Reactors in Aspen Plus® MeOH -Synthesis

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Process Development – ChE459

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Course Outline – Reactors for MeOH Synthesis

1. **General aspects on reactor models in Aspen Plus**

2. **MeOH synthesis reactions**
   - Stoichiometric considerations
   - Operating conditions

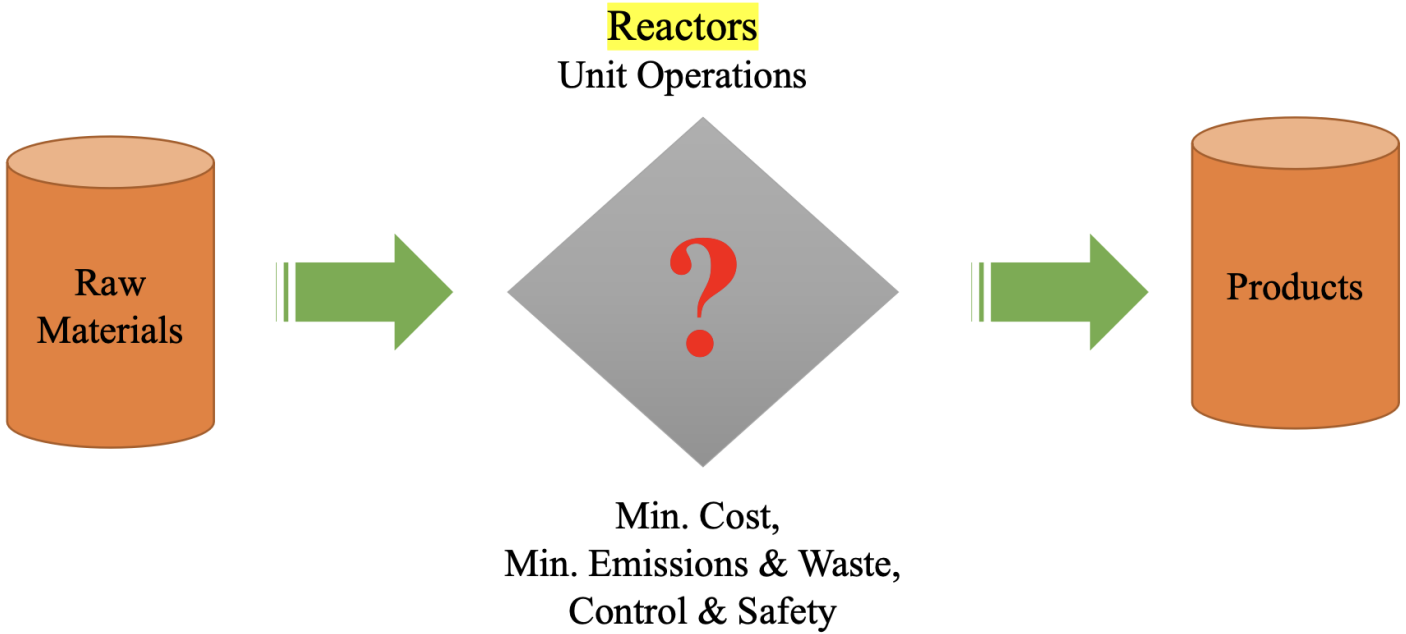
3. **Tutorial in Aspen Plus**
   - Scaling-up: Co-electrolyzer
   - Multi-stage compression (with intercooling)
   - RGibb's reactor model (Equilibrium)
   - Rplug reactor model (Kinetic)

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

Chemical reactors to model … chemical reactions

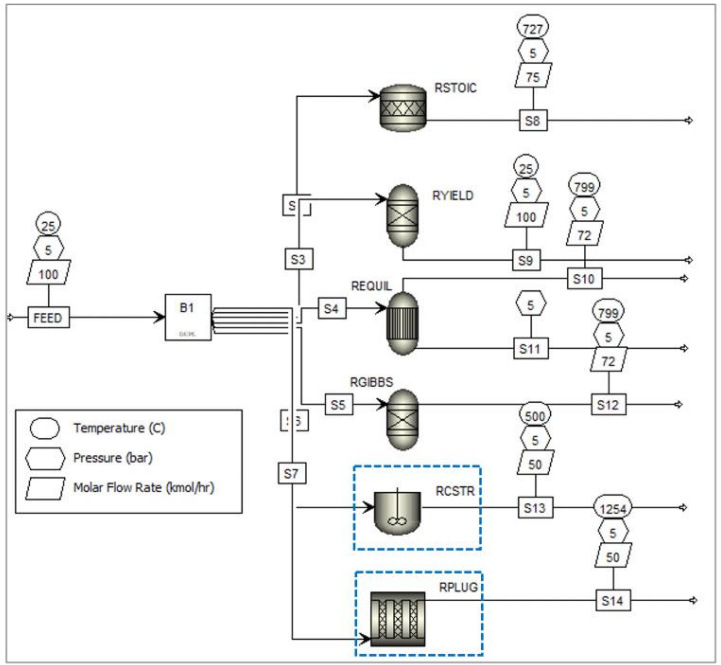


- **Decide the type of reactor**
  Batch, CSTR (continuous stirrer tank), PFR (plug flow), PBR (packed bed), etc,

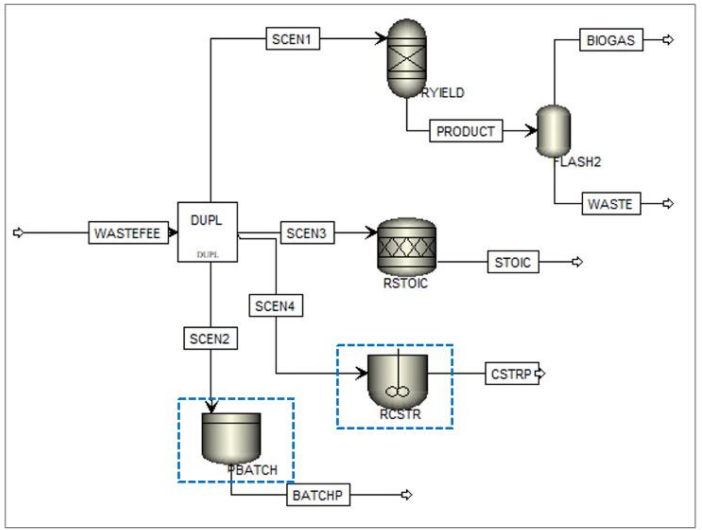
- **Find the information for modelling of reactor**
  Reaction stoichiometry, reaction conversion, reaction yield, reaction kinetics, isothermal/adiabatic

Many different reactor models

C2H4 + H2 <=> C2H6



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

MeOH Synthesis – Co_x hydrogenation reactions

- **3 main chemical reactions in competition:**

A. $CO + 2H_2 \rightleftarrows CH_3OH$	$\Delta H = -90.8$ kJ/mol
B. $CO_2 + H_2 \rightleftarrows CO + H_2O$	$\Delta H = +41.2$ kJ/mol, **Reverse WGS Reaction**
C. $CO_2 + 3H_2 \rightleftarrows CH_3OH + H_2O$	$\Delta H = -49.16$ kJ/mol

