Ammonia Synthesis with Aspen Plus® V8.0

Part 2 Closed Loop Simulation of Ammonia Synthesis

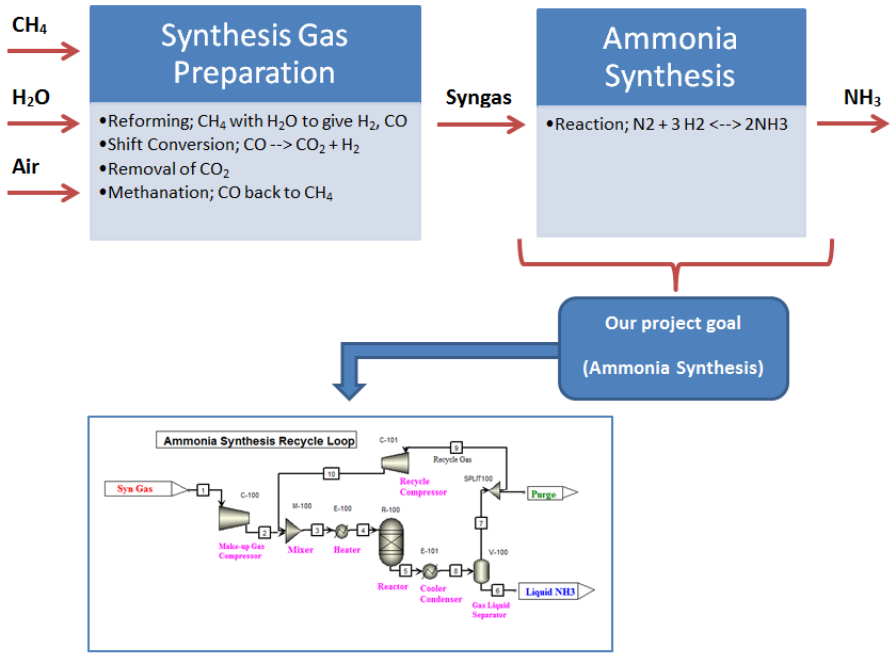
1. Lesson Objectives

- Review Aspen Plus convergence methods
- Build upon the open loop Ammonia Synthesis process simulation
  - Insert a purge stream
  - Learn how to close recycle loops
  - Explore closed loop convergence methods
- Optimize process operating conditions to maximize product composition and flowrate
  - Learn how to utilize the model analysis tools built into Aspen Plus
  - Find the optimal purge fraction to meet desired product specifications
  - Determine the effect on product composition of a decrease in cooling efficiency of the pre-flash cooling unit

2. Prerequisites

- Aspen Plus V8.0
- Design-001 Module (Part 1 of this series)

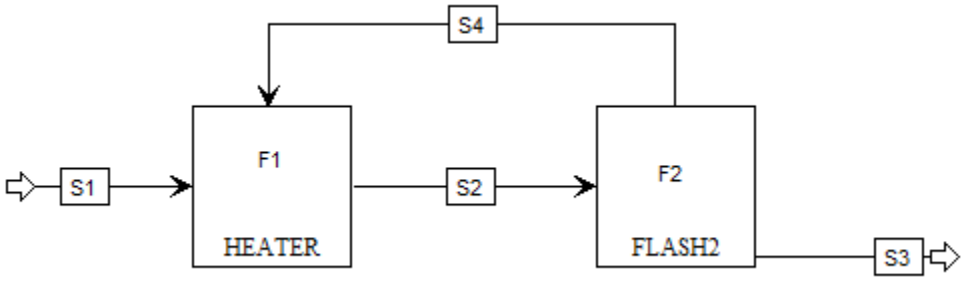
3. Background; Recap of Ammonia Process



The examples presented are solely intended to illustrate specific concepts and principles. They may not reflect an industrial application or real situation.

4. Review of Aspen Plus Convergence Methods

There are several methods Aspen Plus can utilize to converge recycle loops. Convergence in Aspen Plus is an iterative process consisting of making guesses for tear streams and then comparing the calculated stream values with the guessed values. If these values are equivalent within a certain tolerance, then the simulation has successfully converged. Consider the following example shown in the flowsheet below:

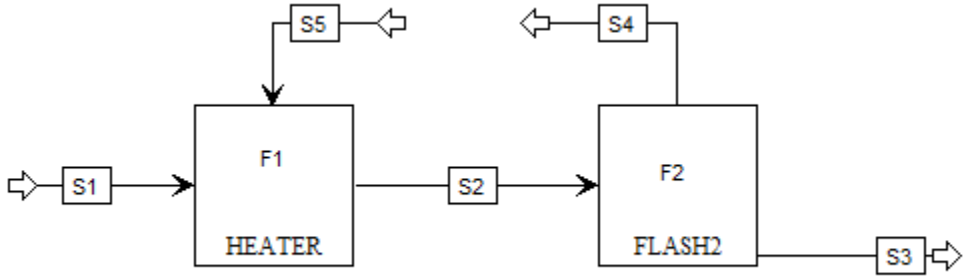


To calculate the properties of stream S4, the properties of stream S2 must be known or calculated. To calculate the properties of stream S2, the properties of streams S1 and S4 must be known or calculated. In mathematical terms we have:

$$S4 = F2(S2)$$

$$S2 = F1(S1, S4)$$

The mutual dependency of streams S4 and S2 creates an algebraic loop. This loop can be removed by 'tearing' a stream apart. For example, we can choose to hypothetically tear stream S4 into two separate streams. This would result in the following flowsheet:



Mathematically we now have the following:

$$S4 = F2(S2)$$
$$S2 = F1(S1, S5)$$

There is no longer mutual dependency between streams S4 and S2. The issue now relies in finding a solution that results in stream S5 being equal to stream S4. This is accomplished by utilizing iterative convergence methods which are briefly described below. Based on the flowsheet you create, Aspen Plus will automatically define tear streams to converge, or alternatively you can input user defined tear streams.

The following methods are available in Aspen Plus:

- Direct substitution
- Wegstein
- Newton
- Secant
- Broyden
- Sequential quadratic programming (SQP)

The direct substitution method is a slow but sure way to reach convergence. For each iteration, this method uses the values calculated from the previous flowsheet pass as the new values of the tear stream. In mathematical terms we have the following, where k is the iteration number.

$$S4_k = F(S5_k)$$

$$S5_{k+1} = S4_k$$

This sequence would be iterated until $S4_k$ and $S5_k$ are equivalent within a specified tolerance.

The Wegstein method is an extrapolation of the direct substitution method used to accelerate convergence. It attempts to estimate what the final solution will be based on the difference between successive iteration values. This is the default convergence method for system generated tear convergence blocks and is usually the quickest and most reliable method for tear stream convergence.

Newton's convergence method for simultaneous nonlinear equations uses matrices of partial derivatives to obtain a set of linear equations which are then solved. This process is iterated until convergence criteria are met. Newton's method requires the evaluation of the function and it's derivative per iteration. This method provides an efficient means of convergence only if a sufficiently good initial guess is provided. Use the Newton method for tear streams only when the number of components is small or when convergence cannot be achieved by other methods.

The secant method uses a succession of roots of secant lines to approximate the root of a function. Compared with Newton's method, the secant method does not require the evaluation of the functions derivative. This enables this method to converge for systems involving non-elementary functions. The secant method can be

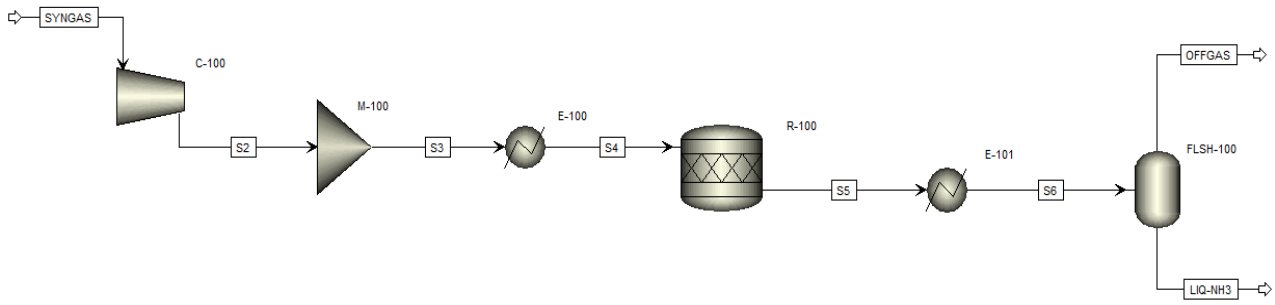
used for converging single design specifications and is the default method in Aspen Plus for design specification convergence.

