Equilibrium Reactors Simulation

Example: Methane steam reforming is the heart of hydrogen, ammonia, and methanol plants. In such fired heaters, methane with steam reacts and as a result, CO and H_2 is produced.

$$CH_4 + H_2O \rightarrow CO + H_2$$

Alongside the reaction, another reaction named water-gas shift reaction occurs at the same time and are in a state of equilibrium.

$$CO + H_2O \rightarrow CO_2 + H_2$$

Here is the K table versus temperature for the first reaction.

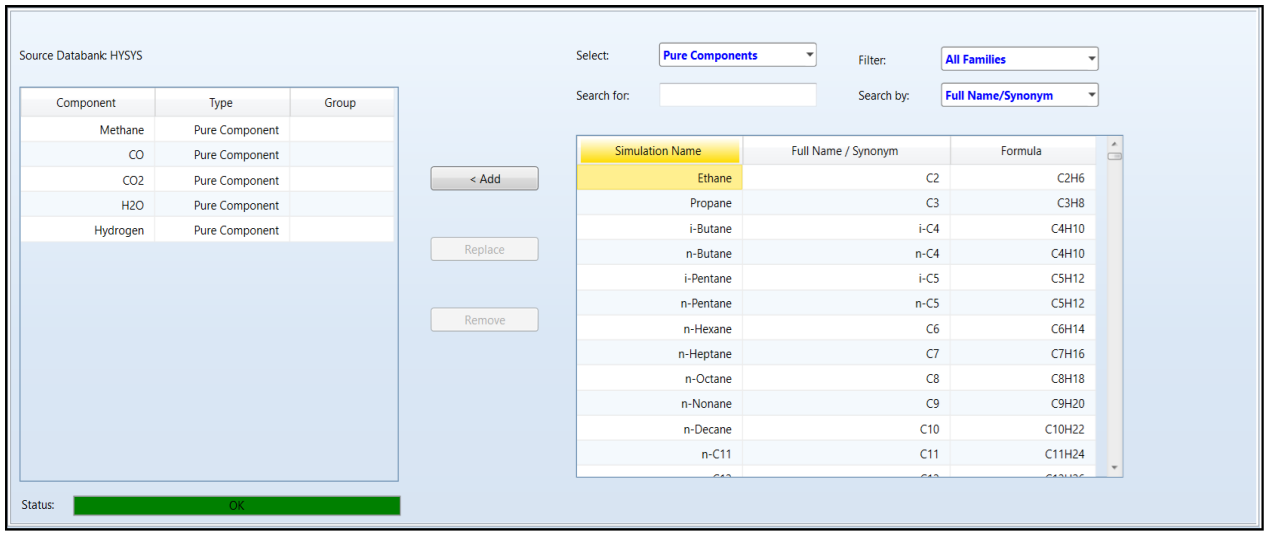
Temperature	Keq
595C	0.5
650C	3
705C	14
760C	63
815C	243
870C	817

In this example, 800 kg/hr. of methane with operating condition of 20 C, 520 kPa reacts with the steam with operating condition of 900 kPa and 180C. The Steam molar flowrate is always 2.5 times the methane molar flowrate. The inlet temperature is 760C and also consider the outlet temperature to be 760C. Determine the amount of hydrogen in the outlet of the reactor.

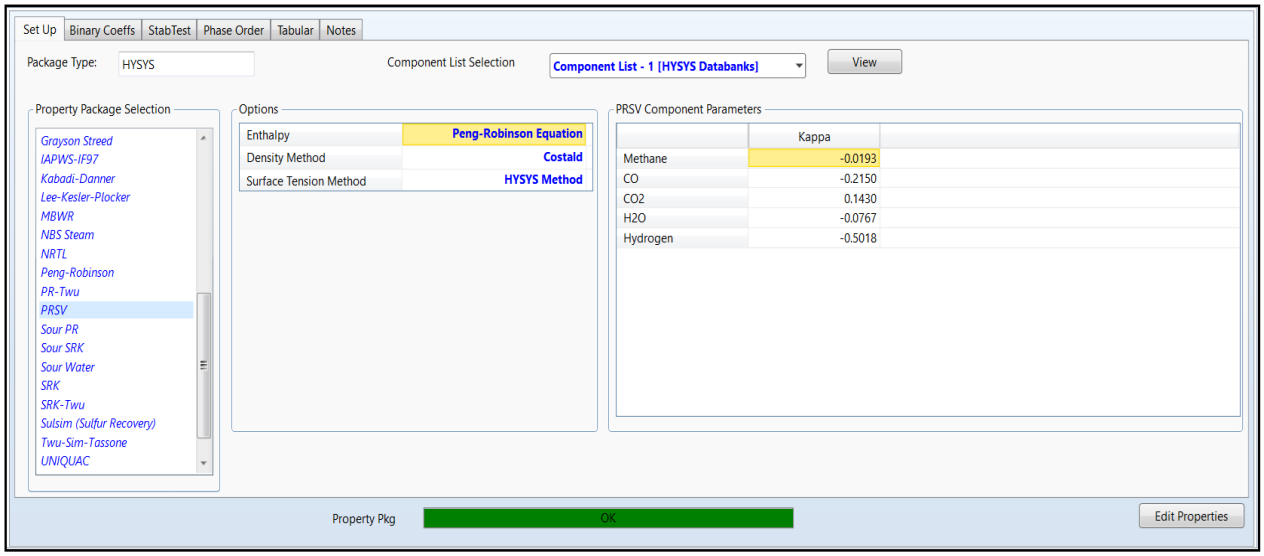
As might have noticed, we have not specified the flowrate of steam. It is typical for ammonia and methanol plants to adjust the steam flowrate in a way that steam/carbon mole ration is between 1.5-3. For this example we consider S/C = 2.5

How to simulate:

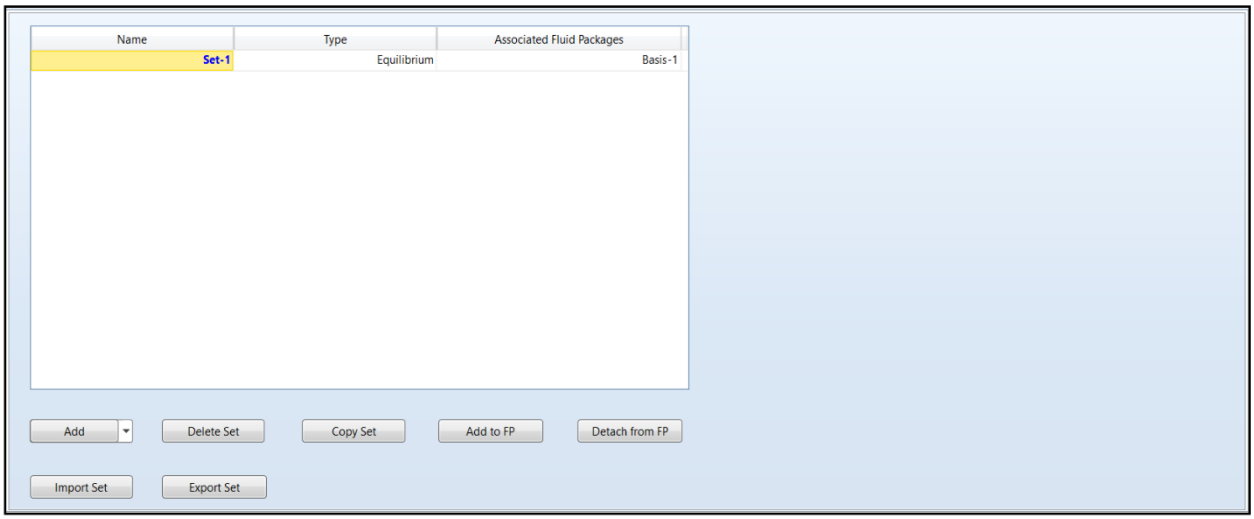
1.Add the reactants and the products to the component list:

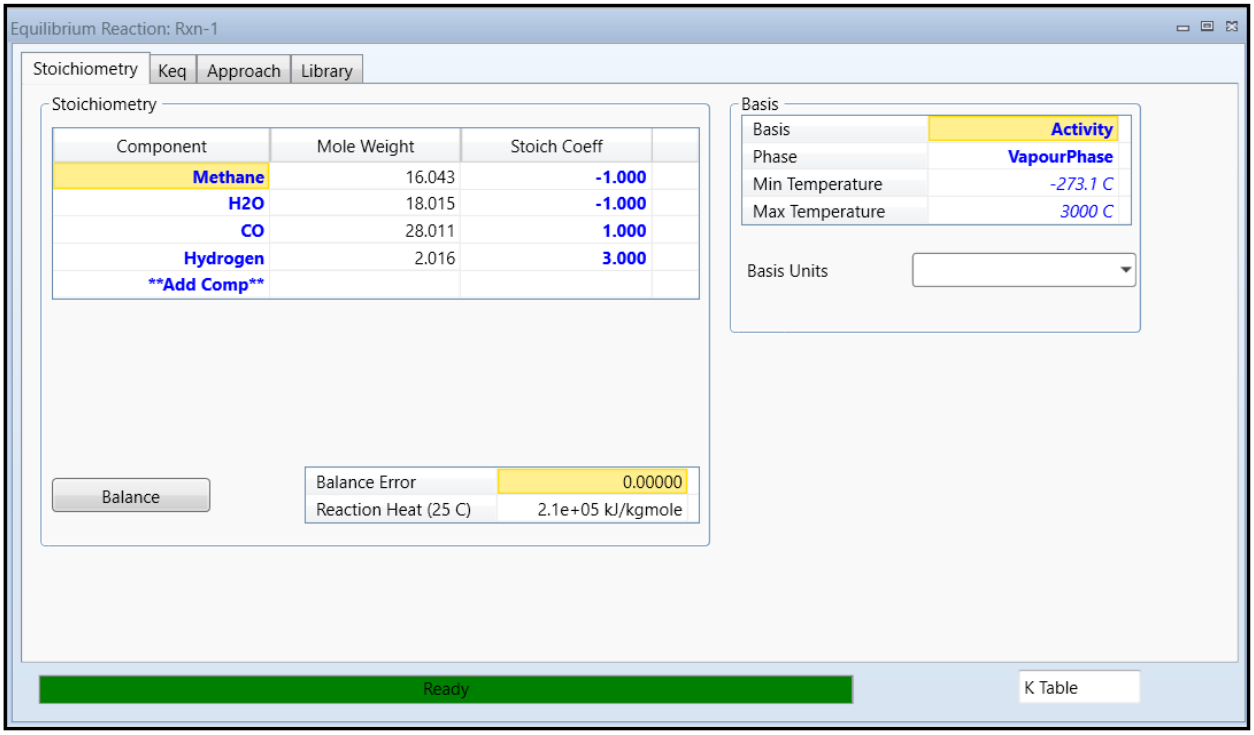


2.Select PRSV as the Fluid Package.

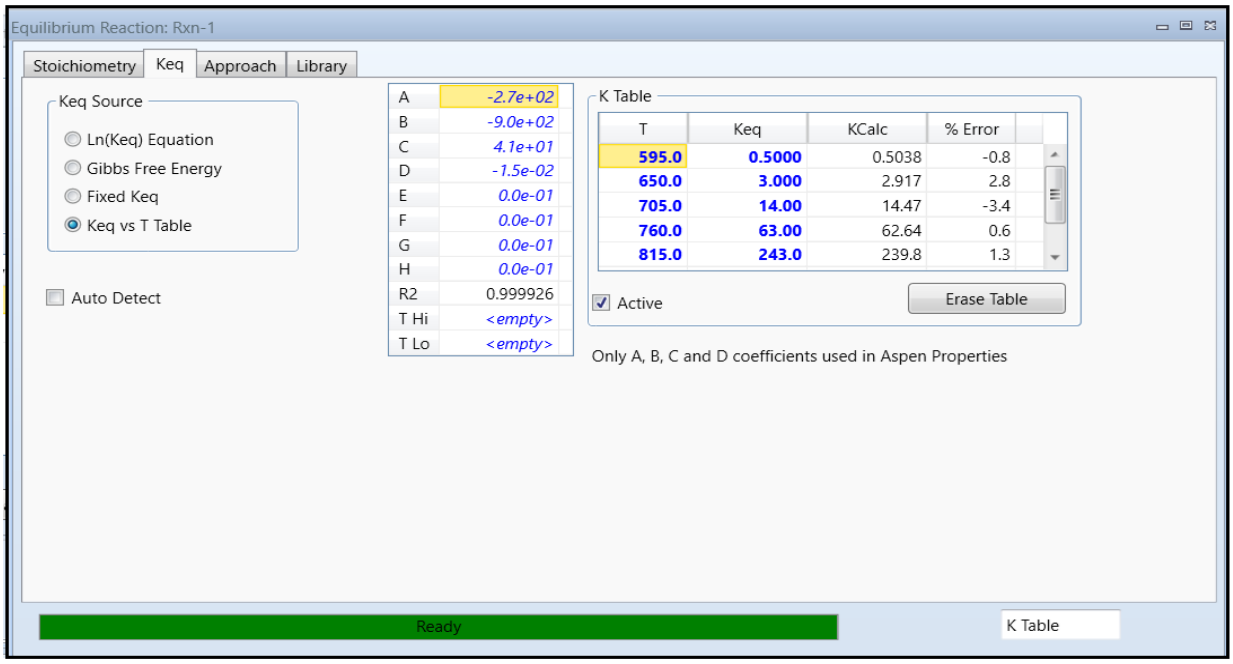


3.Under Properties/Reaction, Add a set, Add Rxn-1 and Rxn-2. For Rxn-1, add the first reaction. Select Equilibrium for both reactions.

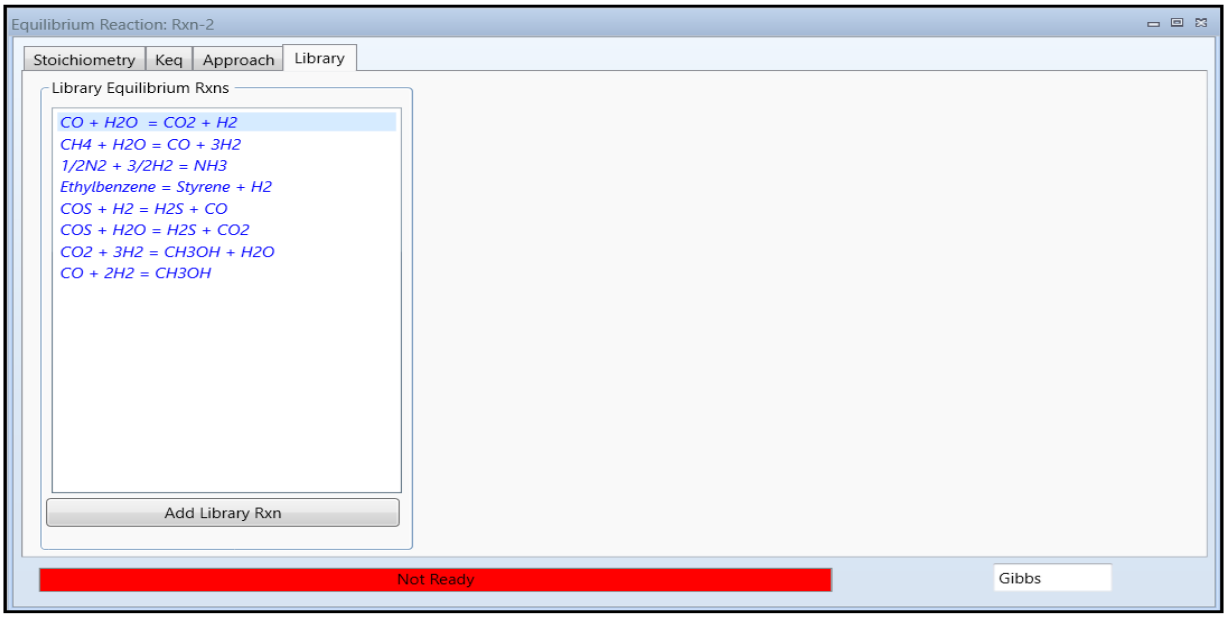




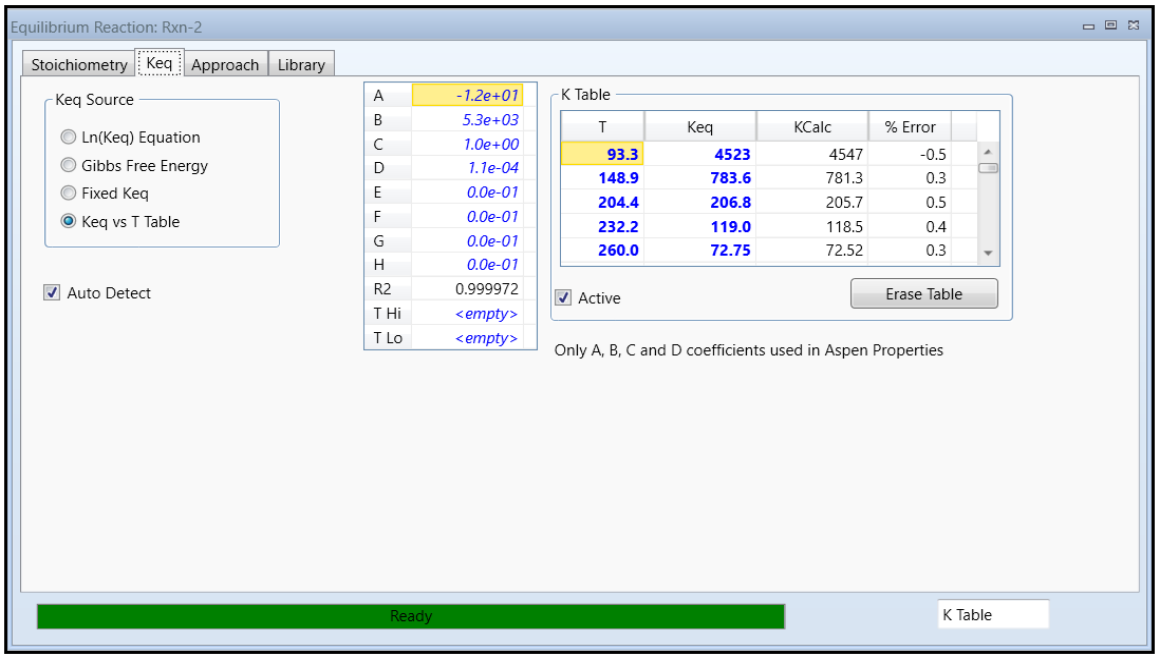
4.Under Keq, add K for different temperatures. By default, Hysys selects Gibbs Free Energy but this source is selected when we don't have that much information but here, we have K table and thus select the last source. Simply add T versus K in the table.