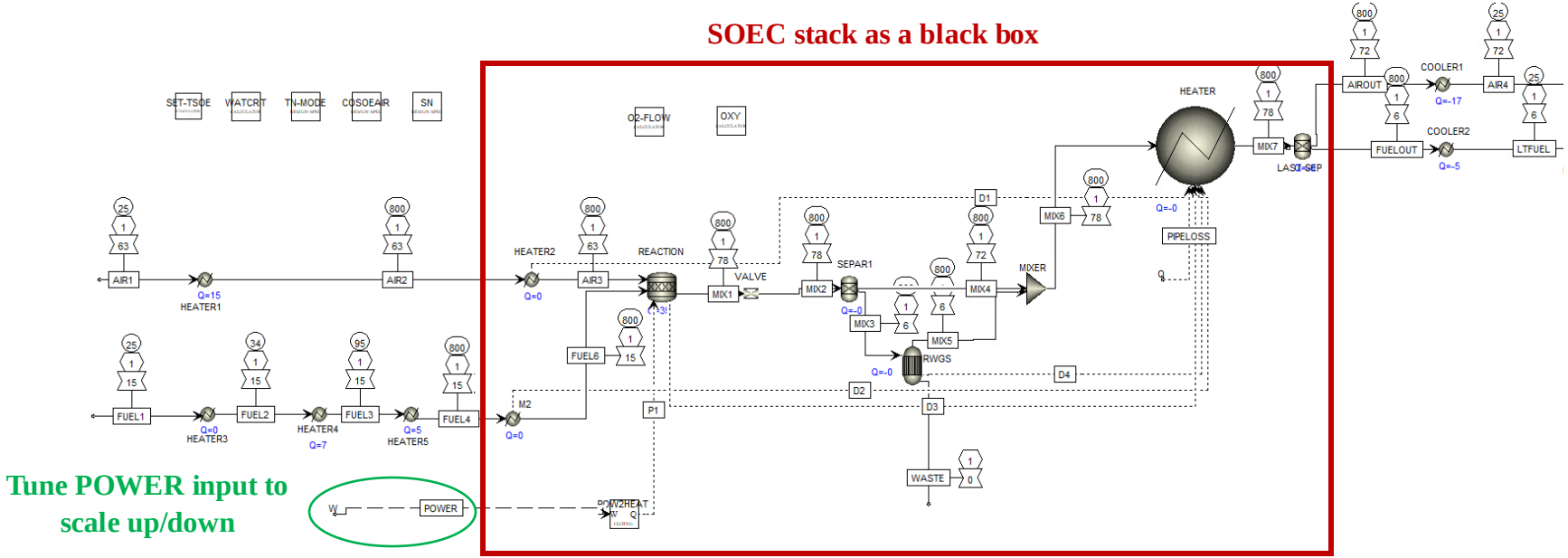
- **The Stoichiometric number (SN) of the feed must be ≥ 2 for good conversion**

$$SN = \frac{y_{H_2} - y_{CO_2}}{y_{CO} + y_{CO_2}}$$

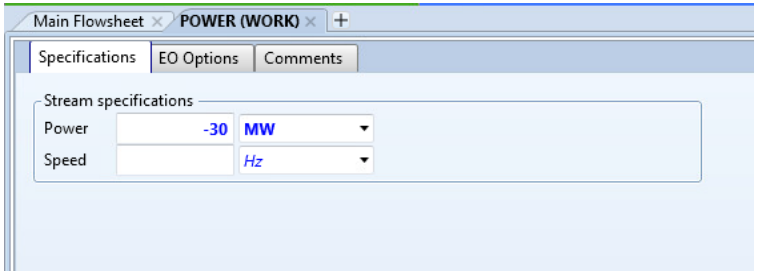
SN = 3 as a design specification in previous tutorial

- **Operating conditions:**
  - **T = [200 – 300] °C**
  - **P = [50 – 100] bar**
  - **SN = 2-3**

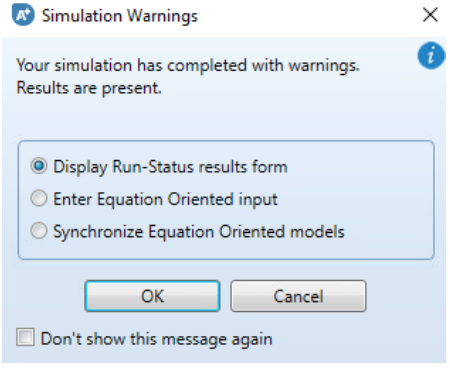
Co-Electrolyzer: Scaling up to achieve ~1 kg/s Syngas output

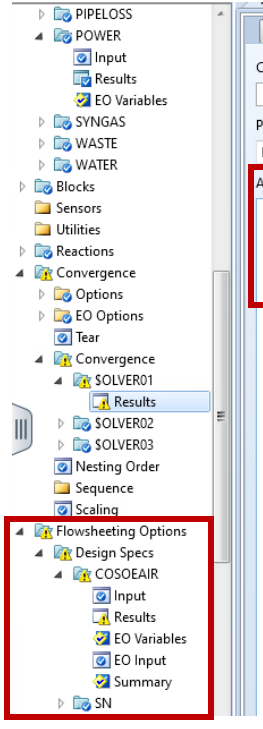


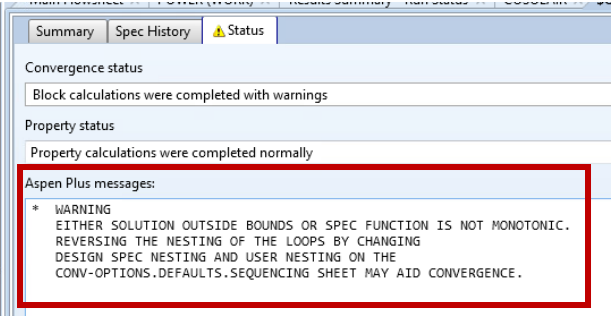
- SN design specification:
  - Get desired Syngas composition
  - varying H2O/CO2 ration at inlet
- POWER stream to scale Syngas flow rate output
  - FUEL1 flow rate changed automatically in OXY

