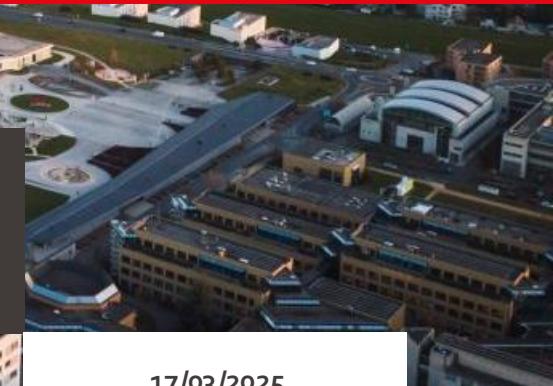




# Co-electrolysis process in Aspen Plus®

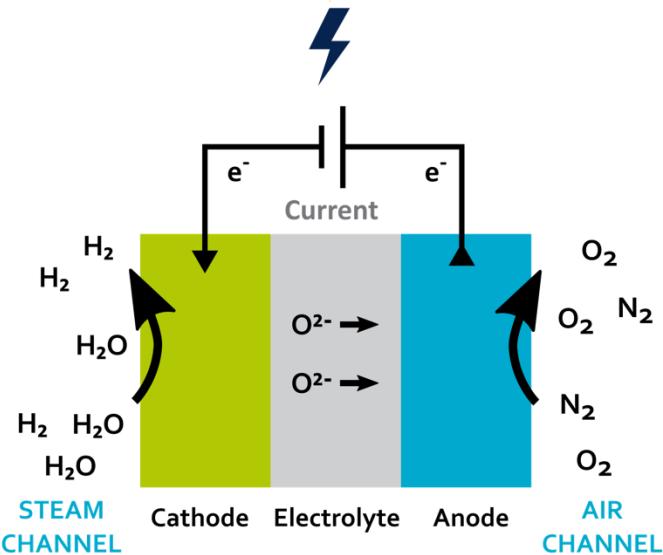
Arthur Waeber

Xinyi Wei

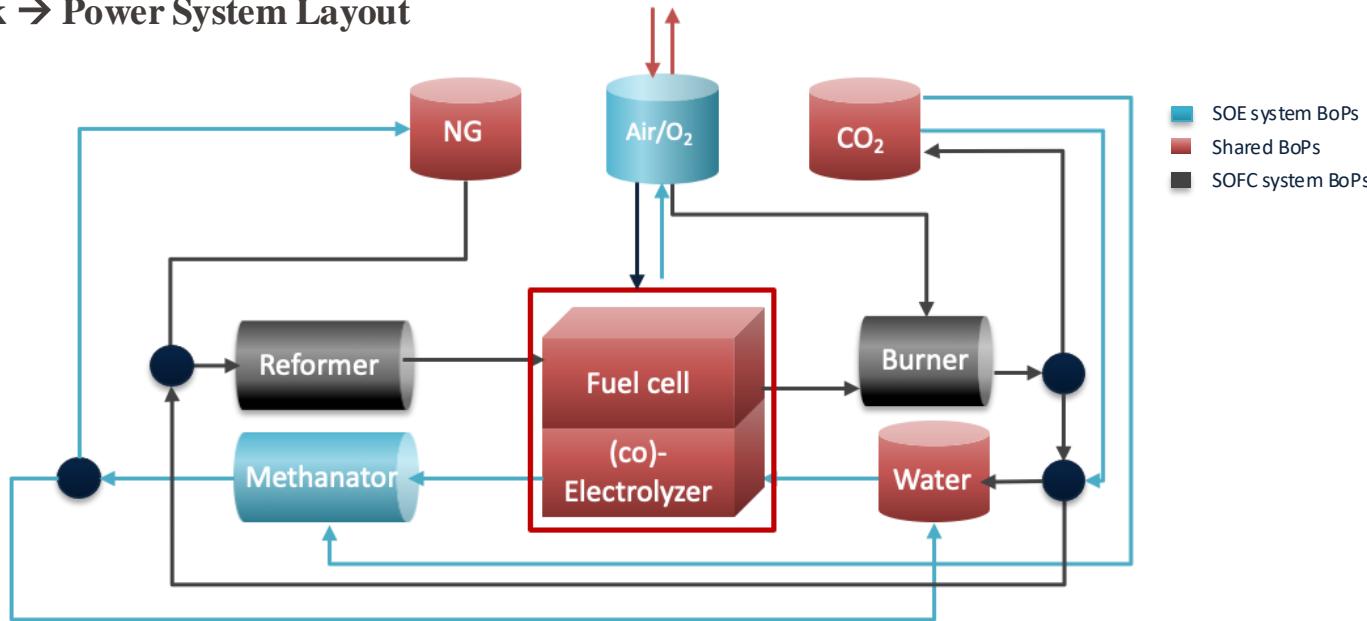


- Electrochemical reduction of  $\text{H}_2\text{O}$  and/or  $\text{CO}_2$
- Solid Oxide Electrolyte at high temperature ( $> 700^\circ\text{C}$ )
- High Temperature:
  - Good conversion efficiency
  - Challenges for integration
  - Necessitate clever heat integration
- Production of  $\text{H}_2$  or Syngas and  $\text{O}_2$  which are all 3 valuable products
- 3 operation modes:
  - Endothermic (need heat at high T)
  - **Thermoneutral (High T heat is balanced)**
  - Exothermic (outputs heat at high T)
- SOC stack is reversible (can operate in fuel cell mode as well)