5.Now for second reaction, click on library, and select the second reaction from the library. Yes, Aspen has it!

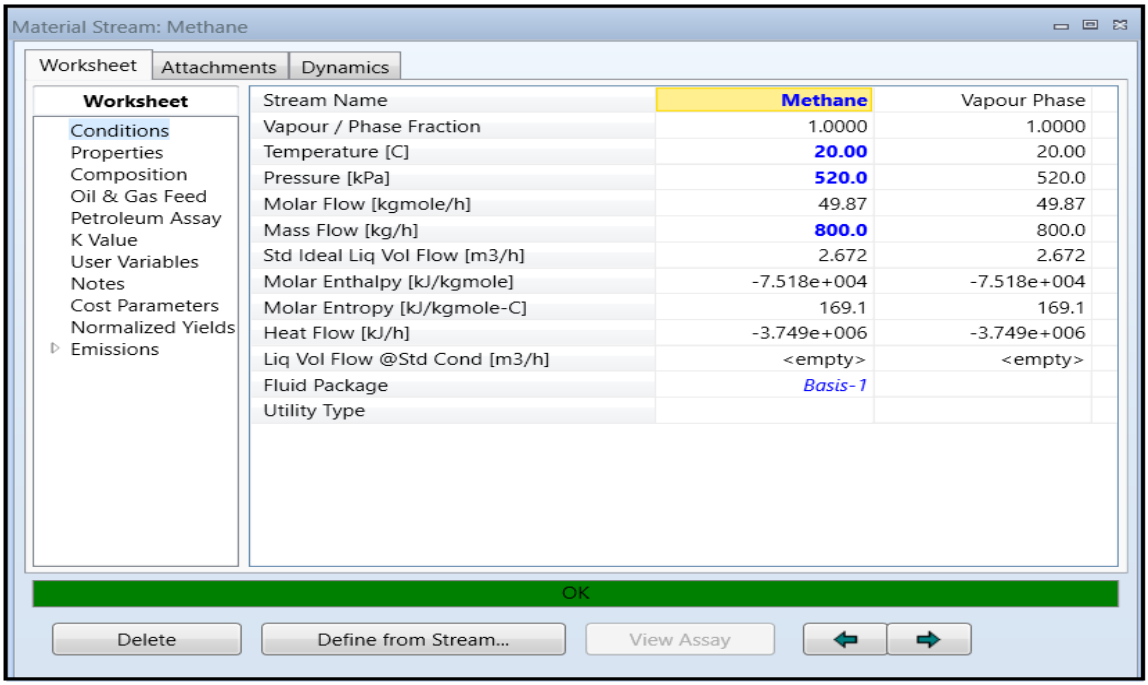


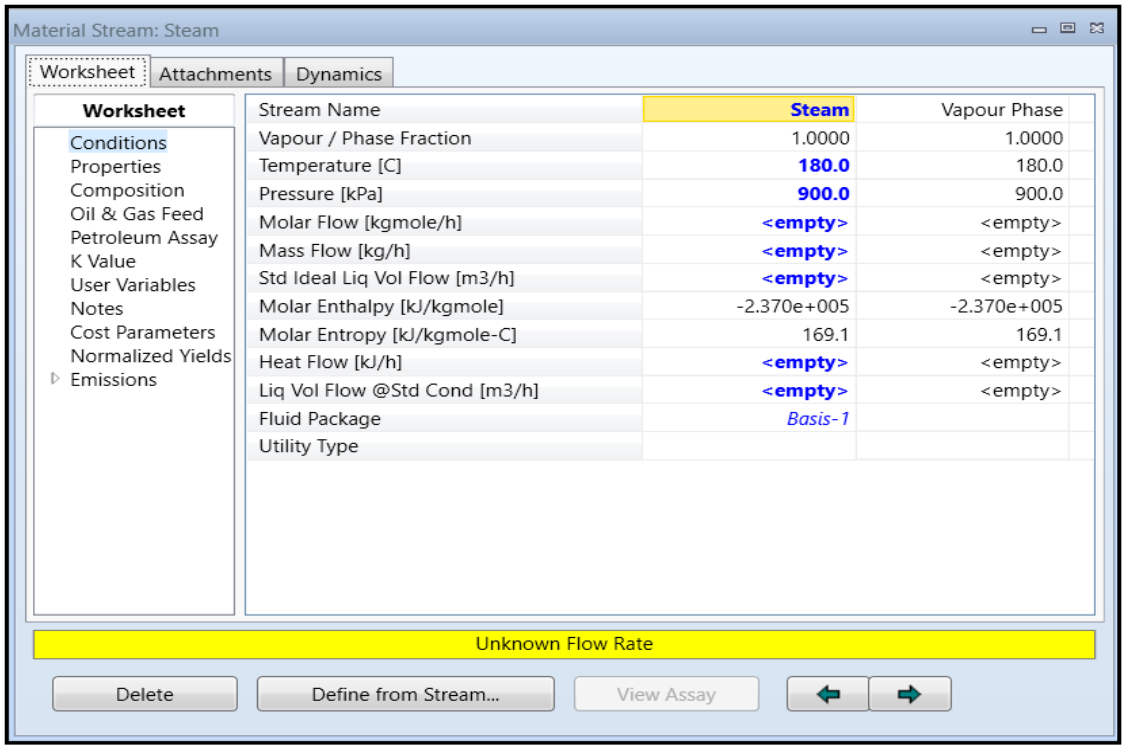
Now if you check the Keq tab, you should see the following:



Finally click add to FP.

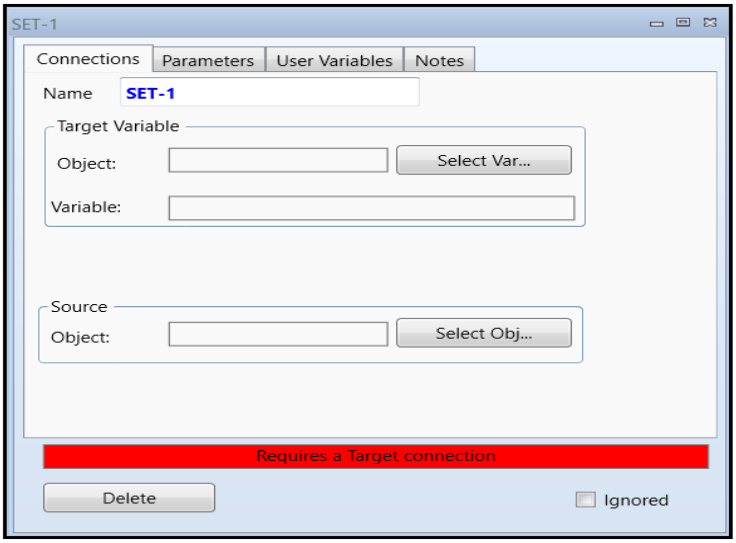
6. Now enter Simulation Environment and define the stream named Methane and Steam.



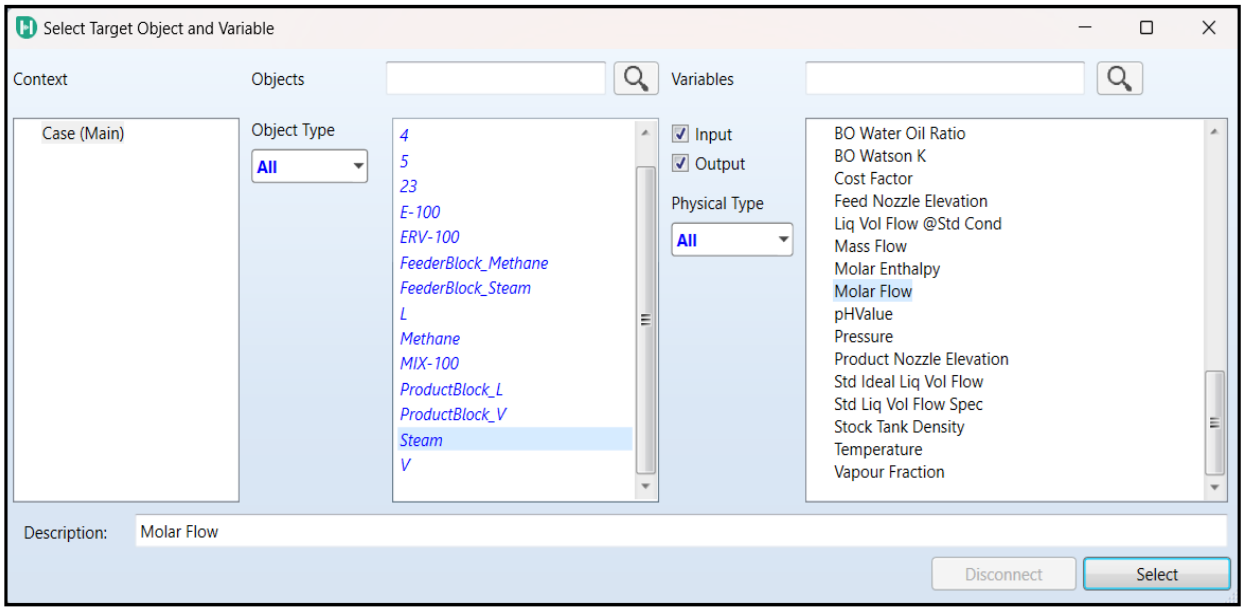


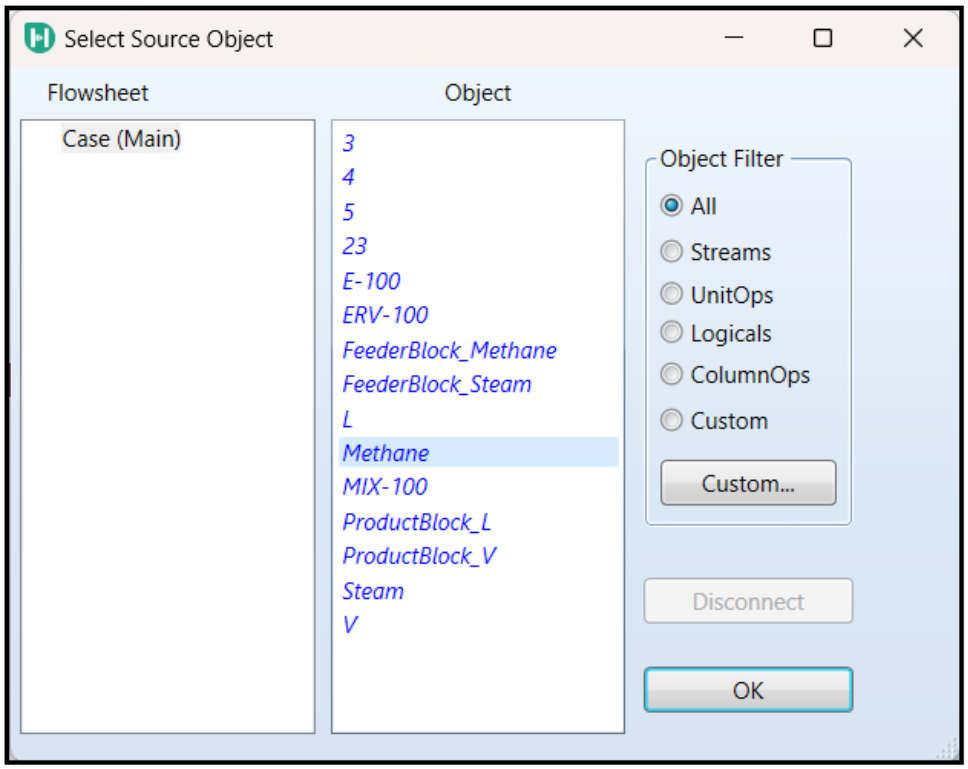
Since we always want the S/C to be 2.5 without changing the flowrate of steam, we can use Set tool in Aspen Plus. The reason we want to happen this way stems from the fact that for methanol or ammonia fired heater, if we deviate from such ratio, cocking happens. So, when the methane flowrate changes, the flowrate of steam should be changed correspondingly by controllers in FCS in monitoring system. How to simulate it in Hysys? We use Set.

7.Select Set from Model Pallete and put it in the flowsheet.

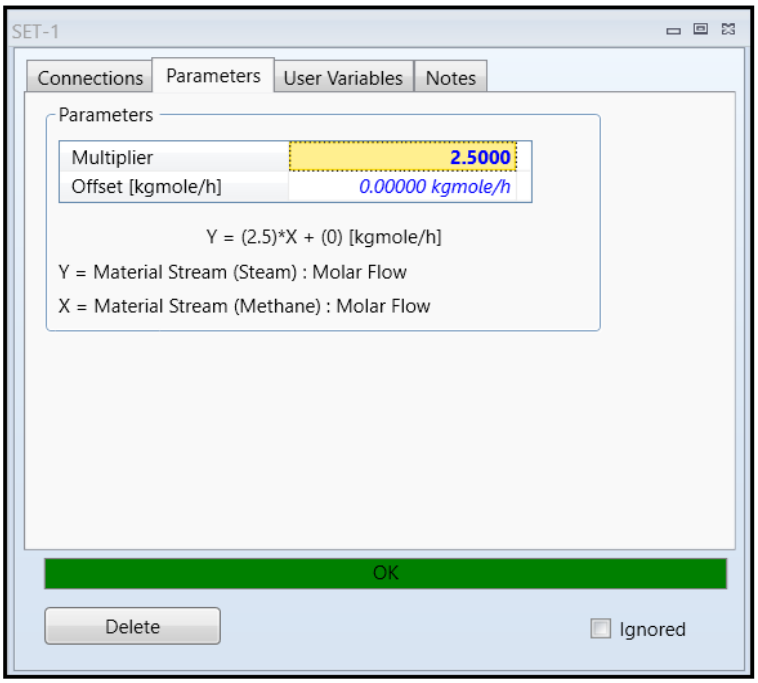


Target Variable in our example is mole flowrate of steam while source is the flowrate of the methane.