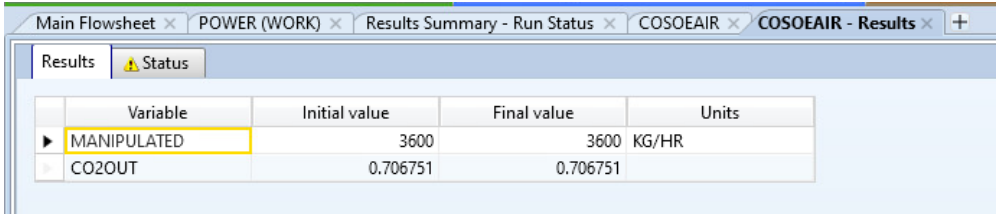


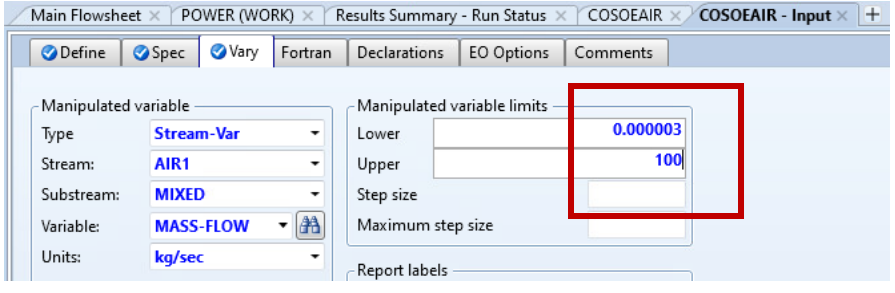
Adapt Design specification: COSOEAIR







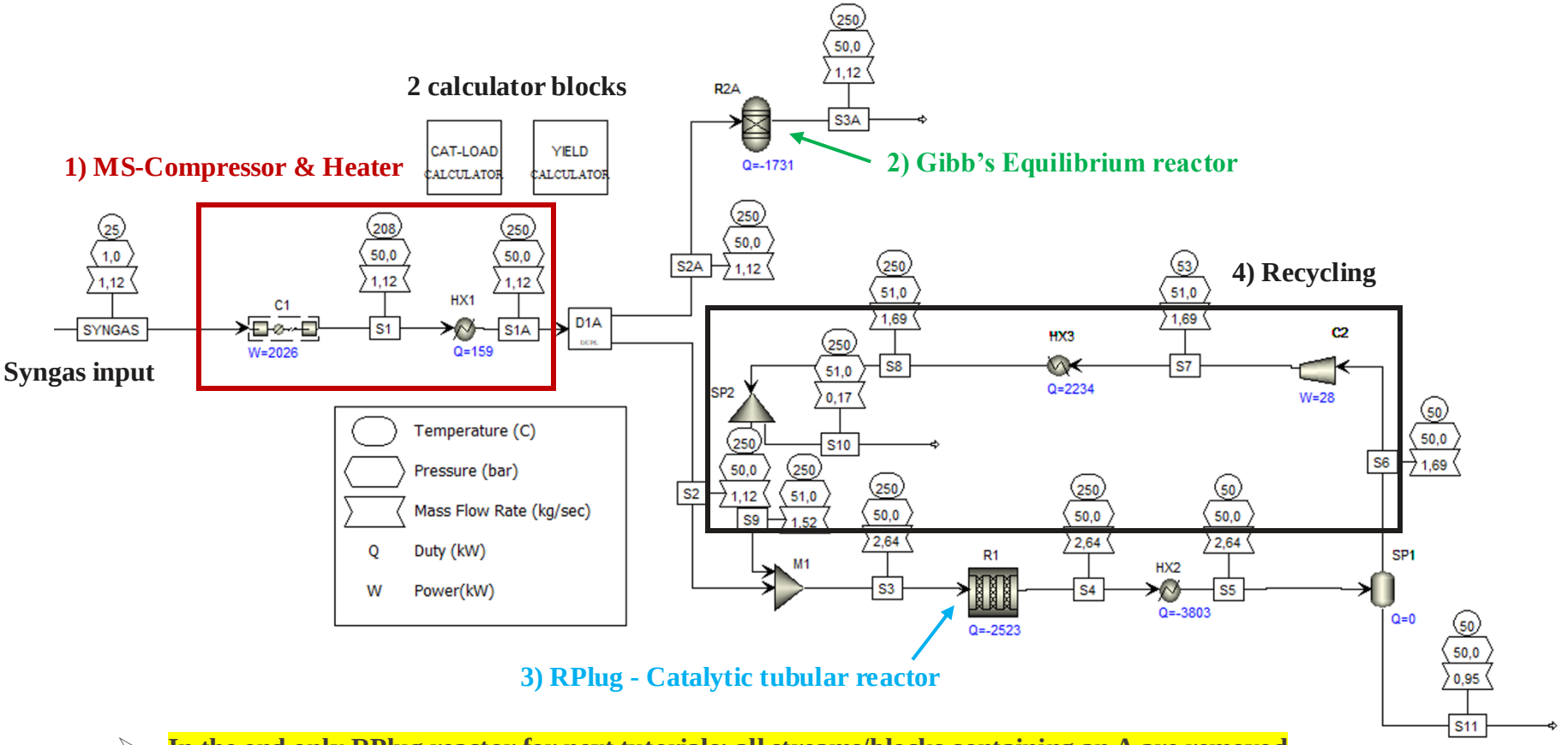




- Results completed with warnings ?
  - Open control panel
  - Read message
  - Locate the error
  - Try to fix it by yourself
- **Always analyse results when computed with warnings**

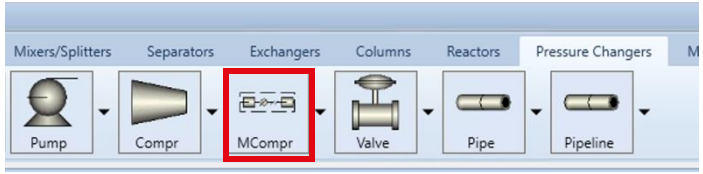
- Final value is at upper bound
  - → Increase bound to 100 kg/s, RESET, RE-RUN

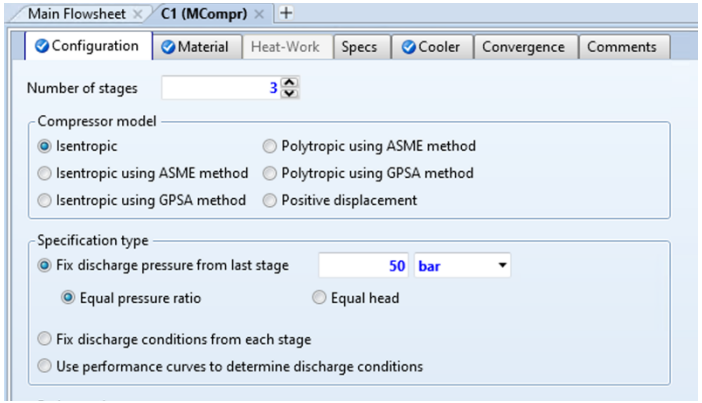
Overview of Aspen Flowsheet



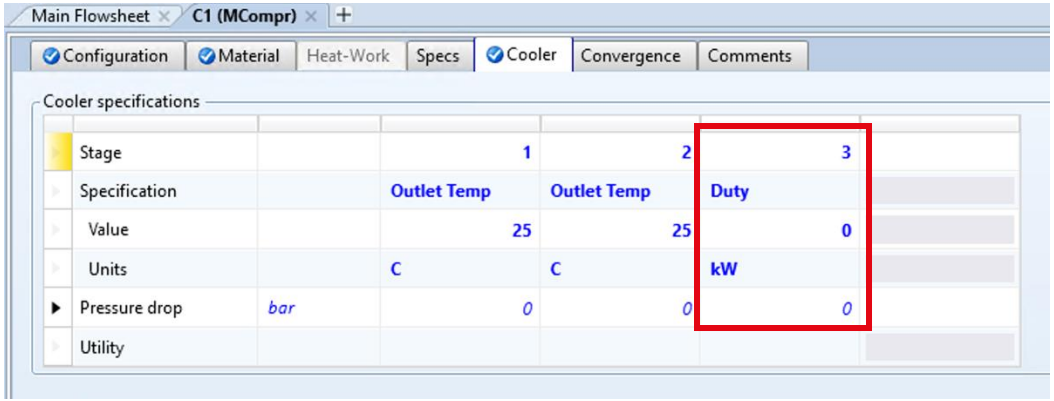
- **In the end only RPlug reactor for next tutorials: all streams/blocks containing an A are removed**

Multistage Compressor with intercooling





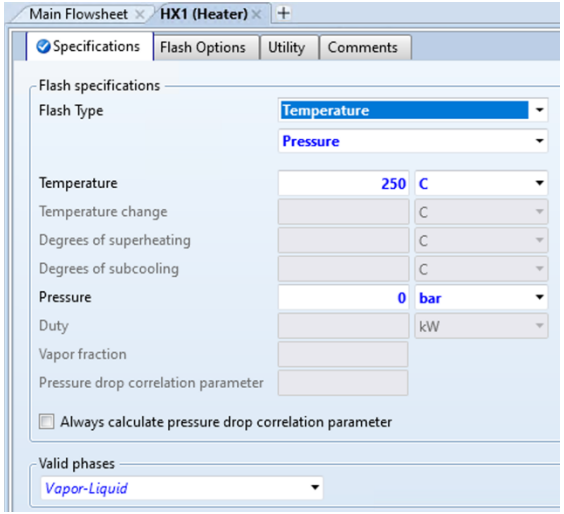
- Compression ratio < 4 to limit Costs & Temperature issues
- Use 3-stage compression to reach 50 bars



