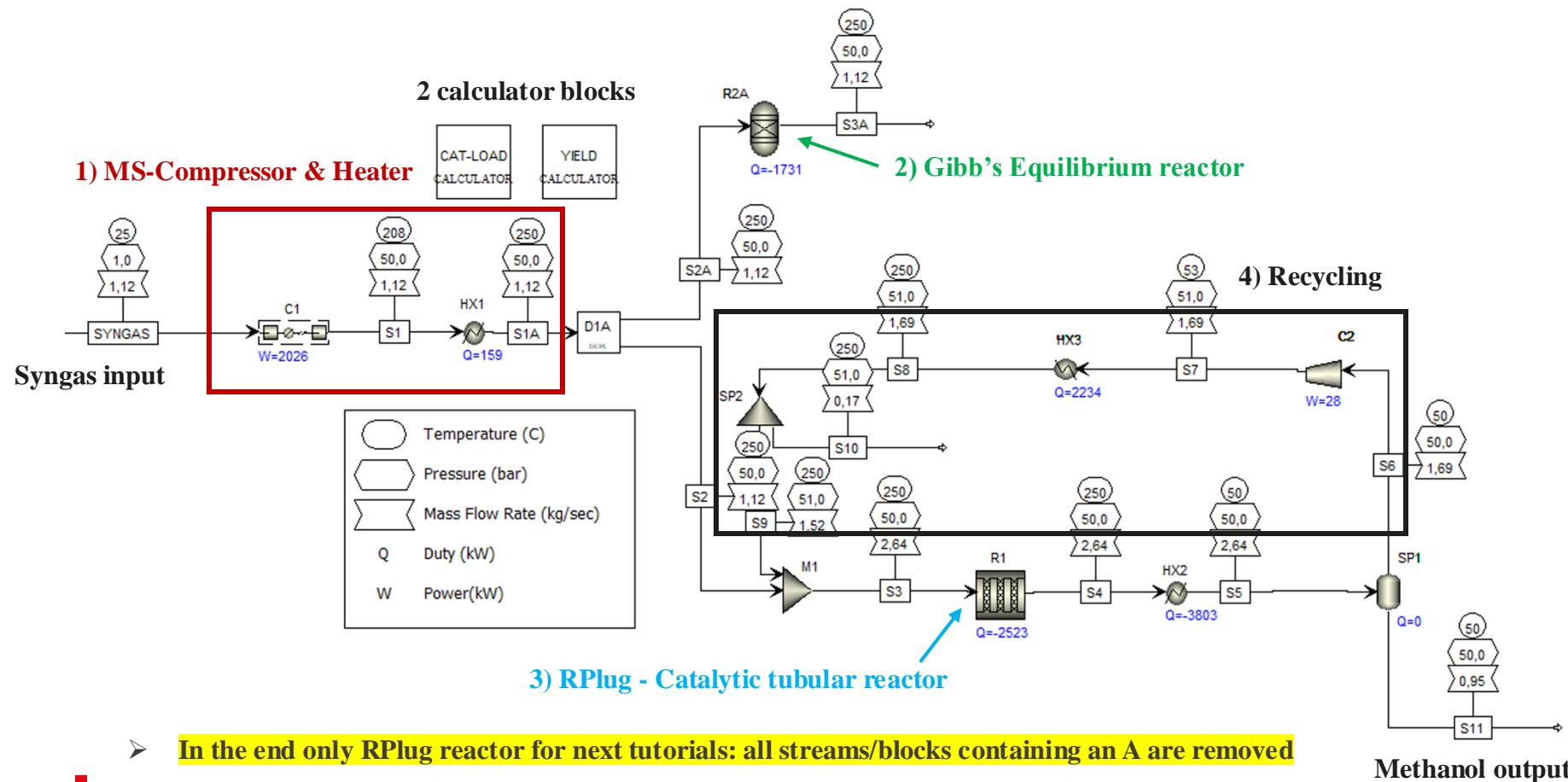
Run the flowsheet and see the results at the outlet

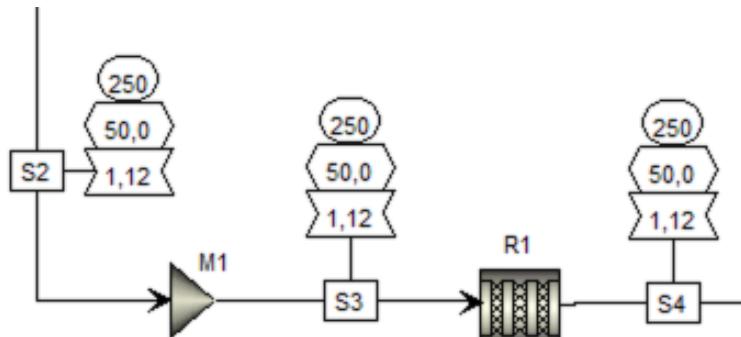
- Mole Fractions		
H2		0.653266
CO		0.0810427
...		...
METHANOL		0.211198