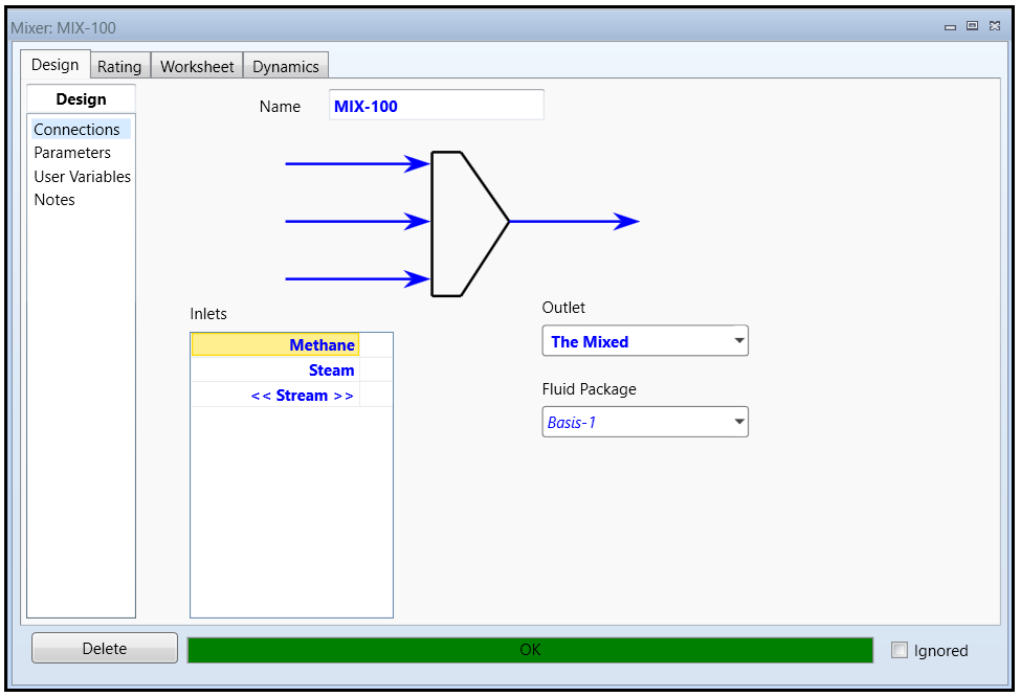




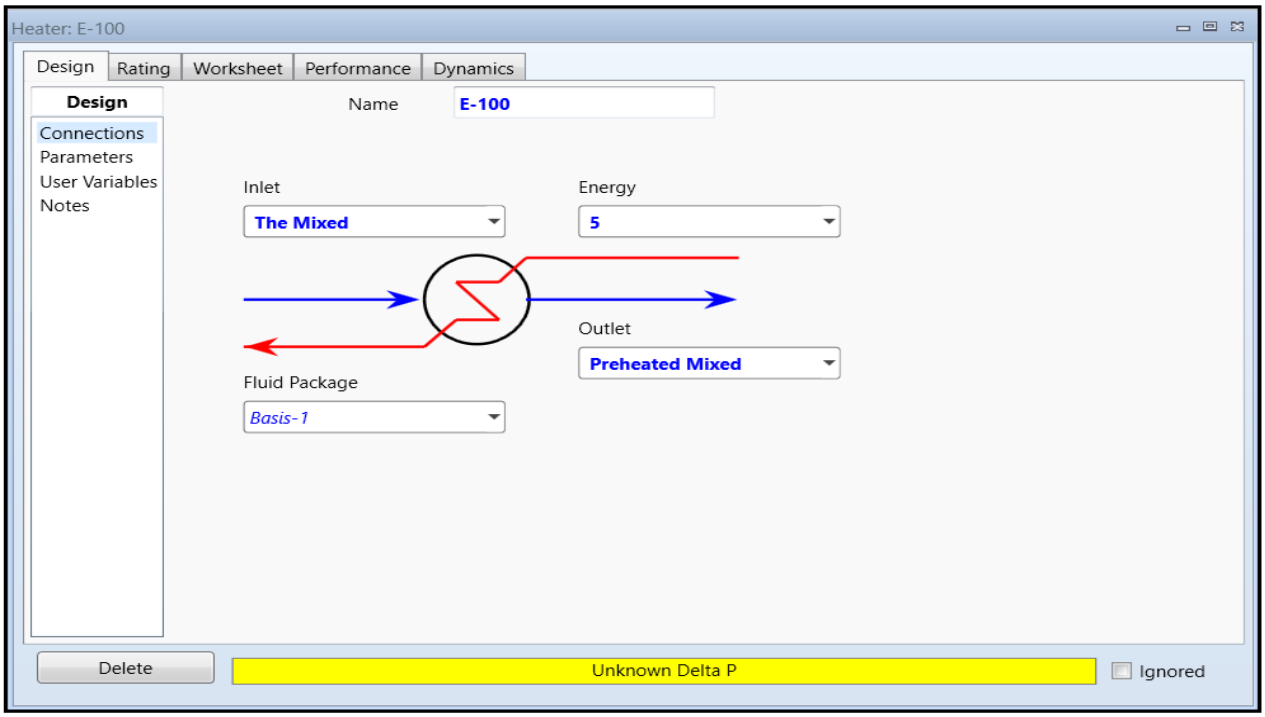
Finally in Parameter tab, the multiplier is changed from 1 to 2.5.

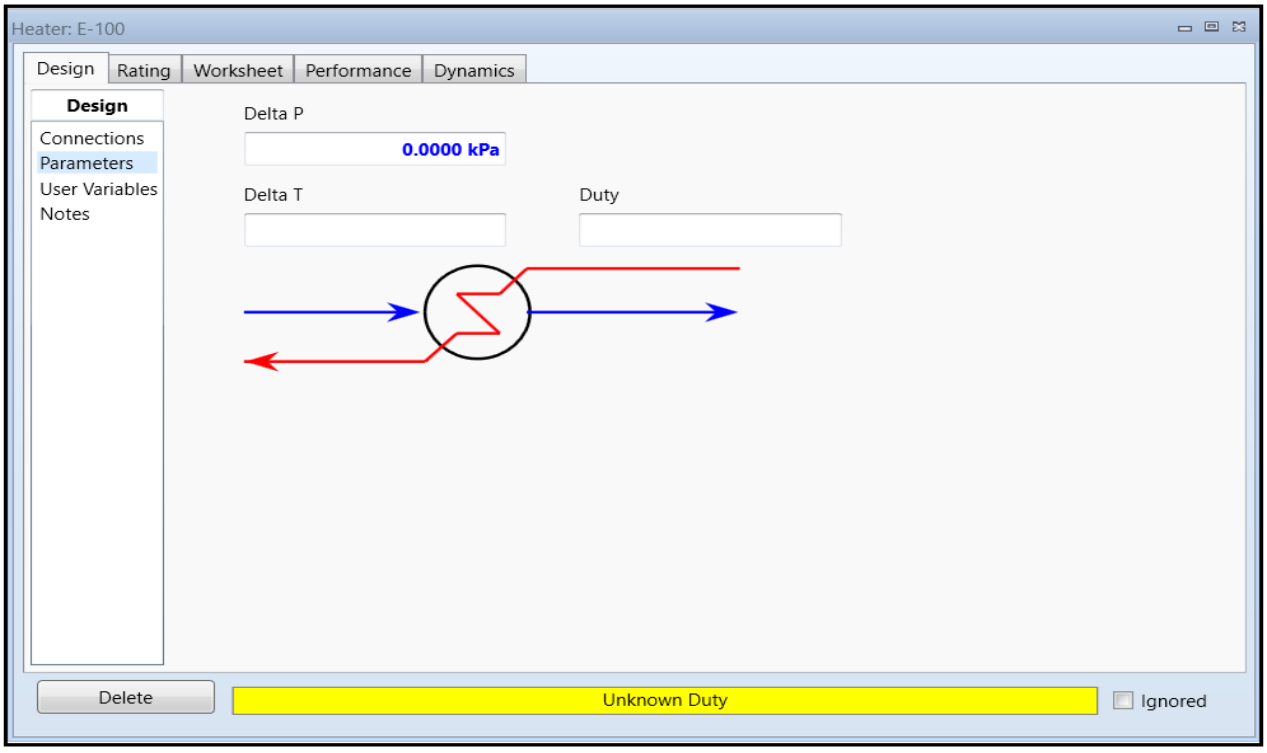


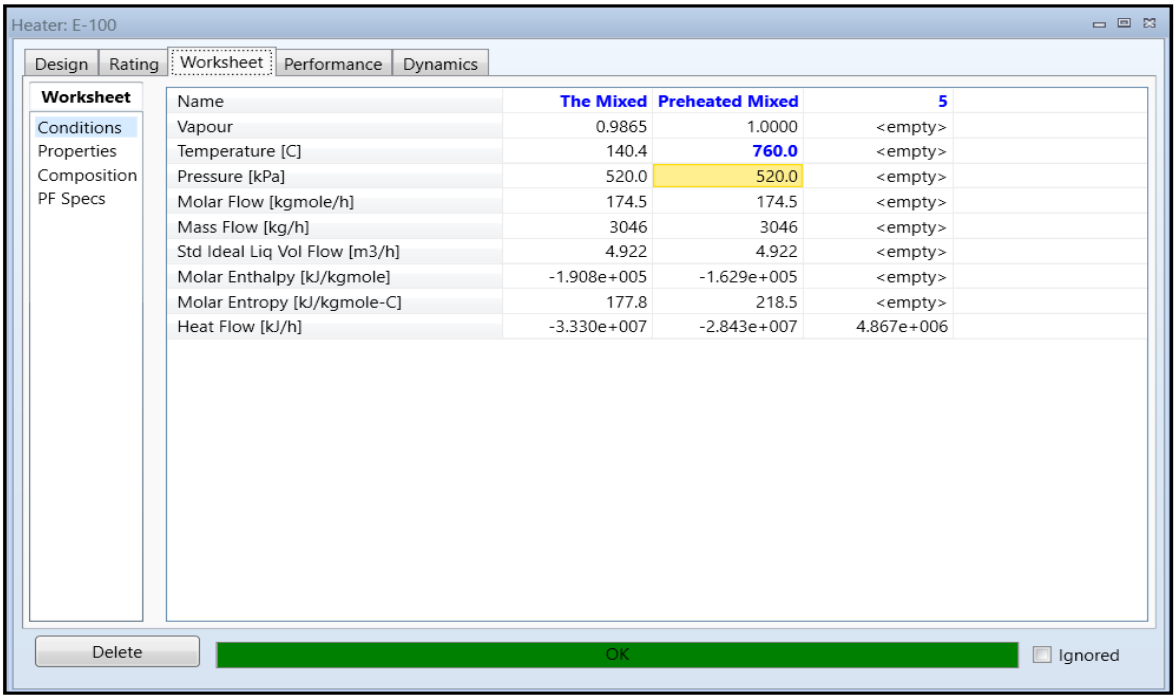
7.Now we add a mixer to mix them. Methane and Steam as inlets are selected and The Mixed stream is defined as the outlet stream.



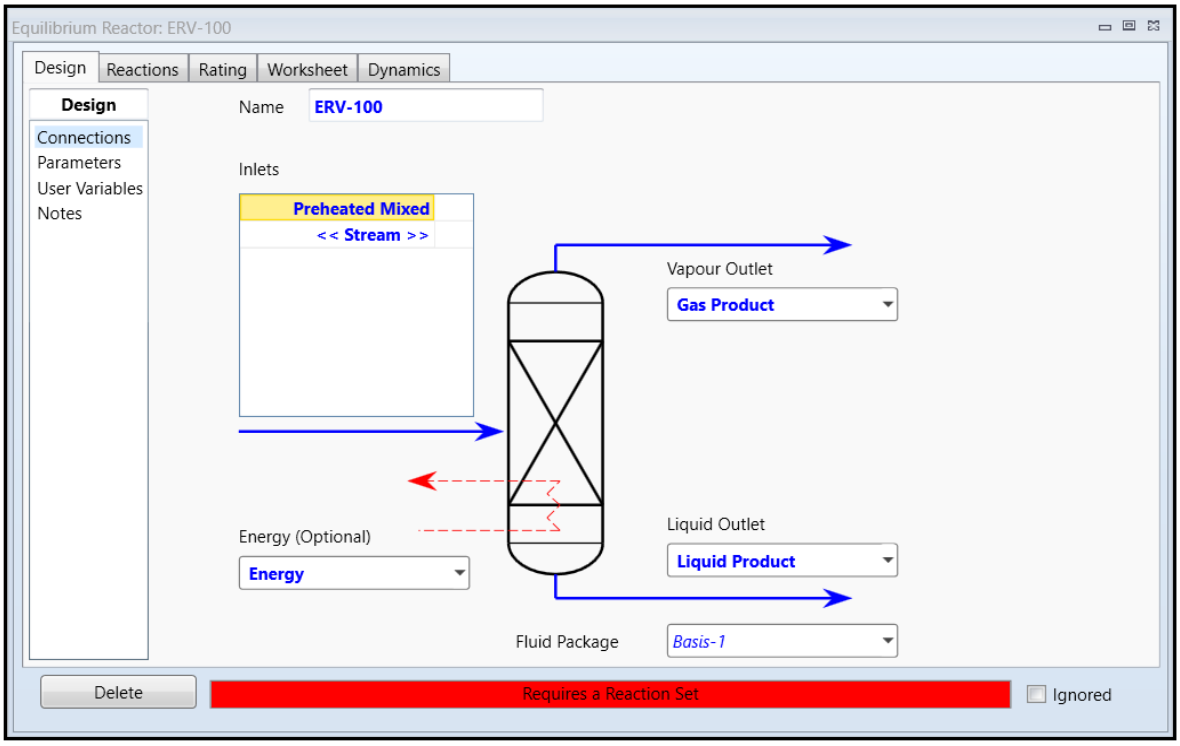
8.Add a heater to the flowsheet and heat The Mixed stream to 760C. Also, the pressure drop is zero. The outlet stream is called Preheat Mixed.



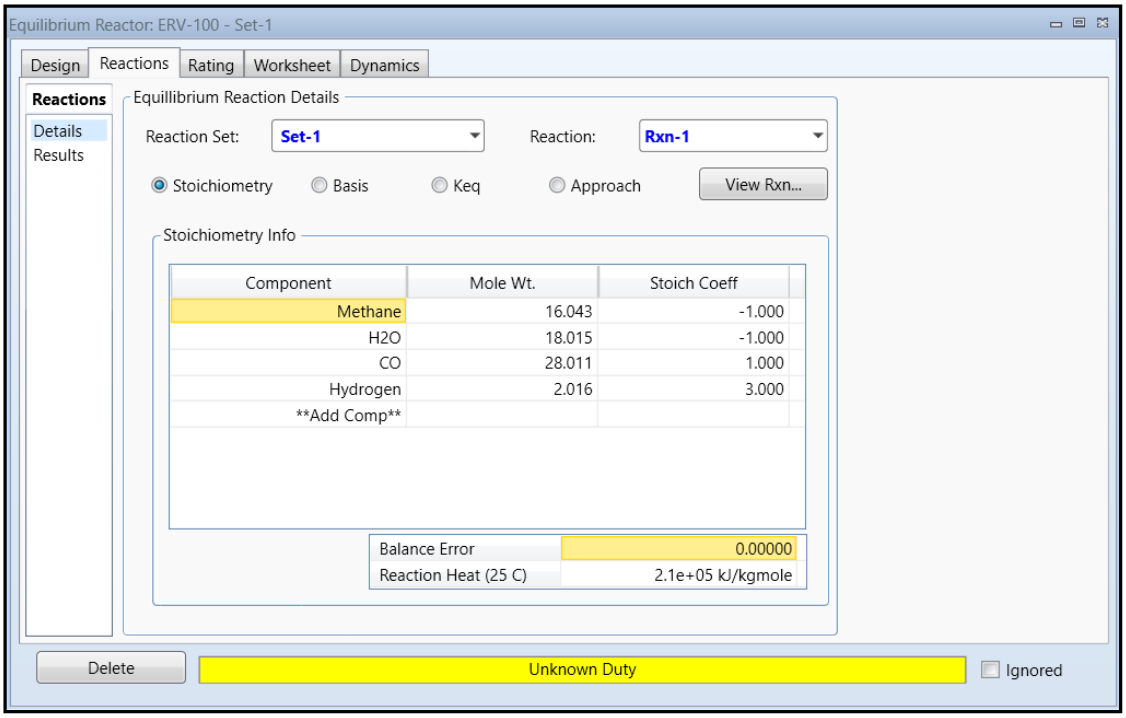




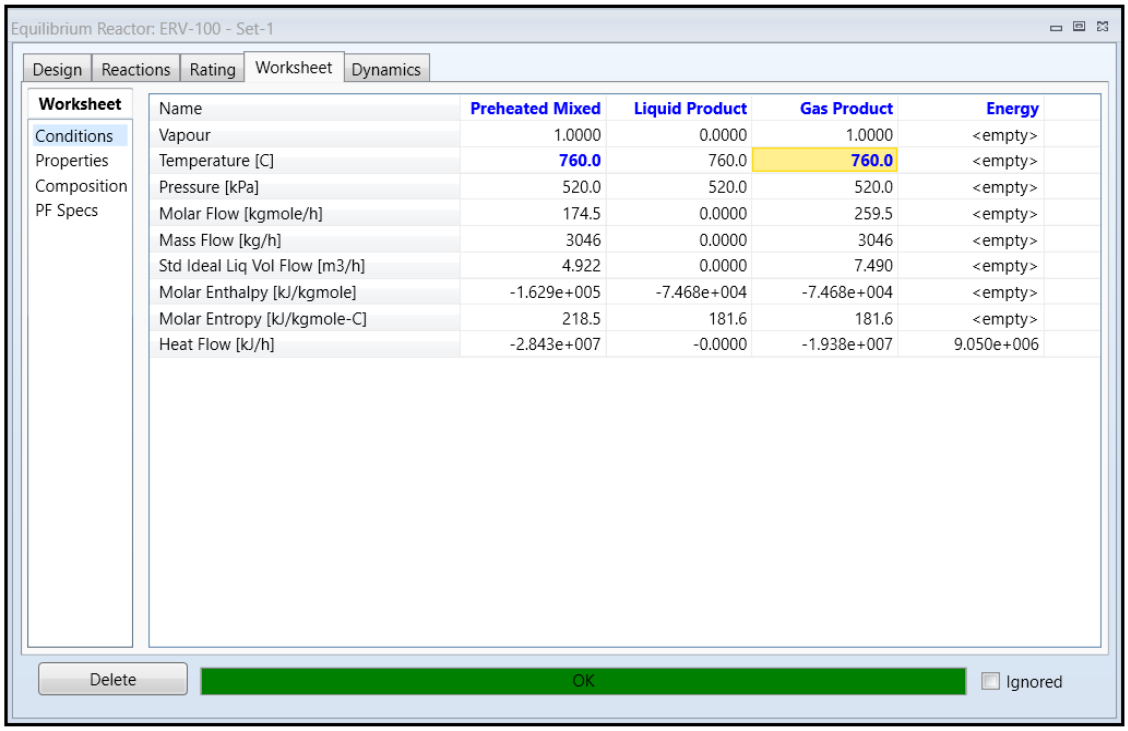
9.Select Equilibrium Reactor from Model Pallete/Reactors. Select Pre-heated Mixed as inlet and define Gas Product and Liquid Product as outlet streams.



