Azeotropic Distillation with Aspen Plus® V8.0

Production of Anhydrous Ethanol Using an Entrainer

1. Lesson Objectives

- Design a separation train for anhydrous ethanol production using cyclohexane as an entrainer
- Include recycle of cyclohexane and the azeotropic mixture so that the recovery of ethanol is >99.9 % and the recovery of cyclohexane is nearly 100%
- Experiment with the Distillation Synthesis tool included in Aspen Plus
- Successfully converge a flowsheet with multiple recycle streams
- Manipulate convergence methods in **RadFrac** to improve convergence

2. Prerequisites

- Aspen Plus V8.0
- Understanding of azeotropes
- Experience using **RadFrac** distillation model
- Experience reading ternary diagrams

3. Background

Ethanol production via fermentation occurs in water, which must later be separated to make anhydrous ethanol (99.95% ethanol). There is an azeotrope in the ethanol-water system at approximately 95 mol-% ethanol which is a barrier to separation. Cyclohexane is one of the solvents used for the production of anhydrous ethanol for food and pharmaceutical usage. It is used as an entrainer: the ternary mixture forms a ternary azeotrope with a different ethanol concentration, which allows ethanol to enrich in the other stream. The azeotropic liquid is separated to recover the entrainer and ethanol which exits the column in the azeotropic mixture.

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

4. Problem Statement and Aspen Plus Solution

Problem Statement

The feed to the separation train is a stream at 100 kmol/hr with 87 mol-% ethanol and 13 mol-% water. Cyclohexane is added to the column, and > 99.95 mol-% ethanol exits the bottom of the column. The distillate is sent to a decanter (described in Thermo-020_Decanter). The cyclohexane-rich stream is recycled directly to the first column, while the water- and ethanol-rich stream is sent to a second column from which almost-pure water exits in the bottoms. The distillate of the second column is recycled to the first column.

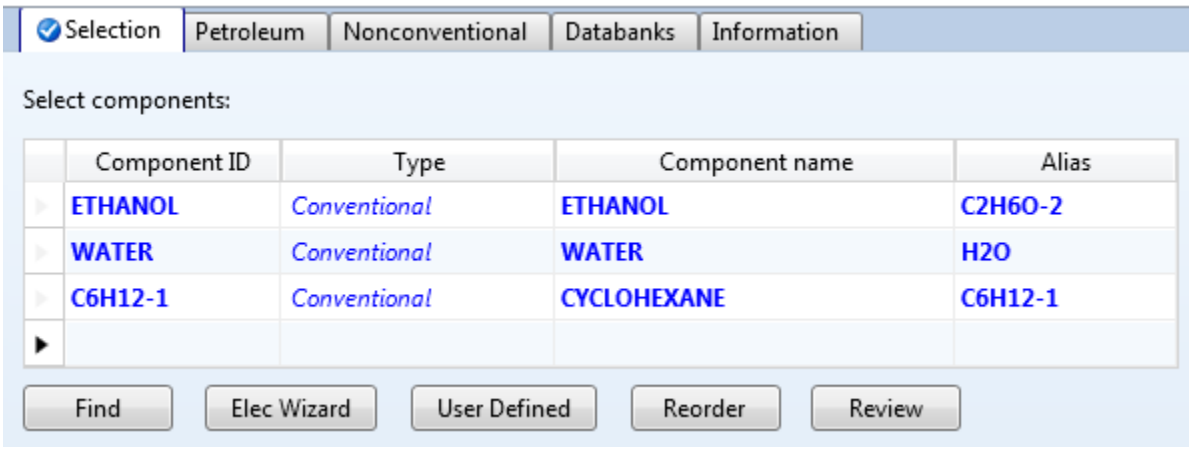
Design the separation train so that the ethanol product stream meets the purity specification, has > 99.9 mol-% recovery, and the water effluent stream is essentially pure water.

Aspen Plus Solution

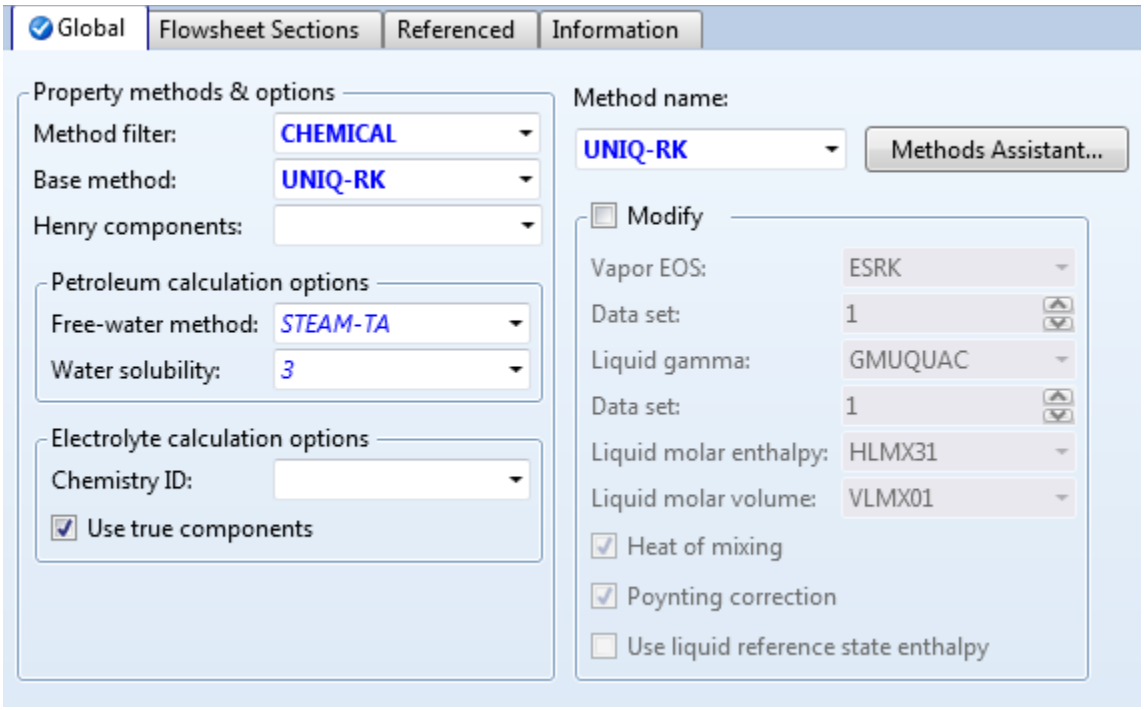
If you are unfamiliar with how to start Aspen Plus, select components, define methods, or construct a flowsheet, consult **Get Started Guide for New Users of Aspen Plus.pdf** for instructions.