The screenshot shows the Aspen Plus software interface with the following details:

- Top Toolbar:** Separators, Exchangers, Columns, **Reactors** (highlighted with a red box), Pressure Changers.
- Flowsheet Window:**
 - Specifications:** Calculate phase equilibrium and chemical equilibrium.
 - Operating conditions:** Pressure: 50 bar, Temperature: 250 C, Heat Duty: kW.
 - Phases:** Maximum number of fluid phases: 2, Maximum number of solid solution phases: 0, Include vapor phase: checked, Merge all CISOLID species into the first CISOLID substream: unchecked.
 - Calculation Options:** A dropdown menu lists:
 - Calculate phase equilibrium and chemical equilibrium
 - Calculate phase equilibrium only
 - Calculate phase equilibrium and chemical equilibrium
 - Restrict chemical equilibrium - specify temperature approach or reaction extents
 - Restrict chemical equilibrium - specify duty and temp, calc temp approach





For recycling stream
(later)

➤ Langmuir-Hinshelwood kinetic model (LHHW)

- To evaluate the effect of catalyst (Cu/Zn/Al/Zr substrate)
- Extension of modified Arrhenius equation: $r = kT^n \exp(-E_a/RT)$
- **r = (kinetic factor) (driving force expression) (adsorption term)**

RPlug Reactor			
Specifications	Reactor type operating condition	Reactor with specified temperature constant at inlet Temperature	
Configuration	number of tubes Length Diameter Valid phases	Single-tube reactor 6 1 m m m Vapor-Only	
Reactions	New	R-1	LHHW
Catalyst	Catalyst loading Catalyst density Bed voidage	865 1500 0.98	kg kg/m³ -

Only useful with rigorous kinetic data

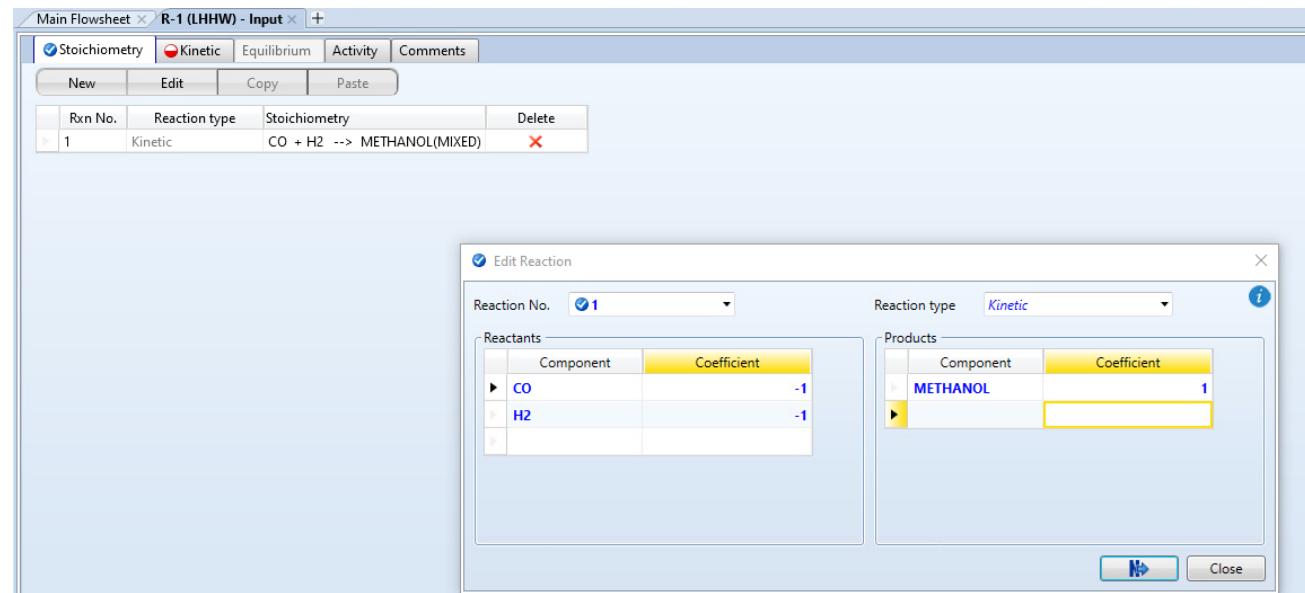
A. Kiss, Novel efficient process for methanol synthesis by CO₂ hydrogenation, 2015,

- Go through first reaction together and then import LHHW reaction set from Moodle (File, import,...)