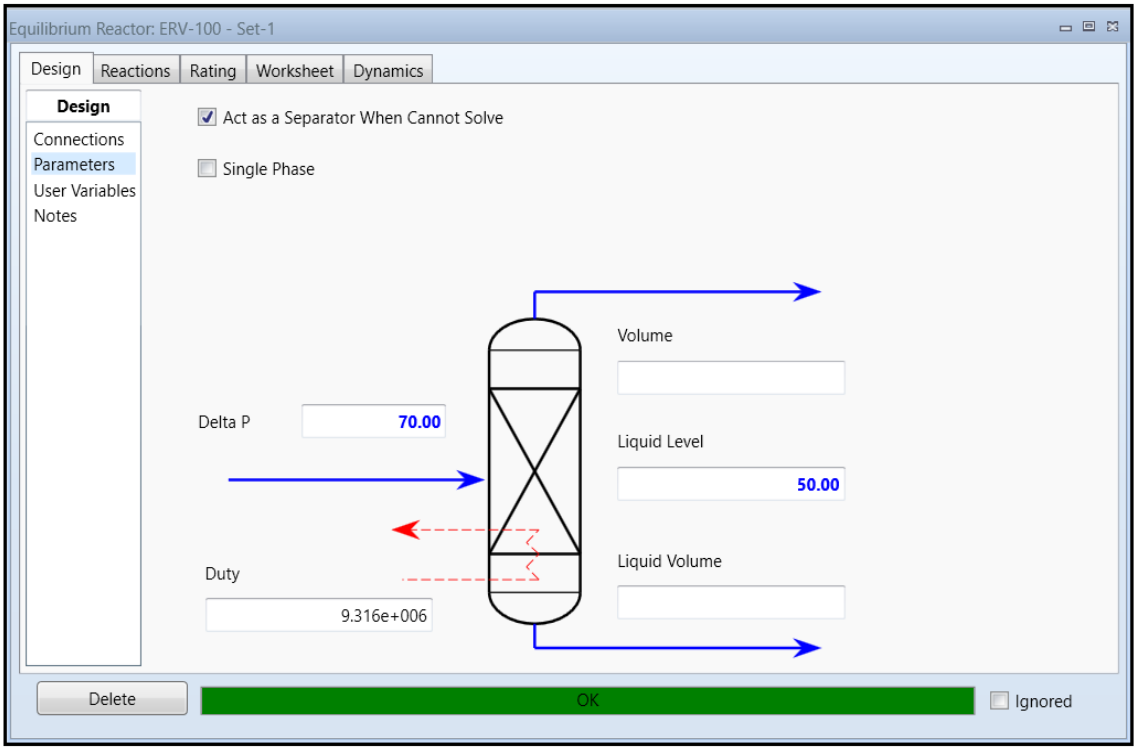
10.As indicated in red indication, a reaction set is required. Under Reaction tab, select Set-1.



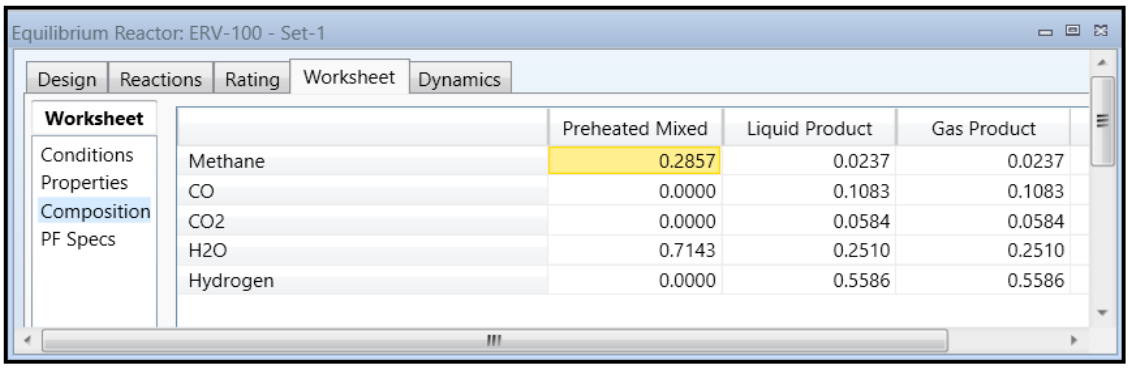
11.Under Worksheet, set the Gas Product stream outlet temperature to 760C.



12.Now under Design/Parameter, change the pressure drop to 70 kPa.

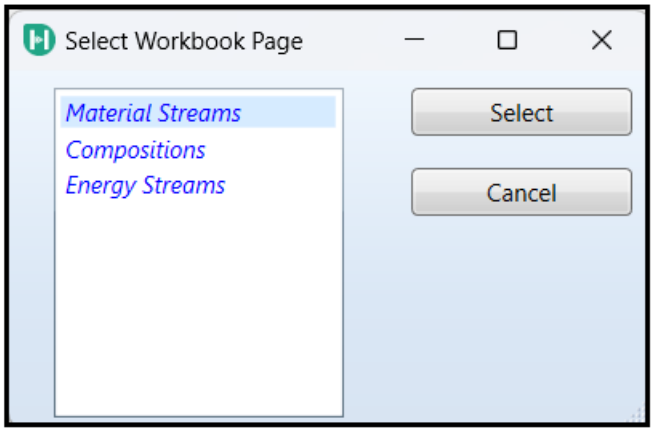


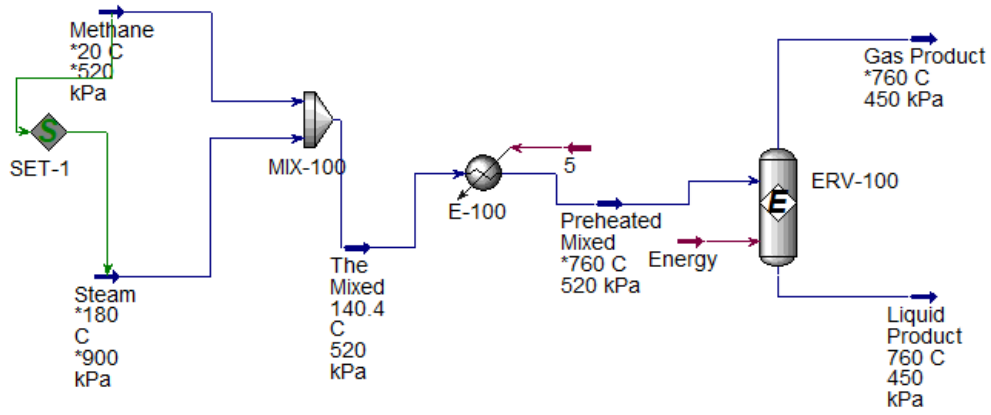
13.Based on the result, 55.8% of Gas Product is made of hydrogen and 2.3% of methane has not reacted.



	Preheated Mixed	Liquid Product	Gas Product
Methane	0.2857	0.0237	0.0237
CO	0.0000	0.1083	0.1083
CO2	0.0000	0.0584	0.0584
H2O	0.7143	0.2510	0.2510
Hydrogen	0.0000	0.5586	0.5586

We are done with simulation but before ending the simulation, let's go to Flowsheet and select Workbook and Material Stream. Also activate temperature and pressure.

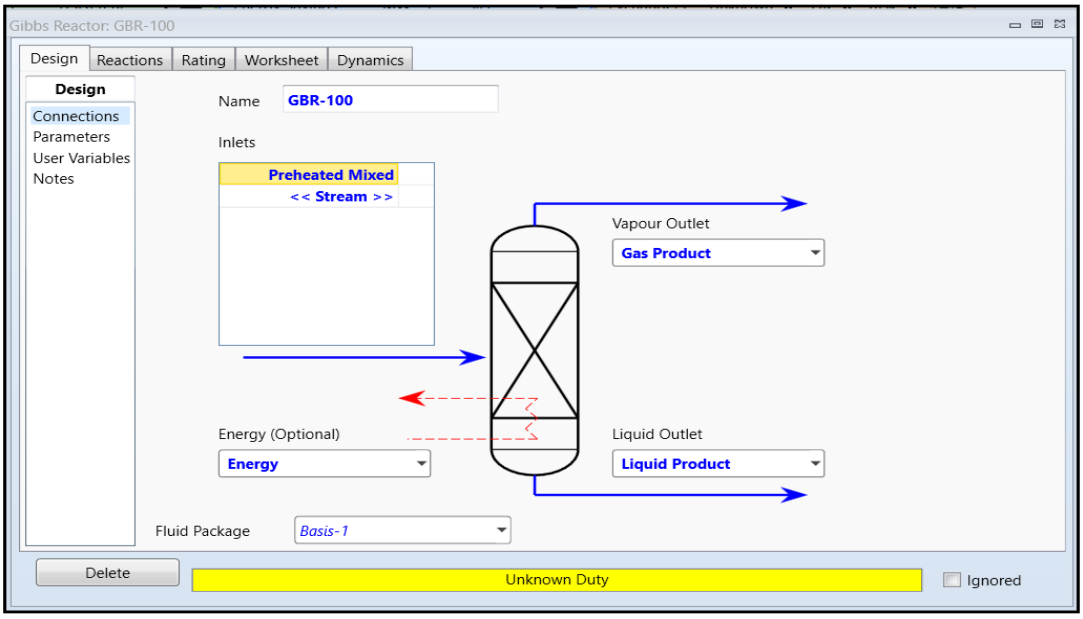




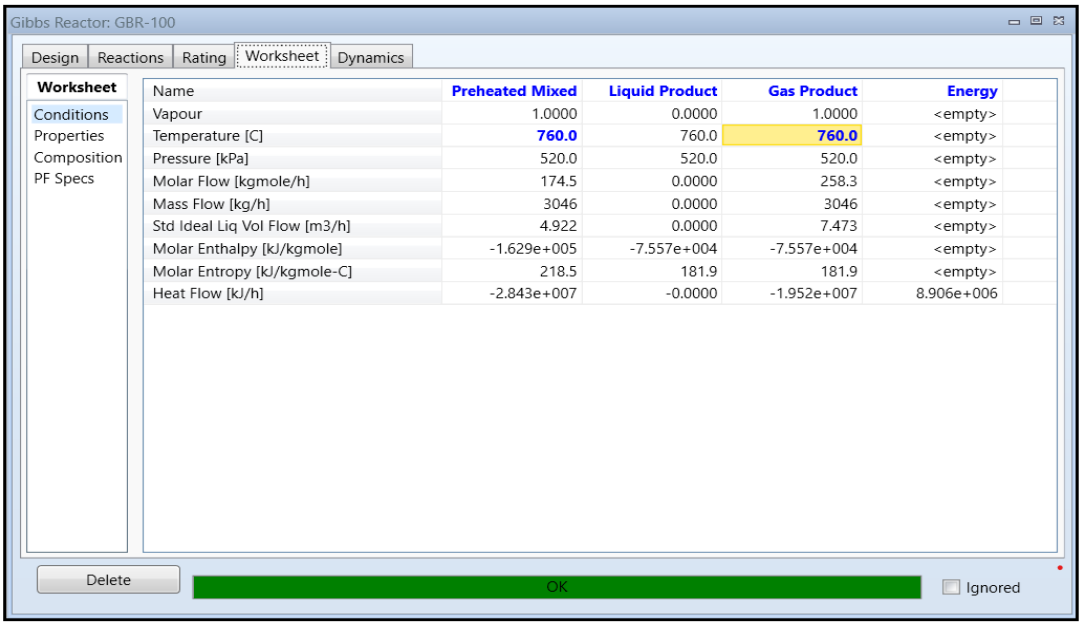
Material Streams							
		Methane	Steam	The Mixed	Preheated Mixed	Gas Product	Liquid Product
Vapour Fraction		1.0000	1.0000	0.9865	1.0000	1.0000	0.0000
Temperature	C	20.00	180.0	140.4	760.0	760.0	760.0
Pressure	kPa	520.0	900.0	520.0	520.0	450.0	450.0
Molar Flow	kgmole/h	49.87	124.7	174.5	174.5	261.8	0.0000
Mass Flow	kg/h	800.0	2246	3046	3046	3046	0.0000
Liquid Volume Flow	m3/h	2.672	2.250	4.922	4.922	7.549	0.0000
Heat Flow	kJ/h	-3.749e+006	-2.955e+007	-3.330e+007	-2.843e+007	-1.911e+007	-0.0000

Example 2: Regarding the first example, use Gibbs Reactor to convert methane to hydrogen. Compare this example result with previous example result.

1.Select Gibbs Reactor from Model Pallete/Reactors. Connect Preheat Mixed stream as the inlet to the reactor, define Gas Product as the outlet and Liquid Product as the second outlet, and Energy as the heat provided to the reactor.

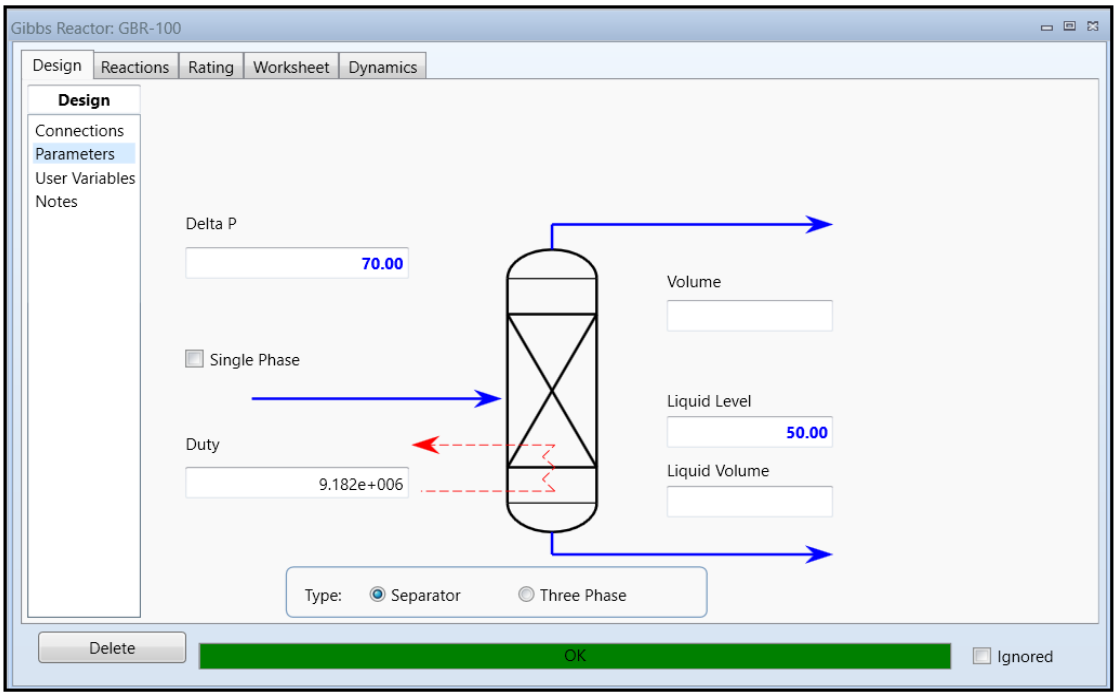


2.Under Worksheet tab, change the Gas Product temperature to 760C.

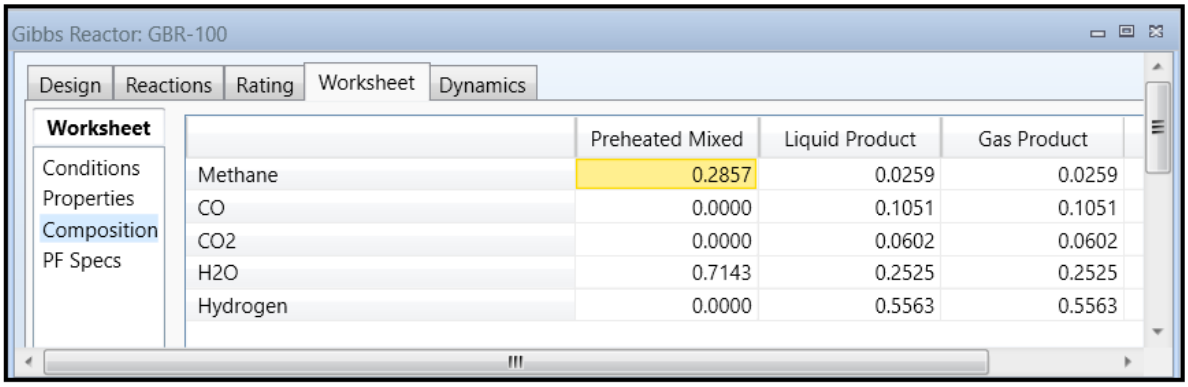


Name	Preheated Mixed	Liquid Product	Gas Product	Energy
Vapour	1.0000	0.0000	1.0000	<empty>
Temperature [C]	760.0	760.0	760.0	<empty>
Pressure [kPa]	520.0	520.0	520.0	<empty>
Molar Flow [kgmole/h]	174.5	0.0000	258.3	<empty>
Mass Flow [kg/h]	3046	0.0000	3046	<empty>
Std Ideal Liq Vol Flow [m3/h]	4.922	0.0000	7.473	<empty>
Molar Enthalpy [kJ/kgmole]	-1.629e+005	-7.557e+004	-7.557e+004	<empty>
Molar Entropy [kJ/kgmole-C]	218.5	181.9	181.9	<empty>
Heat Flow [kJ/h]	-2.843e+007	-0.0000	-1.952e+007	8.906e+006

3.Finally change the pressure drop to 70 kPa



4.Here is the result:



	Preheated Mixed	Liquid Product	Gas Product
Methane	0.2857	0.0259	0.0259
CO	0.0000	0.1051	0.1051
CO2	0.0000	0.0602	0.0602
H2O	0.7143	0.2525	0.2525
Hydrogen	0.0000	0.5563	0.5563