### Electrolyser mode

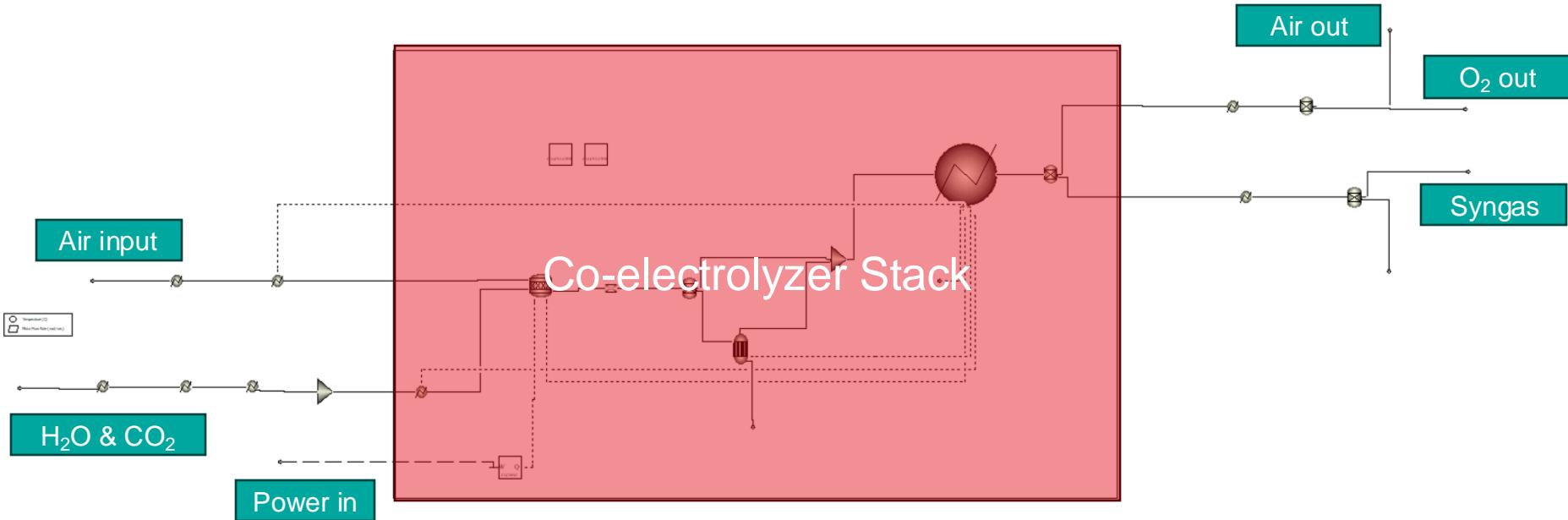


Power → NG Tank → Power System Layout

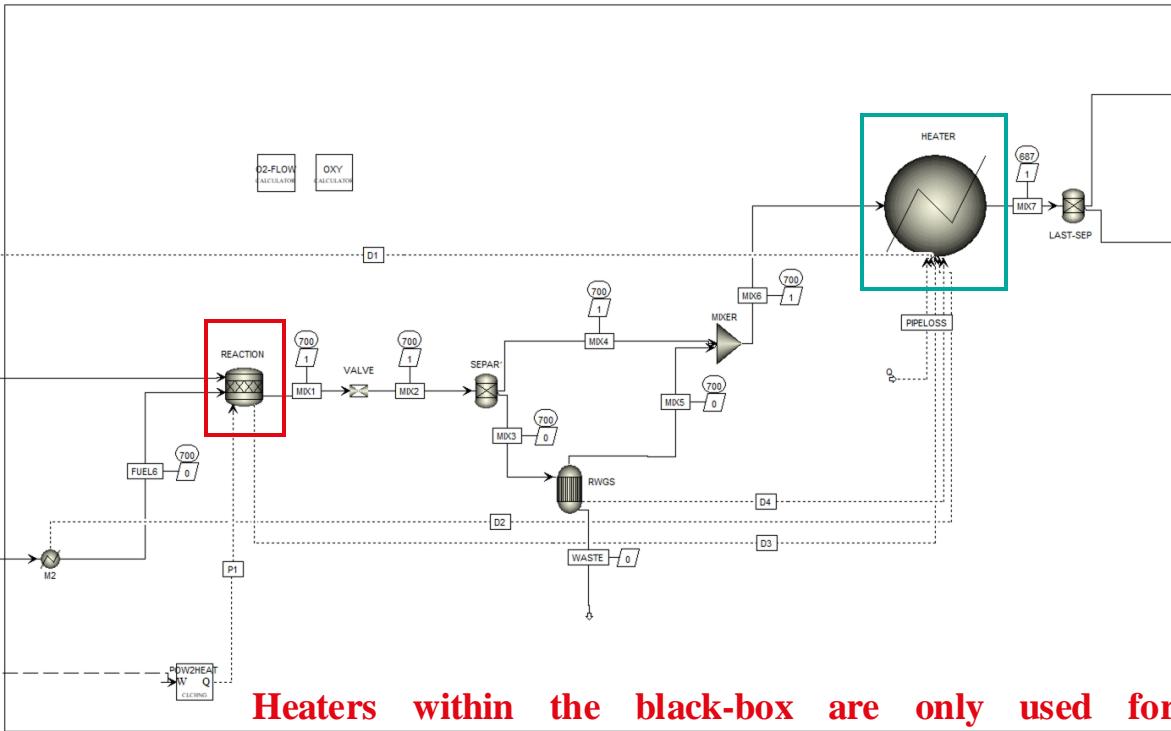


- When renewable electricity is available, methane can be produced *via* electrolyzer-methanation unit.
- When system requires electricity, it can be produced *via* reformer-fuel cell-burner unit.
- Oxy-combustion is considered in fuel cell system (to avoid presence of N<sub>2</sub>).
- High temperature heat is available

Power → H<sub>2</sub> / Syngas via Solid Oxide Electrolyzer (SOE)



## Solid Oxide Electrolyzer (SOE) – Thermoneutral operation



- No need to modify SOE stack model in your project.

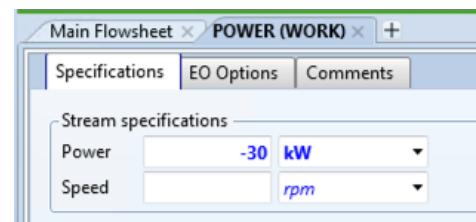
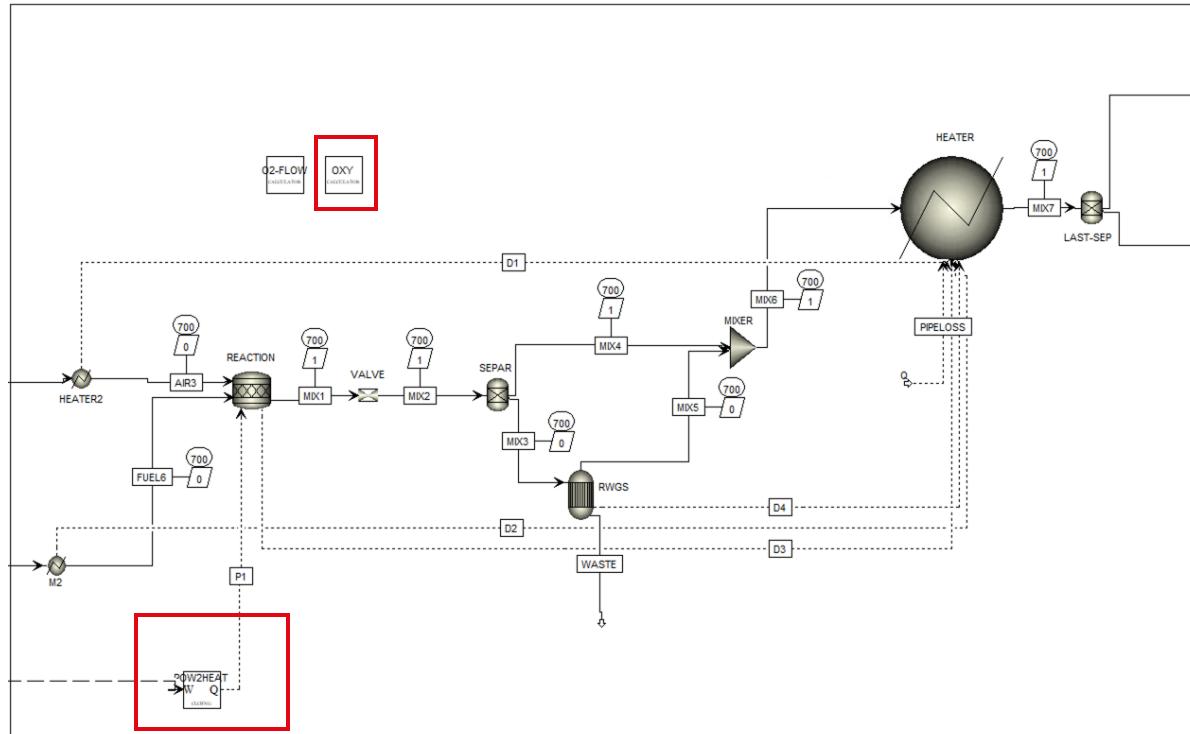
- “REACTION” reactor contains main co-electrolysis reactions.

Component Attr.		
0.85 H <sub>2</sub> O	H <sub>2</sub> O --> H <sub>2</sub> (MIXED) + 0.5 O <sub>2</sub> (MIXED)	
0.85 CO <sub>2</sub>	CO <sub>2</sub> --> CO(MIXED) + 0.5 O <sub>2</sub> (MIXED)	

- “HEATER” is used to count the heat within the stack.

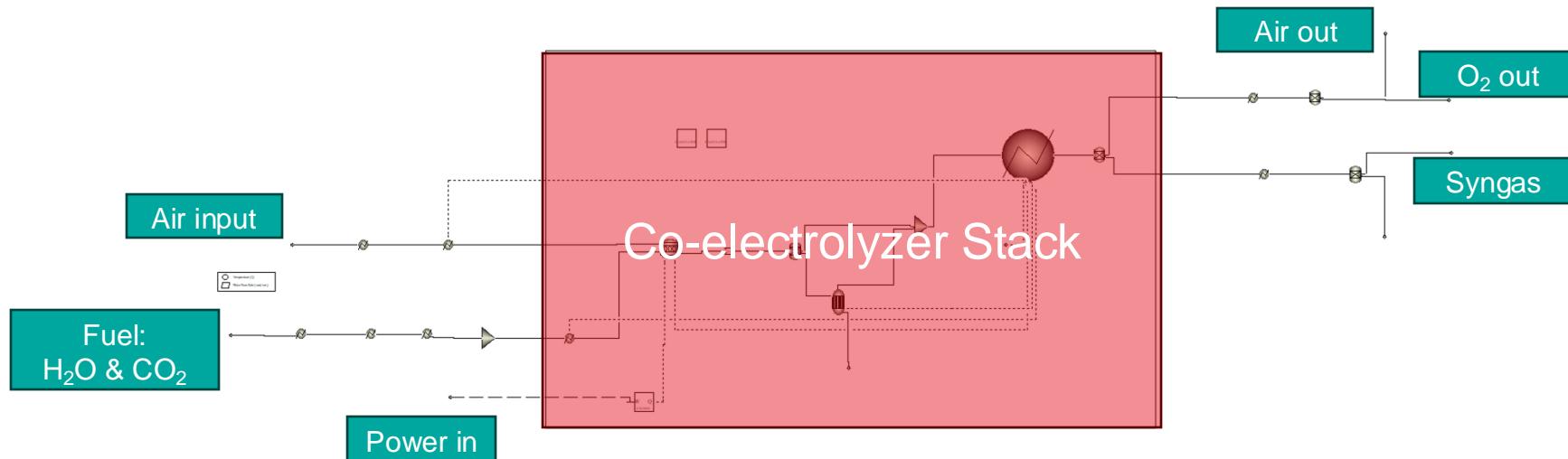
- The HEATER will have a heat output of 0 kW (thermoneutral operation)

## Solid Oxide Electrolyzer (SOE)



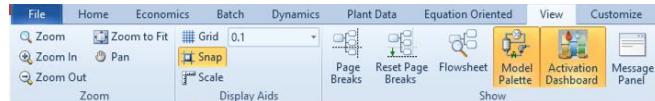
- Power input in current file is 30 kW. (negative as input)
- When you change the electrolyzer power input, the fuel flow rate "FUEL1" will be automatically updated by "OXY" calculator - **no need to change by yourself.**

1. Uniformize all up-stream temperatures (through calculator block)
2. Understand fuel heating-up process (differentiate heaters)
3. Ensure thermoneutral operation ( $T_{SOEC\_in} == T_{SOEC\_out}$ ) through design specification
4. Apply technical constraint on  $O_2$ /Air flow through design specification
5. Define a variable to tune the  $H_2O/CO_2$  ratio in the fuel. (in class)
6. Define the right stoichiometric number for further syngas usage (in class)