Broyden's method is a modification of the Newton and secant methods that uses approximate linearization which can be extended to higher dimensions. This method is faster than Newton's method but is often not as reliable. Broyden's method should be used to converge multiple tear streams or design specifications, and is particularly useful when converging tear streams and design specifications simultaneously.

Sequential quadratic programming is an iterative method for flowsheet optimization. This method is useful for simultaneous convergence of optimization problems with constraints and tear streams.

5. Aspen Plus Solution

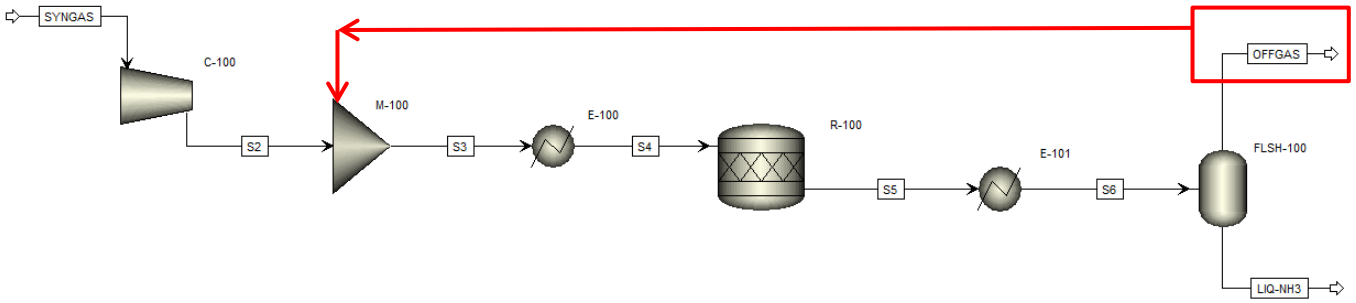
In Part 1 of this series (Design-001), the following flowsheet was developed for an open loop Ammonia Synthesis process.



This process produces two outlet streams; a liquid stream containing the ammonia product and a vapor stream containing mostly unreacted hydrogen and nitrogen. It is desired to capture and recycle these unreacted materials to minimize costs and maximize product yield.

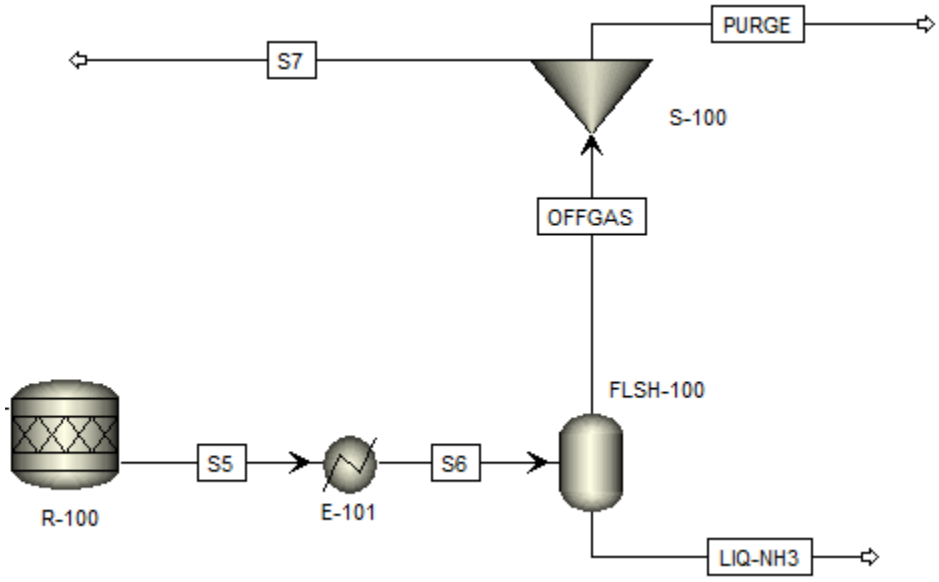
Add Recycle Loop to Ammonia Synthesis Process

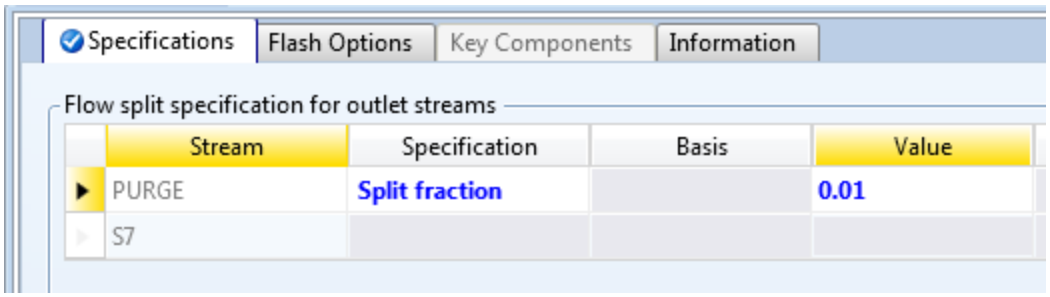
Beginning with the open loop flowsheet constructed in Part 1 of this series, a recycle loop will be constructed to recover unreacted hydrogen and nitrogen contained in the vapor stream named OFFGAS, shown below.



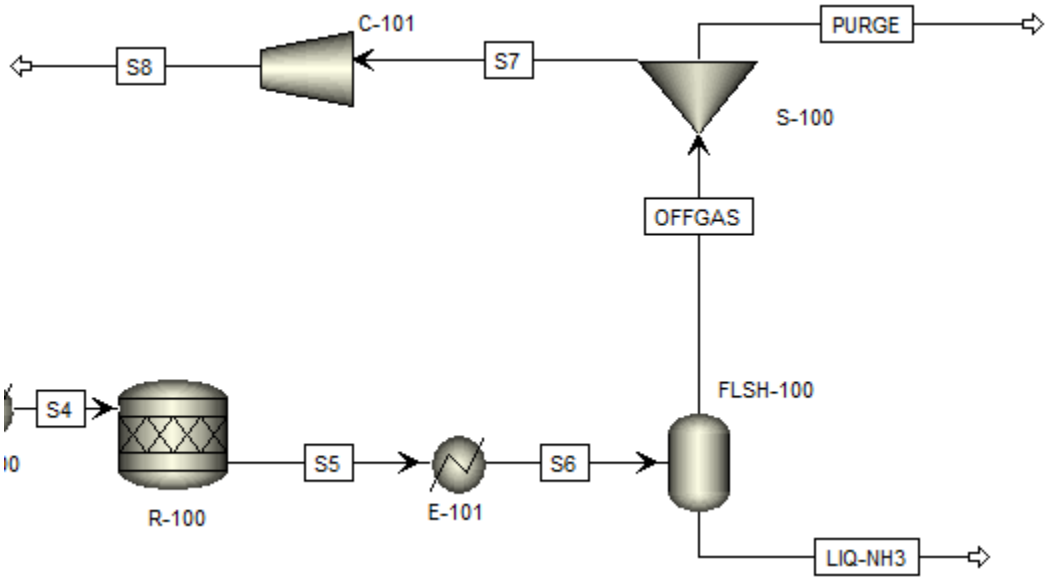
5.01. The first step will be to add a **Splitter** to separate the **OFFGAS** stream into two streams; a purge stream and a recycle stream. As a rule of thumb, whenever a recycle stream exists, there must be an associated purge stream to create an exit route for impurities or byproducts contained in the process. Often times if an exit route does not exist, impurities will build up in the process and the simulation will fail to converge due to a mass balance error.

5.02. On the main flowsheet add an **FSplit** block located in the **Mixers/Splitters** tab in the **Model Palette**. The FSplit block will fractionally split a stream into several streams according to user specifications. Rename this block **S-100** and connect the **OFFGAS** stream to the inlet port. Construct two material outlet streams and label one as the purge stream. This is shown below. Double click on the splitter block to specify the split fraction. Enter a value of **0.01** for the **Split fraction** of the purge stream. This means that 1% of the OFFGAS stream will be diverged to the purge stream.