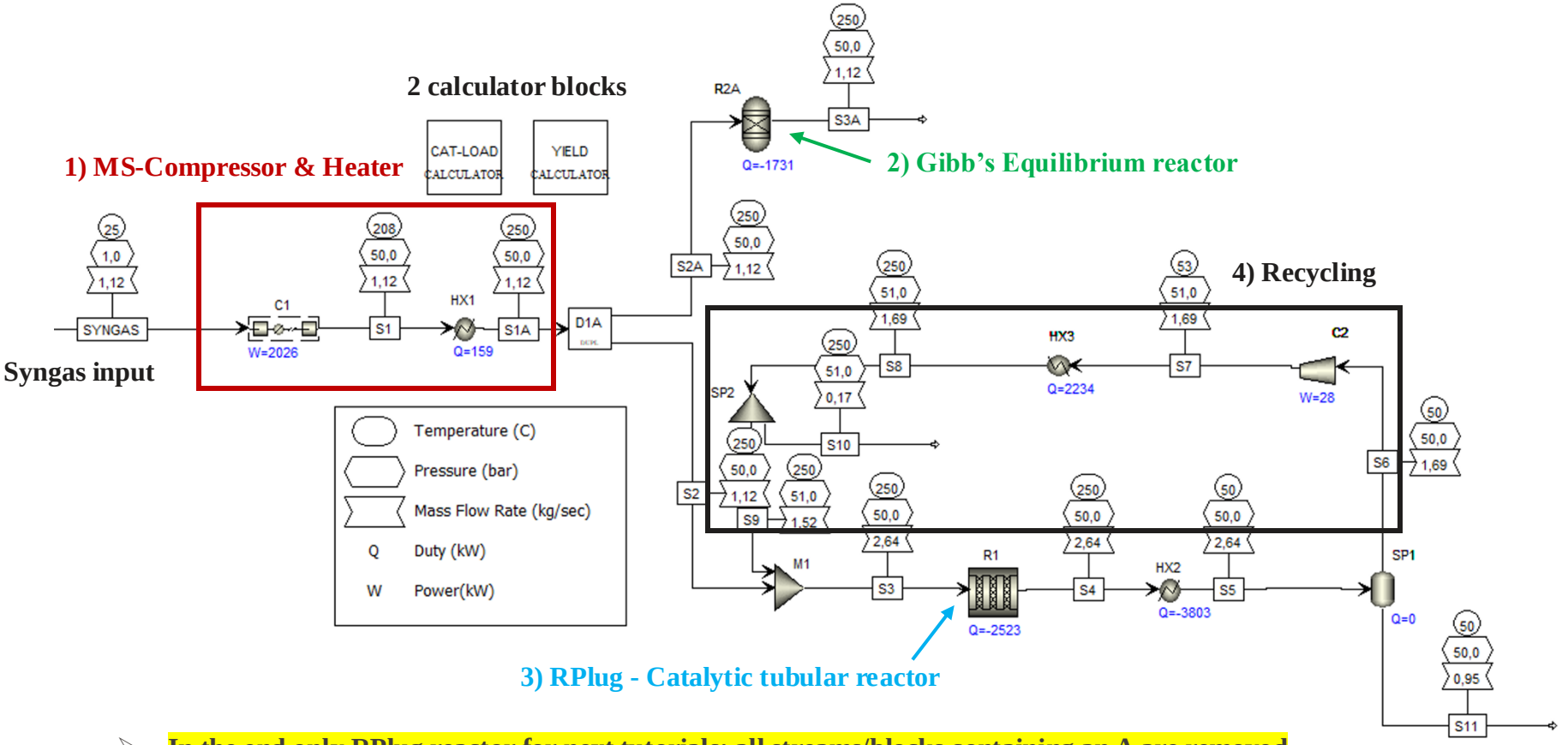
- Intercooling back to 25°C to save electrical power
- No post-compression cooling as high T is desired

Heater

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



Overview of Aspen Flowsheet



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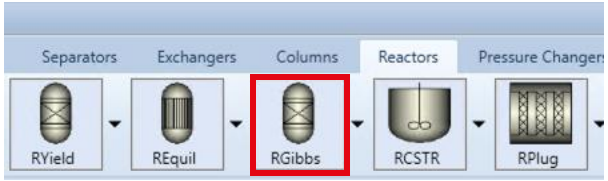
RGibb's equilibrium reactor



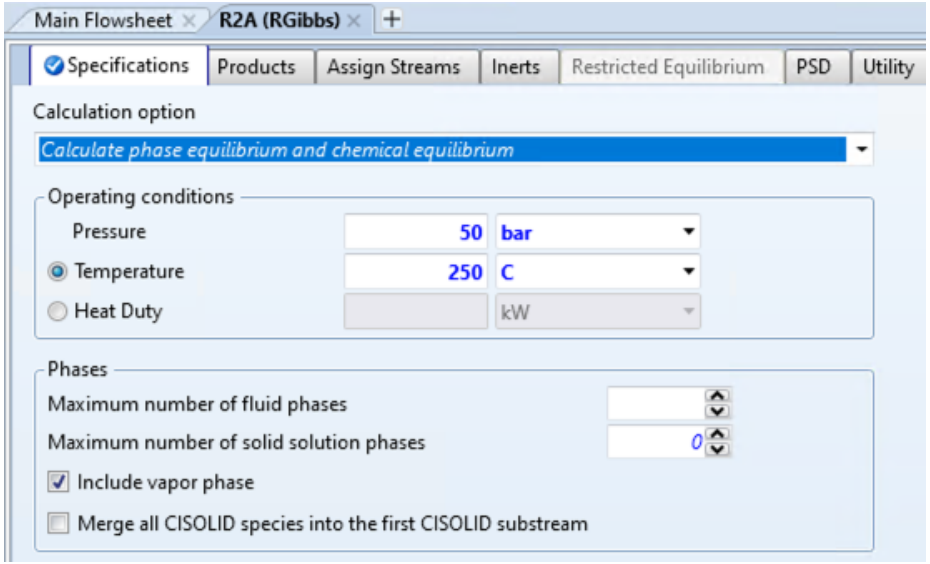
- Add Duplicator block (D1A)
- Add RGibbs reactor model