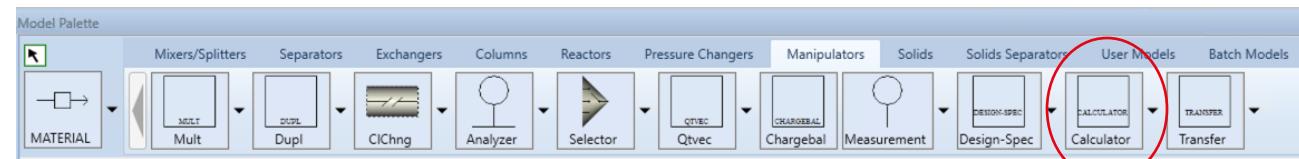
## Step 1: Set SOEC upstream components temperature into 700 °C via calculator

- Go to View → Model Palette



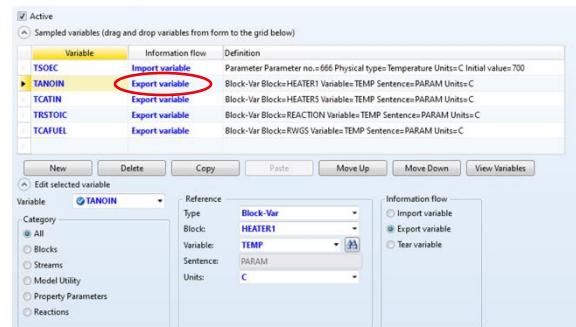
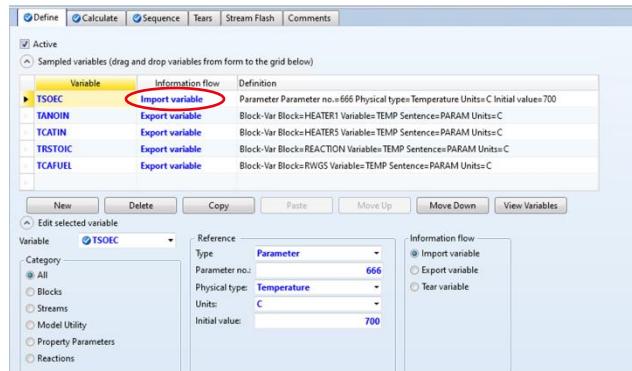
- Go to Manipulators → Calculator

- Name calculator “SET-TSOE”



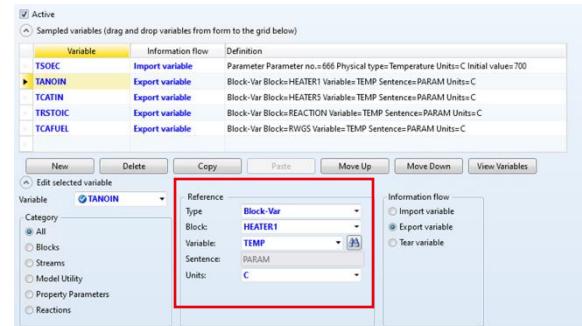
- Target: Set a parameter which is linked with HEATER1, HEATER5, REACTION and RWGS

- Define a new **parameter** “TSOEC”, select it to be the “import variable”.
- Import variable is the input from user.
- Export variable is the output from the calculator, it gives the order to ASPEN.

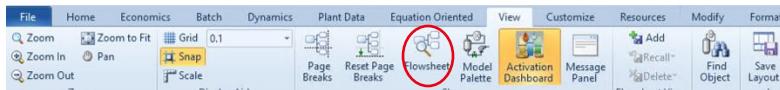


By adding this calculator, if we want to change the stack inlet T, we only need to change Parameter – “TSOEC”

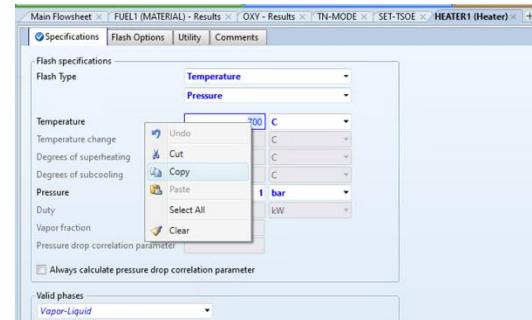
Question: What if we are not sure about “Reference”?



➤ Go to Flowsheet



➤ Find “HEATER1” → “Temperature” → Select value → “Copy”

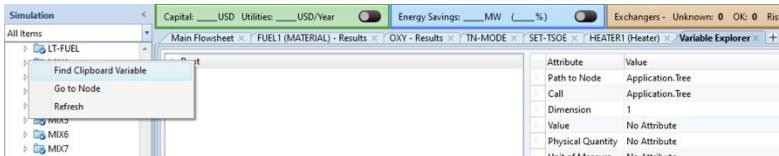


## Question: What if we are not sure about “Reference”?

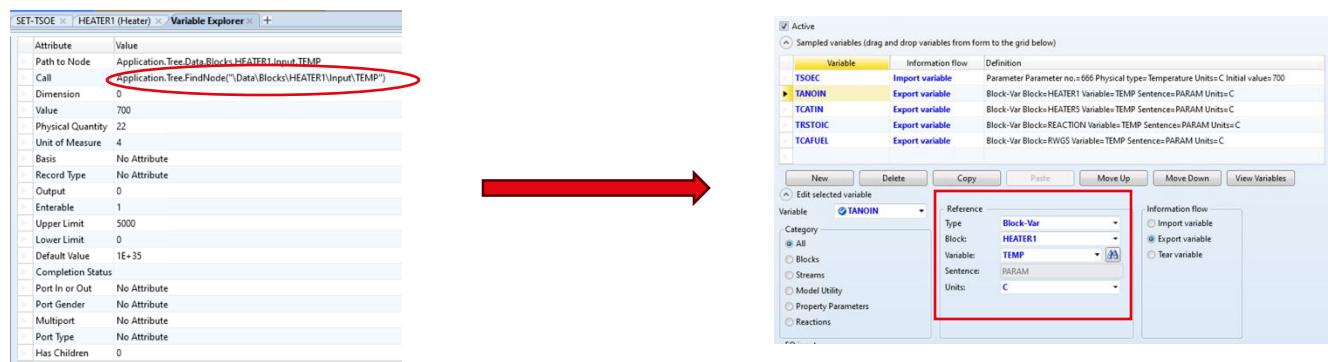
- Go to Customize → Variable Explorer



- Go to Variable Explorer → Right Click “Root” → “Find Clipboard Variable”

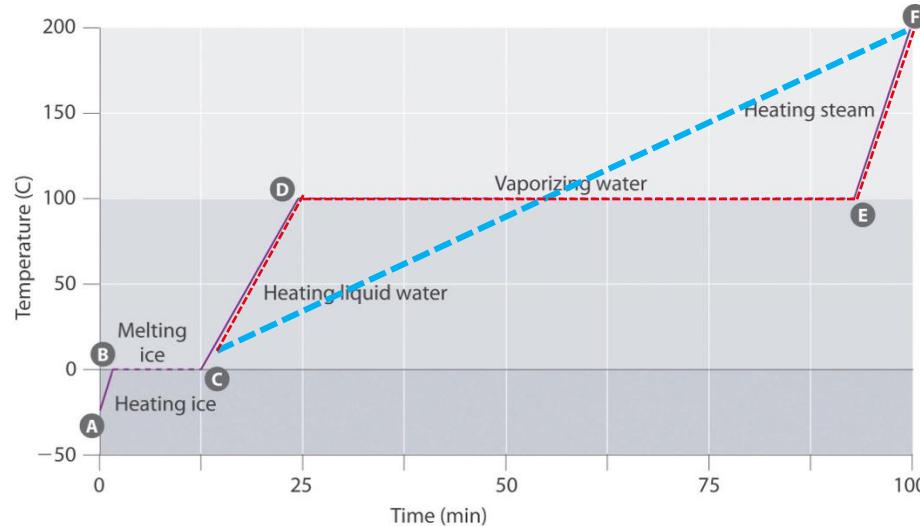


- “Call” → the “path” of one variable → Provide hint for “Reference”



## Step 2: Set “Fuel” heating up process

- “Fuel1” contains  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  → How to heat it up?
  - $\text{CO}_2$  is easy to be heated up, as it is gas.
  - Water has three stages in heating up process: Liquid heating, evaporation, steam superheating



If only 1 heater was used:

inlet T, outlet T and average cp → linear interpolation

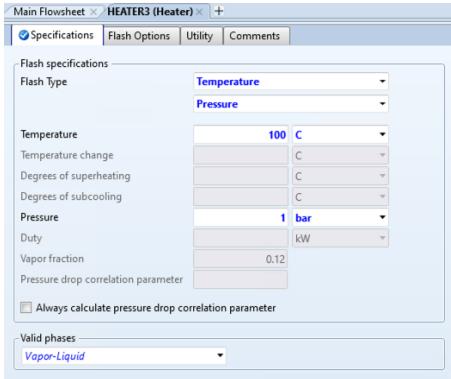
3 Three heaters:

To capture each stage temperature changing and the duties

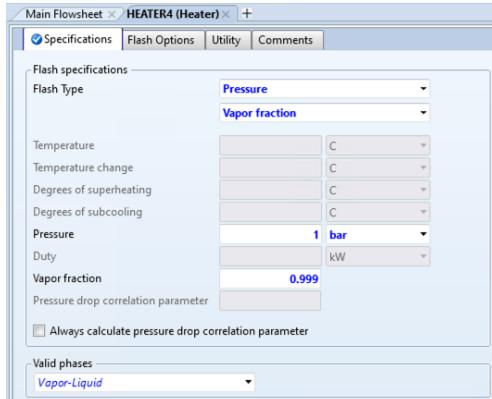
## Step 2: Set “Fuel” heating up process