- 3 main chemical reactions in competition:



- Operating conditions are a priori fulfilled



The image shows a software interface for process simulation. At the top, a tab labeled "R-1 (LHHW) - Input" is active, showing a table of stoichiometric data. The table has columns for Rxn No., Reaction type, Stoichiometry, and Delete. One row is shown: Rxn No. 1, Reaction type Kinetic, Stoichiometry CO + H2 --> METHANOL(MIXED), with a delete button. Below this, a modal dialog titled "Edit Reaction" is open. It shows the reaction number as 1, reaction type as Kinetic, and two tables: "Reactants" and "Products". The "Reactants" table has rows for CO and H2 with coefficients -1. The "Products" table has a row for METHANOL with a coefficient of 1. The "Edit Reaction" dialog has a "Close" button at the bottom right.

Rxn No.	Reaction type	Stoichiometry	Delete
1	Kinetic	CO + H2 --> METHANOL(MIXED)	X

Edit Reaction			
Reaction No.	1	Reaction type	Kinetic
Reactants			
Component	Coefficient		
CO	-1		
H2	-1		
Products			
Component	Coefficient		
METHANOL	1		

$$(\text{kinetic factor}) = kT^n \exp(-E_a/RT)$$

Table 1

Kinetic factor for reactions A, B and C (based on data from [2]) – the units used are [Pa] for fugacity and [mol/g_{catalyst} s] = [kmol/kg_{catalyst} s] for reaction rate.

Reaction	<i>k</i>	<i>n</i>	<i>E_a</i> [J/mol]
A	4.0638×10^{-6} [kmol/kg _{cat} s Pa]	0	11,695
B	9.0421×10^8 [kmol/kg _{cat} s Pa ^{1/2}]	0	112,860
C	1.5188×10^{-33} [kmol/kg _{cat} s Pa]	0	266,010

A. Kiss, Novel efficient process for methanol synthesis by CO₂ hydrogenation, 2015,

Be careful on the units !

They depend on the dimension of the driving force and the adsorption term

Catalytic reaction

$$r = \frac{(\text{kinetic factor})(\text{driving force expression})}{(\text{adsorption term})}$$

Main Flowsheet x R-1 (LHHW) - Input x +

Stoichiometry Kinetic Equilibrium Activity Comments

1) CO + H₂ --> METHANOL(MIXED)

Reacting phase: Vapor Rate basis: Cat (wt)

LHHW kinetic expression

$r = \frac{[\text{Kinetic factor}][\text{Driving force expression}]}{[\text{Adsorption expression}]}$

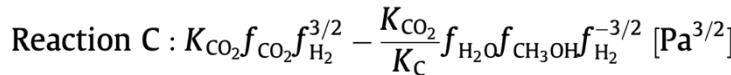
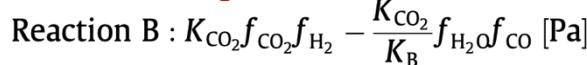
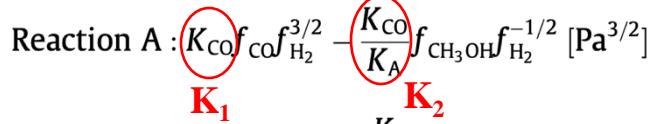
Kinetic factor

If T₀ is specified: Kinetic factor = $k(T/T_0)^n e^{-(E/R)(1/T-1/T_0)}$
 If T₀ is not specified: Kinetic factor = $kT^n e^{-E/RT}$

k: 4.0638e-06
 n: 0
 E: 11695 kJ/kmol
 T₀: C

Solids
 Driving Force
 Adsorption

The driving force expressions are as follows:



A. Kiss, Novel efficient process for methanol synthesis by CO₂ hydrogenation, 2015,

Concentration exponents								
Reactions	Term1			Term 2				
A)	CO	H ₂	CH ₃ OH	CO	H ₂	CH ₃ OH		
	1	1,5	0	0	-0,5	1		
B)	CO ₂	H ₂	CO	H ₂ O	CO ₂	H ₂	CO	H ₂ O
	1	1	0	0	0	0	1	1
C)	CO ₂	H ₂	CH ₃ OH	H ₂ O	CO	H ₂	CH ₃ OH	H ₂ O
	1	1,5	0	0	0	-1,5	1	1