This model is built using a specific path. The order in which things are done is important for successful convergence of the model. Do not reinitialize the run unless asked to, and if steps are skipped or done out of order you may need to be start at the beginning or from a previously saved version.

4.01. Start a new simulation using the **Blank Simulation** template in Aspen Plus. The **Components | Specification | Selection** sheet is displayed. Enter the components as shown below.

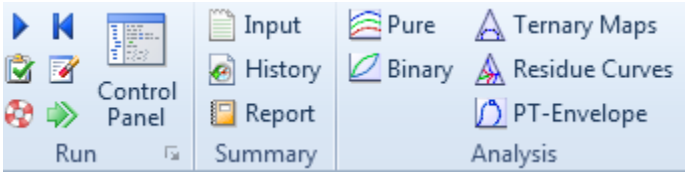


4.02. Click on the **Methods** button in the **Navigate** group under the **Home** tab of the ribbon. Change the **Method filter** to **CHEMICAL** and select **UNIQ-RK** as the **Base method**.



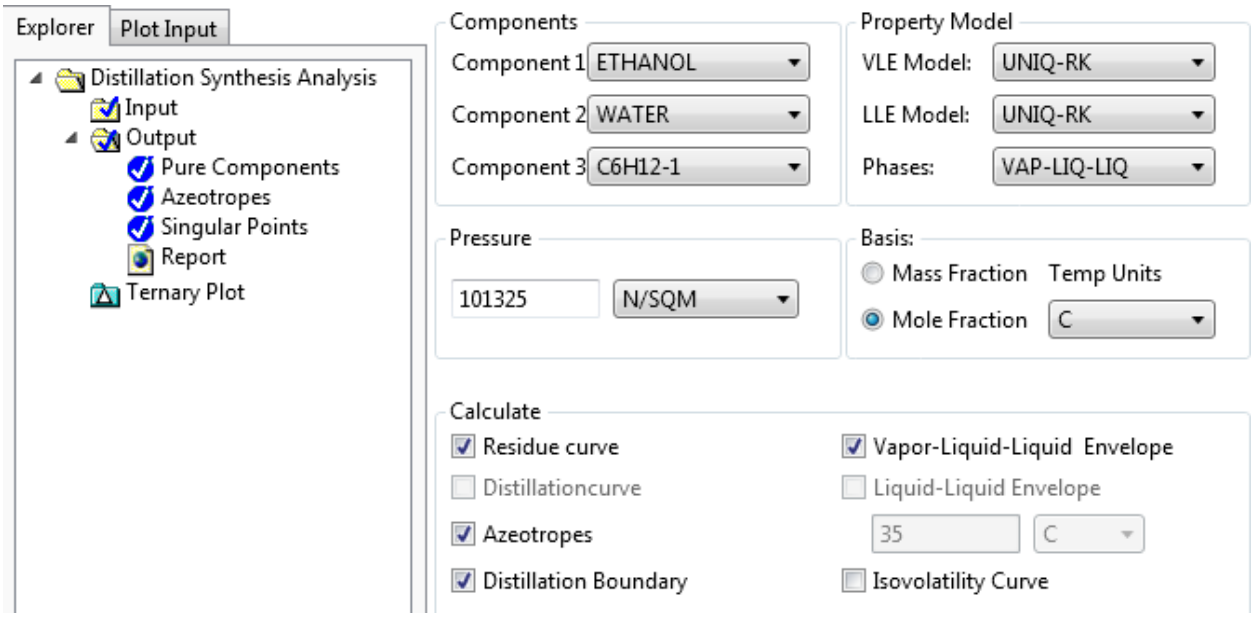
4.03. Press the **F4** key. Note that the **Methods | Parameters | Binary Interaction | UNIQ-1 | Input** sheet is displayed and binary parameters are filled automatically.