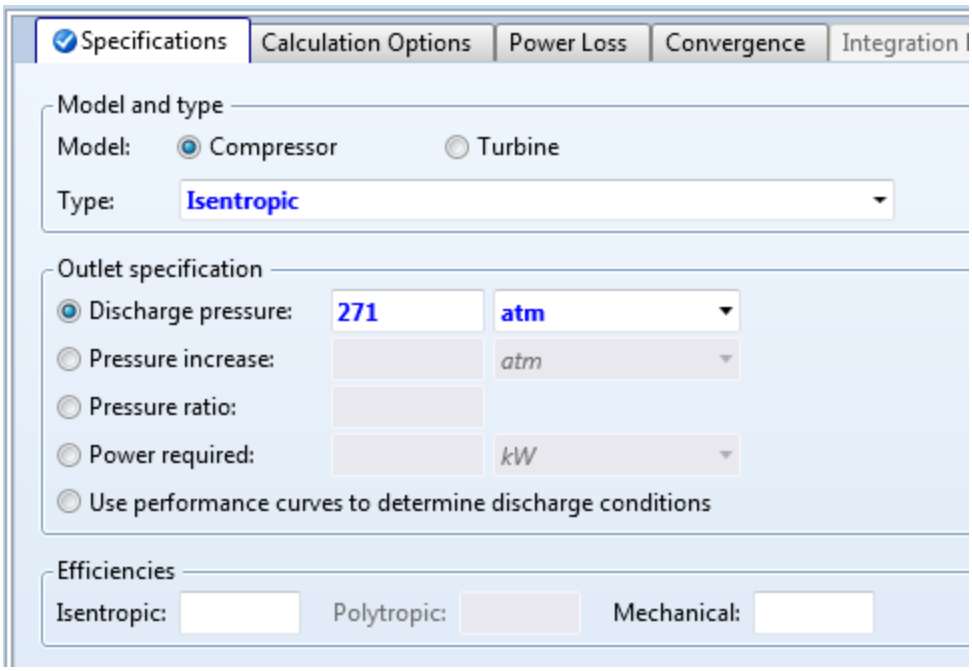




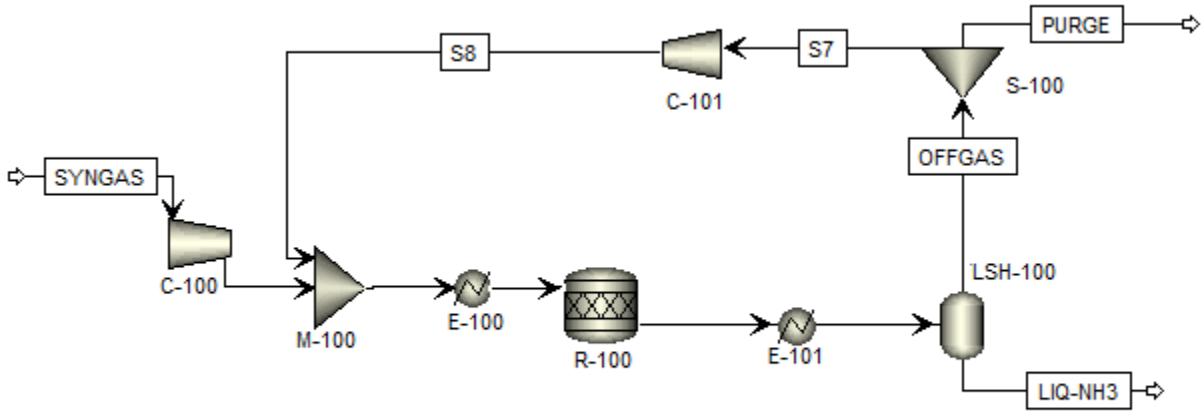
5.03. Next, we must add a compressor to bring the pressure of the recycle stream back up to the feed conditions. Add a compressor (**Compr**) block from the **Pressure Changers** tab in the **Model Palette**. Connect stream **S7** to the inlet port and construct a material stream for the outlet port. Remember that you can rotate and resize the block icons by right clicking the block and selecting either **Rotate Icon** or **Resize Icon**.



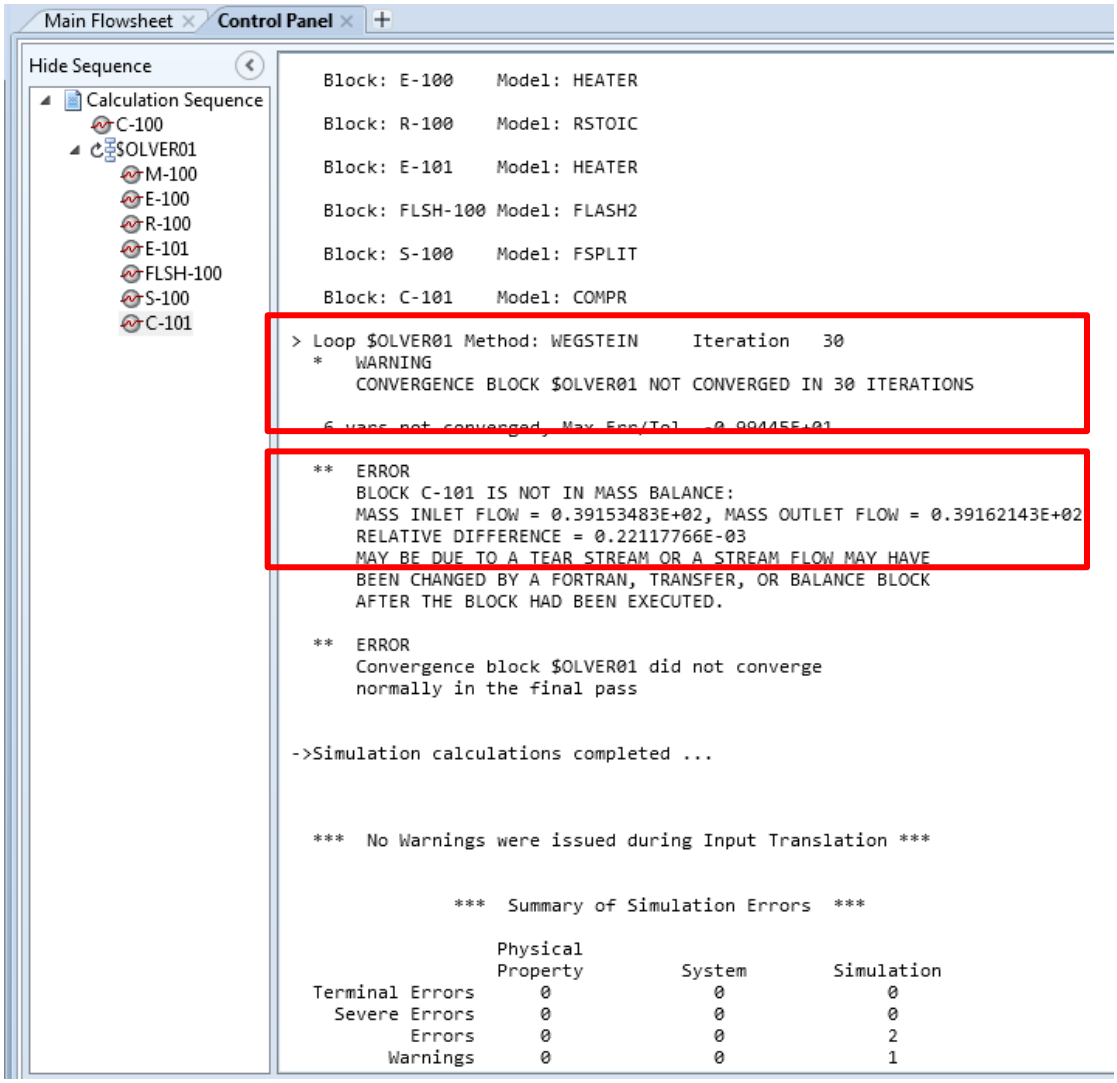
5.04. Double click on the compressor block to specify the operating conditions. Select **Isentropic** as the **Type** and enter a **Discharge pressure** of **271 atmospheres**.