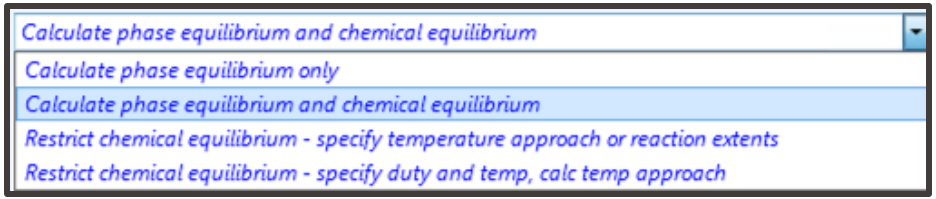
RGibbs models reactions at equilibrium

- 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

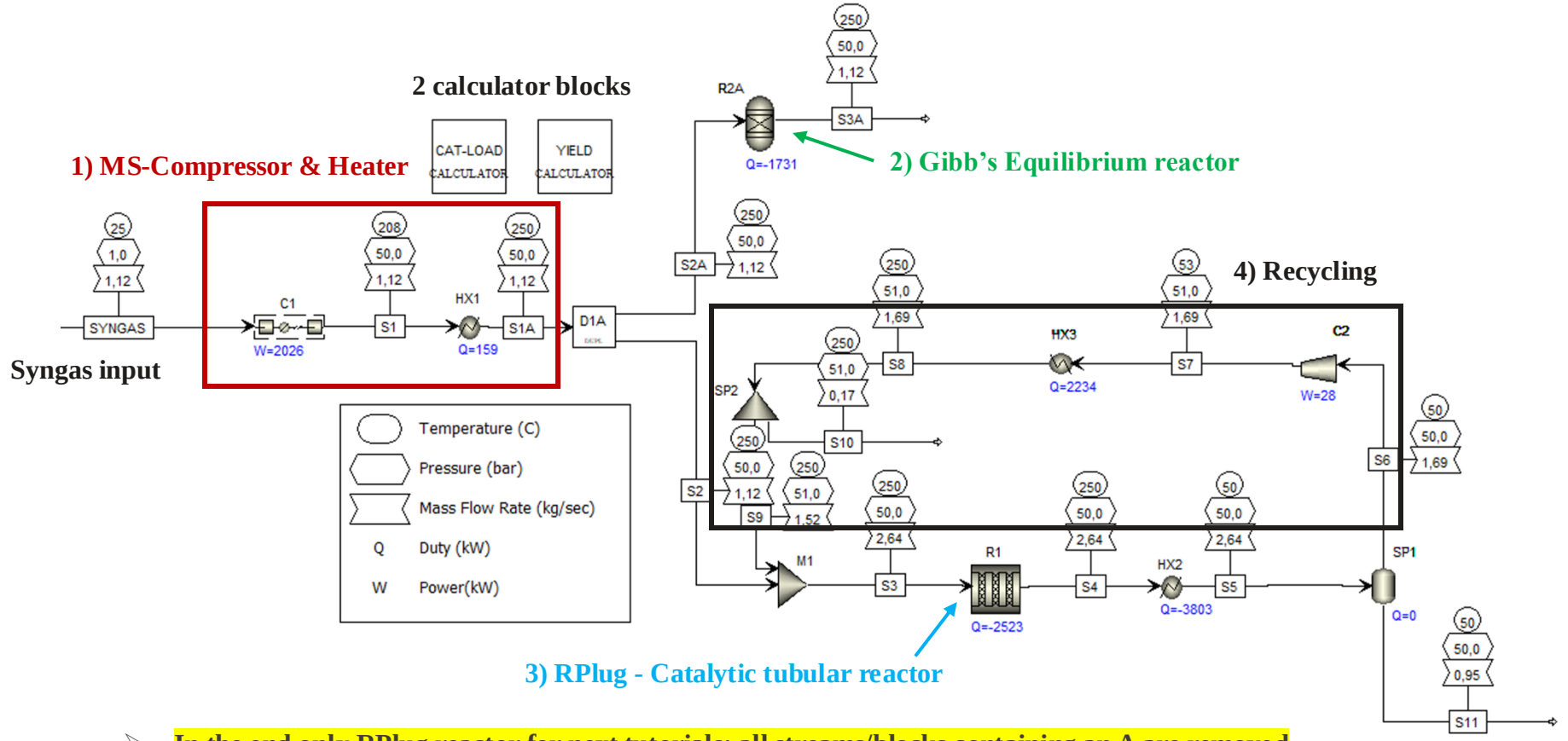
Run the flowsheet and see the results at the outlet

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



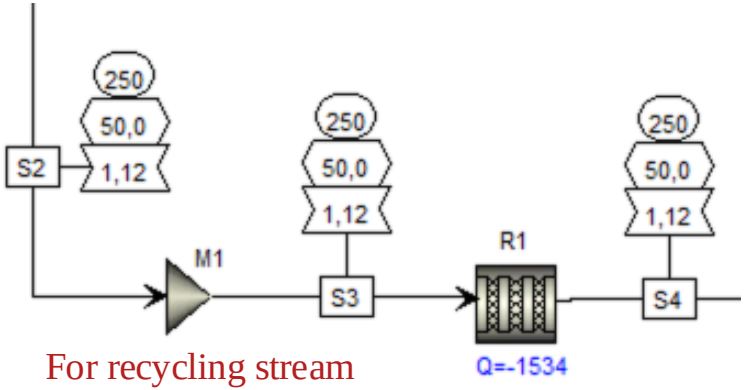


Overview of Aspen Flowsheet



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

RPlug reactor – kinetic modelling



RPlug Reactor			
Specifications	Reactor type operating condition	Reactor with specified temperature constant at inlet Temperature	
Configuration	number of tubes	Single-tube reactor	
	Length	6	m
	Diameter	1	m
	Valid phases	Vapor-Only	
Reactions	New	R-1	LHHW
Catalyst	Catalyst loading	865	kg
	Catalyst density	1500	kg/m^3
	Bed voidage	0.98	-

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

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,…)

MeOH Synthesis – Co_x hydrogenation reactions

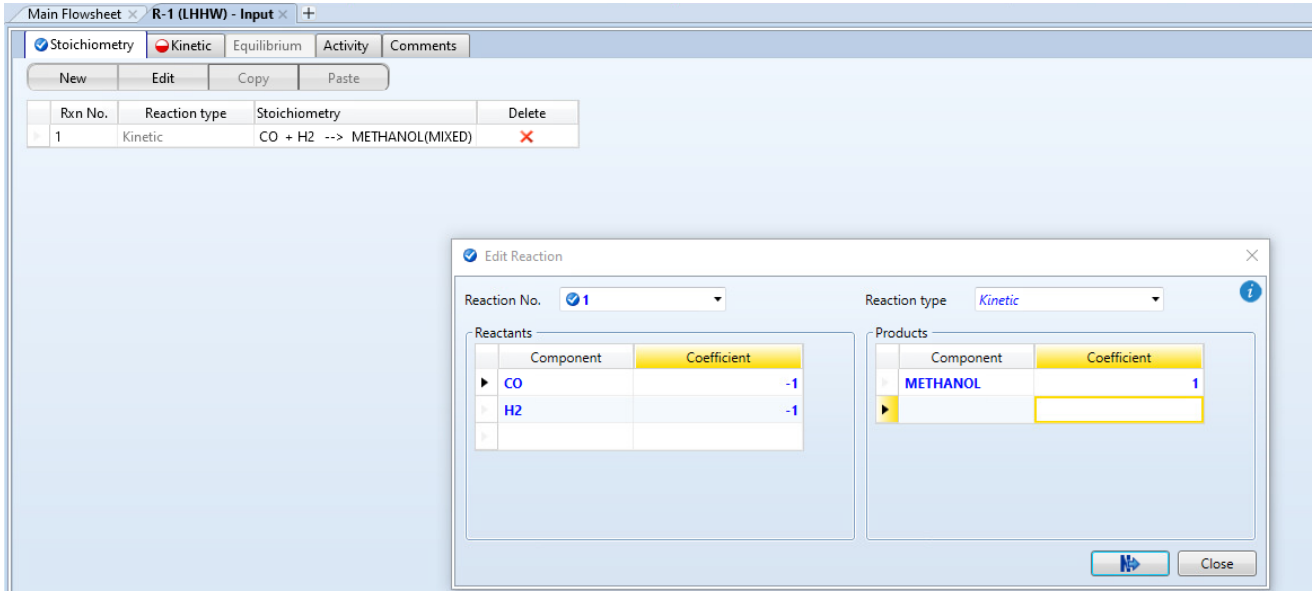
- **3 main chemical reactions in competition:**

A. $CO + 2H_2 \rightleftarrows CH_3OH$ $\quad \Delta H = -90.8$ kJ/mol

B. $CO_2 + H_2 \rightleftarrows CO + H_2O$ $\quad \Delta H = +41.2$ kJ/mol, **Reverse WGS Reaction**

C. $CO_2 + 3H_2 \rightleftarrows CH_3OH + H_2O$ $\quad \Delta H = -49.16$ kJ/mol

- **Operating conditions are a priori fulfilled**



MeOH Synthesis – LHHW kinetic model

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

Catalytic reaction

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

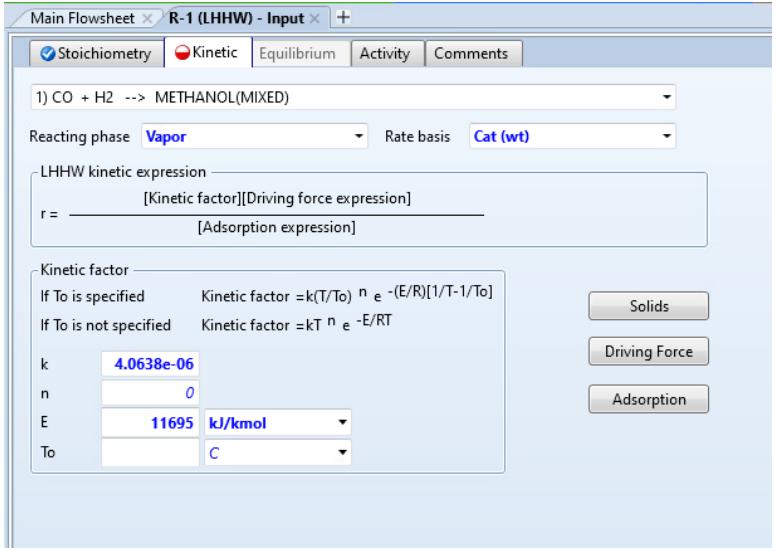
Table 1
Kinetic factor for reactions A, B and C (based on data from [2]) – the units used are [Pa] for fugacity and [mol/$g_{catalyst}$ s] = [kmol/$kg_{catalyst}$ s] for reaction rate.