4.04. Click on the **Analysis | Residue Curves** button in the **Home** tab of the ribbon.

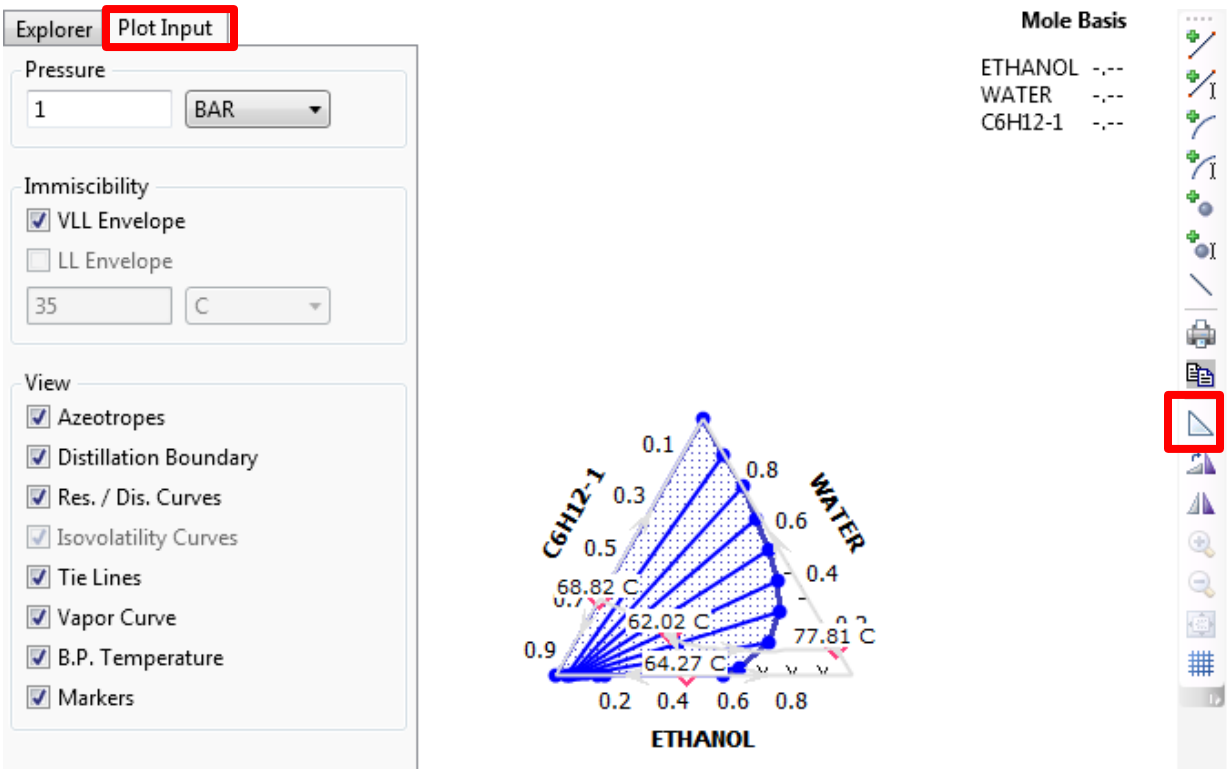


4.05. In the popup dialog box, click the **Use Distillation Synthesis ternary maps** button.

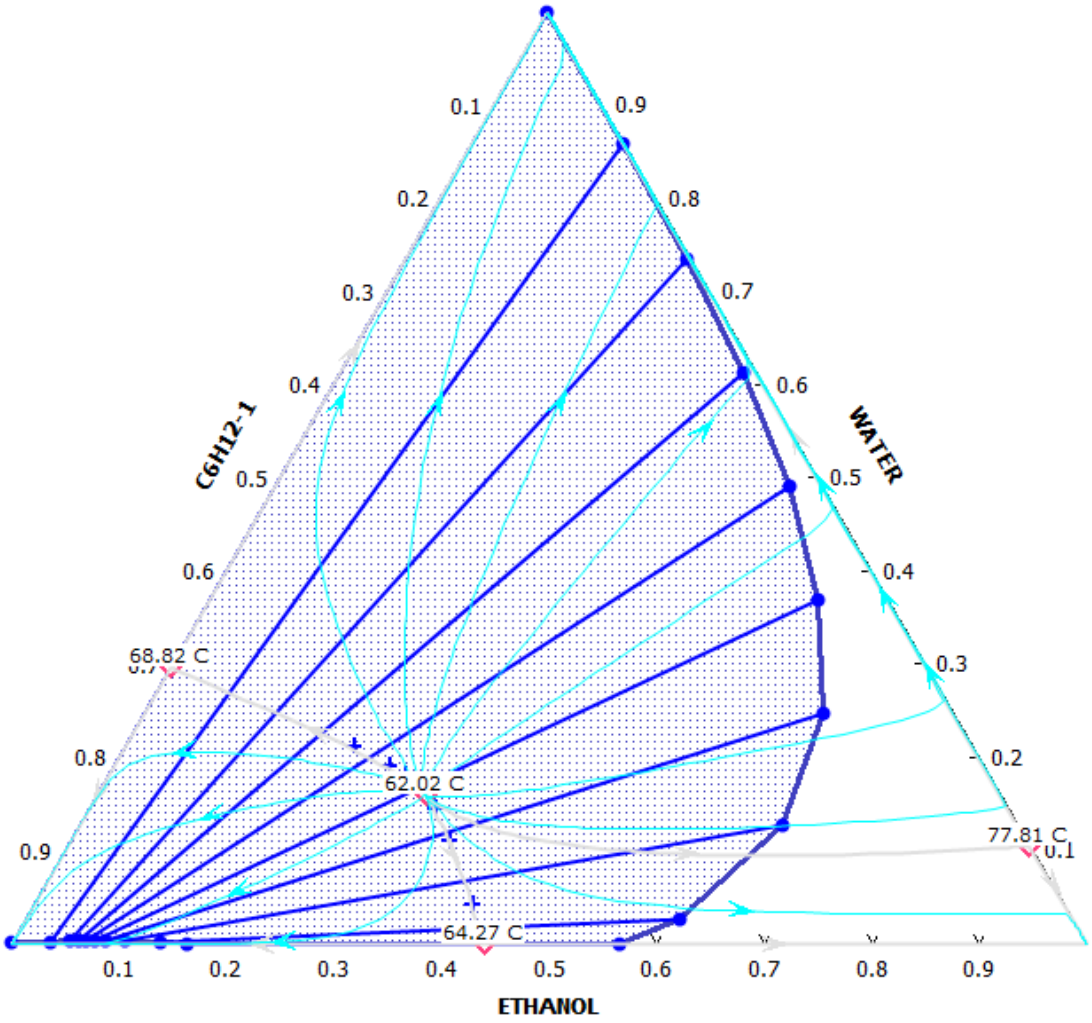
4.06. Ensure that the components are in the same order so that the axes match. Ensure that the **Phases** field is **VAP-LIQ-LIQ** so that the model is accurate.