- If “Fuel1” only contains H<sub>2</sub>O

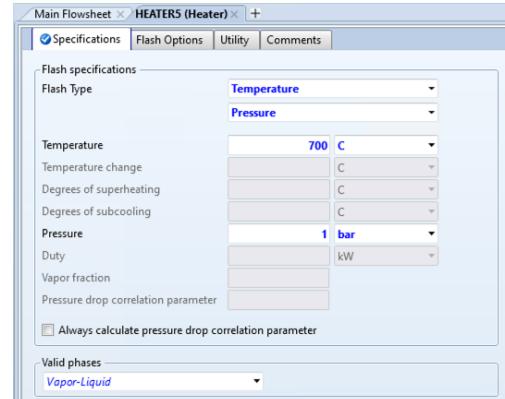
- HEATER3



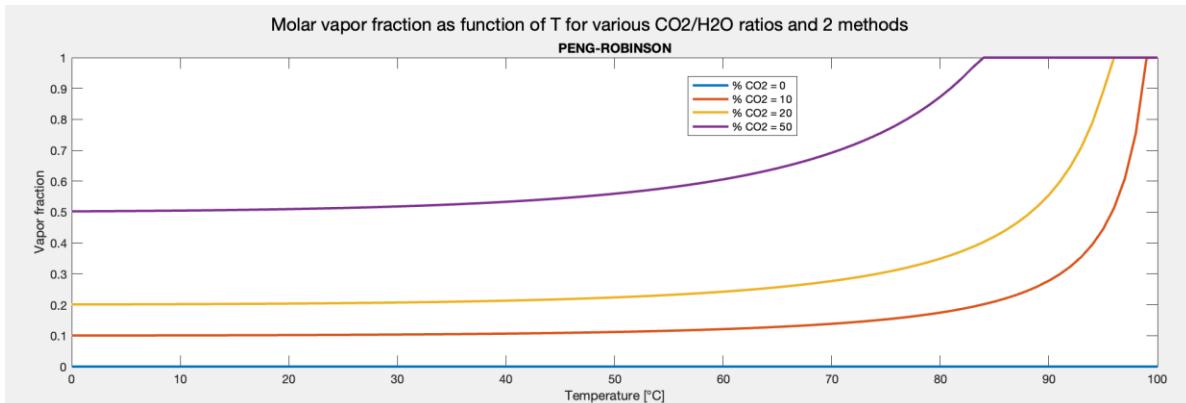
- HEATER4



- HEATER5

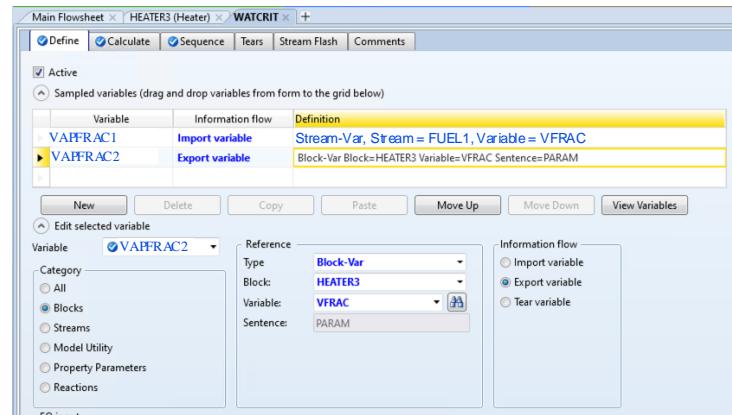
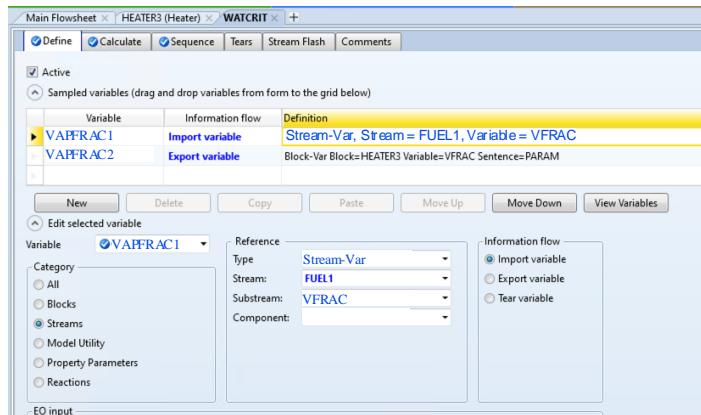
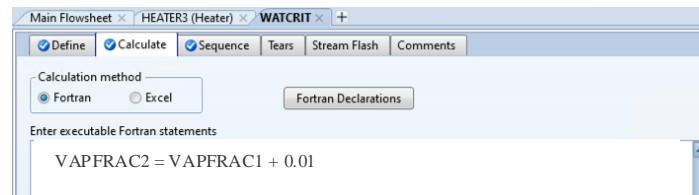


- If “Fuel1” contains both H<sub>2</sub>O and CO<sub>2</sub> → “HEATER3” needs to be updated → Boiling point of H<sub>2</sub>O will change as the pressure change



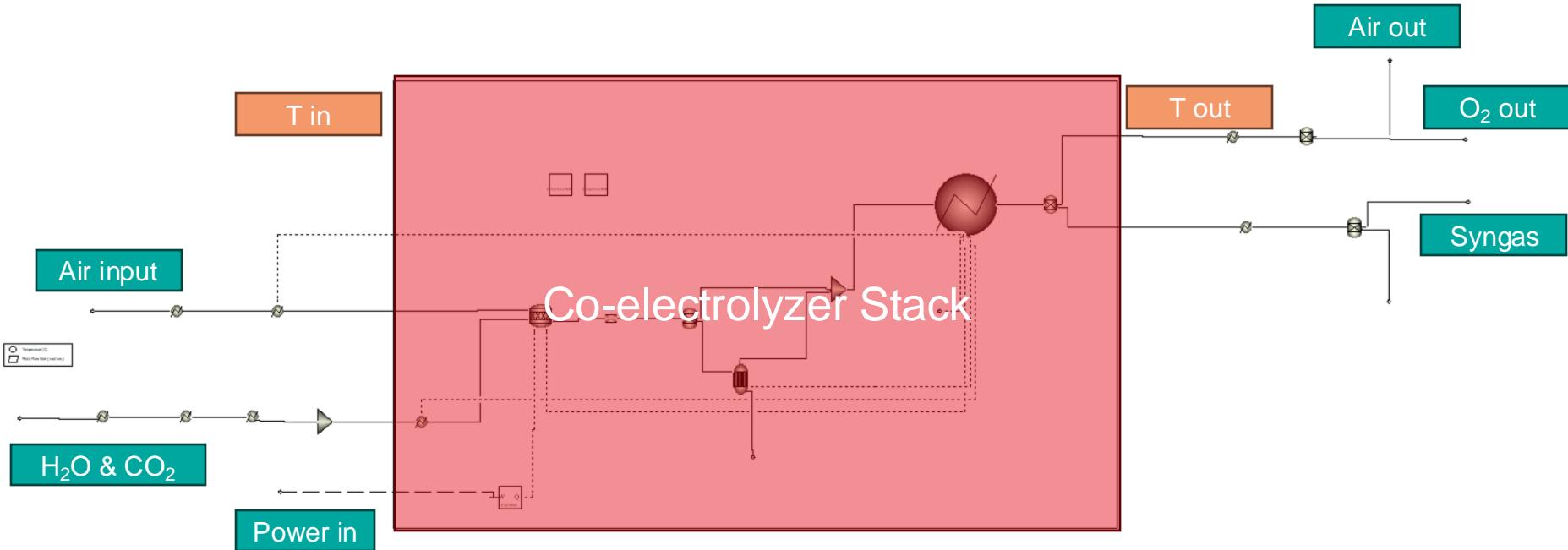
## Step 2: Set “Fuel” heating up process

- After “HEATER3”,  $\text{H}_2\text{O}$  is going to evaporate further → stream “FUEL2” vapor fraction shall be slightly higher than “FUEL1”
- Add a calculator, name it as “WATCRIT”
  - Import “FUEL1” vapor mole fraction as “VAPFRAC1”
  - Export “HEATER3” vapor fraction as “VAPFRAC2”
  - “HEATER3” vapor fraction = “FUEL1” vapor mole fraction + 0.01

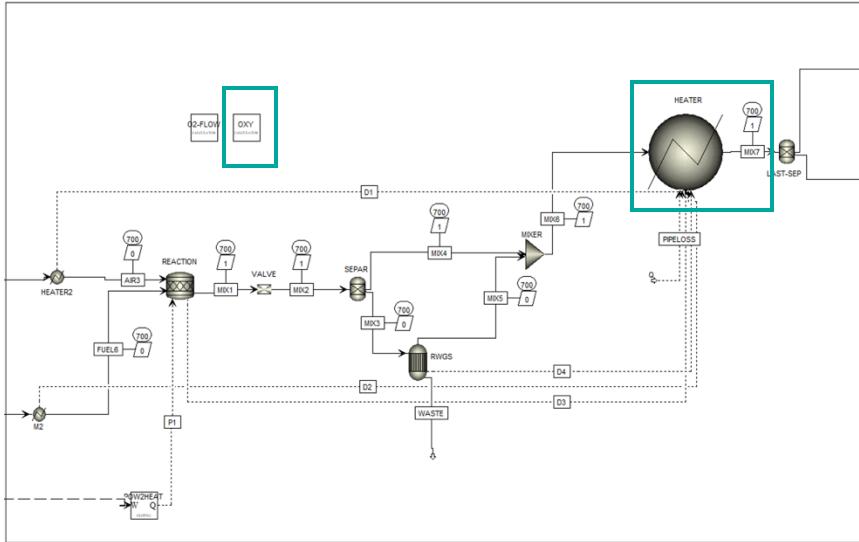


- Note: “HEATER3” shall have pressure and vapor fraction as the specifications, otherwise, calculator CAN NOT give order

Step 3: operate in thermoneutral mode, dictated by the operating voltage applied



## Solid Oxide Electrolyzer (SOE)



- “CVCELL” IN “OXY” calculator is an “**Import variable**”, it is used as a **parameter** to influence SOE outlet T – “MIX7”.