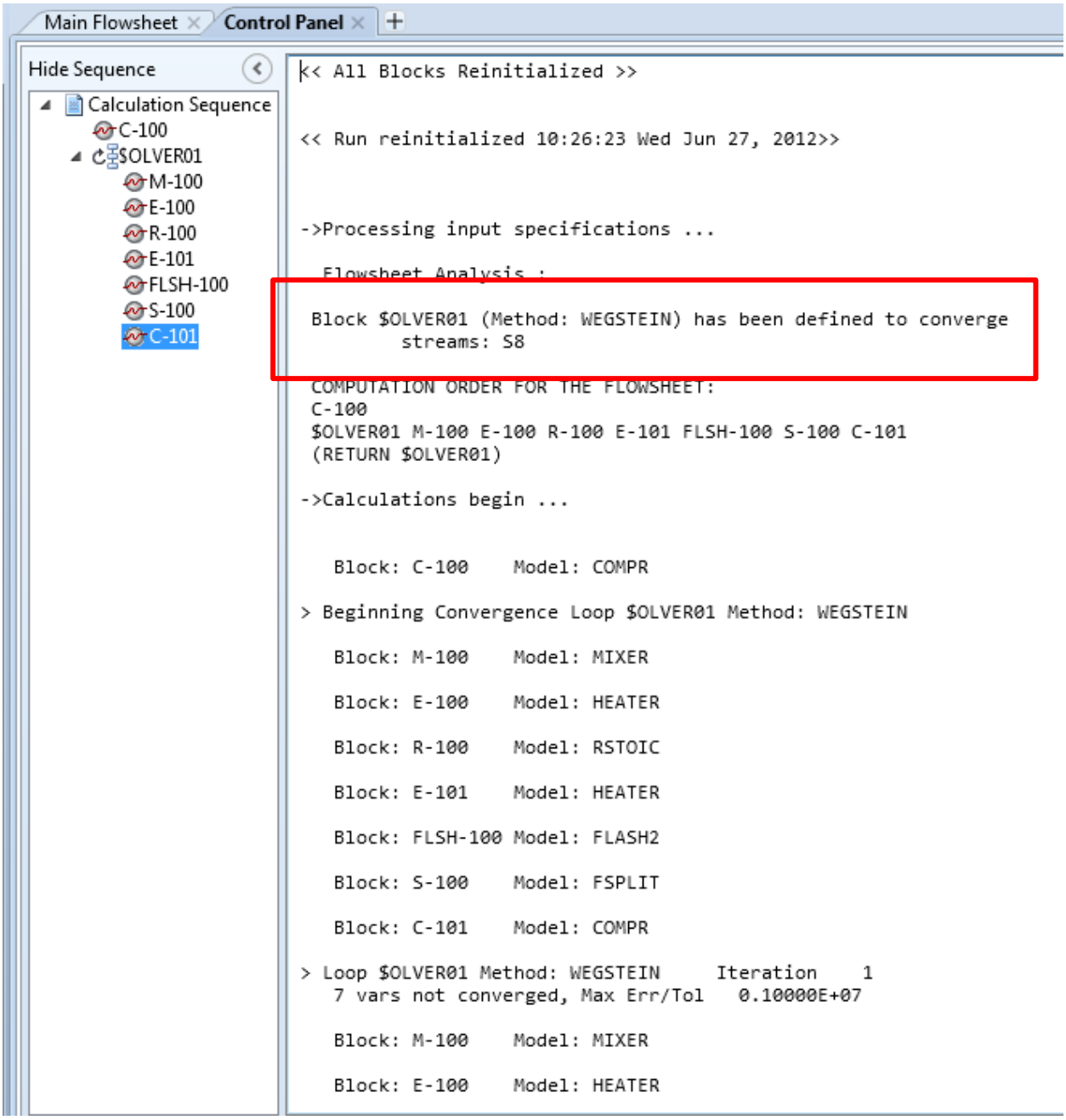
5.05. The recycle stream is now ready to be connected back to the mixer block to close the loop. Right click on the recycle stream, select **Reconnect Destination**, and connect the stream to the inlet port of the mixer block. This can also be done by double clicking the arrow of the disconnected recycle stream. This stream (S8) will be the tear stream in this simulation. Aspen Plus automatically recognizes and assigns tear streams; however you can also specify which streams you would like to be tear streams.



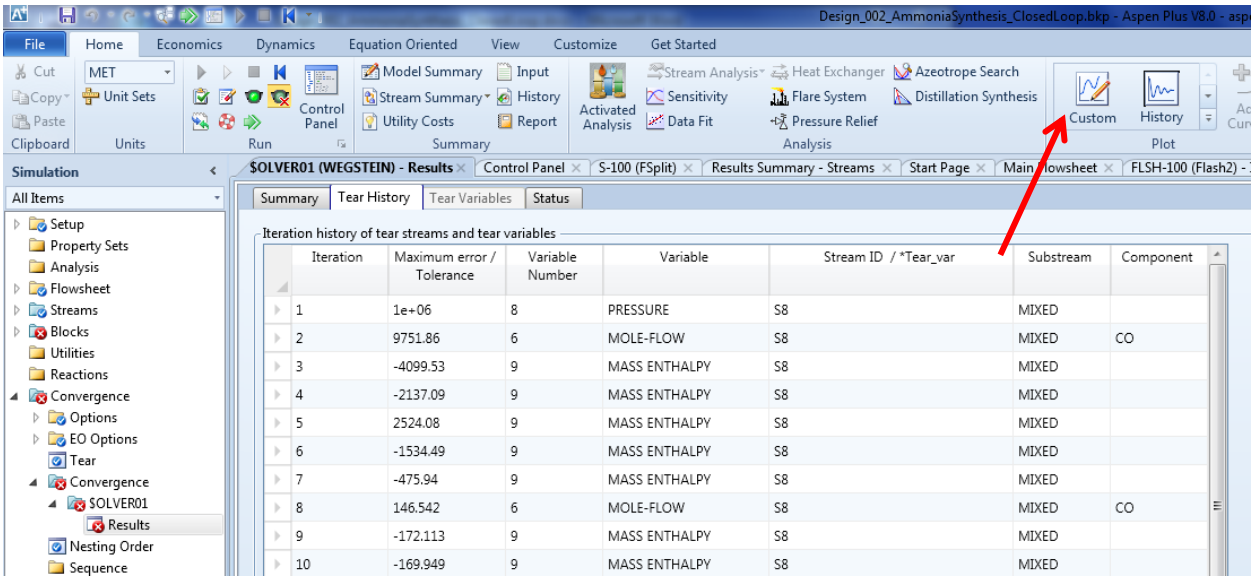
5.06. Open the **Control Panel** and run the simulation (**F5**). You should result in an error stating that block **C-101** is **not in mass balance** and that the simulation failed to converge after 30 iterations.



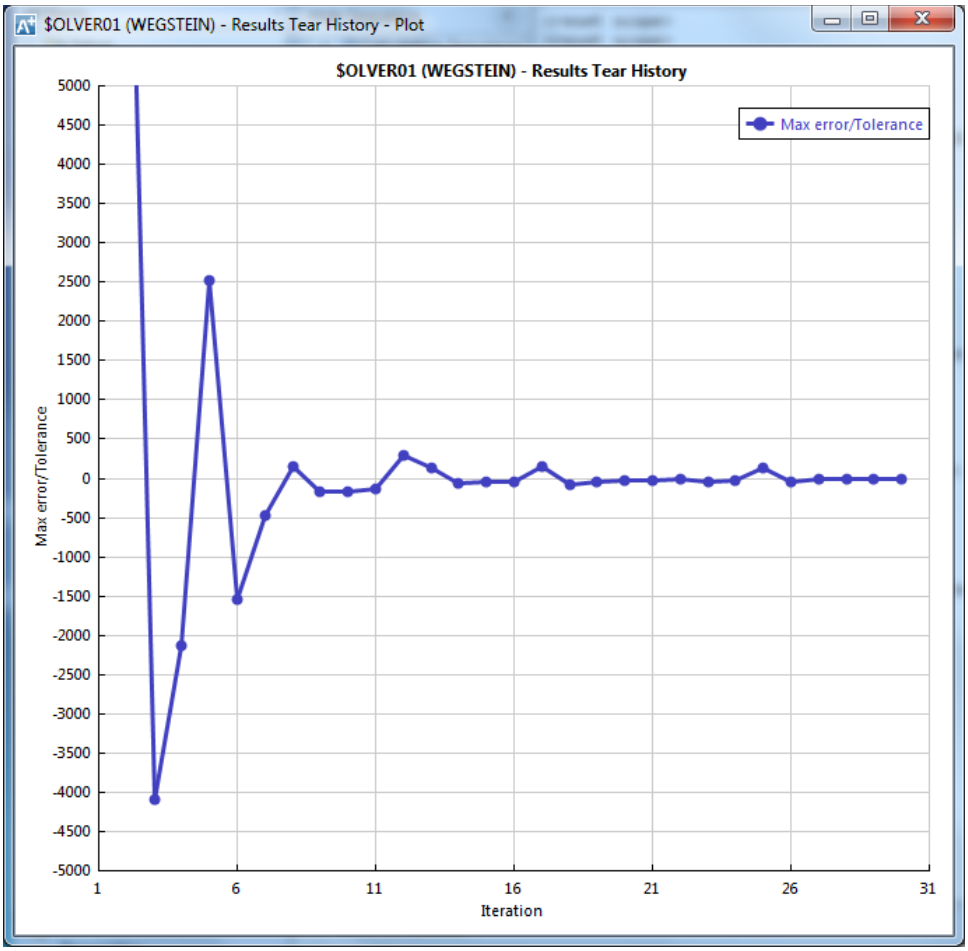
There are several steps you can take to overcome this issue. First, check to see which convergence method is being used and check which stream is being converged. Scroll up to the very top of the **Control Panel**.