4.07. Change the **Pressure** to **1 bar**, as this will be the pressure for the columns. Click on the **Plot Input** sheet (it may take 8-15 seconds for this sheet to be displayed) and select the **Switch Coordinates** option to change the format of the graph.

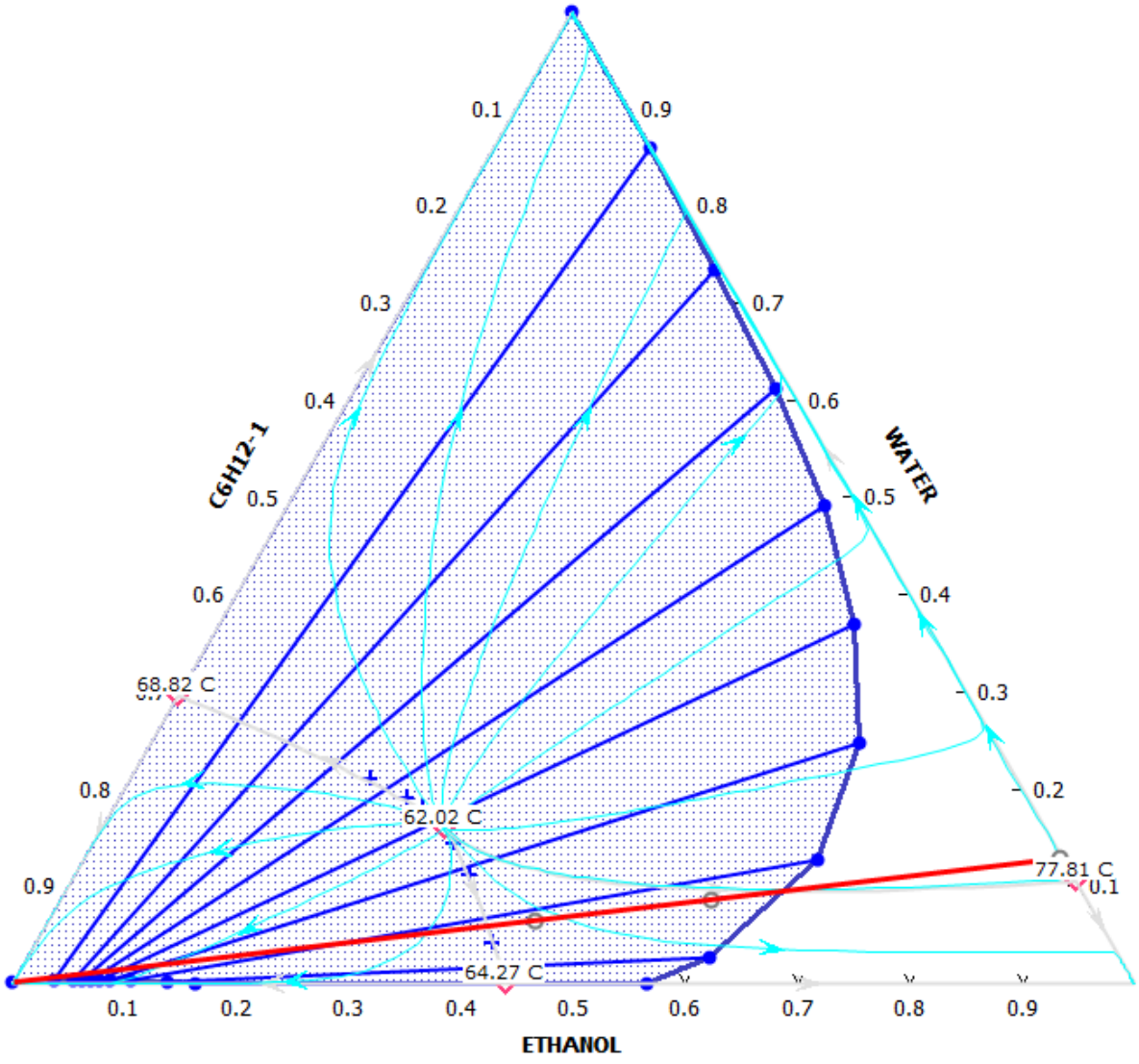


4.08. You can increase the size of the graph by dragging a corner of the **Aspen Plus** window. For help on reading ternary diagrams, refer to **Thermo-016_Ternary_Maps**. The gray lines are the boundaries for the distillation regions. The arrows point towards higher boiling point mixtures. Red diamonds are azeotropes. The dark blue line is the LLE envelope. The slightly lighter blue lines are tie lines for the LLE split. Select the **Add Curve** button and click the plot to add residue curves at specific points in diagram. These curves will be light blue.