5.Comparison

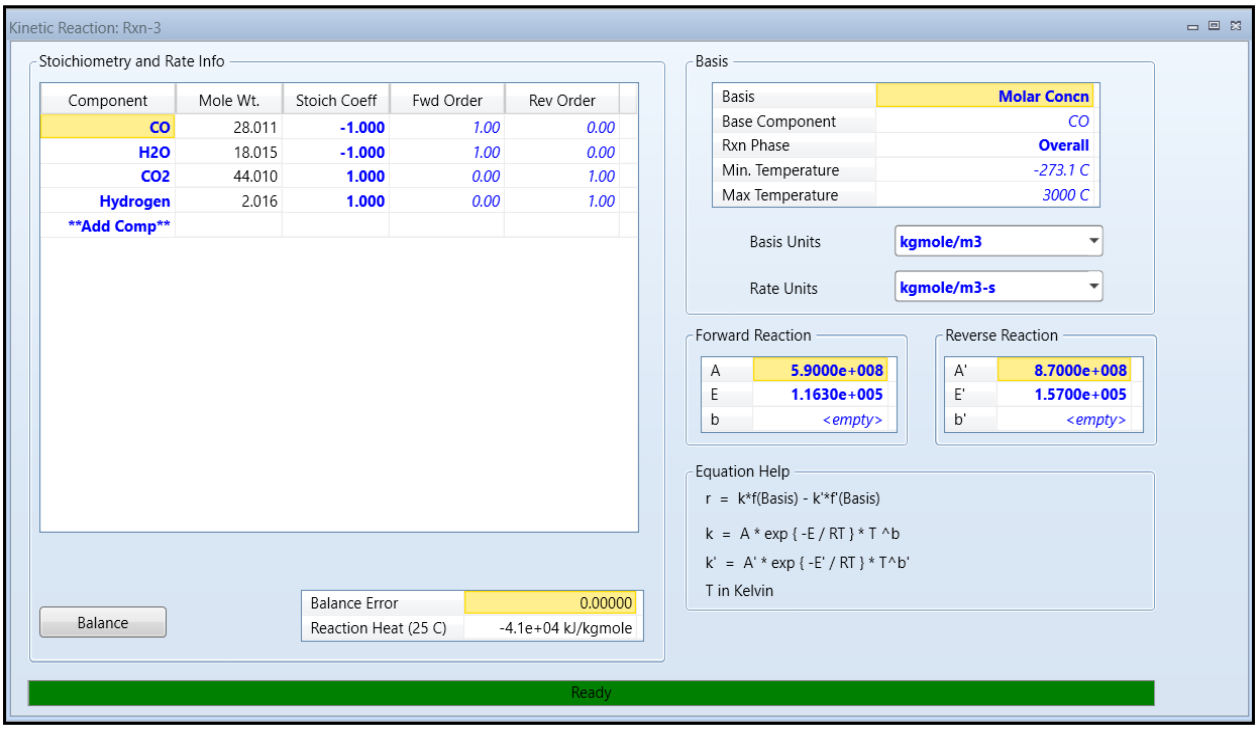
Example 3: Regarding the first example result, CO mole fraction in the stream is approximately 10%. In this example we will show how to convert all CO to hydrogen via water-gas-shift reaction in a Plug Flow Reactor or PFR.

$$CO + H_2O \rightarrow CO_2 + H_2$$

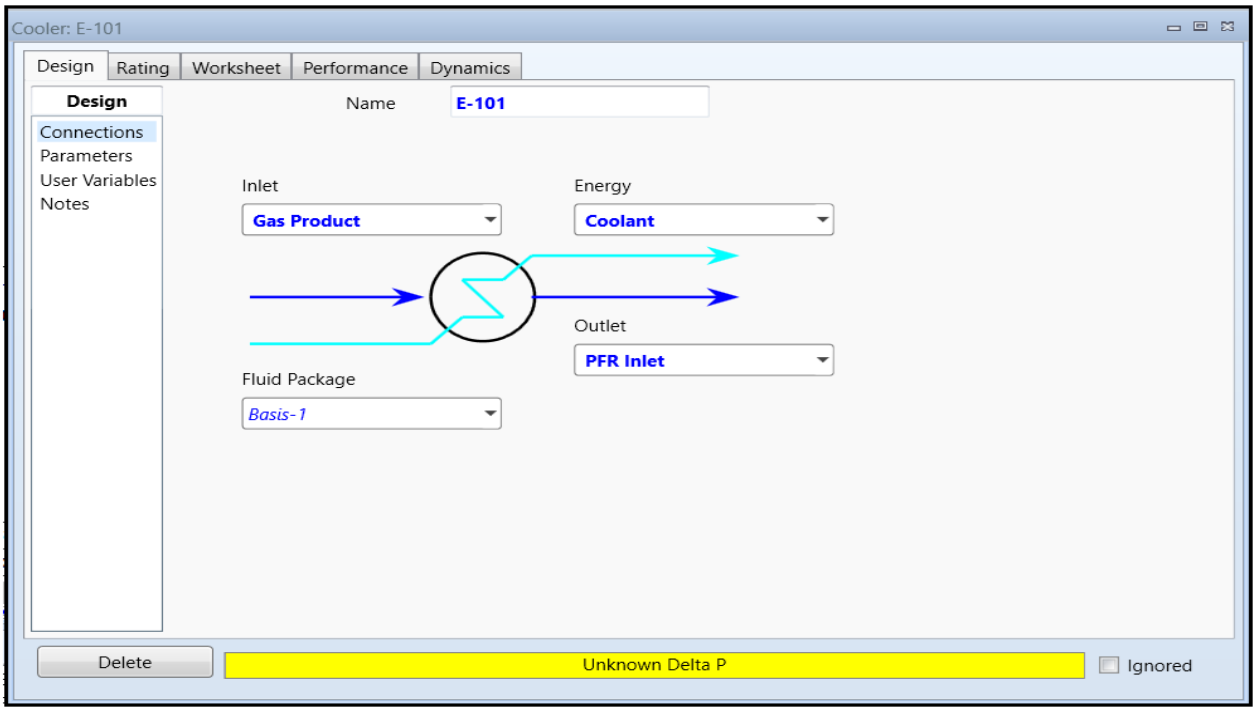
The reaction takes place around 430C. Run the software for two scenarios; in first scenario, the length and diameter of reactor are 15m and 3m respectively while in second scenario, the length and diameter of the reactor are 12m and 2.4m.

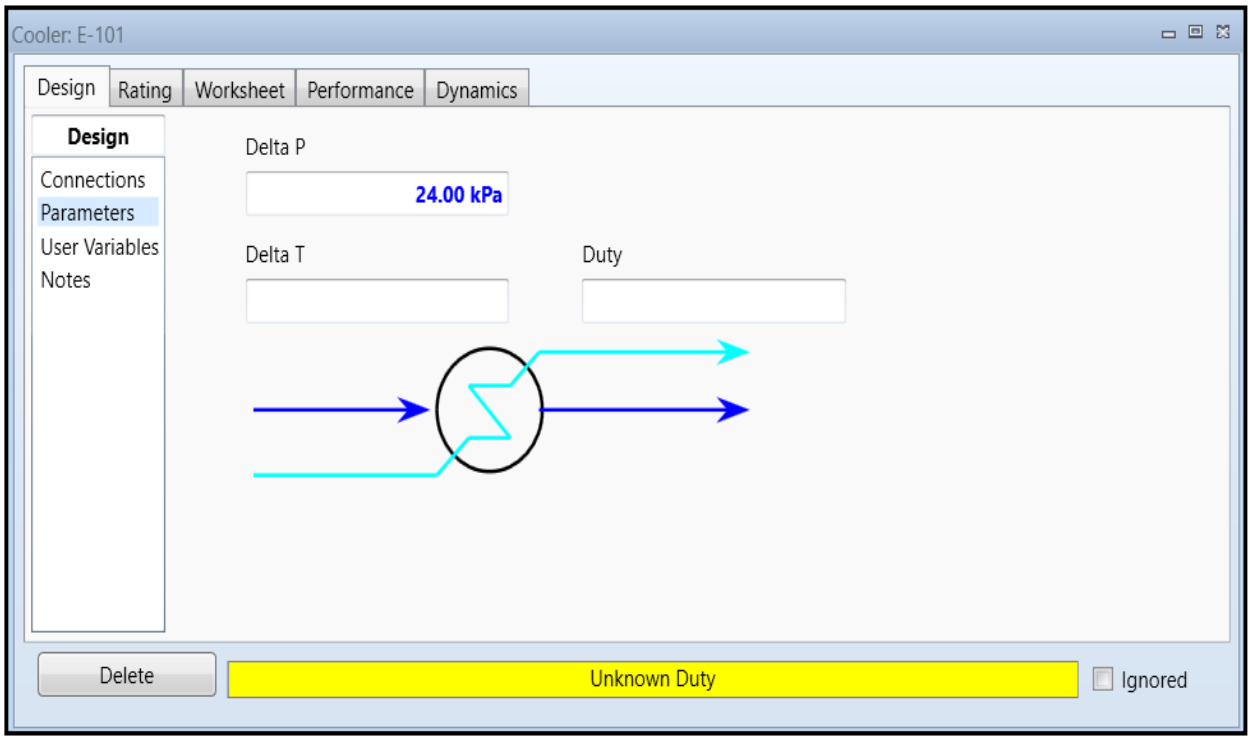
Note: It is not possible to use equilibrium reaction for PFR. Only kinetic reactions are used inside such reactors.

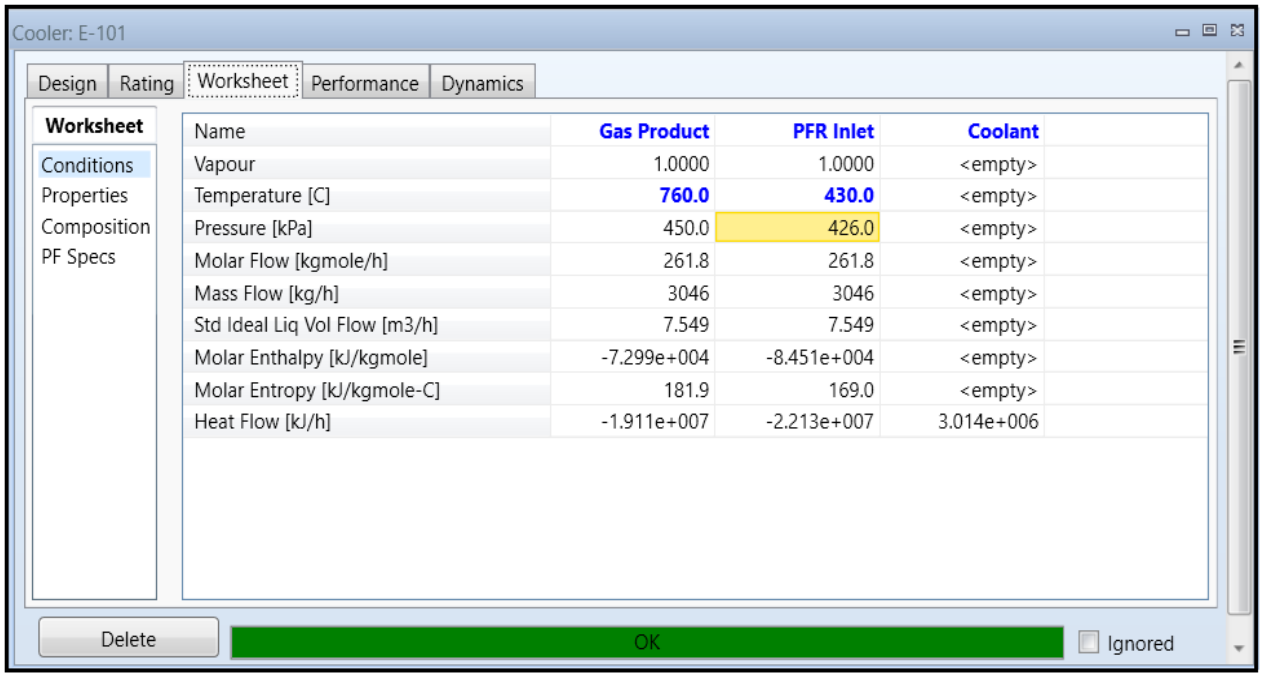
1.Open the first example file and define new set in which new reaction is added and the information like below is provided:



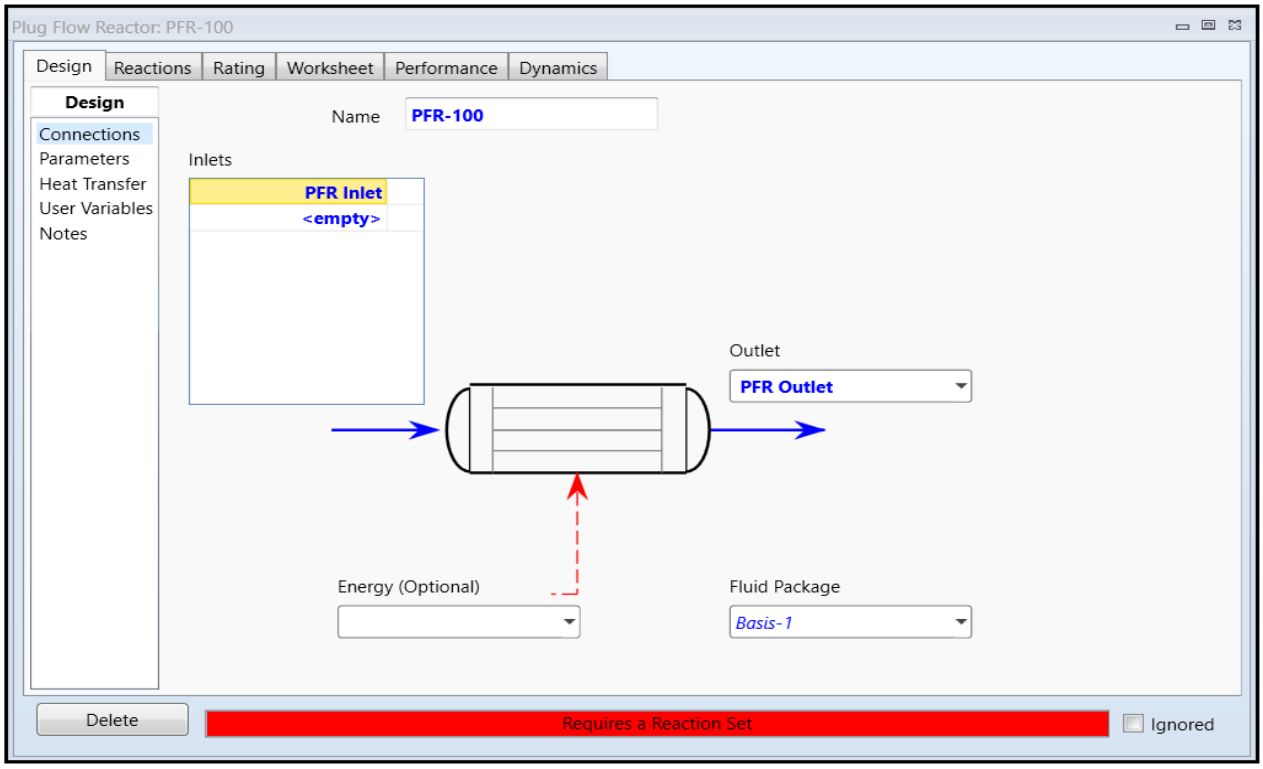
2.Enter Simulation Environment and set-up the simple heater and reduce the temperature to 430C.