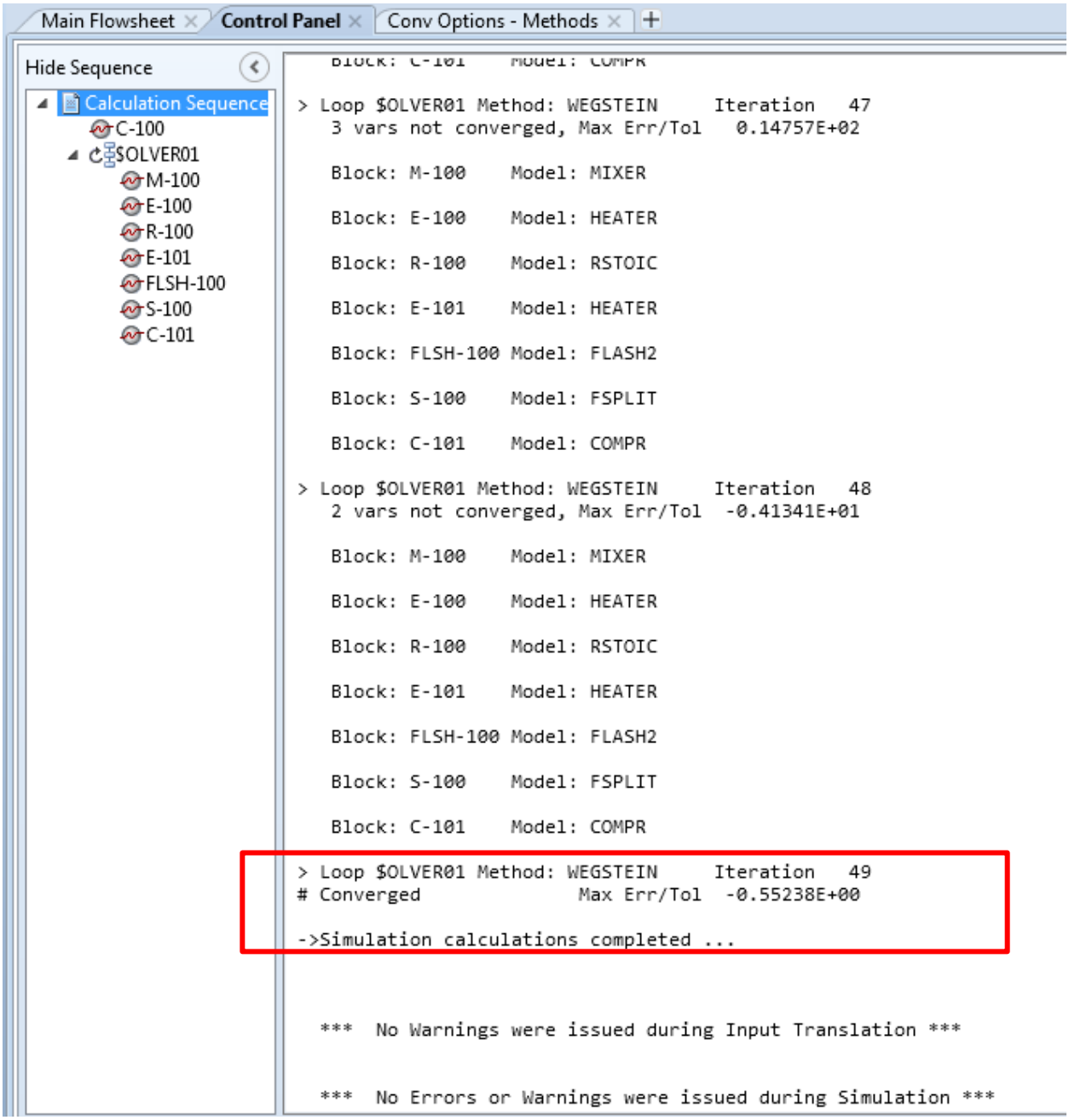
5.07. Aspen Plus is using the **Wegstein** method to converge recycle stream **S8**. The Wegstein method is a good method to use when trying to converge a single recycle stream, and stream S8 is an appropriate stream to attempt to converge. The next thing you can do is to check the maximum error per iteration to see whether the solver is heading towards convergence or not. In the navigation pane, go to **Convergence | Convergence | $OLVER01 | Results**. In the **Summary** tab you can see which variables have converged and which haven't after 30 iterations. Click the **Tear History** tab where you can view the maximum error that occurs each iteration and which variable it occurs in. Click the **Custom** plot button at the top of the screen.



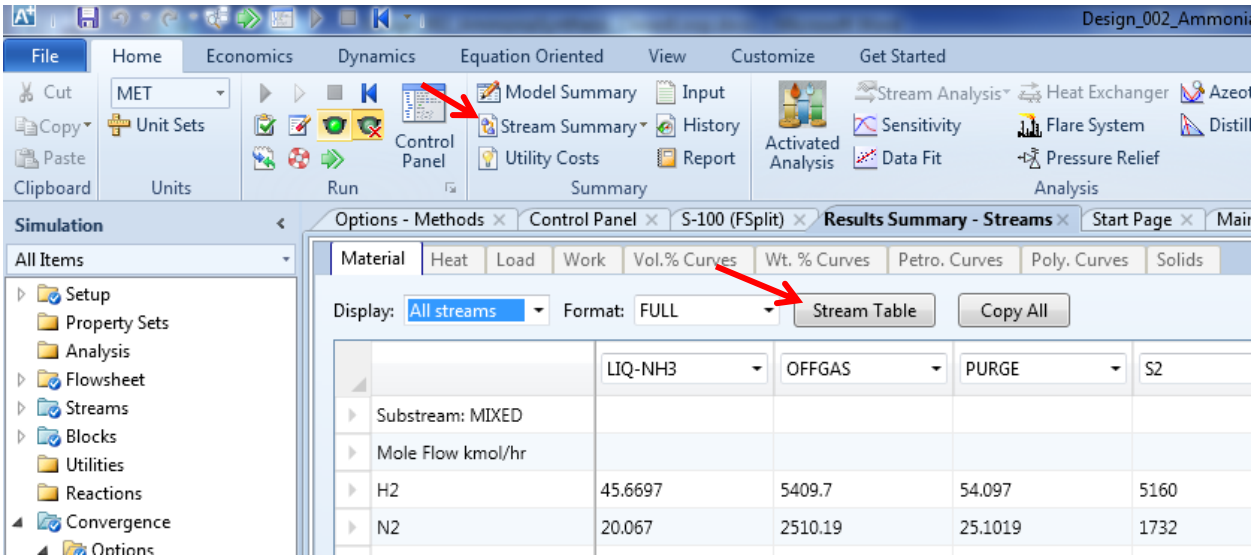
5.08. Select **Iteration** as the **x-axis** and **Maximum error/Tolerance** as the **y-axis**. Change the **y-axis min** to **-5000** and change the **max** to **5000**. The plot should appear as below.



5.09. By looking at the plot, it is clear that the Wegstein method is on the right track towards finding the solution. It may be that the solver just needs a few more iterations to converge. In the navigation pane, go to **Convergence | Options | Methods**. Click the **Wegstein** tab and increase the **Maximum flowsheet evaluations** to **50**. Run the simulation again. In the control panel you will see that the solver has now converged after only **20** iterations. This is because the solver used the last calculation from the previous run that failed to converge as the initial guess for the second run. If you reinitialize and run the simulation again you will notice that the simulation converged after **49** iterations.



5.10. Now that the simulation has converged, check the results. In the **Home** ribbon click **Stream Summary** and then click **Stream Table**.