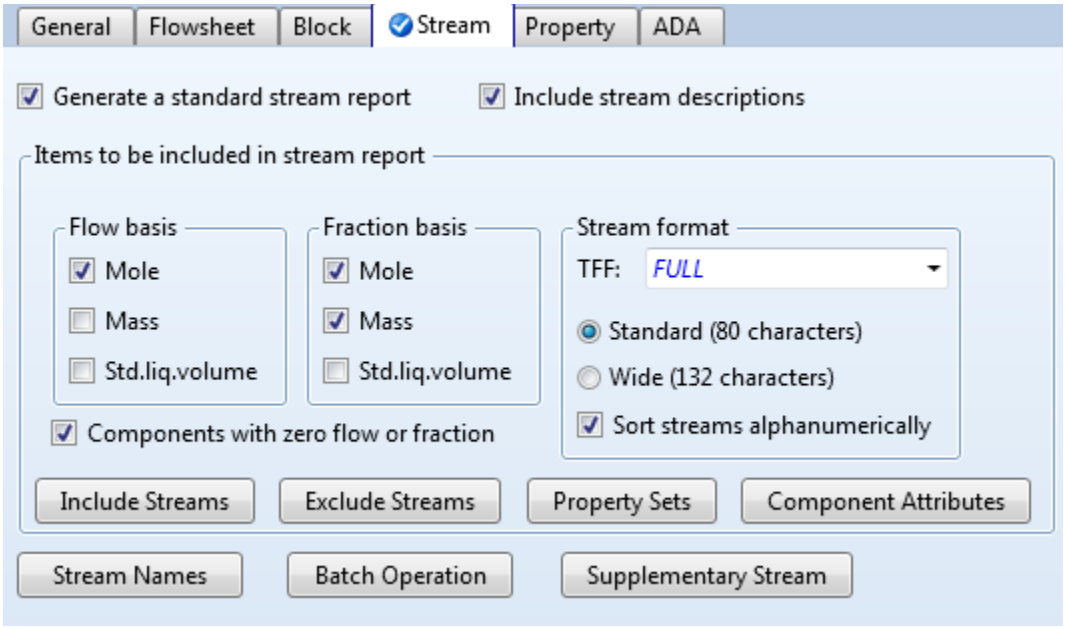
4.09. All residue curves point towards the vertices, which represent pure components. A distillation column will enrich a single component in the bottoms, and the enriched component depends on which distillation region the feed composition is in. We plan to enrich ethanol from the bottom of the first column.

4.10. Use the **Add Marker By Value** button to put a marker at the feed composition (**0.87**, **0.13**, and **0.0**, respectively). Use the **Draw Line** button to draw a line between the marker you just made and the 100% cyclohexane vertex. A combination of a pure cyclohexane stream and the feed stream will have a composition somewhere along this line, depending on the ratio of the flow rates. A section of this line goes through the region which enriches ethanol in the bottoms. Calculate the composition of adding 50 kmol/hr of cyclohexane to the feed stream and adding 100 kmol/hr of cyclohexane to the feed stream. Remember, the feed stream has a flow rate of 100 kmole/hr. Use the **Add Marker By Value** button to put markers at these locations.



4.11. Both points are within the correct distillation region, but the 100 kmol/hr addition marker is farther in the region. Because of this, the initial feed of solvent to the column will be 100 kmol/hr. Use this tool throughout the simulation construction to understand what the decanter or distillation columns are doing. Now, close the **Distillation Synthesis** window.

4.12. Switch to the **Simulation** environment by clicking the **Simulation** bar in the navigation pane. In the navigation pane, go to the **Set up | Report Options | Stream** sheet. Check the **Mole** and **Mass** boxes in the **Fraction basis** frame. This changes the default information shown in stream results which makes it easier to determine what section of the ternary map the stream falls in. This information will also be used later on when closing recycle loops.