Cooler: E-101
Design
Rating
Worksheet
Performance
Dynamics
Design
Connections
Parameters
User Variables
Notes
Name
E-101
Inlet
Gas Product
Energy
Coolant
Outlet
PFR Inlet
Fluid Package
Basis-1
Delete
Unknown Delta P
Ignored

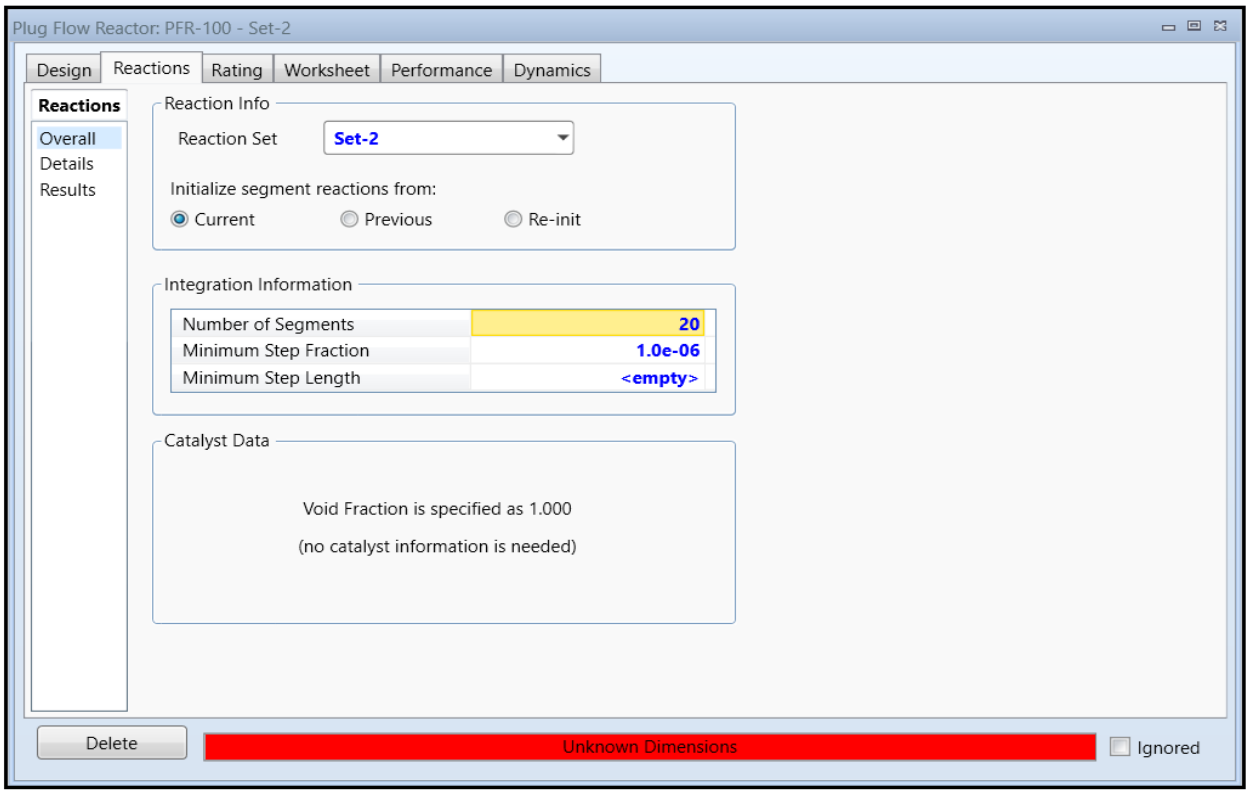

Cooler: E-101
Design
Rating
Worksheet
Performance
Dynamics
Design
Connections
Parameters
User Variables
Notes
Delta P
24.00 kPa
Delta T
Duty
Delete
Unknown Duty
Ignored



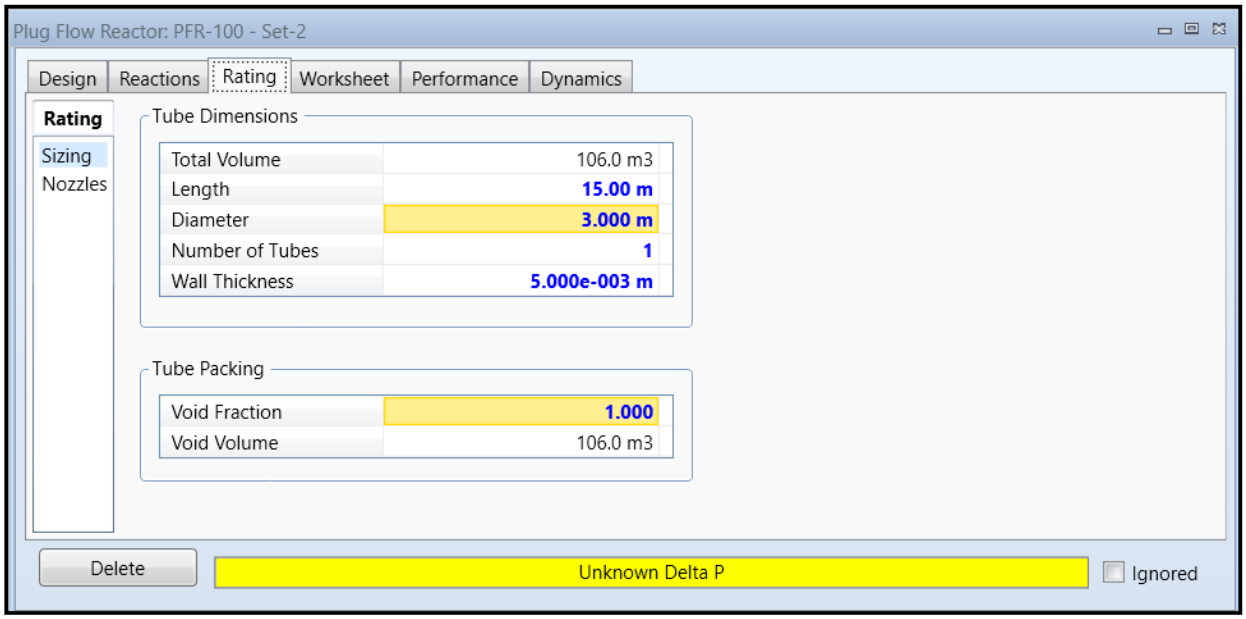
3.Select a PFR from Model Pallete/Reactor, select PFR Inlet as the inlet, and define PFR Outlet as the outlet stream.



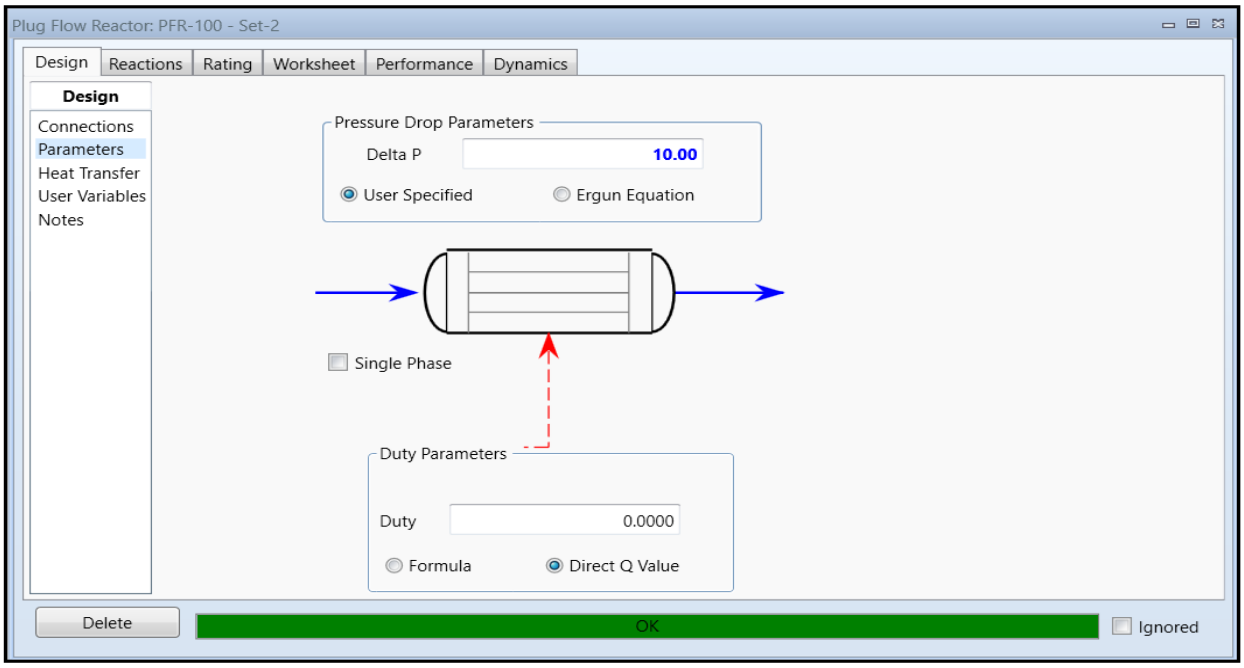
4.The red indication states that a reaction set is required. Under Reaction tab, select Set-2.



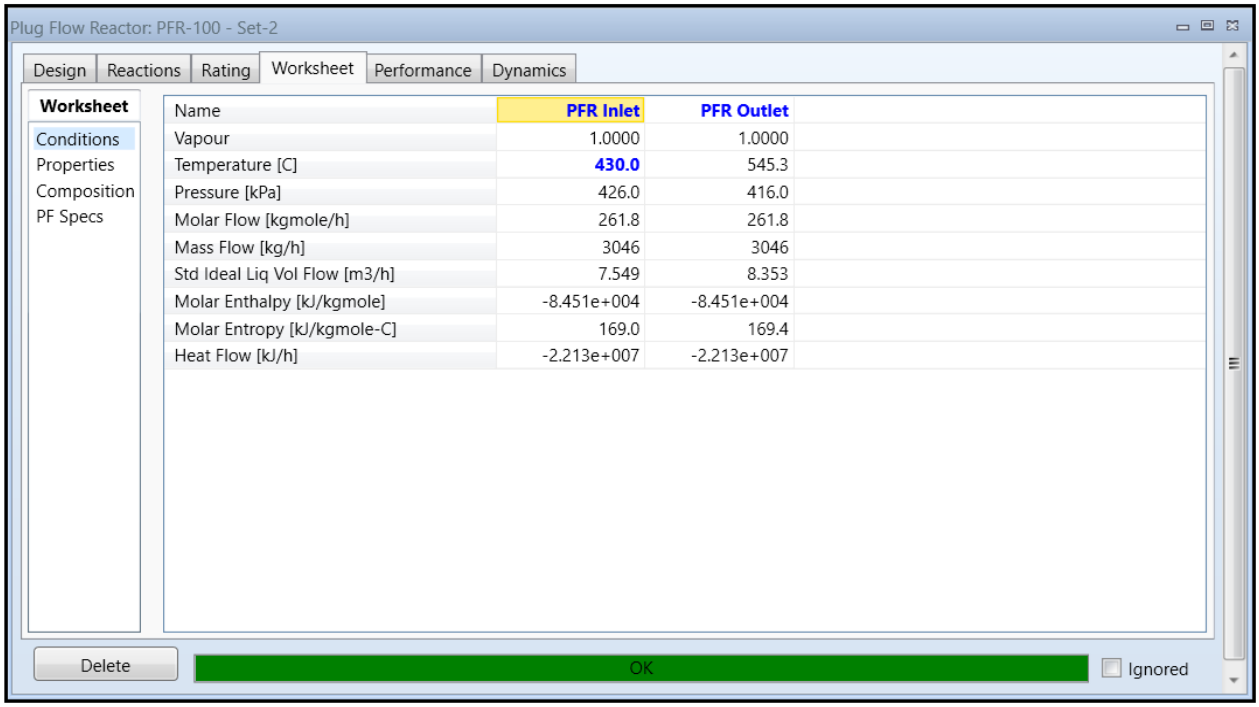
5.Under Rating/Sizing, specify length and diameter for first scenario.

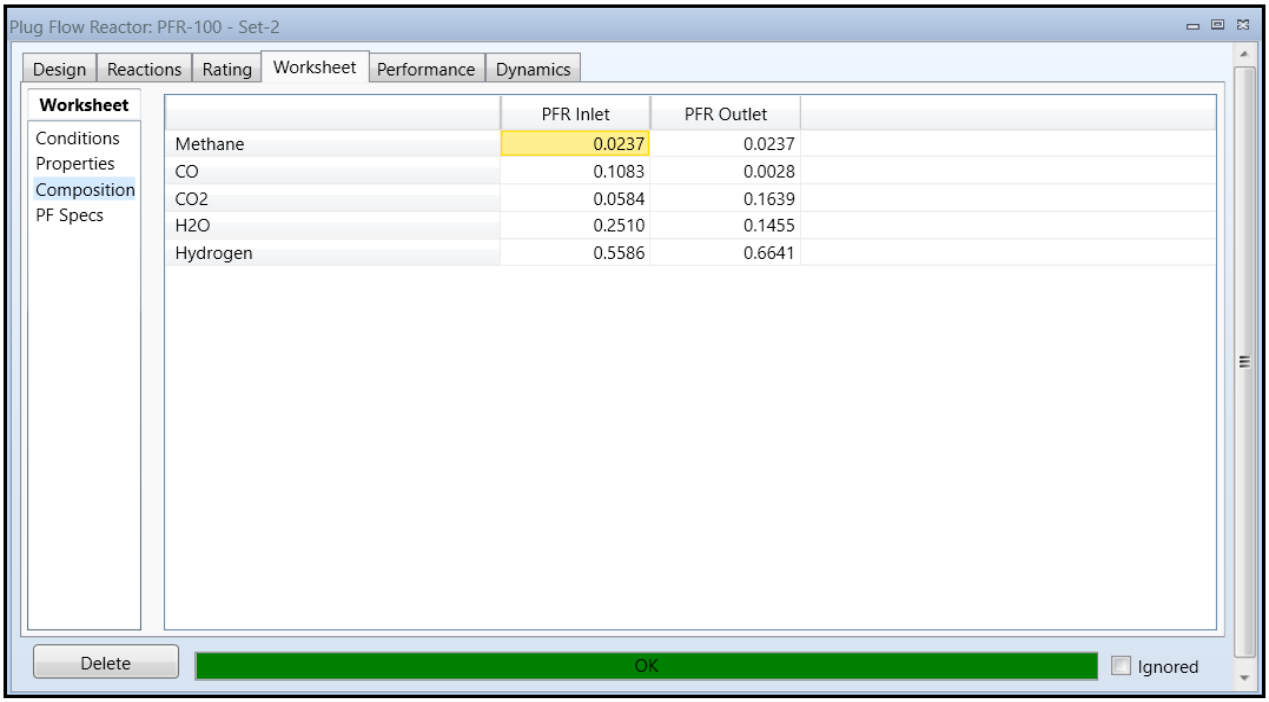


6.Based on yellow indication, the pressure drop should be specified. To do so, Under Design/Parameter, specify 10 kPa as the pressure drop.

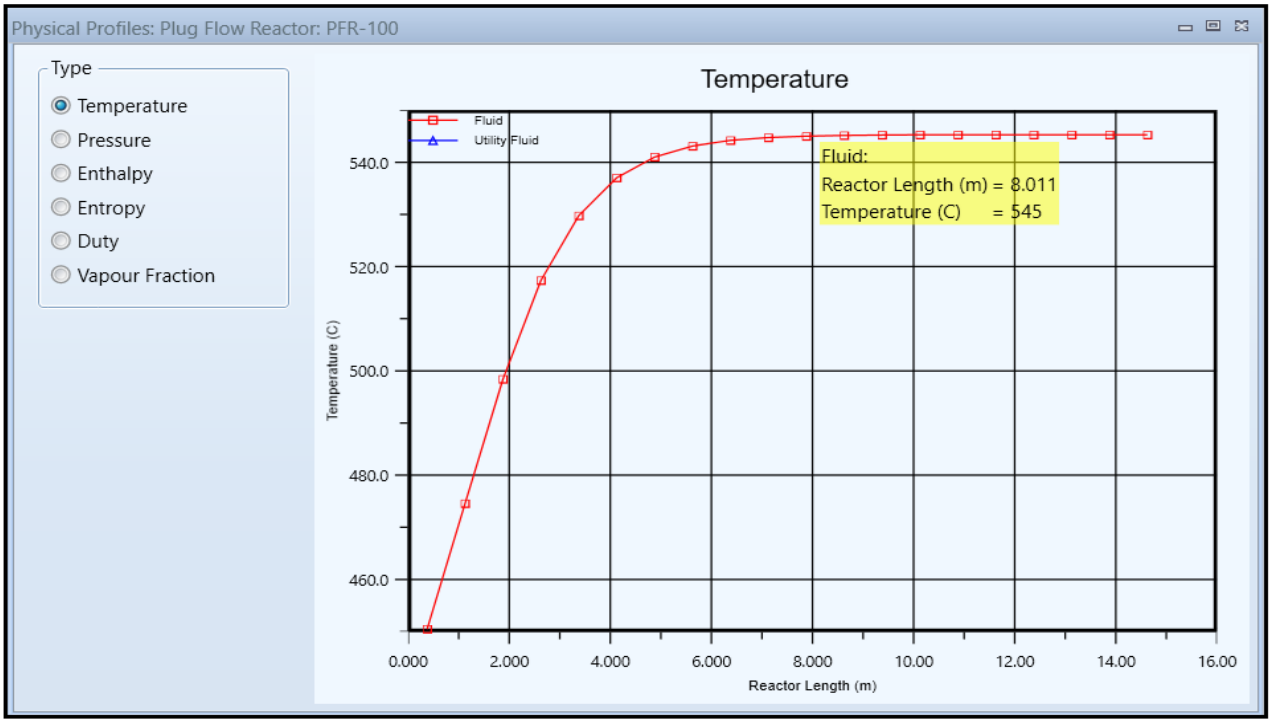


7.Results:

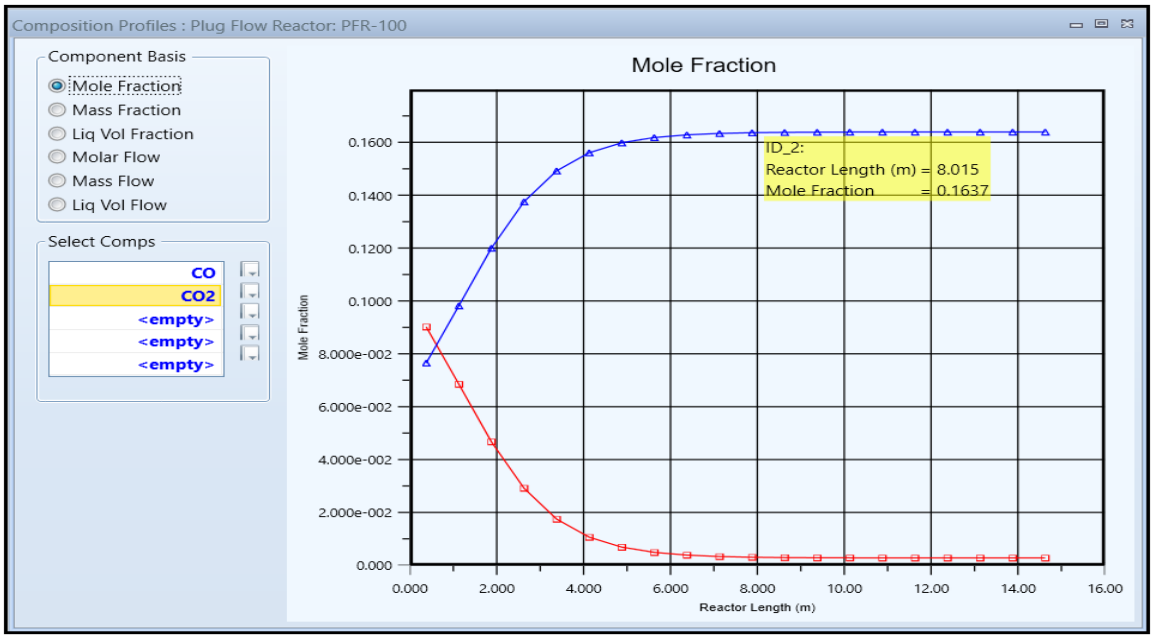




8.Under Performance select Plot.