Reaction	k	n	E_a [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



MeOH Synthesis – LHHW kinetic model

The driving force expressions are as follows:

Reaction A : $K_{CO} f_{CO} f_{H_2}^{3/2} - \frac{K_{CO}}{K_A} f_{CH_3OH} f_{H_2}^{-1/2}$ [Pa$^{3/2}$]

K_1 K_2

Reaction B : $K_{CO_2} f_{CO_2} f_{H_2} - \frac{K_{CO_2}}{K_B} f_{H_2O} f_{CO}$ [Pa]

Reaction C : $K_{CO_2} f_{CO_2} f_{H_2}^{3/2} - \frac{K_{CO_2}}{K_C} f_{H_2O} f_{CH_3OH} f_{H_2}^{-3/2}$ [Pa$^{3/2}$]

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

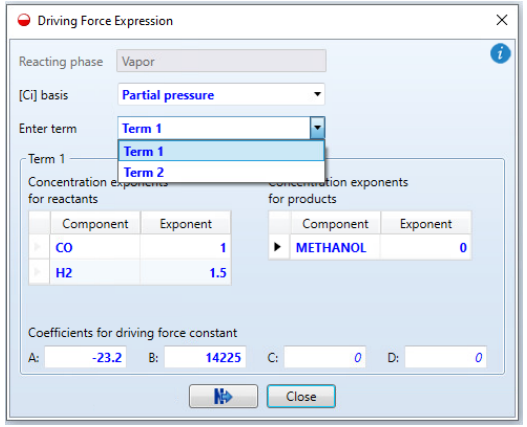
Table 3
Constants for driving force (from [2]) using the format for Aspen Plus.

	K_1		K_2	
Reaction	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

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

Concentration exponents								
Reactions	**Term1**				**Term 2**			
A)	CO	H2	CH3OH		CO	H2	CH3OH	
	1	1,5	0		0	-0,5	1	
B)	CO2	H2	CO	H2O	CO2	H2	CO	H2O
	1	1	0	0	0	0	1	1
C)	CO2	H2	CH3OH	H2O	CO	H2	CH3OH	H2O
	1	1,5	0	0	0	-1,5	1	1



Ideal gas law → partial pressure to express fugacity

MeOH Synthesis – LHHW kinetic model

Catalytic reaction

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

(adsorption term) = f(T, P, C, catalyst)

Same for all reactions, exponent =1

K_2 K_3

$$\sqrt{f_{H_2}} + \frac{K_{H_2O}}{\sqrt{K_H}} f_{H_2O} + K_{CO} f_{CO} \sqrt{f_{H_2}} + \dots$$

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

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

Catalytic reactions – Effect of operating conditions

Temperature

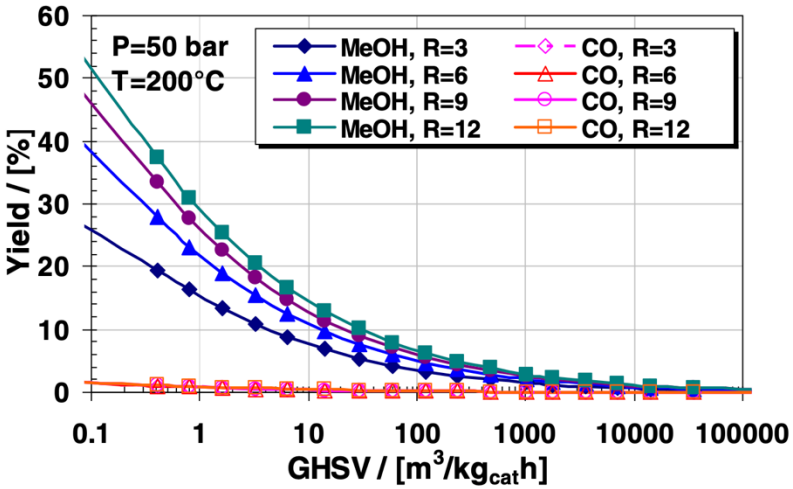
- Impact Equilibrium constant of the reaction
  - For $\Delta H < 0$, $T \nearrow \Longrightarrow K_{eq} \searrow$
  - For $\Delta H > 0$, $T \nearrow \Longrightarrow K_{eq} \nearrow$
- Impact kinetics (increase probability of collisions)
  - $T \nearrow \Longrightarrow r \nearrow$

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 [$m^3/(kg\ h)$]
  - V_{flow} is the volumetric flow rate [m^3/h]
  - m_{cat} is the mass of catalyst present in the reactor [kg]
- $GHSV \nearrow \Longrightarrow YIELD \searrow$