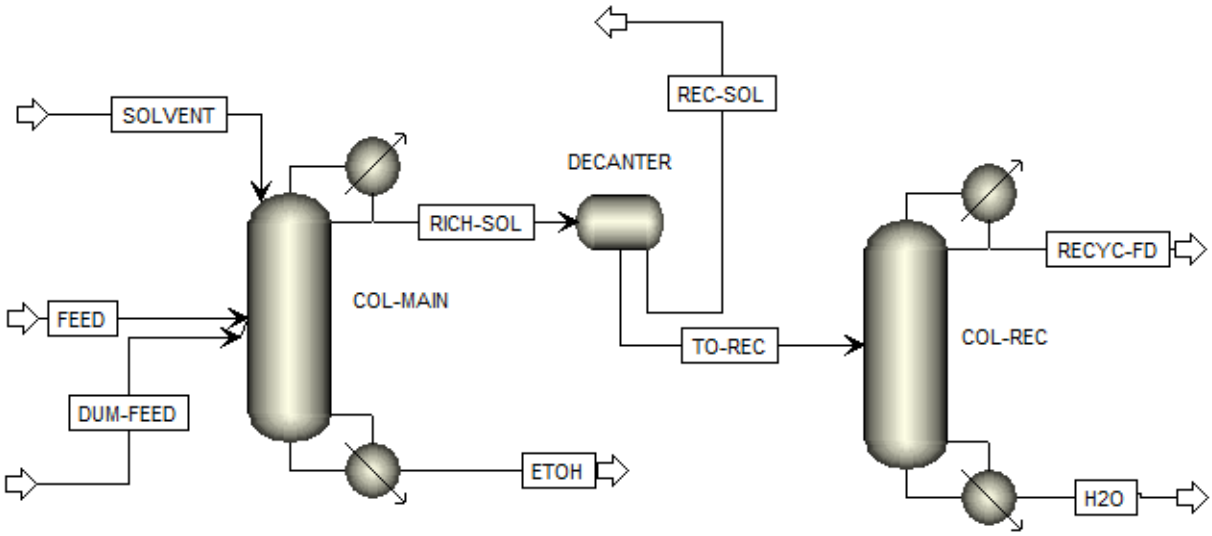


4.13. Create a flowsheet that consists of the following blocks and streams.

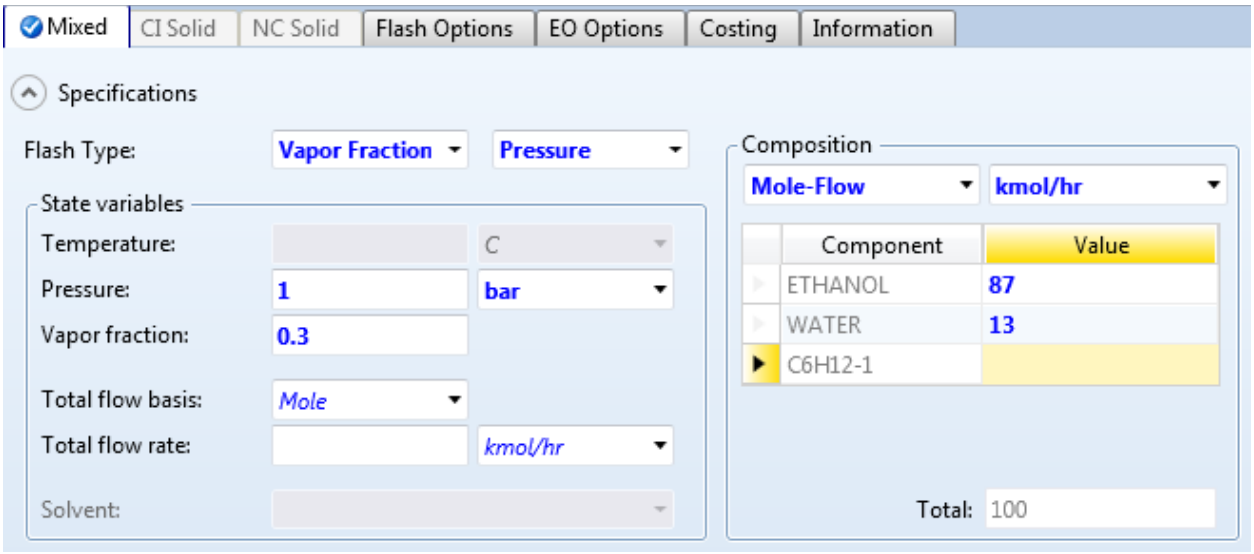
Name	Type
COL-MAIN	RadFrac
COL-REC	RadFrac
DECANTER	Decanter

Name	Type
DUM-FEED	MATERIAL
ETOH	MATERIAL
FEED	MATERIAL
H2O	MATERIAL
REC-SOL	MATERIAL
RECYC-FD	MATERIAL
RICH-SOL	MATERIAL
SOLVENT	MATERIAL
TO-REC	MATERIAL

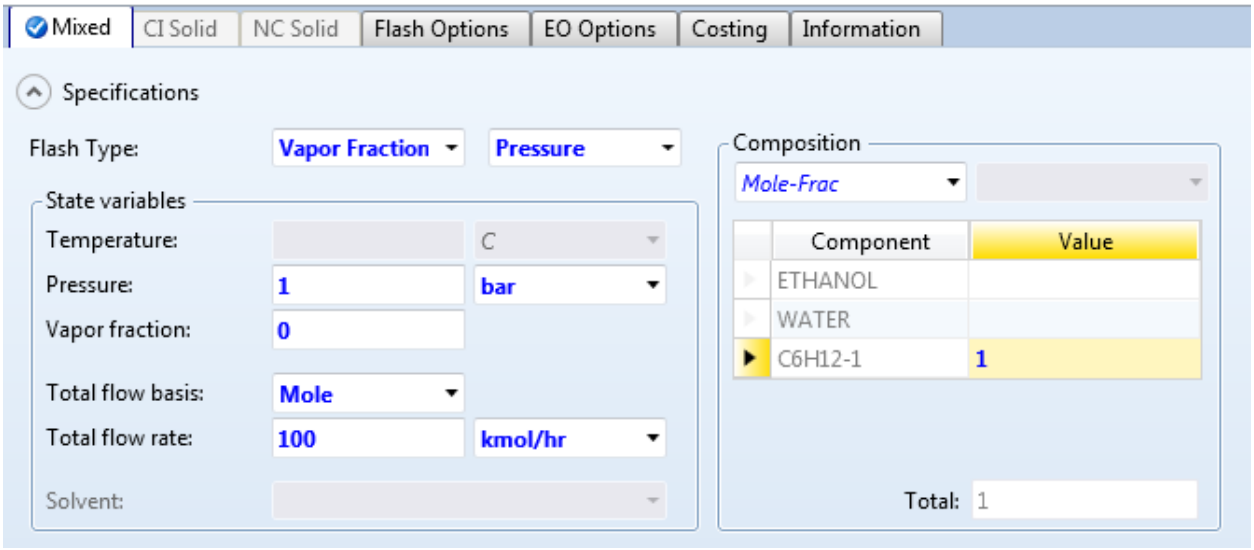
4.14. These blocks and streams should be connected in the following way.