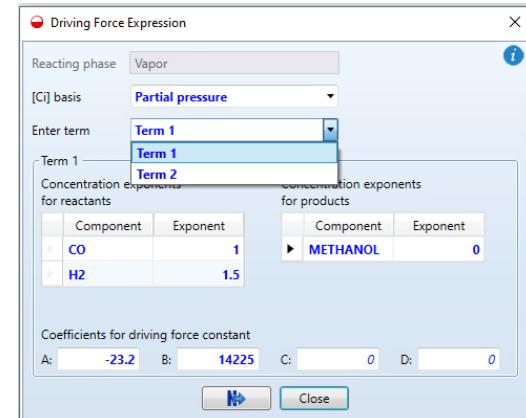
$$\ln(K) = A + \frac{B}{T}$$

Table 3

Constants for driving force (from [2]) using the format for Aspen Plus.

Reaction	K_1		K_2	
	A	B	A	B
A	-23.20	14,225	28.895	2385
B	-22.48	9777	-28.12	15,062
C	-22.48	9777	23.974	3222

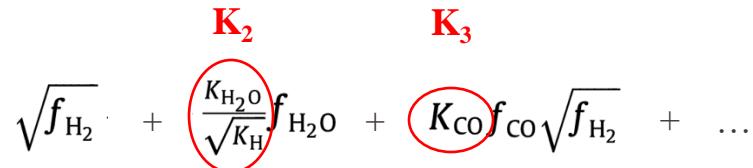
A. Kiss, Novel efficient process for methanol synthesis by CO₂ hydrogenation, 2015



Ideal gas law → partial pressure to express fugacity

(adsorption term) = $f(T, P, C, \text{catalyst})$

Same for all reactions, exponent = 1



Catalytic reaction

$$r = \frac{(\text{kinetic factor}) (\text{driving force expression})}{(\text{adsorption term})}$$

$$\ln(K_i) = A_i + \frac{Bi}{T}$$

Component	Term no. 1	Term no. 2	Term no. 3	Term no. 4	Term no. 5	Term no. 6
H2	0,5	0	0,5	0	0,5	0
H2O	0	1	0	1	0	1
CO	0	0	1	1	0	0
CO2	0	0	0	0	1	1
Term no.	1	2	3	4	5	6
Coefficient A	0	-26,1568	-23,2006	-49,3574	-22,4827	-48,6395
Coefficient B	0	13842	14225	28067	9777	23619
Coefficient C	0	0	0	0	0	0
Coefficient D	0	0	0	0	0	0

Temperature

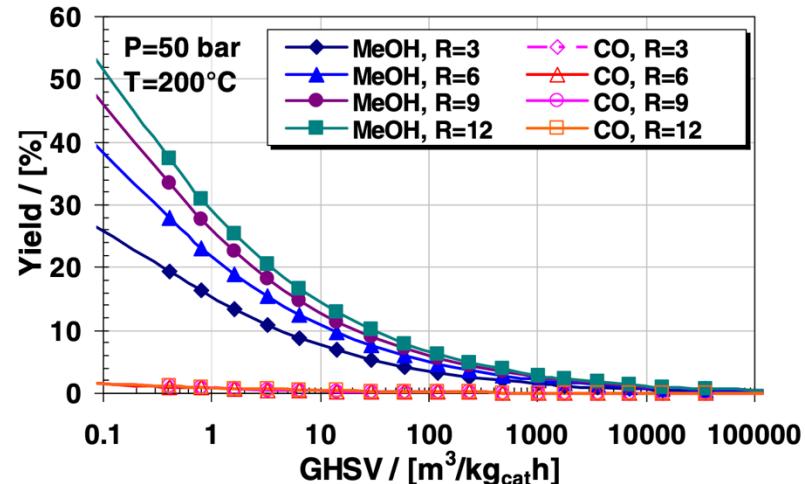
- Impact Equilibrium constant of the reaction
 - For $\Delta H < 0$, $T \uparrow \Rightarrow K_{eq} \downarrow$
 - For $\Delta H > 0$, $T \uparrow \Rightarrow K_{eq} \uparrow$
- Impact kinetics (increase probability of collisions)
 - $T \uparrow \Rightarrow r \uparrow$