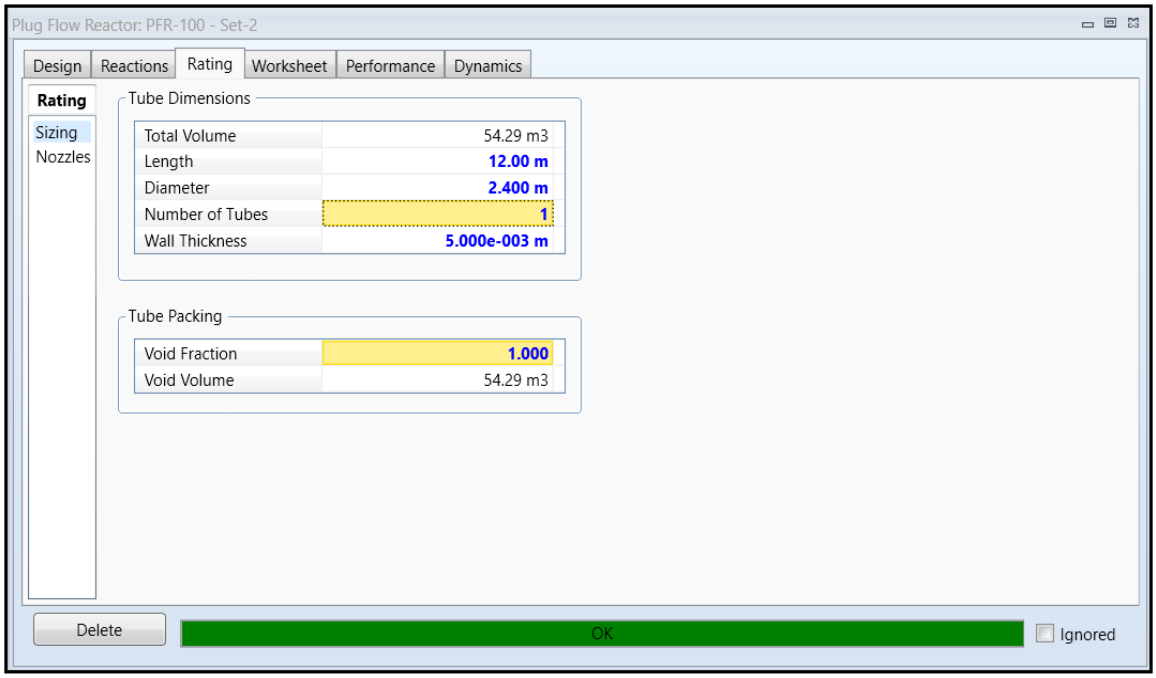


9.Under Performance, click on composition and then plot it. Select CO and CO_2.

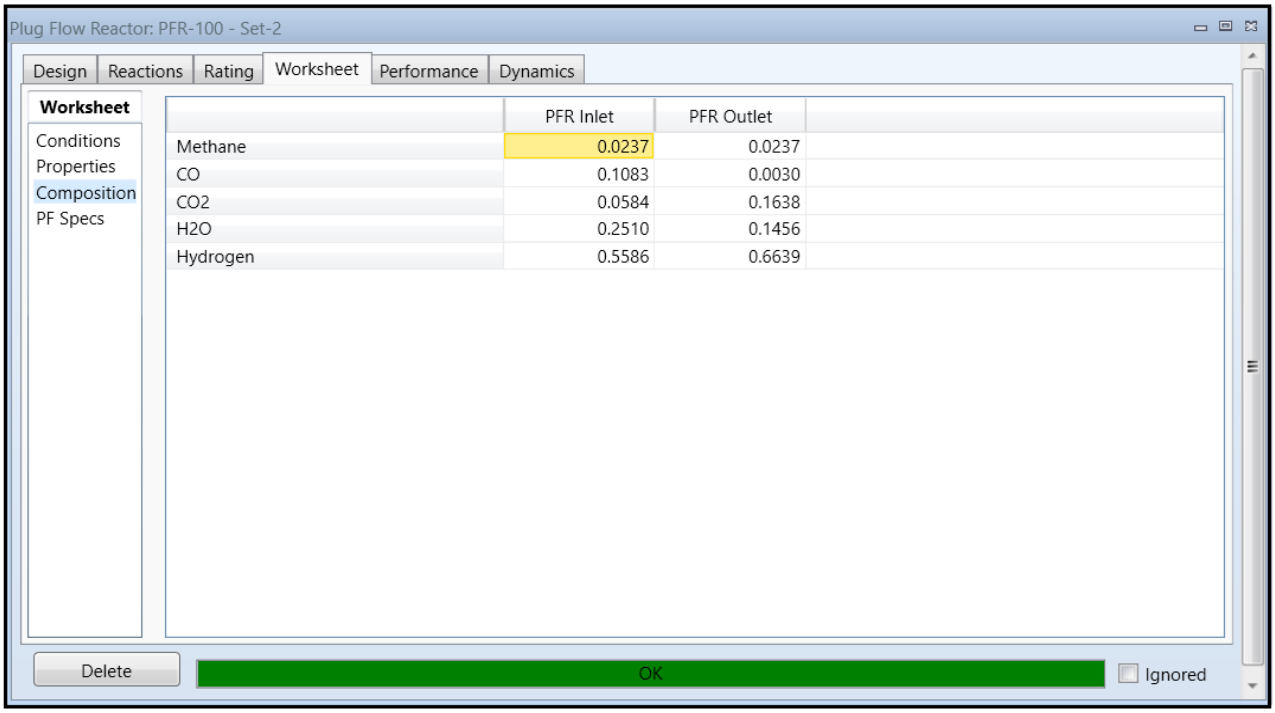


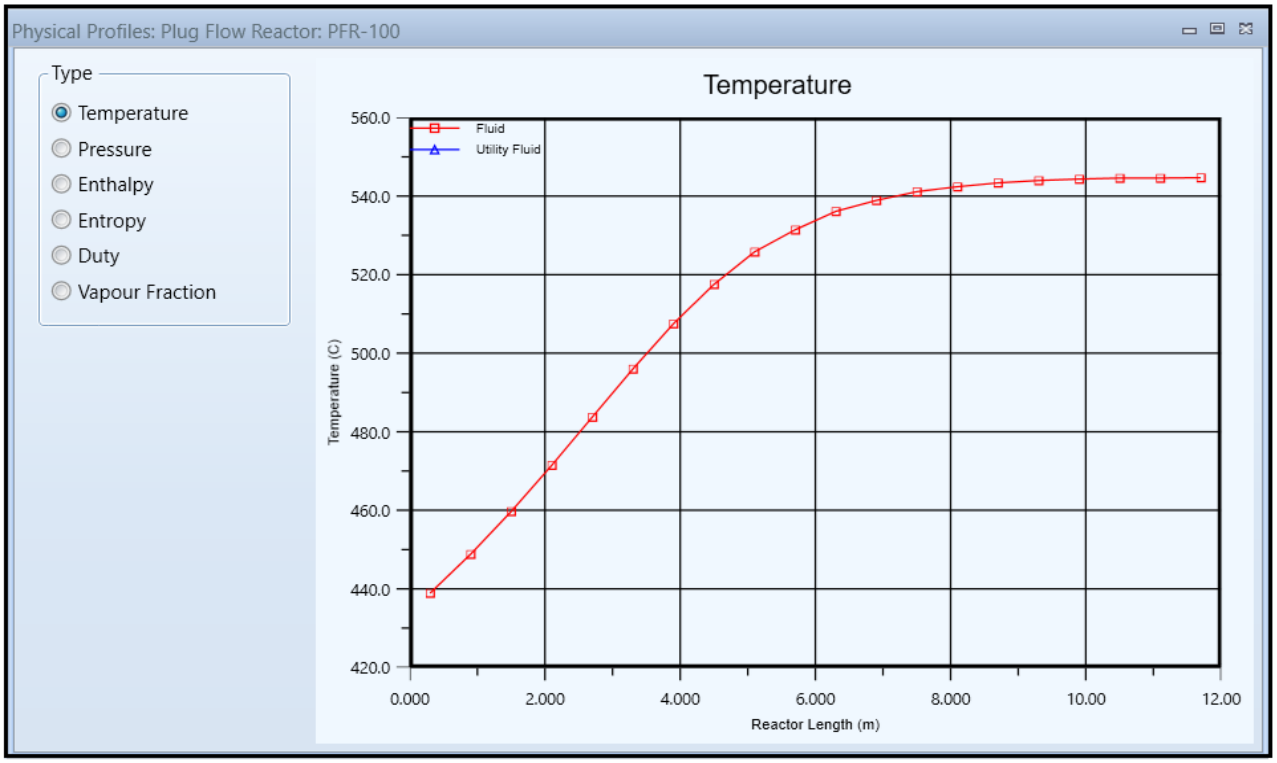
It is clear that after 8m of the length, temperature and compositions are unchanged. It means the reactor is oversized.

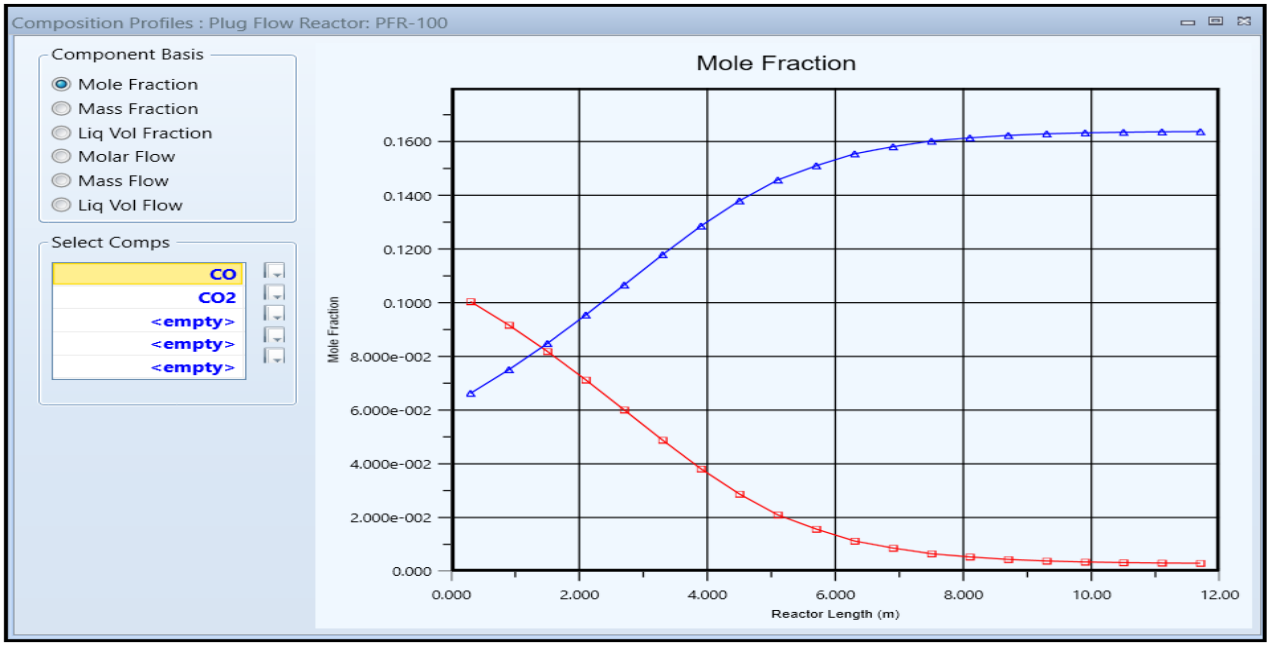
10.For the second scenario, under Rating/Sizing, change the length to 12m and diameter to 2.4m.



11.Results

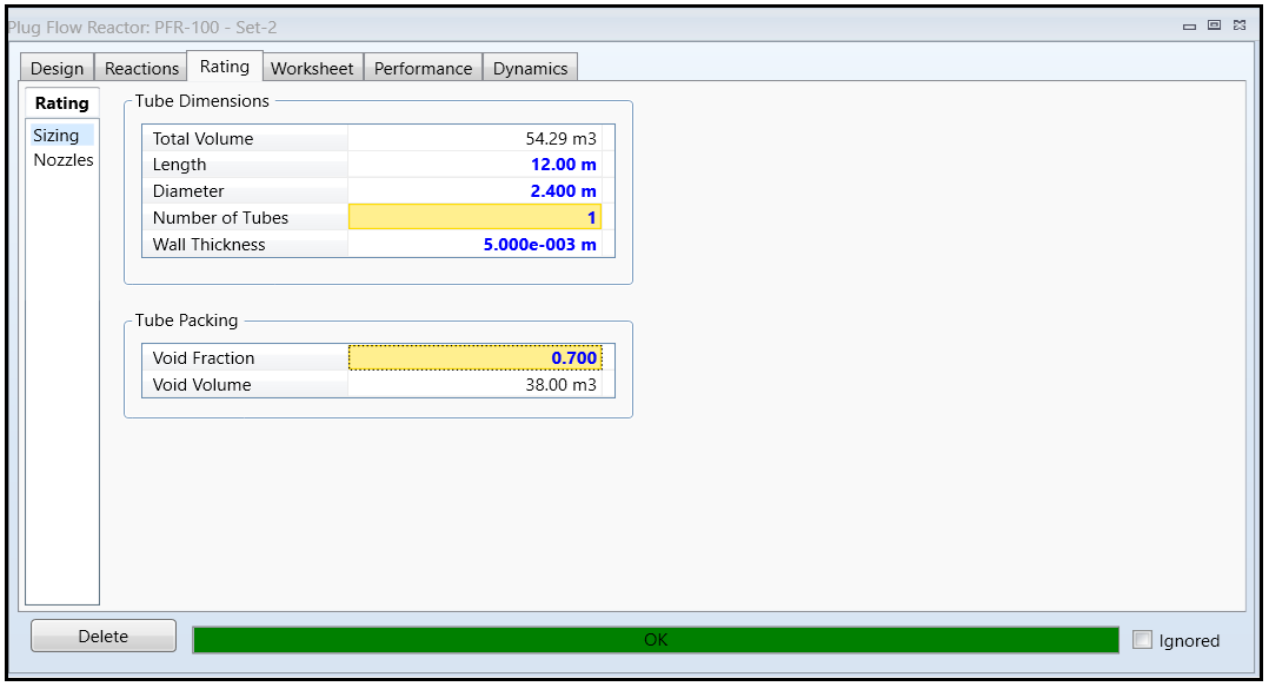

Plug Flow Reactor: PFR-100 - Set-2
Design
Reactions
Rating
Worksheet
Performance
Dynamics
Worksheet
Conditions
Properties
Composition
PF Specs
PFR Inlet
PFR Outlet
Methane 0.0237 0.0237
CO 0.1083 0.0030
CO2 0.0584 0.1638
H2O 0.2510 0.1456
Hydrogen 0.5586 0.6639
Delete
OK
Ignored


Physical Profiles: Plug Flow Reactor: PFR-100
Type
Temperature
Pressure
Enthalpy
Entropy
Duty
Vapour Fraction
Temperature
Fluid
Utility Fluid
560.0
540.0
520.0
500.0
480.0
460.0
440.0
420.0
Temperature (C)
0.000
2.000
4.000
6.000
8.000
10.00
12.00
Reactor Length (m)

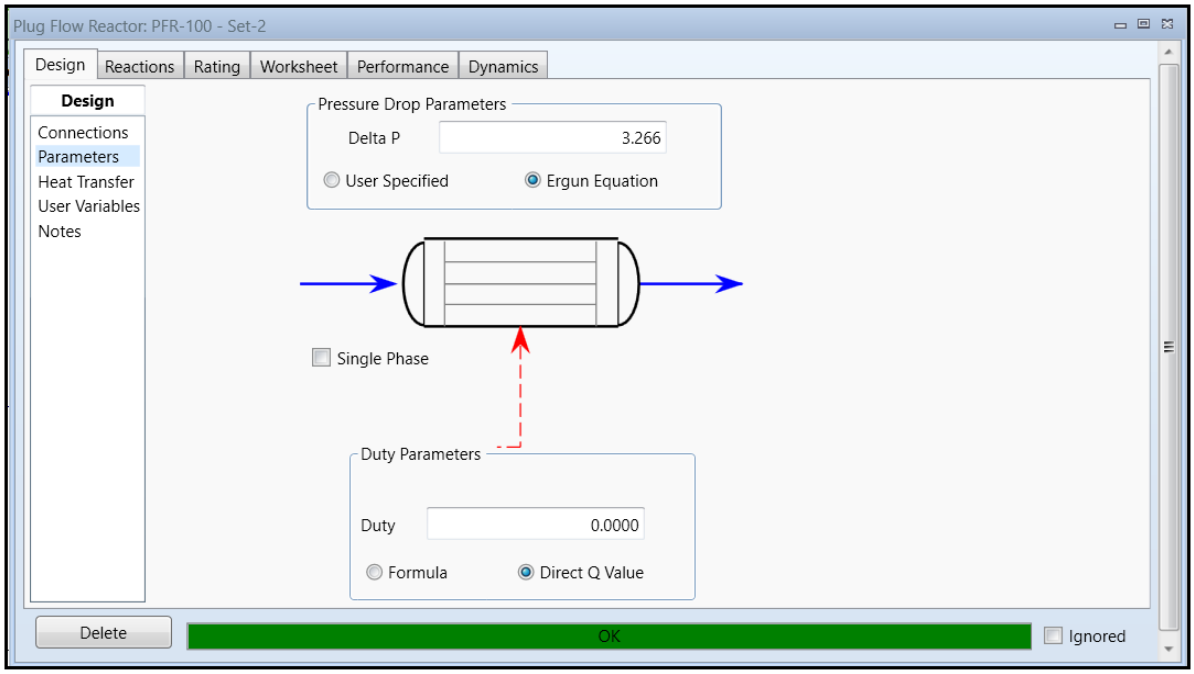


Based on the plots, it seems that the PFR in second scenario is better sized.