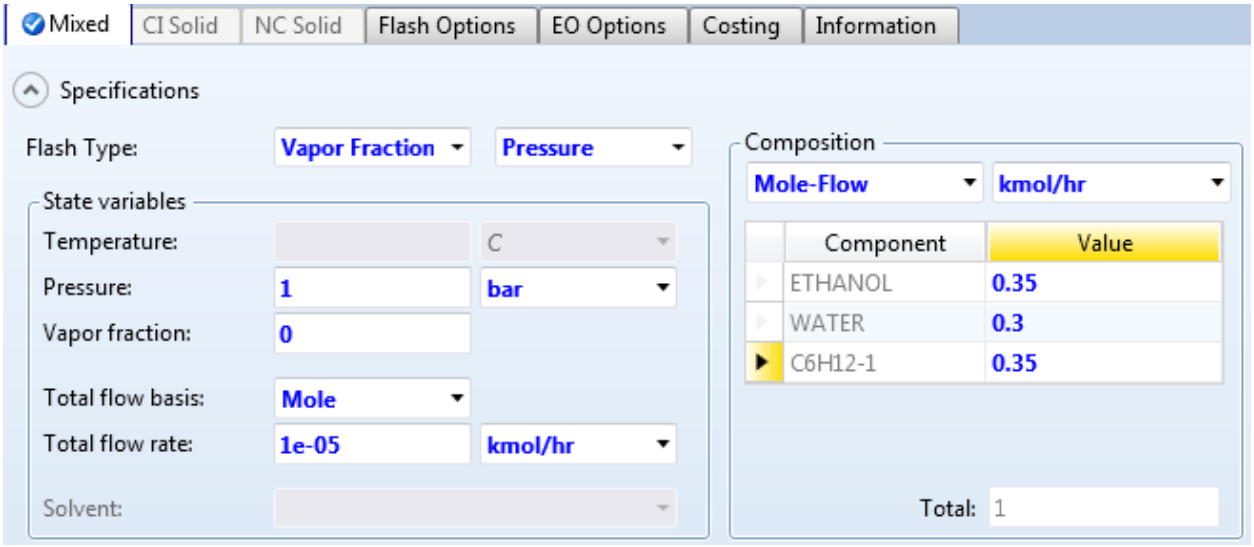
4.15. Enter the feed conditions. Go to the **Streams | FEED | Input | Mixed** sheet and specify **FEED** as shown below.



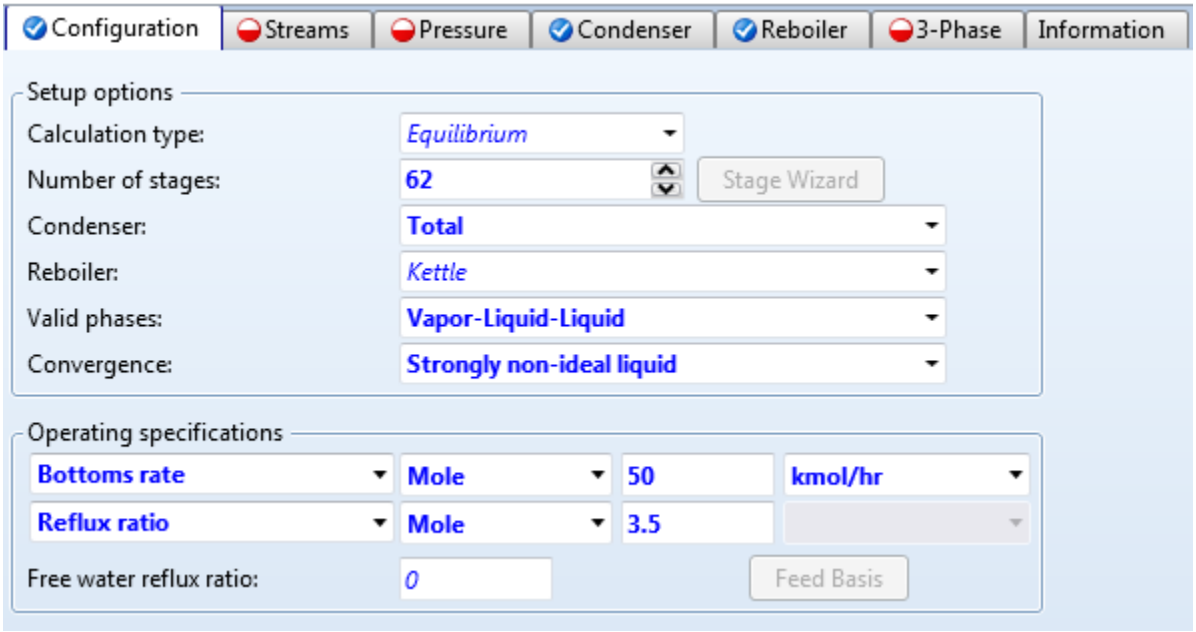
4.16. Go to the **Streams | SOLVENT | Input | Mixed** sheet and specify **SOLVENT** as shown below. This stream will eventually be connected with a stream recycled from **DECANTER**. The specifications here serve as an initial guess.