Main Flowsheet x OXY x

Variable	Information flow	Definition
CIMAX	Export variable	Parameter Parameter no.=2002 Physical type=Current Units=amp Initial value=10
CI	Export variable	Parameter Parameter no.=2003 Physical type=Current Units=amp
CUF	Export variable	Parameter Parameter no.=2004 Physical type=Dimensions Units=Unitless Initial value=0.85
CEXTENH2	Export variable	Block-Var Block=REACTION Variable=CONV Sentence=CONV ID1=1
CEXTENCO	Export variable	Block-Var Block=REACTION Variable=CONV Sentence=CONV ID1=2
<b>CVCELL</b>	<b>Import variable</b>	Parameter Parameter no.=2013 Physical type=Voltage Units=volt Initial value=1.3
CELEPOW	Import variable	Work-Power Stream=POWER Units=kW
FUELIN	Export variable	Stream-Var Stream=FUEL1 Substream=MIXED Variable=MOLE-FLOW Units=moL/sec
FUEINH2O	Export variable	Mole-Flow Stream=FUEL1 Substream=MIXED Component=H2O Units=moL/sec
FUEINCO2	Export variable	Mole-Flow Stream=FUEL1 Substream=MIXED Component=CO2 Units=moL/sec
RATIO2	Import variable	Parameter Parameter no.=10002 Physical type=Dimensions Units=Unitless Initial value=0.9

New Delete Copy Paste Move Up Move Down View Variables

Edit selected variable

Variable: **CVCELL** Reference: Parameter Type: **Parameter** Parameter no.: **2013** Physical type: **Voltage** Units: **volt** Initial value: **1.3**

Category:  All  Blocks  Streams  Model Utility  Property Parameters  Reactions

Information flow

- Import variable
- Export variable
- Tear variable

- We have defined a calculator for the inlet T of SOE, **how about the outlet T of SOE?**
- “HEATER” is used to count all the heat within the stack and calculate the outlet T of SOE.

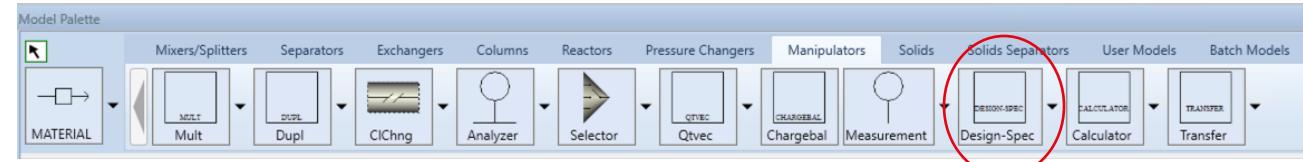
### Step 3: Create a design specification block, which is able to make SOE inlet T = SOE outlet T

- Go to View → Model Palette



- Go to Manipulators → Design-Spec

- Name it as “TN-MODE”



- Target: “MIX7” temperature = “FUEL4” temperature, by varying “CVCELL”

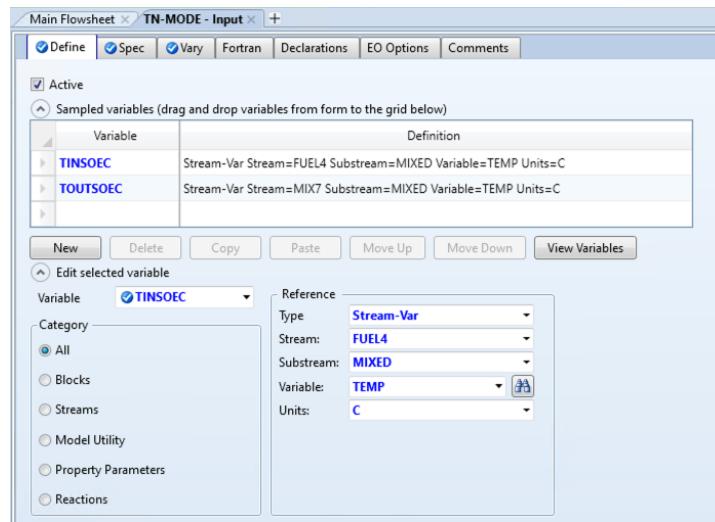
- “FUEL4” temperature is fixed by the previous calculator
  - “MIX7” temperature is calculated by using “CVCELL” parameter value
  - The temperature difference of these two streams shall be 0 by varying CVCELL value

### Step 3: Create a design specification block, which is able to make SOE inlet T = SOE outlet T

- Target: “MIX7” temperature = “FUEL4” temperature, by varying “CVCELL”

- “FUEL4” temperature is fixed by the previous calculator
- “MIX7” temperature is calculated by using “CVCELL” parameter value
- The temperature difference of these two streams shall be 0 by varying CVCELL value

- Define SOEC inlet T



Main Flowsheet / TN-MODE - Input

Variable	Definition
TINSOEC	Stream-Var Stream=FUEL4 Substream=MIXED Variable=TEMP Units=C
TOUTSOEC	Stream-Var Stream=MIX7 Substream=MIXED Variable=TEMP Units=C

New Delete Copy Paste Move Up Move Down View Variables

Active

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

Variable: TINSOEC

Category: All

Streams: TINSOEC

Model Utility: TINSOEC

Property Parameters: TINSOEC

Reactions: TINSOEC

Reference

Type: Stream-Var

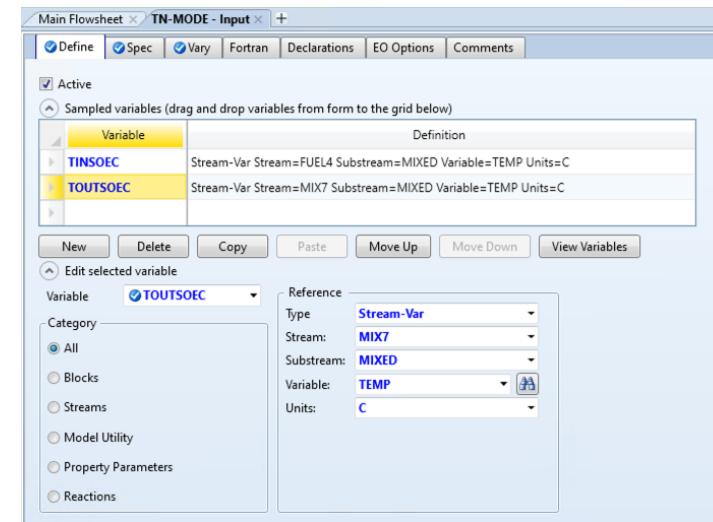
Stream: FUEL4

Substream: MIXED

Variable: TEMP

Units: C

- Define SOEC outlet T



Main Flowsheet / TN-MODE - Input

Variable	Definition
TINSOEC	Stream-Var Stream=FUEL4 Substream=MIXED Variable=TEMP Units=C
TOUTSOEC	Stream-Var Stream=MIX7 Substream=MIXED Variable=TEMP Units=C

New Delete Copy Paste Move Up Move Down View Variables

Active

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

Variable: TOUTSOEC

Category: All

Streams: TOUTSOEC

Model Utility: TOUTSOEC

Property Parameters: TOUTSOEC

Reactions: TOUTSOEC

Reference

Type: Stream-Var

Stream: MIX7

Substream: MIXED

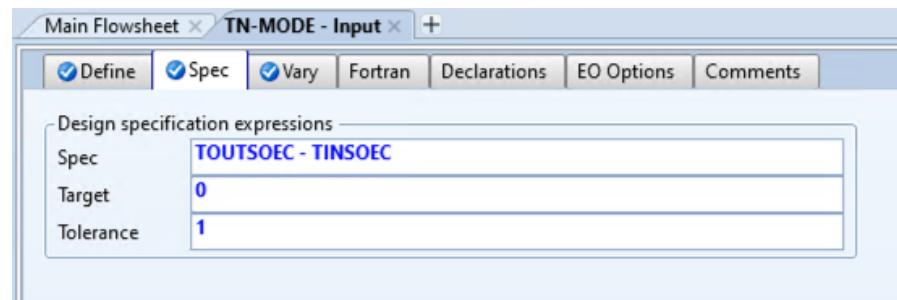
Variable: TEMP

Units: C

### Step 3: Create a design specification block, which is able to make SOE inlet T = SOE outlet T

- Target: “MIX7” temperature = “FUEL4” temperature, by varying “CVCELL”
  - “FUEL4” temperature is fixed by the previous calculator
  - “MIX7” temperature is calculated by using “CVCELL” parameter value
  - The temperature difference of these two streams shall be 0 by varying CVCELL value