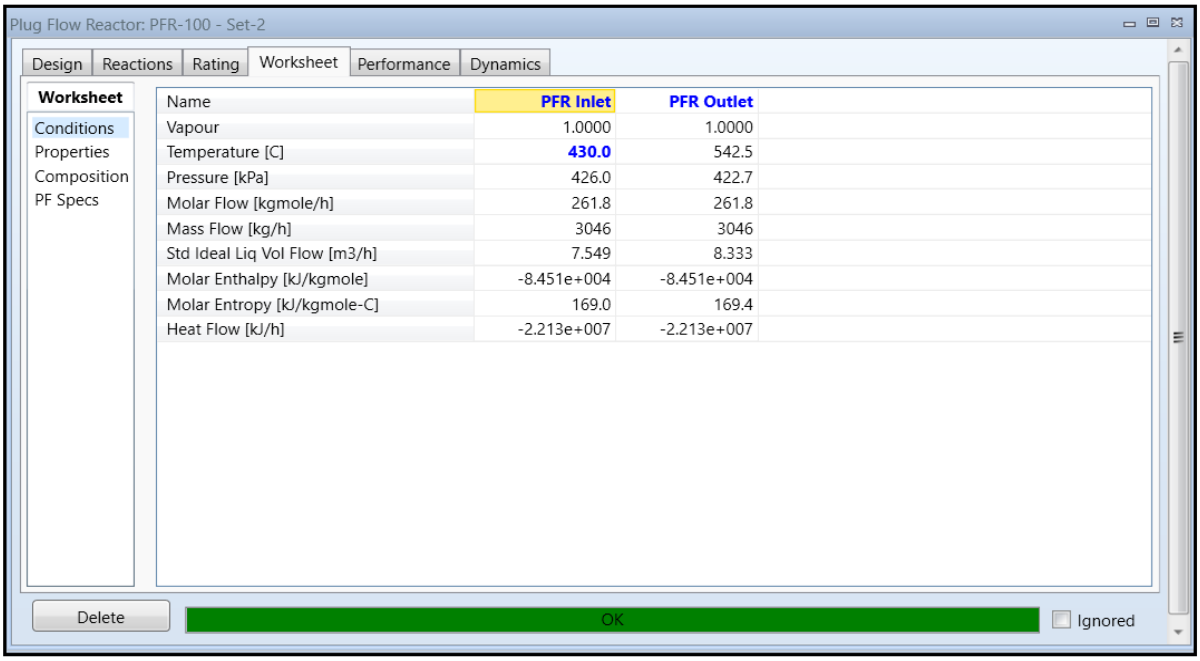
12.If we want to include catalysts in our simulation, under Rating/Sizing, void fraction could be changed. By default, the value is 1 but in reality, it is between 0.6-0.8. The void fraction is a function of reactor and catalyst design.



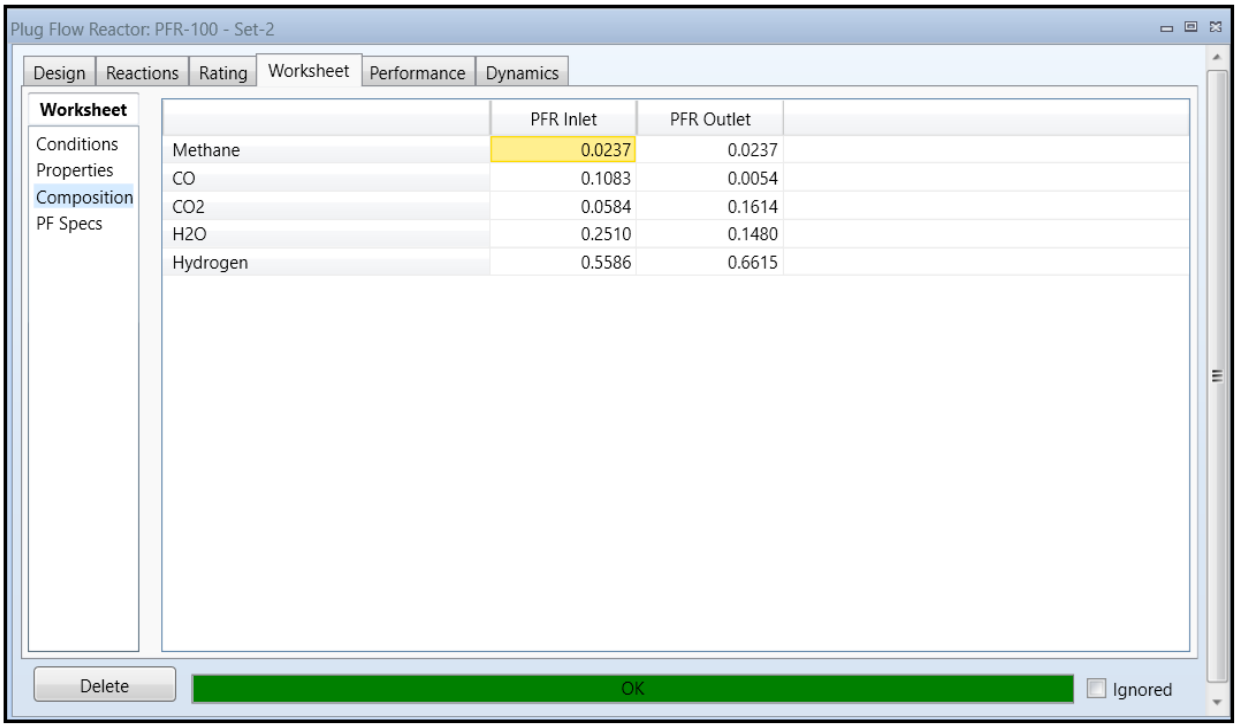
13.In previous steps, we dictate the pressure drop to the software. Now we can select Ergun Equation to calculate the pressure drop.

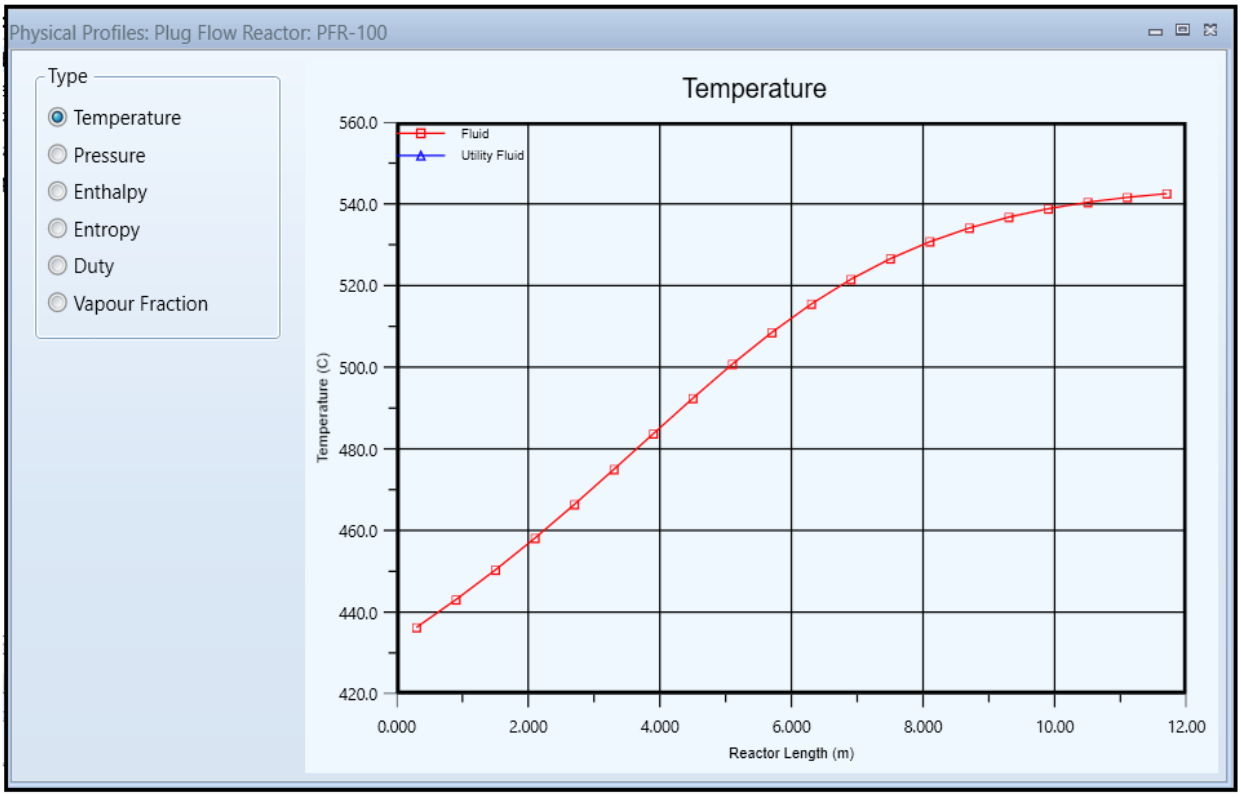


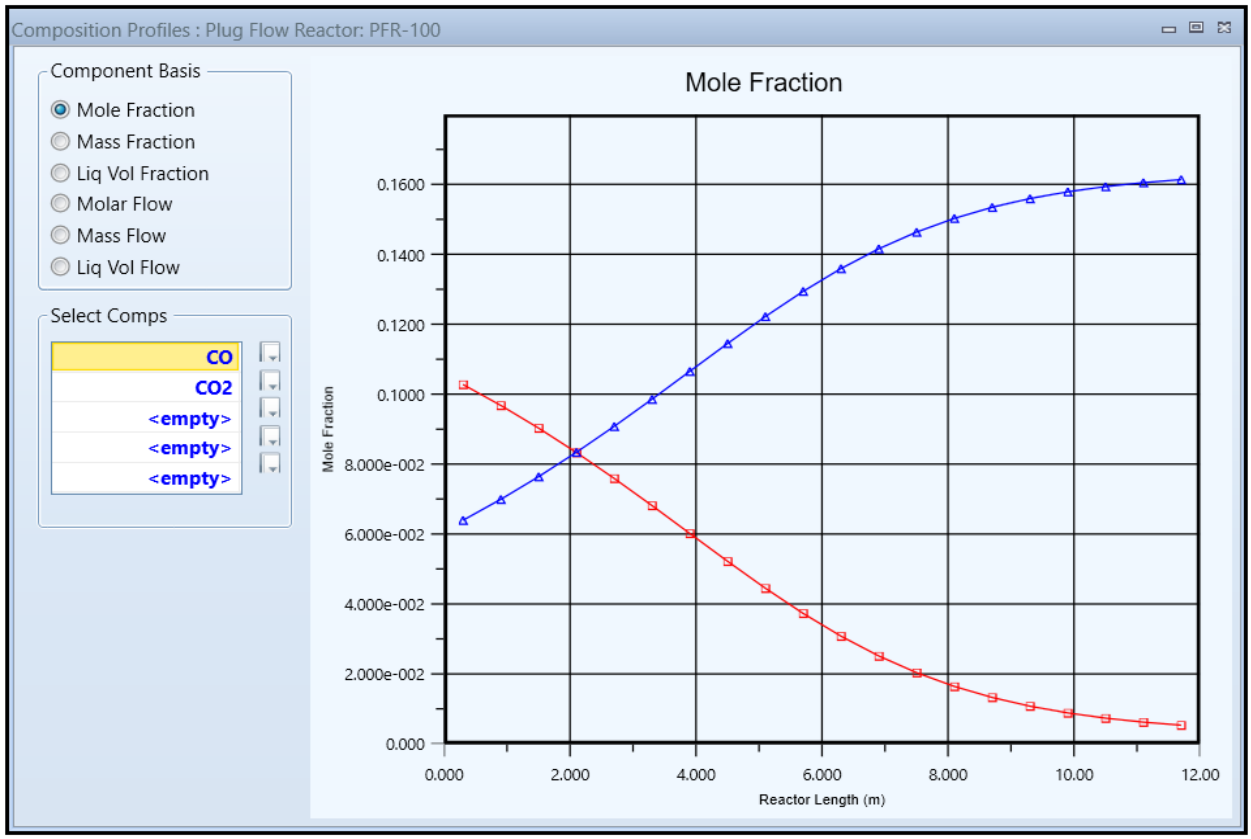
14. Here is the final result:

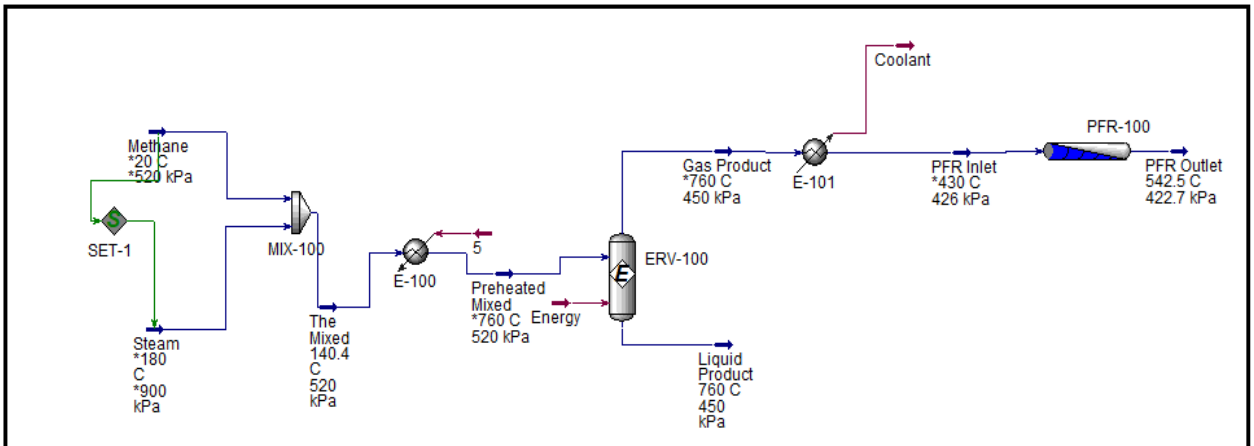


Name	PFR Inlet	PFR Outlet
Vapour	1.0000	1.0000
Temperature [C]	430.0	542.5
Pressure [kPa]	426.0	422.7
Molar Flow [kgmole/h]	261.8	261.8
Mass Flow [kg/h]	3046	3046
Std Ideal Liq Vol Flow [m3/h]	7.549	8.333
Molar Enthalpy [kJ/kgmole]	-8.451e+004	-8.451e+004
Molar Entropy [kJ/kgmole-C]	169.0	169.4
Heat Flow [kJ/h]	-2.213e+007	-2.213e+007


Plug Flow Reactor: PFR-100 - Set-2
Design
Reactions
Rating
Worksheet
Performance
Dynamics
Worksheet
Conditions
Properties
Composition
PF Specs
PFR Inlet
PFR Outlet
Methane 0.0237 0.0237
CO 0.1083 0.0054
CO2 0.0584 0.1614
H2O 0.2510 0.1480
Hydrogen 0.5586 0.6615
Delete
OK
Ignored


Physical Profiles: Plug Flow Reactor: PFR-100
Type
Temperature
Pressure
Enthalpy
Entropy
Duty
Vapour Fraction
Temperature
Fluid
Utility Fluid
560.0
540.0
520.0
500.0
480.0
460.0
440.0
420.0
Temperature (C)
0.000
2.000
4.000
6.000
8.000
10.00
12.00
Reactor Length (m)





Material Streams									
		Methane	Steam	The Mixed	Preheated Mixed	Gas Product	Liquid Product	PFR Inlet	PFR Outlet
Vapour Fraction		1.0000	1.0000	0.9865	1.0000	1.0000	0.0000	1.0000	1.0000
Temperature	C	20.00	180.0	140.4	760.0	760.0	760.0	430.0	542.5
Pressure	kPa	520.0	900.0	520.0	520.0	450.0	450.0	426.0	422.7
Molar Flow	kgmole/h	49.87	124.7	174.5	174.5	261.8	0.0000	261.8	261.8
Mass Flow	kg/h	800.0	2246	3046	3046	3046	0.0000	3046	3046
Liquid Volume Flow	m3/h	2.672	2.250	4.922	4.922	7.549	0.0000	7.549	8.333
Heat Flow	kJ/h	-3.749e+006	-2.955e+007	-3.330e+007	-2.843e+007	-1.911e+007	0.0000	-2.213e+007	-2.213e+007