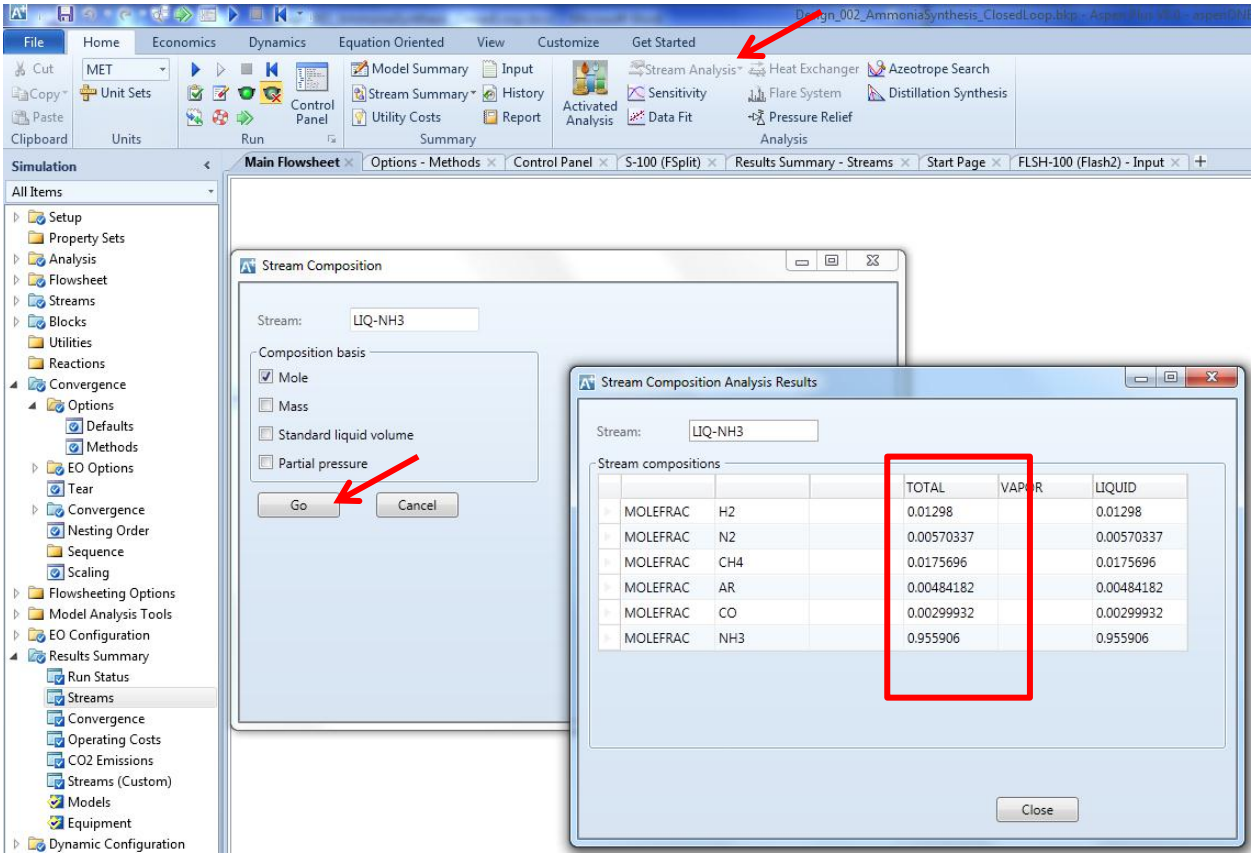
This will generate a stream table that will appear on the main flowsheet. Here you can see the flow and composition of each stream.

Heat and Material Balance Table

Stream ID		LIQ-NH3	OFFGAS	PURGE	S2	S3	S4	S5	S6	S7	S8	SYNGAS
Temperature	K	300.0	300.0	300.0	1240.0	646.6	755.0	755.0	300.0	300.0	300.4	553.1
Pressure	atm	270.00	270.00	270.00	271.40	271.00	271.00	270.00	270.00	270.00	271.00	26.17
Vapor Frac		0.000	1.000	1.000	1.000	1.000	1.000	1.000	0.755	1.000	1.000	1.000
Mole Flow	kmol/hr	3518.395	10823.793	108.238	7000.000	17715.983	17715.983	14342.189	14342.189	10715.555	10715.983	7000.000
Mass Flow	kg/hr	59901.649	141351.238	1413.512	61311.556	201252.887	201252.887	201252.887	201252.887	139937.726	139941.332	61311.556
Volume Flow	l/min	2069.230	18492.138	184.921	46125.997	63945.655	73768.573	59633.951	20561.368	18307.217	18279.014	204640.320
Enthalpy	MMBtu/hr	-217.397	-191.330	-1.913	187.074	-2.205	58.056	-118.229	-408.727	-189.417	-189.279	43.064
Mole Flow	kmol/hr											
H2		45.523	5407.587	54.076	5160.000	10513.802	10513.802	5453.110	5453.110	5353.511	5353.802	5160.000
N2		20.009	2510.337	25.103	1732.000	4217.243	4217.243	2530.346	2530.346	2485.234	2485.243	1732.000
CH4		61.812	1024.040	10.240	72.000	1085.852	1085.852	1085.852	1085.852	1013.800	1013.852	72.000
AR		17.036	197.454	1.975	19.000	214.491	214.491	214.491	214.491	195.480	195.491	19.000
CO		10.546	648.893	6.489	17.000	659.439	659.439	659.439	659.439	642.404	642.439	17.000
NH3		3363.470	1035.481	10.355		1025.156	1025.156	4398.951	4398.951	1025.126	1025.156	

Optimize the Purge Rate to Deliver Desired Product

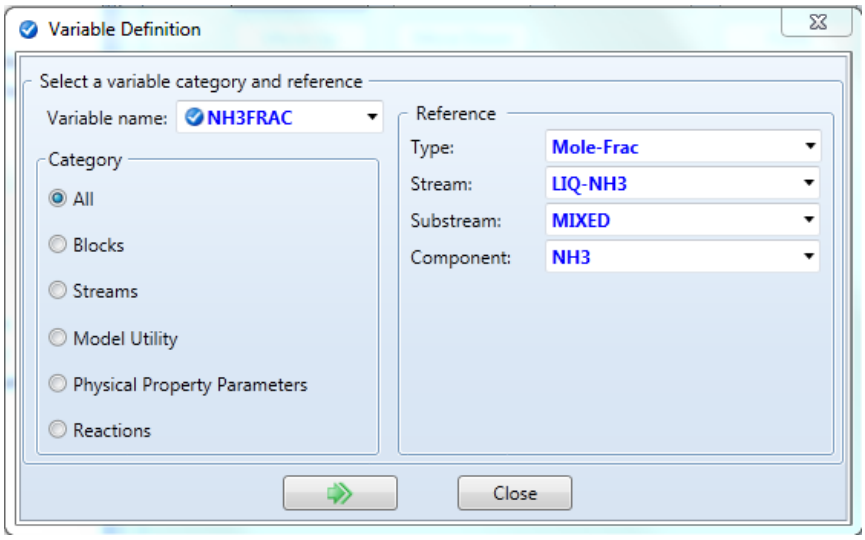
5.11. We now wish determine the purge rate required to deliver a product with a mole fraction of 0.96 ammonia. First, check the composition of the current ammonia stream by clicking on the product stream (LIQ-NH3) and clicking **Stream Analysis | Composition** in the **Home** ribbon. Select **Mole** for **Composition basis** and press **Go**.



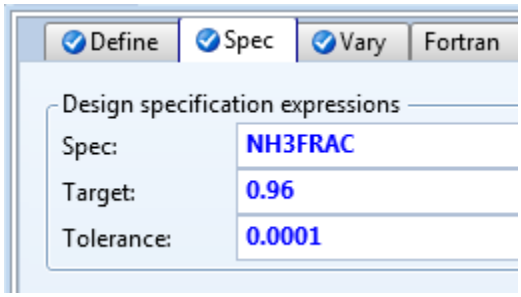
From the composition analysis results, the mole fraction of ammonia in the product stream is only **0.955**, which is below the specification of **0.96**. We need to determine the purge rate required to reach this product specification.

5.12. Go to the navigation pane and select **Flowsheeting Options | Design Spec** and click **New**. This will create a design spec which we will use to vary the purge fraction in order to reach 0.96 mole fraction ammonia in the product stream.