- Set target/objective of this design **specification**

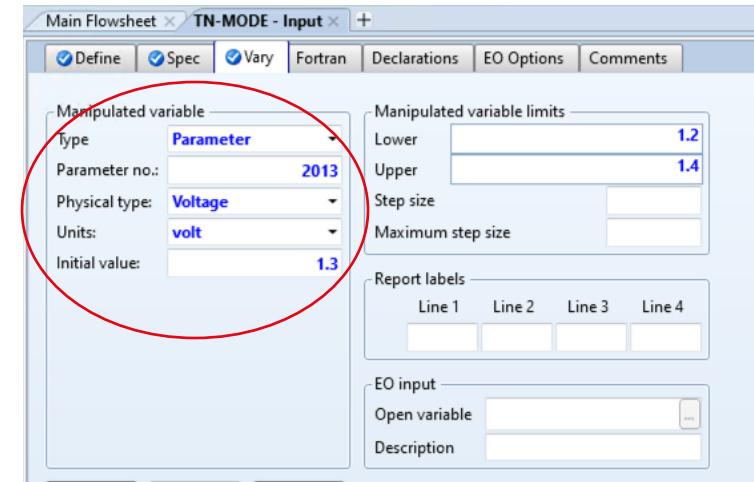
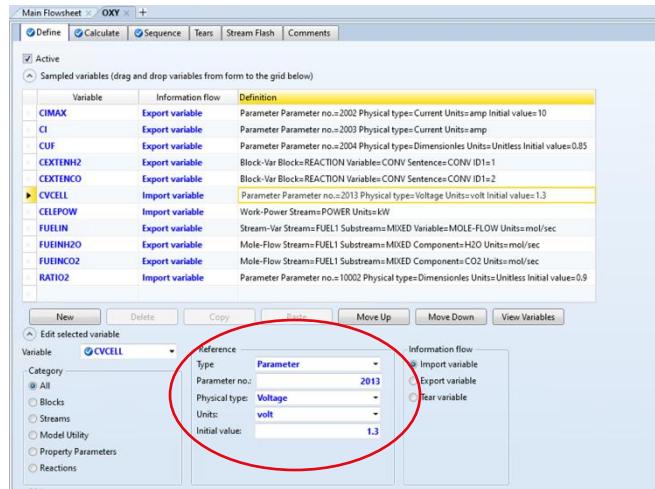


### Step 3: Create a design specification block, which is able to make SOE inlet T = SOE outlet T

- Target: “MIX7” temperature = “FUEL4” temperature, by varying “CVCELL”

- “FUEL4” temperature is fixed by the previous calculator
- “MIX7” temperature is calculated by using “CVCELL” parameter value
- The temperature difference of these two streams shall be 0 by varying CVCELL value

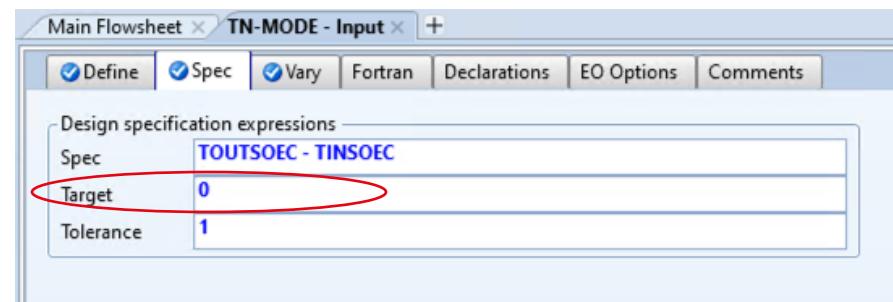
- By varying parameter “CVCELL”, set lower and upper bound



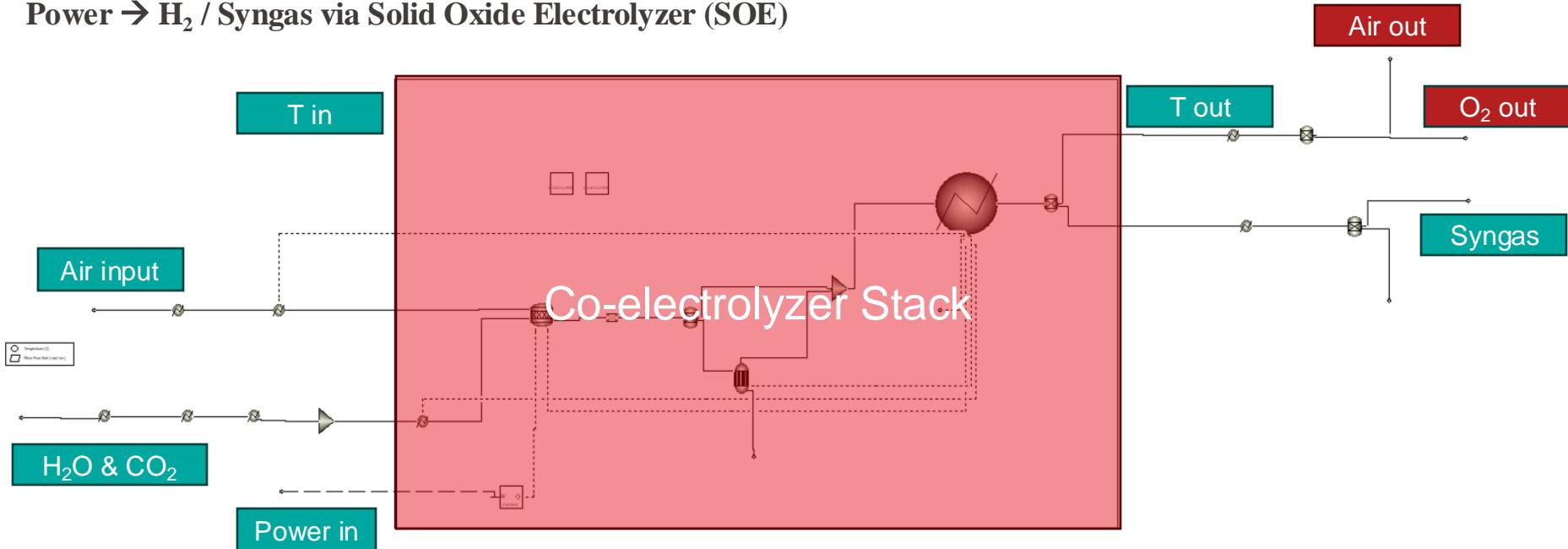
### Step 3: Create a design specification block, which is able to make SOE inlet T = SOE outlet T

- Target: “MIX7” temperature = “FUEL4” temperature, by varying “CVCELL”
  - “FUEL4” temperature is fixed by the previous calculator
  - “MIX7” temperature is calculated by using “CVCELL” parameter value
  - The temperature difference of these two streams shall be 0 by varying CVCELL value
- SOE normally can be operated in the thermal neutral mode →  $T_{in} = T_{out}$ 
  - $T_{in} > T_{out}$ , it is called as endothermic mode
  - $T_{in} < T_{out}$ , it is called as exothermic mode

**Rule: Maximum temperature difference between inlet and outlet of SOE shall be smaller than 100C**



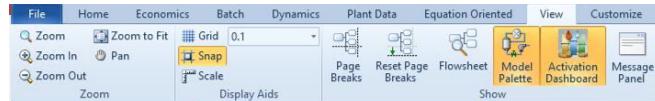
Power → H<sub>2</sub> / Syngas via Solid Oxide Electrolyzer (SOE)



- ✓ For SOE, fuel flow rate is automatically calculated by **Power input**
- ✓ For SOE, O<sub>2</sub> mole fraction normally shall be smaller than 0.3, to prevent any material degradation and oxidation

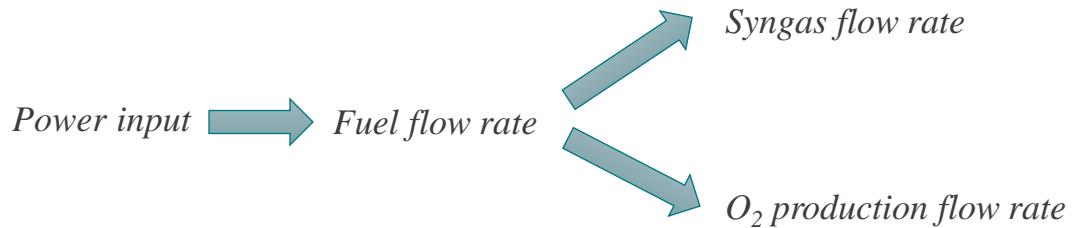
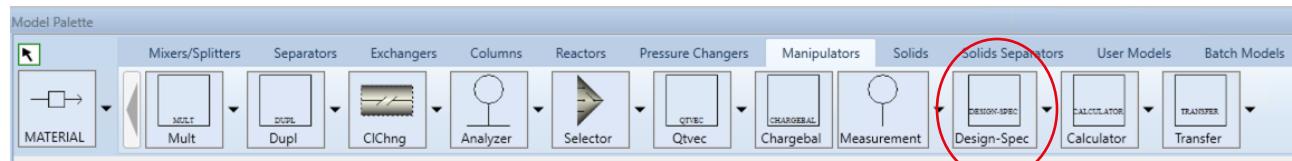
## Step 4: Create a design specification block, define the air flow rate input