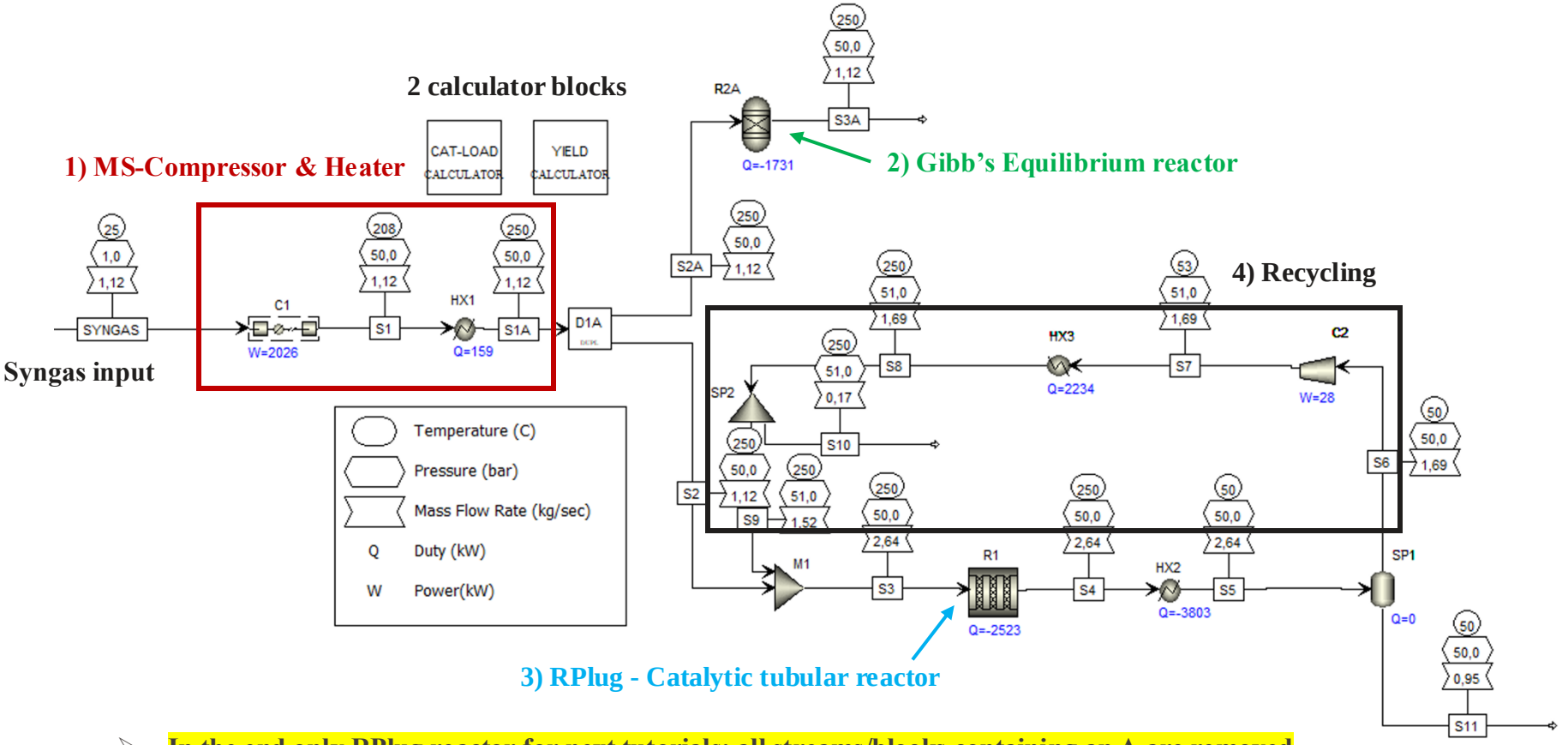
Pressure

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



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

Overview of Aspen Flowsheet



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

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 Declaratio

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

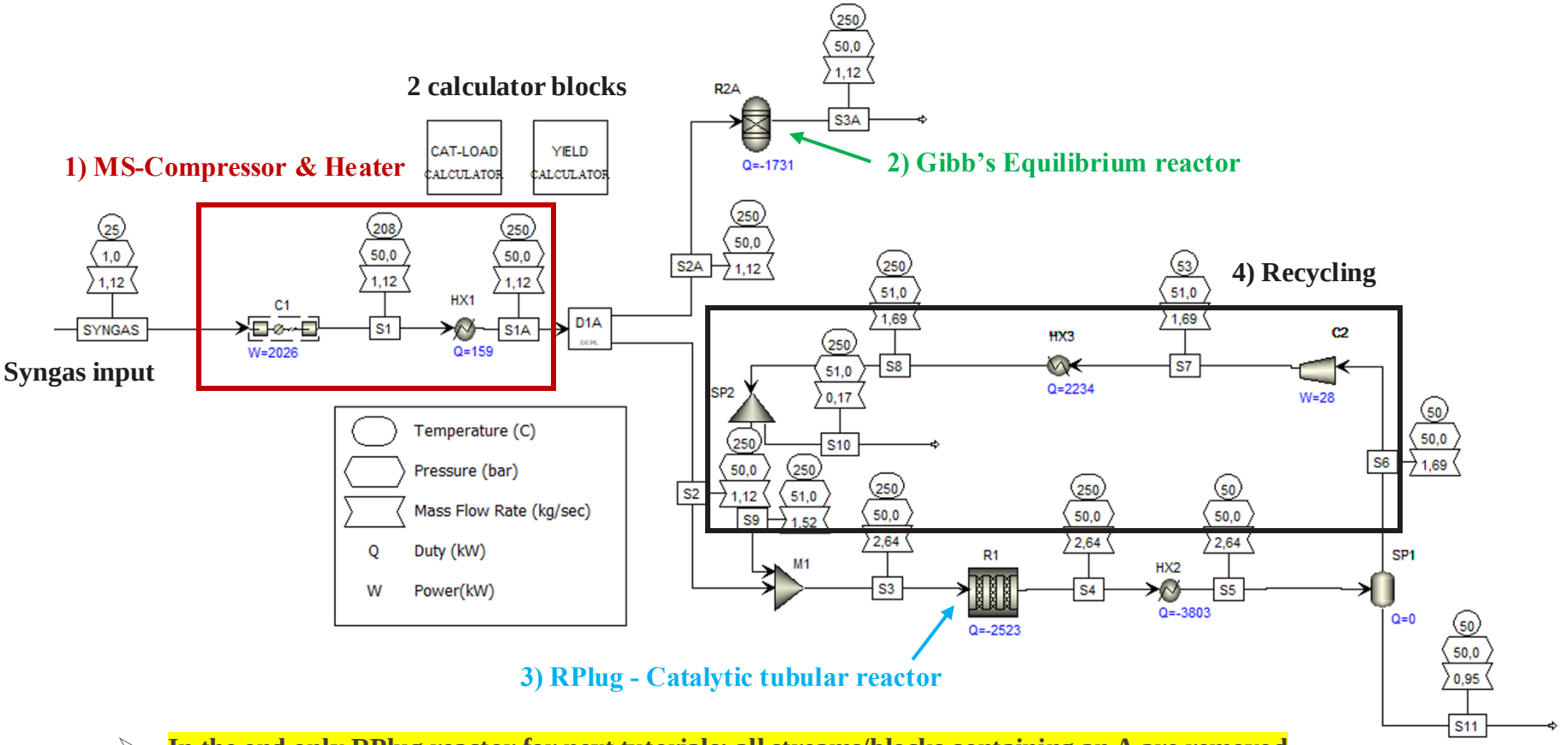
Enter executable Fortran statements

```
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

Overview of Aspen Flowsheet



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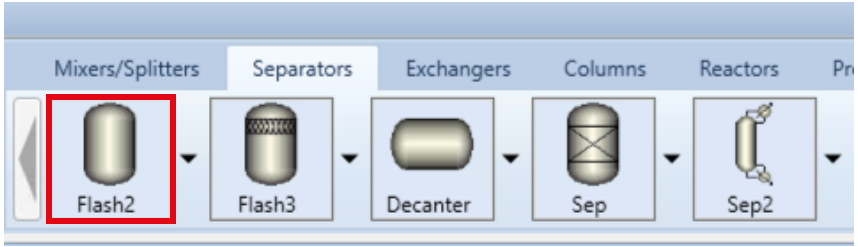
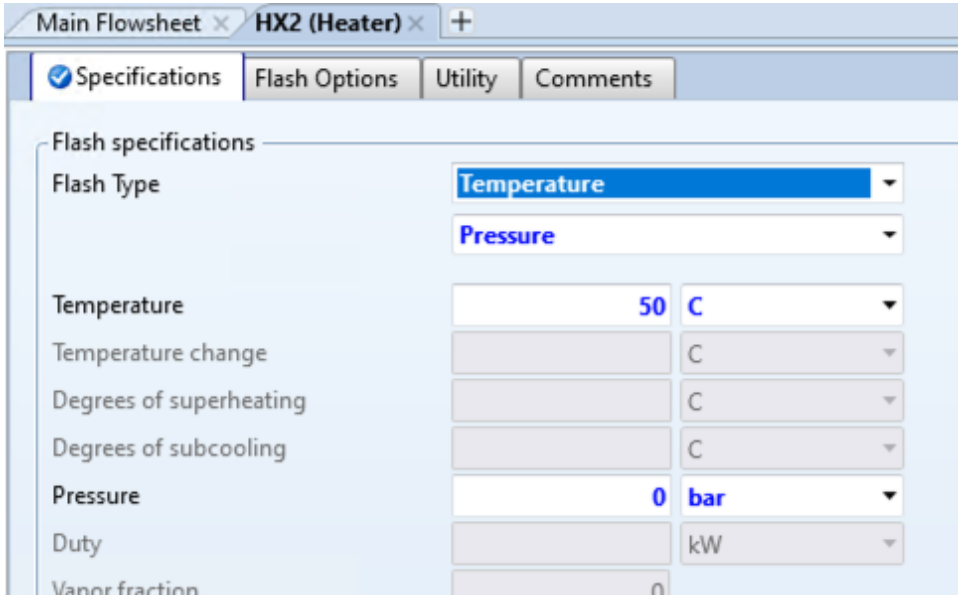
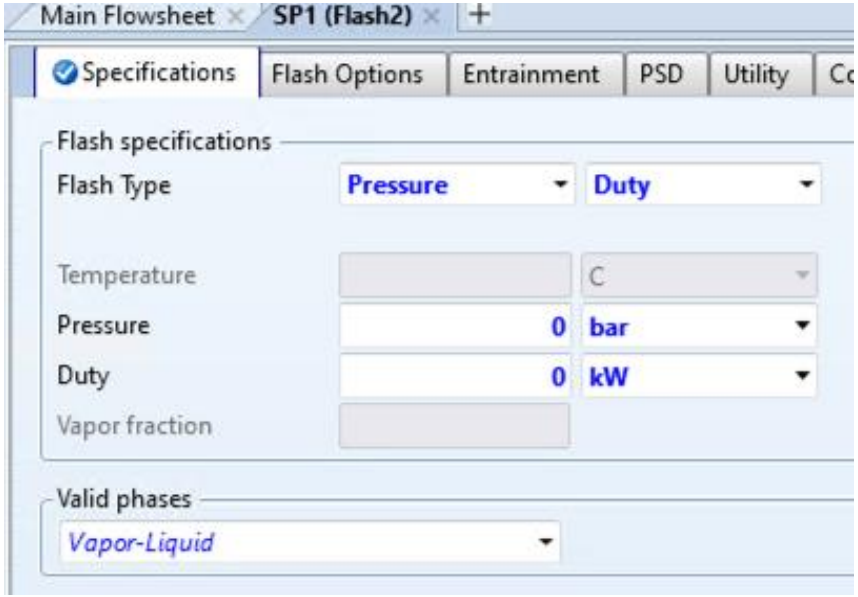
Isolate produced MeOH – Cooler & Flash Separator

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







Recycling stream

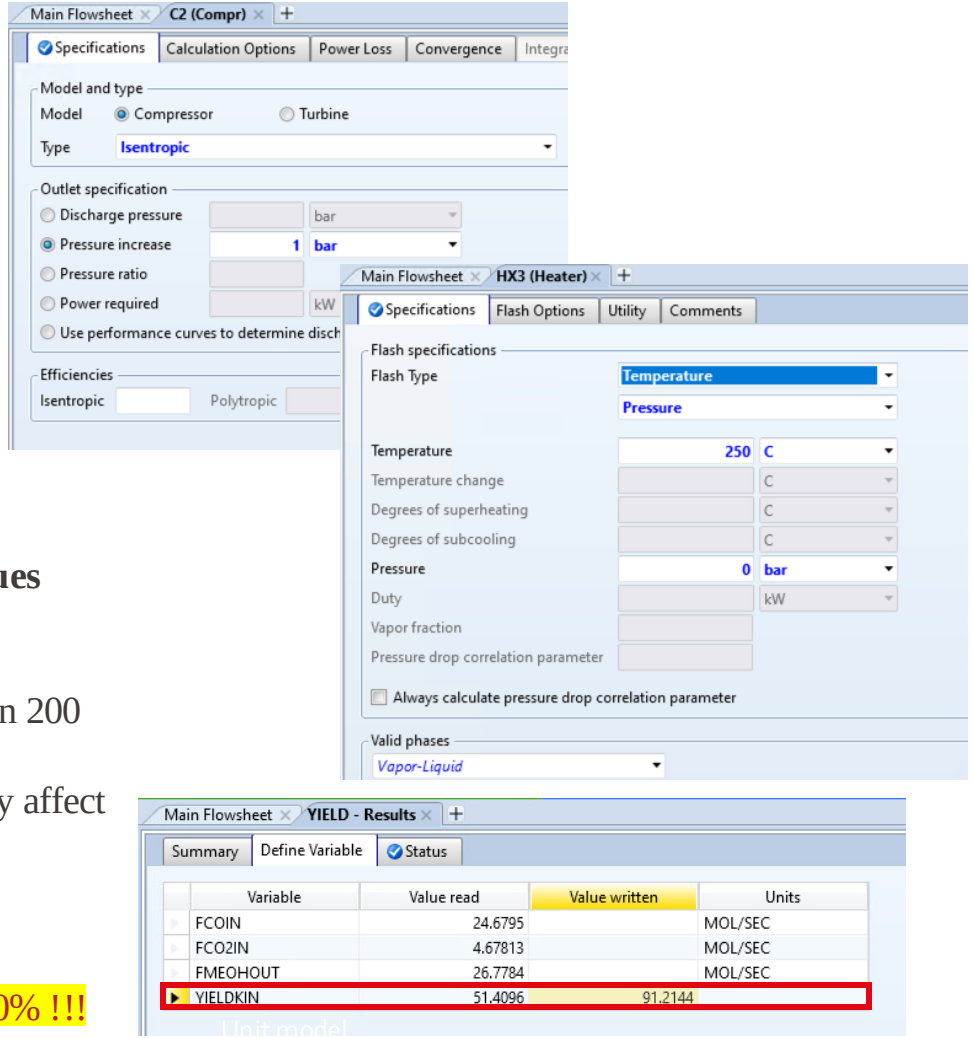
- Needs to be at higher pressure (+1 bar) to be reinjected