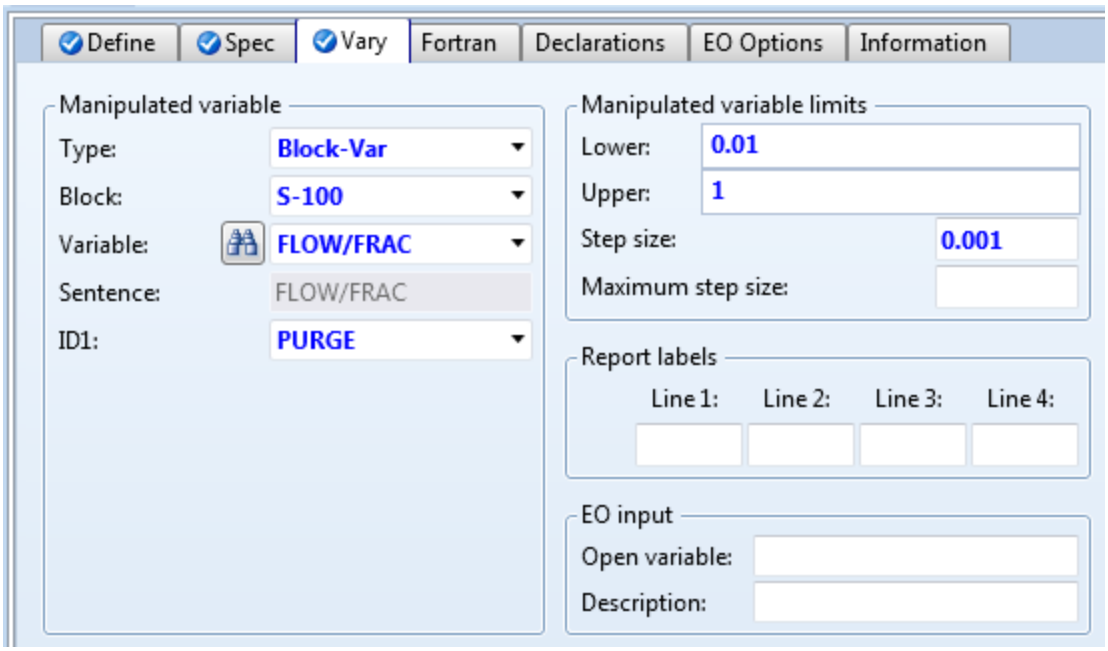
5.13. Under the **Define** tab select **New**. Enter the variable name **NH3FRAC**. A window will appear where you must define the variable. Select **Mole-Frac** as type, **LIQ-NH3** for **Stream**, and **NH3** for **Component**.



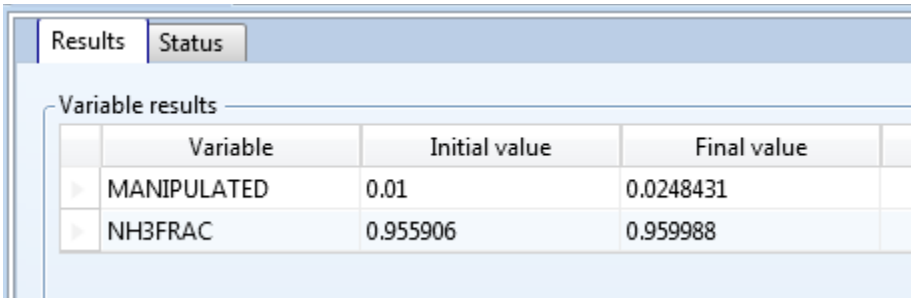
5.14. Next, move to the **Spec** tab and enter **NH3FRAC** for **Spec**, **0.96** as **Target**, and **0.0001** for **Tolerance**.



5.15. Move to the **Vary** tab and define the purge fraction from the splitter as the manipulated variable. Select **Block-Var** for **Type**, **S-100** for **Block**, **FLOW/FRAC** for **Variable**, and **Purge** for **ID1**. Enter **0.01** and **1** as the **Upper** and **Lower** limits and a **Step size** of **0.001**.

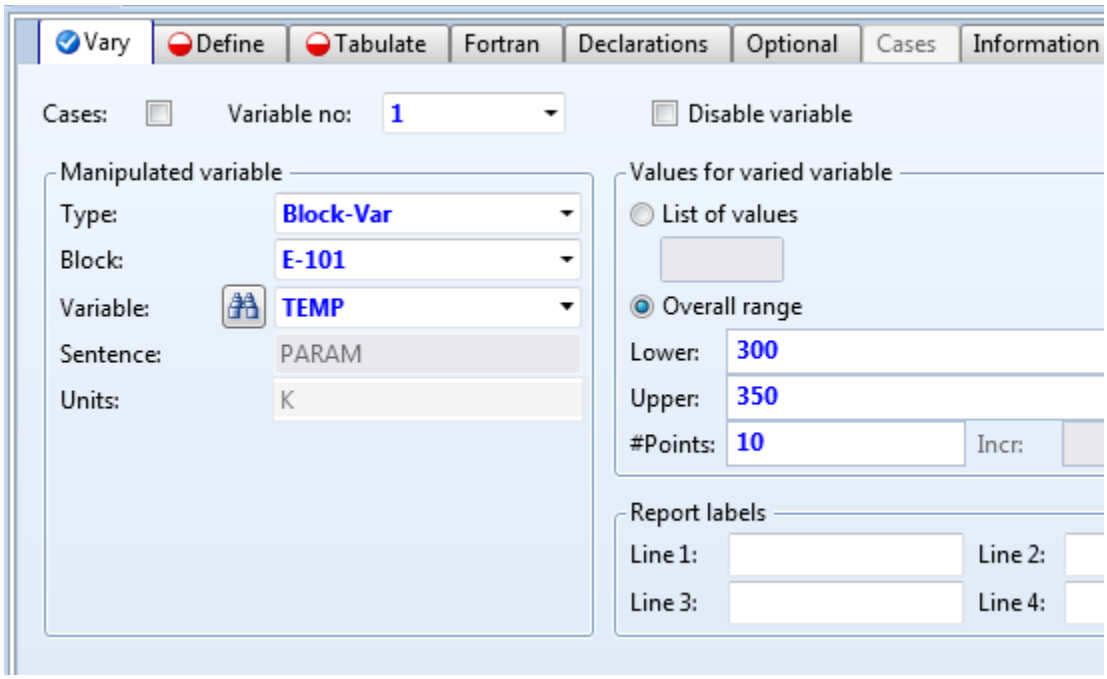


5.16. Open the **Control Panel** and run the simulation (**F5**). Go to **Flowsheeting Options | Design Spec | DS-1 | Results**. You will see that the mole fraction of ammonia in the product stream has reached **0.96** at a purge fraction of **2.48%.**

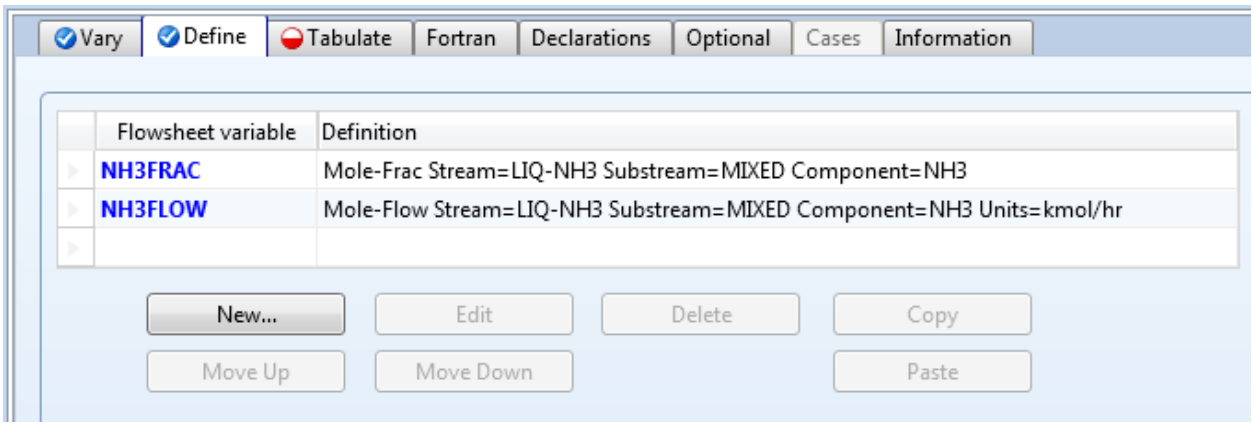


Investigate the Effect of Flash Feed Temperature on Product Composition

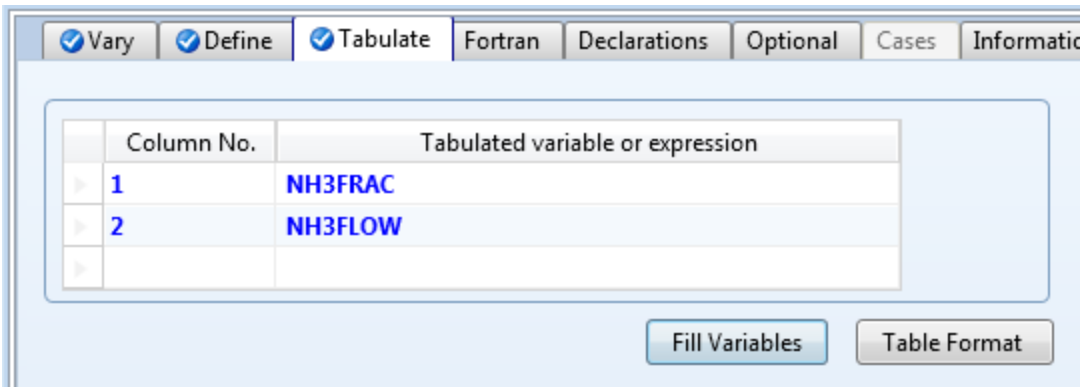
5.17. We would now like to determine how fluctuations in flash feed temperature will affect the product composition and flowrate. Changes in cooling efficiency or utility fluid temperature can change the temperature of the flash feed stream. This change in temperature will change the vapor fraction of the stream, thus changing the composition and flowrate of the product and recycle streams. To do this analysis go to **Model Analysis Tools | Sensitivity** and click **New**. Define the **Manipulated variable** to be the **Outlet temperature of the cooler block (E-101).** Enter a **Temperature range** from **300 to 350 K** for a total of **10 points**.