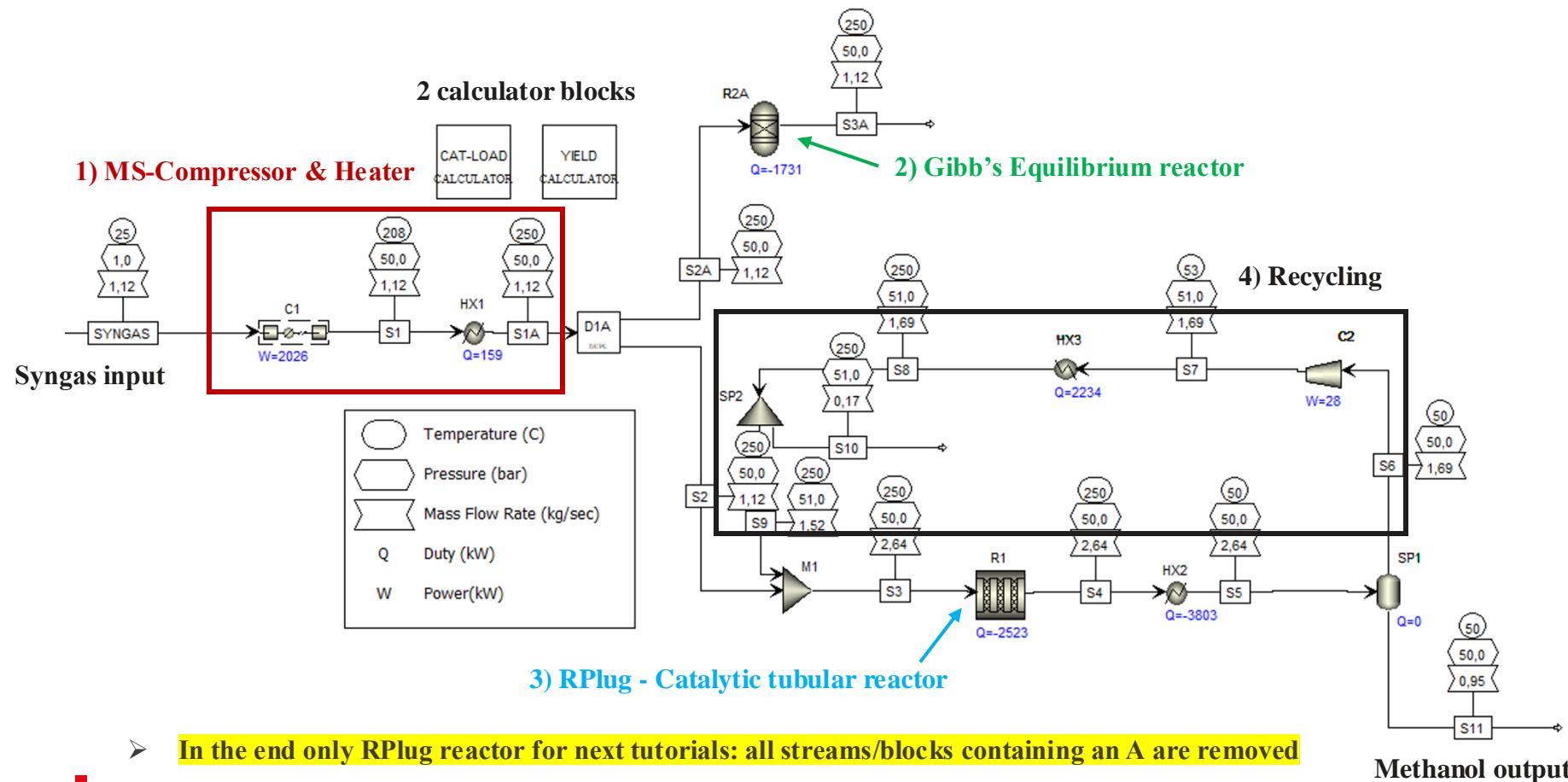
Catalyst Loading

- How much reactants are present for a given amount of catalyst
- $GHSV = \frac{V_{flow}}{m_{cat}}$, where:
 - GHSV is the gas hourly space velocity [$m^3/(kg \cdot h)$]
 - V_{flow} is the volumetric flow rate [m^3/h]
 - m_{cat} is the mass of catalyst present in the reactor [kg]
- $GHSV \uparrow \Rightarrow \text{YIELD} \downarrow$

Pressure

- Impact Equilibrium constant of the reaction
 - Mole decreasing reactions favored at high P
- Impact kinetics (increase probability of collisions)
 - $P \uparrow \Rightarrow r \uparrow$





- In the end only RPlug reactor for next tutorials: all streams/blocks containing an A are removed