- Needs to be reheated up to 250°C

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%)

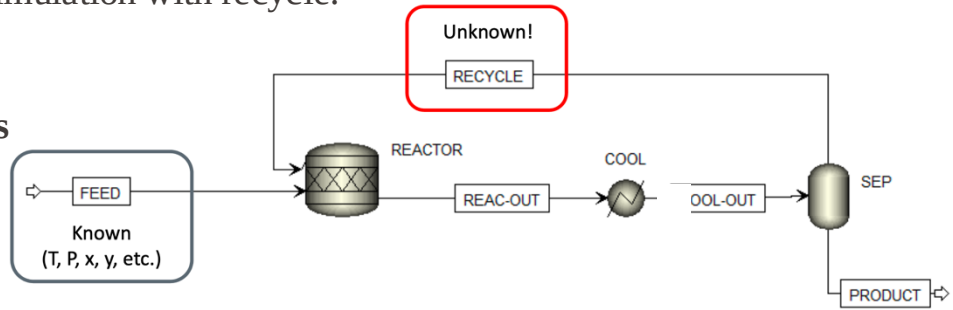
- Huge jump in MeOH yield with purge 10% !!!



Tear streams and Convergence in Aspen

- **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%)

Conclusions and outlook

- **The Shunli plant in Anyang, China**
  ≈ 500'000 tons CO_2 into MeOH per year

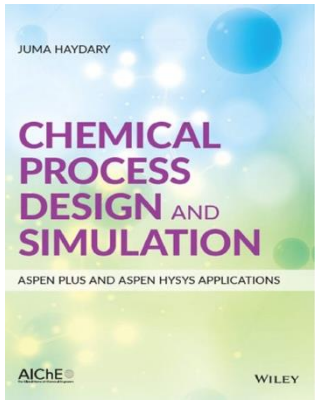
New Scientist, Michel Le Page, Nov. 2022

Summary of learning outcomes

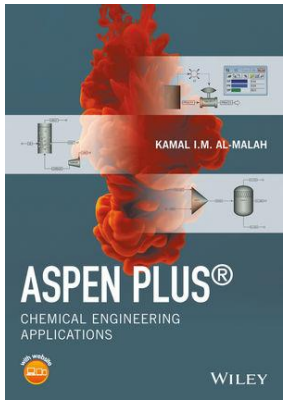
- ✓ Differentiate the several reactor models
- ✓ Select the correct model based on provided information (literature, available data,…)
- ✓ Handle reactions in Aspen Plus
- ✓ Understand and differentiate equilibrium from kinetic reactions
- ✓ Understand the impact of operating conditions on kinetic reactions
- ✓ 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