- Go to View → Model Palette



- Go to Manipulators → Design-Spec

- Name it as “COSOEAIR”



Activity		
Fractional conversion	Fractional Conversion of Component	Stoichiometry
0.85 H <sub>2</sub> O		H <sub>2</sub> O → H <sub>2</sub> (MIXED) + 0.5 O <sub>2</sub> (MIXED)
0.85 CO <sub>2</sub>		CO <sub>2</sub> → CO(MIXED) + 0.5 O <sub>2</sub> (MIXED)

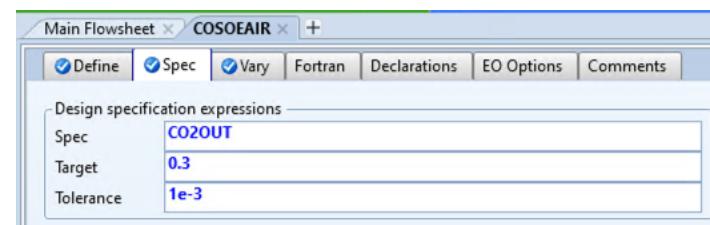
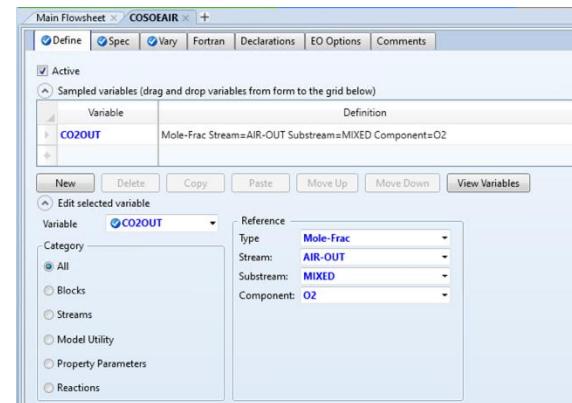
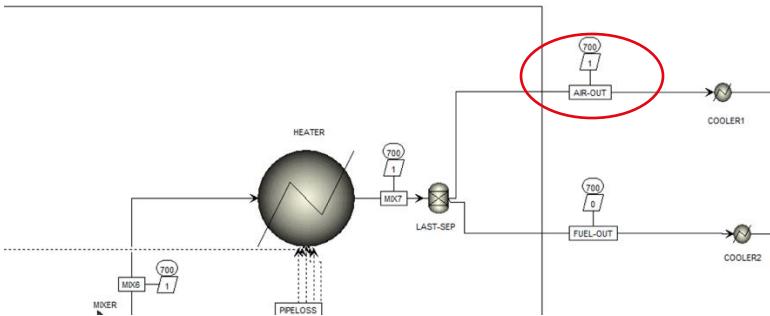
- Target: “AIR-OUT” O<sub>2</sub> mole fraction = 0.3

- If there is no air flow input, then the O<sub>2</sub> mole fraction is 1, which is dangerous for stack material, and also it is not SAFE!
  - “AIR1” mole flow rate can be adjusted, to reach this target, as it contains N<sub>2</sub> and it can dilute the concentration of O<sub>2</sub>

## Step 4: Create a design specification block, define the air flow rate input

- Target: “AIR-OUT” O<sub>2</sub> mole fraction = 0.3
  - If there is no air flow input, then the O<sub>2</sub> mole fraction is 1, which is dangerous for stack material, and also it is not SAFE!
  - “AIR1” mole flow rate can be adjusted, to reach this target, as it contains N<sub>2</sub> and it can dilute the concentration of O<sub>2</sub>

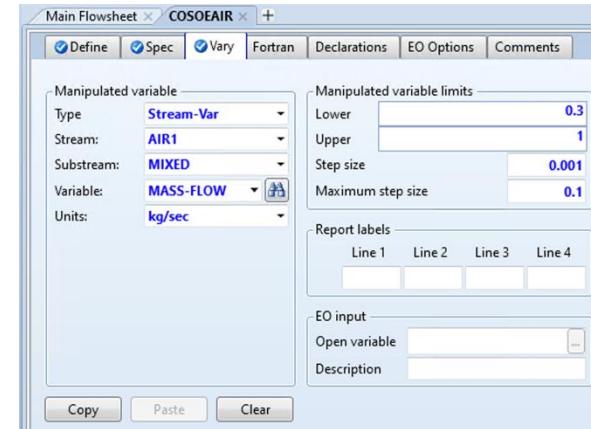
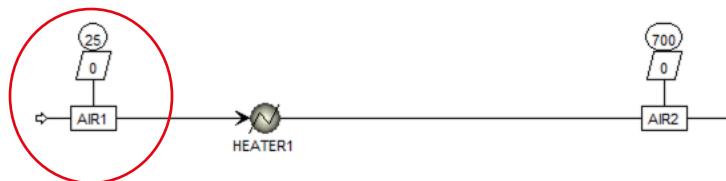
**Define** your target and specification: "AIR-OUT" O<sub>2</sub> mole fraction = 0.3



## Step 4: Create a design specification block, define the air flow rate input

- Target: “AIR-OUT” O<sub>2</sub> mole fraction = 0.3
  - If there is no air flow input, then the O<sub>2</sub> mole fraction is 1, which is dangerous for stack material, and also it is not SAFE!
  - “AIR1” mole flow rate can be adjusted, to reach this target, as it contains N<sub>2</sub> and it can dilute the concentration of O<sub>2</sub>

- Varying “AIR1” mass flow rate, to achieve your target and specification: “AIR-OUT” O<sub>2</sub> mole fraction = 0.3



Note: If you are sure about the lower and upper limits, you can put a very big range, but it will increase the calculation time.

## Step 4: Create a design specification block, define the air flow rate input

- Target: “AIR-OUT” O<sub>2</sub> mole fraction = 0.3

- If there is no air flow input, then the O<sub>2</sub> mole fraction is 1, which is dangerous for stack material, and also it is not SAFE!
- “AIR1” mole flow rate can be adjusted, to reach this target, as it contains N<sub>2</sub> and it can dilute the concentration of O<sub>2</sub>

- Varying “AIR1” mass flow rate, to achieve your target and specification: “AIR-OUT” O<sub>2</sub> mole fraction = 0.3

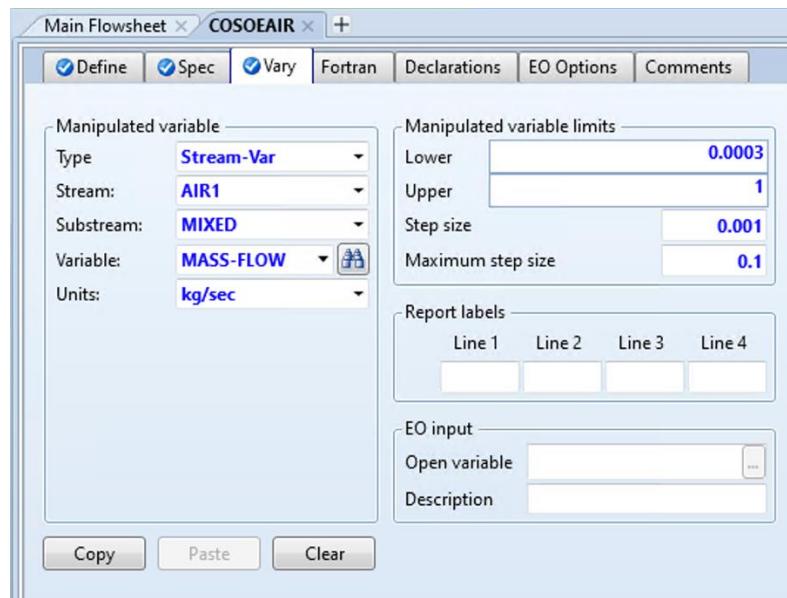
The screenshot shows the Aspen Plus software interface with the following windows:

- Main Flowsheet (COSOEAIR):** This window is used for defining manipulated variables. It shows the following settings:
  - Type: Stream-Var
  - Stream: AIR1
  - Substream: MIXED
  - Variable: MASS-FLOW
  - Units: kg/sec
  - Manipulated variable limits: Lower = 0.3, Upper = 1
  - Report labels: Line 1, Line 2, Line 3, Line 4
  - EO input: Open variable
- Simulation:** This window displays the simulation setup. The 'Results Summary' node is expanded, showing 'Run Status' and other convergence-related nodes. A message in the 'Properties' pane states: "The following Convergence blocks were completed with warnings: C-AIR1O".
- Aspen Plus messages:** This window lists several warning messages:
  - \* WARNING INITIAL VALUE FOR DESIGN SPEC VARIABLE 1 IS BELOW LOWER BOUND. VALUE = 0.129476E-01 KG/SEC LOWER BOUND = 0.300000 KG/SEC UPPER BOUND = 1.000000 KG/SEC VARIABLE RESET TO 0.370000 KG/SEC
  - \* WARNING MAX-STEP-SIZE VIOLATED. STEP ATTEMPTED: .245E-02 STEP APPLIED: .243E-02
  - \* WARNING EITHER SOLUTION OUTSIDE BOUNDS OR SPEC FUNCTION IS NOT MONOTONIC.