Methanol output

Create Calculator blocks (YIELD & CAT-LOAD)

- Make sure streams and blocks are correctly named (cf. slide 8)

Main Flowsheet × YIELD × +

Define Calculate Sequence Tears Stream Flash Comments

Active

Sampled variables (drag and drop variables from form to the grid below)

Variable	Information flow	Definition
FCOIN	Import variable	Mole-Flow Stream=S2 Substream=MIXED Component=CO Units=mol/sec
FCO2IN	Import variable	Mole-Flow Stream=S2 Substream=MIXED Component=CO2 Units=mol/sec
FMEOHOUT	Import variable	Mole-Flow Stream=S11 Substream=MIXED Component=METHANOL Units=mol/sec
YIELDKIN	Export variable	Parameter Parameter no.=4002

Main Flowsheet × YIELD × +

Define Calculate Sequence Tears Stream Flash

Calculation method

Fortran Excel Fortran Declaration

Enter executable Fortran statements

```
YIELDKIN = FMEOHOUT/ (FCOIN + FCO2IN)*100
```

Main Flowsheet × CAT-LOAD × +

Define Calculate Sequence Tears Stream Flash Comments

Active

Sampled variables (drag and drop variables from form to the grid below)

Variable	Information flow	Definition
MFLOW	Import variable	Stream-Var Stream=S3 Substream=MIXED Variable=MASS-FLOW Units=kg/hr
GHSV	Import variable	Parameter Parameter no.=4001 Initial value=10
DENS	Import variable	Stream-Prop Stream=S3 Prop-Set=RHO Units=kg/cum
MCAT	Export variable	Block-Var Block=R1 Variable=CATWT Sentence=PARAM Units=kg
LREAC	Export variable	Block-Var Block=R1 Variable=LENGTH Sentence=PARAM Units=meter
VREAC	Export variable	Parameter Parameter no.=4003
DREAC	Import variable	Block-Var Block=R1 Variable=DIAM Sentence=PARAM Units=meter