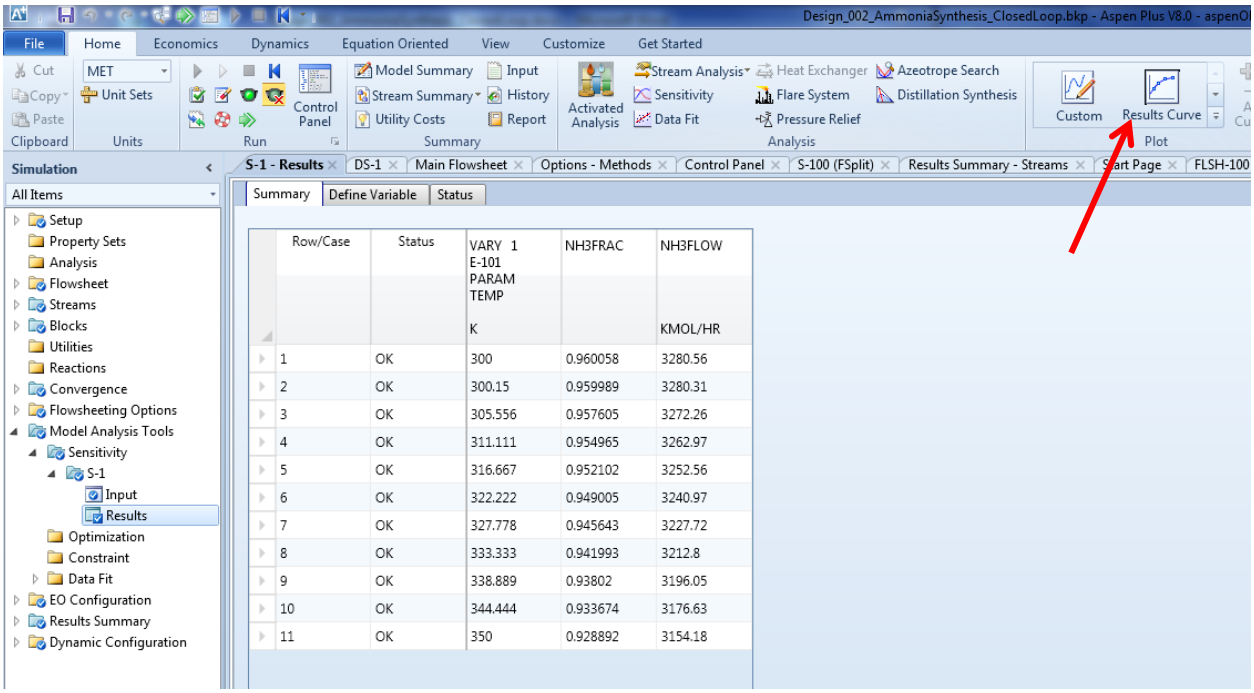
5.18. In the **Define** tab, define the variables that you wish to measure, in this case **ammonia mole fraction** and **flowrate** in the **product stream**.



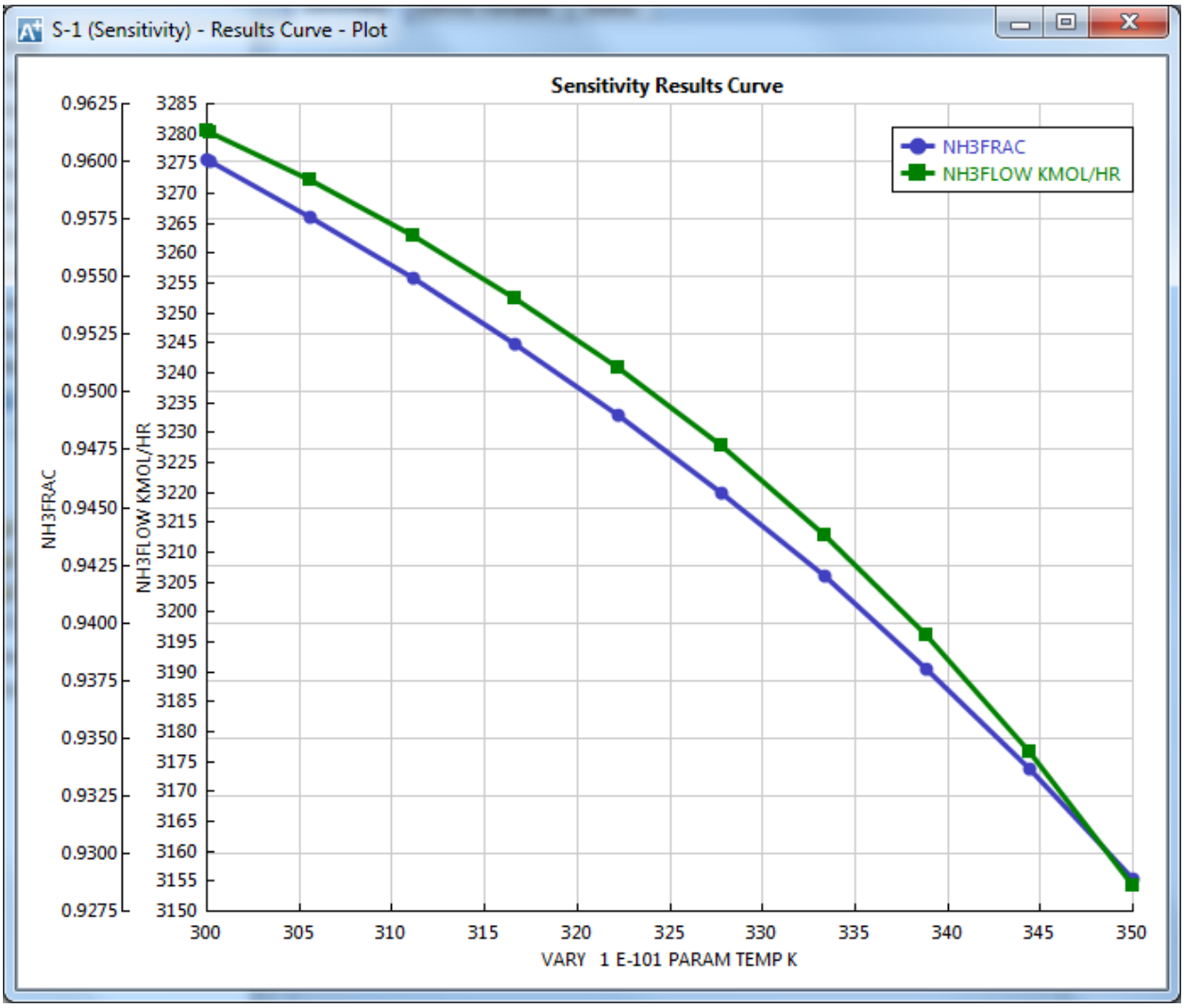
5.19. In the **Tabulate** tab, select which variables you wish to view results for. Manually enter the variables that you just created, or press the **Fill variables** button.



5.20. Before running the simulation, be sure to deactivate the design spec we created in **Flowsheeting Options.** This can be done by going to **Flowsheeting Options** and right clicking on the design spec and selecting **Deactivate**. Once this is done, run the simulation. Check results by going to **Model Analysis Tools | Sensitivity | S-1 | Results**. Click the **Results Curve** plot button on the **Home** ribbon. Select both **Mole fraction** and **Flowrate** to plot against the varied parameter on the x-axis.



The results plot should look like the following.



5.21. You will see that as temperature increases, both the product flowrate and product quality decrease, which means that when operating this process it will be very important to monitor the flash feed temperature in order to deliver high quality product.

6. Conclusion

This simulation has proved the feasibility of this design by solving the mass and energy balances. It is now ready to begin to analyze this process for its economic feasibility. See module **Design-003** to being the economic analysis.

7. Copyright