## Step 4: Create a design specification block, define the air flow rate input

- Target: “AIR-OUT” O<sub>2</sub> mole fraction = 0.3
  - If there is no air flow input, then the O<sub>2</sub> mole fraction is 1, which is dangerous for stack material, and also it is not SAFE!
  - “AIR1” mole flow rate can be adjusted, to reach this target, as it contains N<sub>2</sub> and it can dilute the concentration of O<sub>2</sub>

- Varying “AIR1” mass flow rate, to achieve your target and specification: “AIR-OUT” O<sub>2</sub> mole fraction = 0.3

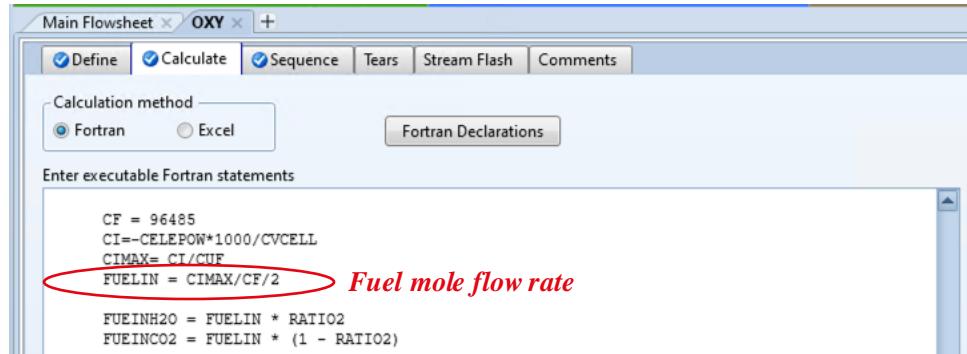


If you are not sure about the lower and upper limits, you can set it as a big range, but it can increase the calculation time.

*Now you can change the power input, the fuel and air flow rate can be calculated automatically!!*

## Step 5: Create a design specification block, define “FUEL1” H<sub>2</sub>O and CO<sub>2</sub> mole fraction

- “FUEL1” mole flow rate is automatically calculated by SOE power input ---- In “OXY” block



Main Flowsheet x OXY x +

Define Calculate Sequence Tears Stream Flash Comments

Calculation method

Fortran  Excel

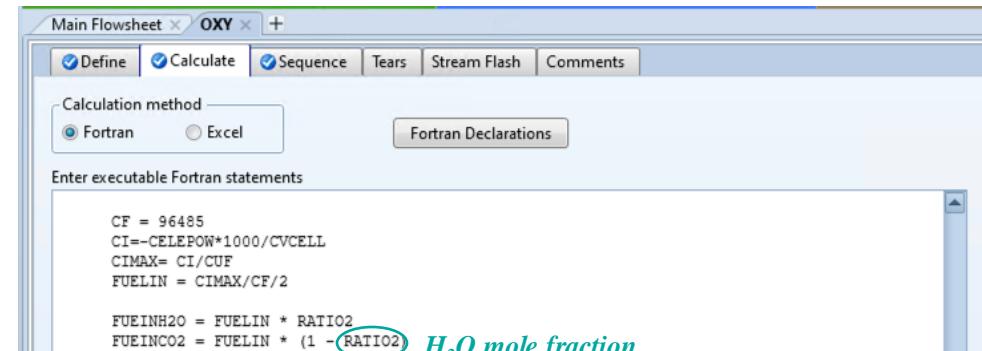
Fortran Declarations

Enter executable Fortran statements

```
CF = 96485
CI=CELEPOW*1000/CVCELL
CIMAX= CI/CF
FUELIN = CIMAX/CF/2
Fuel mole flow rate
FUEINH2O = FUELIN * RATIO2
FUEINCO2 = FUELIN * (1 - RATIO2)
```

*How about the mole fraction of H<sub>2</sub>O and CO<sub>2</sub>?*

- In “OXY” block, input parameter “RATIO2” is considered as the H<sub>2</sub>O mole fraction of fuel input “FUEL1”



Main Flowsheet x OXY x +

Define Calculate Sequence Tears Stream Flash Comments

Calculation method

Fortran  Excel

Fortran Declarations

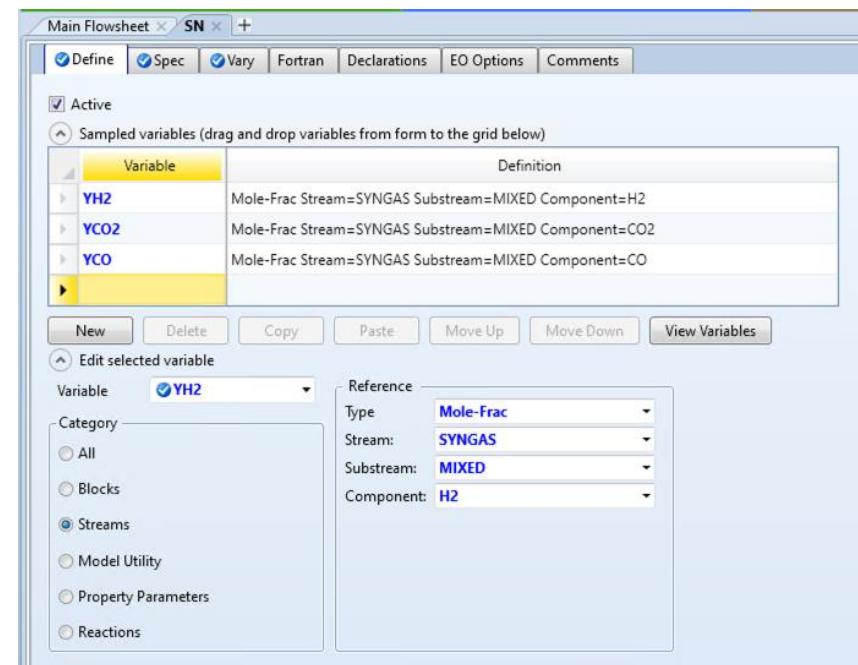
Enter executable Fortran statements

```
CF = 96485
CI=CELEPOW*1000/CVCELL
CIMAX= CI/CF
FUELIN = CIMAX/CF/2
H2O mole fraction
FUEINH2O = FUELIN * RATIO2
FUEINCO2 = FUELIN * (1 - RATIO2)
```

Step 5: Create a design specification block, define “FUEL1” H<sub>2</sub>O and CO<sub>2</sub> mole fraction

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

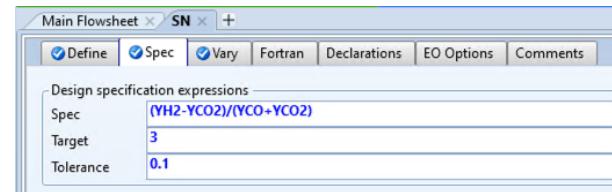
- Requirement: “SYNGAS” SN = 3, by varying parameter “RATIO2”
- **Define** all the information that you need to calculate SN



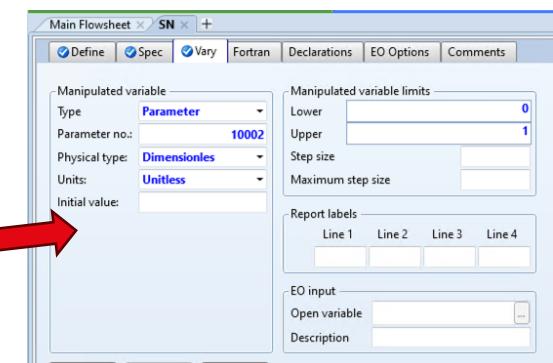
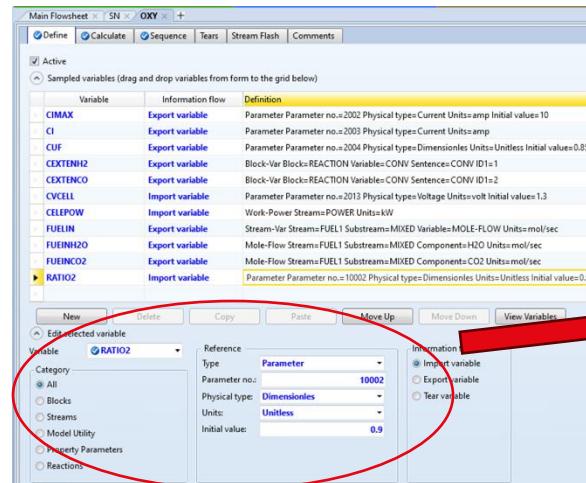
Step 5: Create a design specification block, define “FUEL1” H<sub>2</sub>O and CO<sub>2</sub> mole fraction

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

- Define how to calculate SN in specification



- Varying “RATIO2”, to reach this target



- Calculator and Design Spec implementation in ASPEN
- Understand “Import variable” and “Export variable”.
- Use “Variable explorer” to find the “path” of variable
- Water needs three heaters to be heated up to the right temperature
- “Power” is the input that you can change, in order to achieve the syngas flow rate
- If you have the “warning message”, please read the status, to understand where is the error.