Define Calculate Sequence Tears Stream F

Calculation method

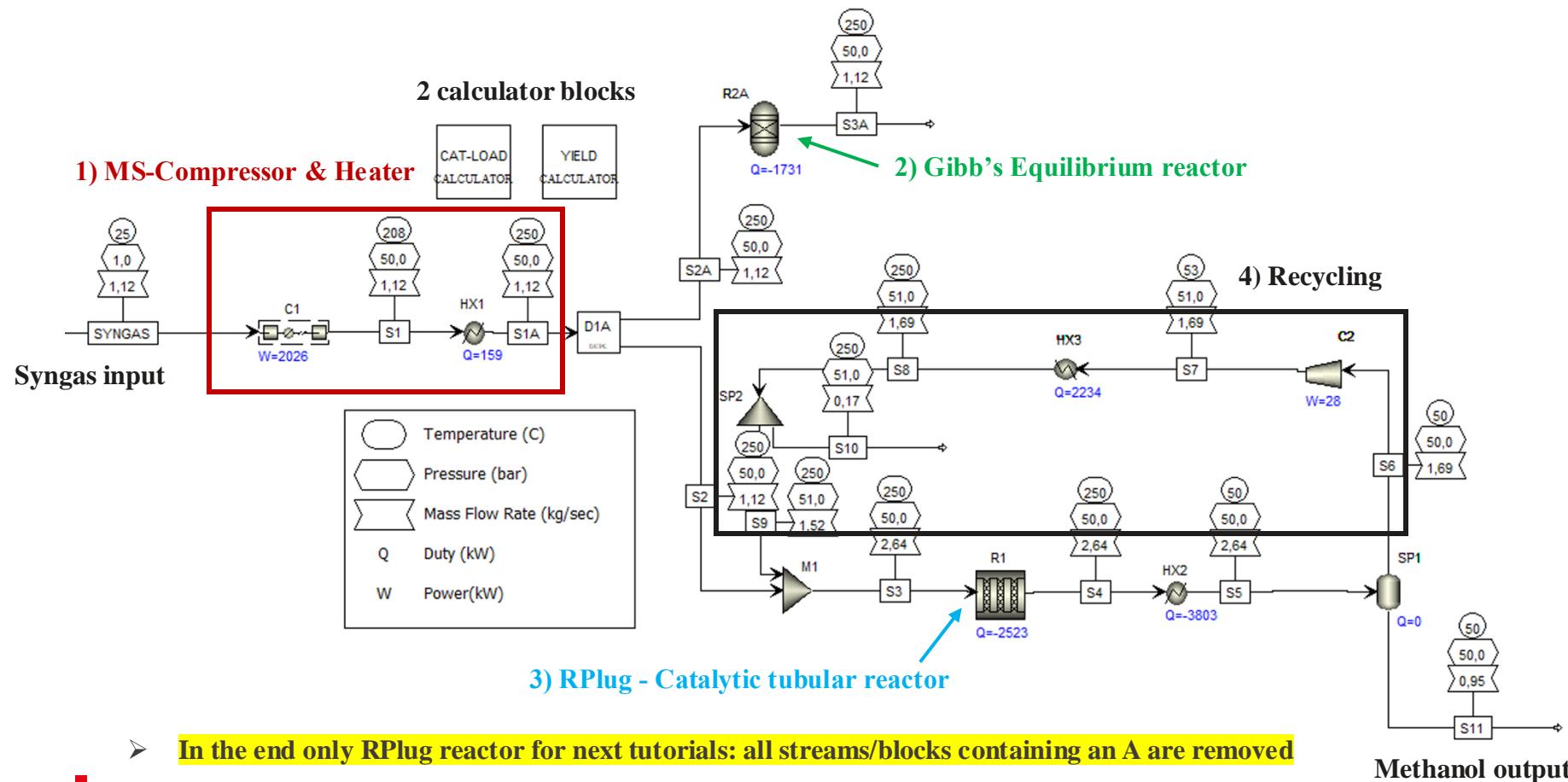
Fortran Excel Neural Network

Enter executable Fortran statements

```
VFLOW = MFLOW/DENS
MCAT = VFLOW/GHSV
CATDENS = 1500
BEDVOID = 0.98

VREAC = MCAT/CATDENS/ (1-BEDVOID)
LREAC = VREAC*4/ (3.14*DREAC*DREAC)
```

First add this in Property Sets

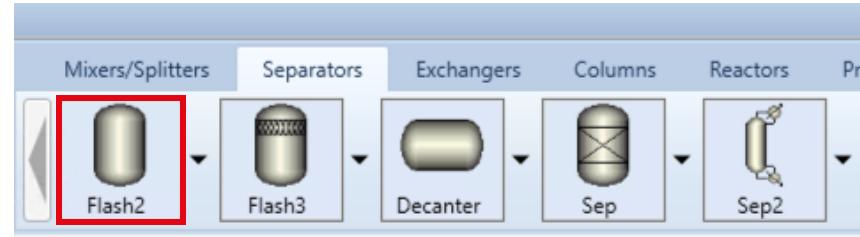


- In the end only RPlug reactor for next tutorials: all streams/blocks containing an A are removed

EPFL Isolate produced MeOH – Cooler & Flash Separator

22

- Cool down to 50°C → MeOH condensation
- Add an adiabatic Flash Separator
- Make sure vapor and liquid are valid phases
- Recycle unreacted Syngas



Main Flowsheet HX2 (Heater) +

Specifications Flash Options Utility Comments

Flash specifications

Flash Type Temperature Pressure

Temperature	50	C
Temperature change		C
Degrees of superheating		C
Degrees of subcooling		C

Pressure Duty

Pressure	0	bar
Duty		kW

Vapor fraction

Main Flowsheet SP1 (Flash2) +

Specifications Flash Options Entrainment PSD Utility Co

Flash specifications

Flash Type Pressure Duty

Temperature		C
Pressure	0	bar
Duty	0	kW

Vapor fraction

Valid phases Vapor-Liquid

Recycling stream

- Needs to be at higher pressure (+1 bar) to be reinjected
- Needs to be reheated up to 250°C

Fix convergence issue

- Strategies for troubleshooting convergence issues

1. View Control Panel and localize error
2. Increase number of iterations (to 100 or even 200 loops)
3. Change tolerance (use with caution as it may affect the overall mass/energy balance)
4. Add a purge (max. 5-10%)

The image displays three windows from a process simulation software:

- Main Flowsheet x C2 (Compr) x**: Shows the 'Specifications' tab for a compressor. The 'Model' is set to 'Compressor' and 'Type' to 'Isentropic'. Under 'Outlet specification', 'Pressure increase' is selected with a value of 1 bar. The 'Efficiencies' section shows 'Isentropic' as the selected type.
- Main Flowsheet x HX3 (Heater) x**: Shows the 'Specifications' tab for a heater. The 'Flash Type' is set to 'Temperature'. The 'Temperature' section shows a value of 250 °C. The 'Pressure' section shows a value of 0 bar. The 'Valid phases' section is set to 'Vapor-Liquid'.
- Main Flowsheet x YIELD - Results x**: Shows a table of results. The table has columns for 'Variable', 'Value read', 'Value written', and 'Units'. The rows are:

Variable	Value read	Value written	Units
FCOIN	24.6795		MOL/SEC
FCO2IN	4.67813		MOL/SEC
FMOHOUT	26.7784		MOL/SEC
YIELDKIN	51.4096	91.2144	

 The row for 'YIELDKIN' is highlighted with a red border. The bottom of the window says 'Unit model'.

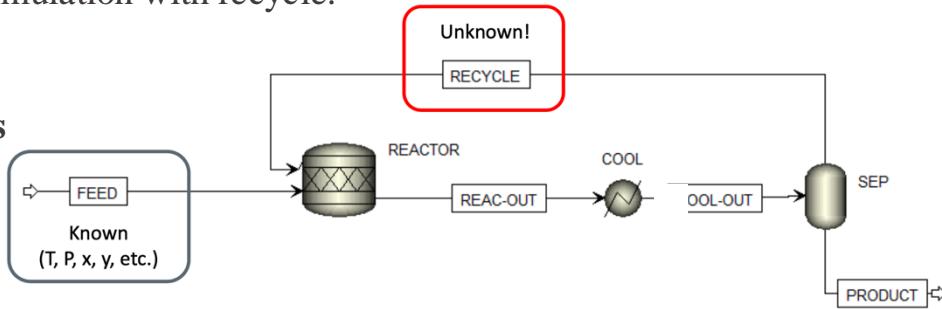
■ Huge jump in MeOH yield with purge 10% !!!

- Aspen plus uses a sequential modular technique to solve a simulation
 - Each unit operation block is solved in a certain sequence, called “calculation sequence”
 - Need to know the feed stream
 - Aspen Plus uses an iterative process to solve a simulation with recycle:

- Recycling streams may lead to mass balance issues
 - non-converging flowsheet

- Strategies for troubleshooting convergence issues

1. View Control Panel and localize error
2. Change tolerance (use with caution as it may affect the overall mass/energy balance)
3. Increase number of iterations (to 100 or even 200 loops)
4. Add a transfer block (Changes the way Aspen Plus treats the problem)
5. Add a purge (max. 5-10%)



- The Shunli plant in Anyang, China
 $\approx 500'000$ tons CO₂ into MeOH per year

New Scientist, Michel Le Page, Nov. 2022

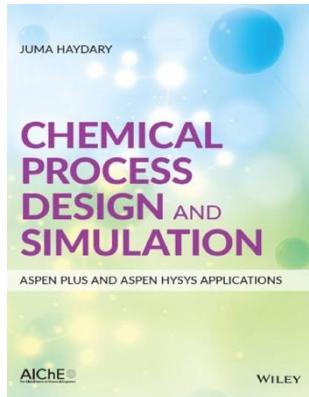
Conclusions and outlook



- ✓ Differentiate the several reactor models
- ✓ Select the correct model based on provided information (literature, available data,...)
- ✓ Handle reactions in Aspen Plus
- ✓ Understand and differentiate equilibrium from kinetic reactions
- ✓ Understand the impact of operating conditions on kinetic reactions
- ✓ Perform pre-sizing of a reactor based on catalyst loading
- ✓ Perform sensitivity analysis
- ✓ Plot and visualize the results
- ✓ Recognize tear stream and find strategies for convergence issues

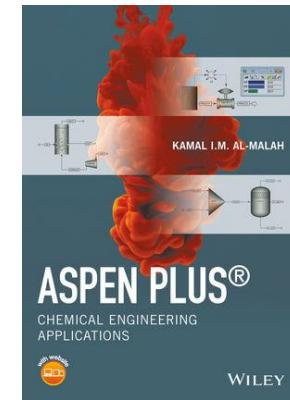
Useful resources - Literature

- Aspen Help Window
- YouTube Aspen tutorials on specific units
- Examples from textbooks



[Chemical Process Design and Simulation: Aspen Plus and Aspen Hysys Applications](#)

[Aspen Plus®: Chemical Engineering Applications](#)



- Aspen simulations provided on Moodle
- A. Kiss et al., Novel efficient process for methanol synthesis by CO₂ hydrogenation, 2015
- M. Domingos et al., Techno-economic and environmental analysis of methanol and dimethyl ether production from syngas in a kraft pulp process, 2021
- William L. Luyben, Design and Control of a Methanol Reactor/Column Process, 2010