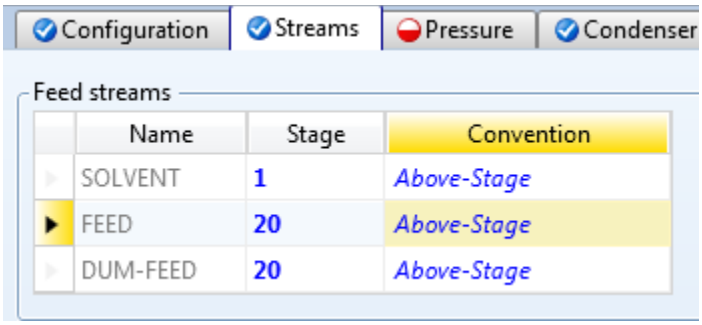
4.17. Go to the **Streams | DUM-FEED | Input | Mixed** sheet. This steam will later on be connected with a recycle stream from the top of **COL-REC**. The dummy feed stream is a place holder for the recycle stream from the top of the recycle column. For now, we enter a tiny flowrate with a rough guess for compositions as shown below.



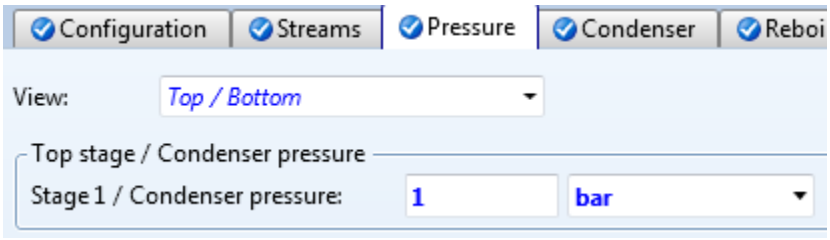
4.18. Go to the **Blocks | COL-MAIN | Specifications | Setup | Configuration** sheet. Enter **62** for **Number of stages.** Select **Total** for **Condenser**, **Vapor-Liquid-Liquid** for **Valid phases** and **Strongly non-ideal** for **Convergence**. In the **Operating specifications** frame, enter **3.5** for **Reflux ratio**. Then, select **Bottoms rate** as the other specification and enter **50** for **Bottoms rate**. **Blocks | COL-MAIN | Specifications | Setup | Configuration** sheet should look like this.



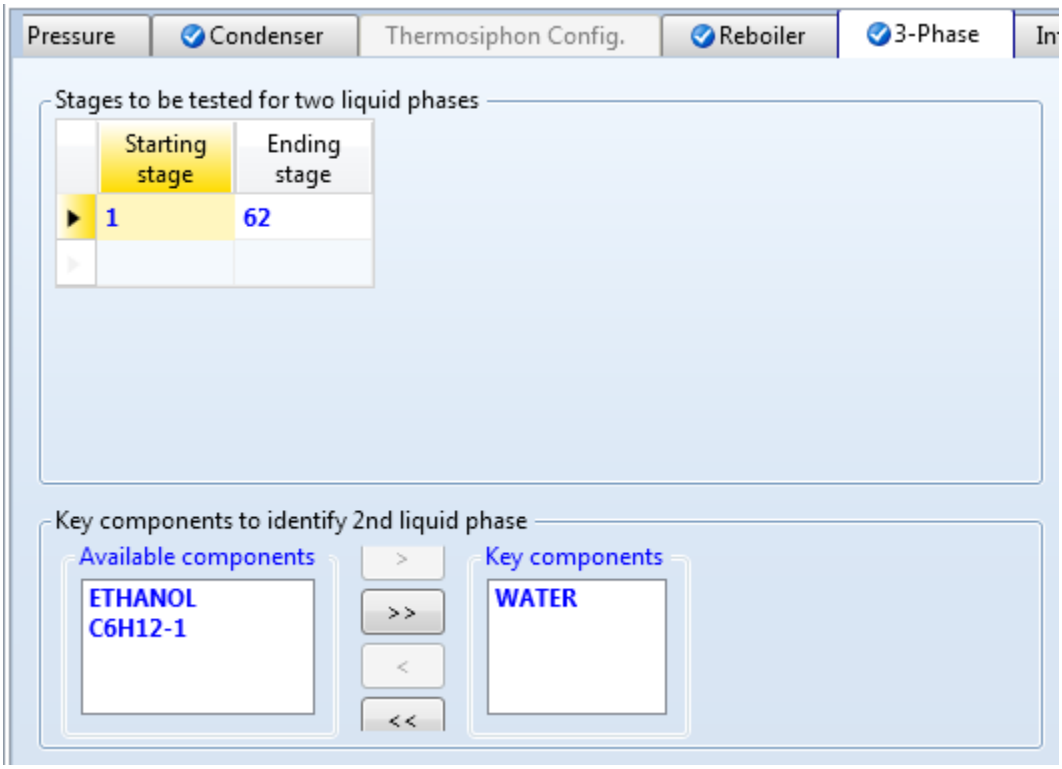
4.19. Go to the **Blocks | COL-MAIN | Specifications | Setup | Streams** sheet. In the **Feed streams** frame, enter **20** in the **Stage** column for **FEED** and **DUM-FEED**. Enter **1** for **SOLVENT** as shown below.



4.20. Go to the **Blocks | COL- MAIN | Specifications | Setup | Pressure** sheet. Enter **1** for **Stage 1 / Condenser pressure**.

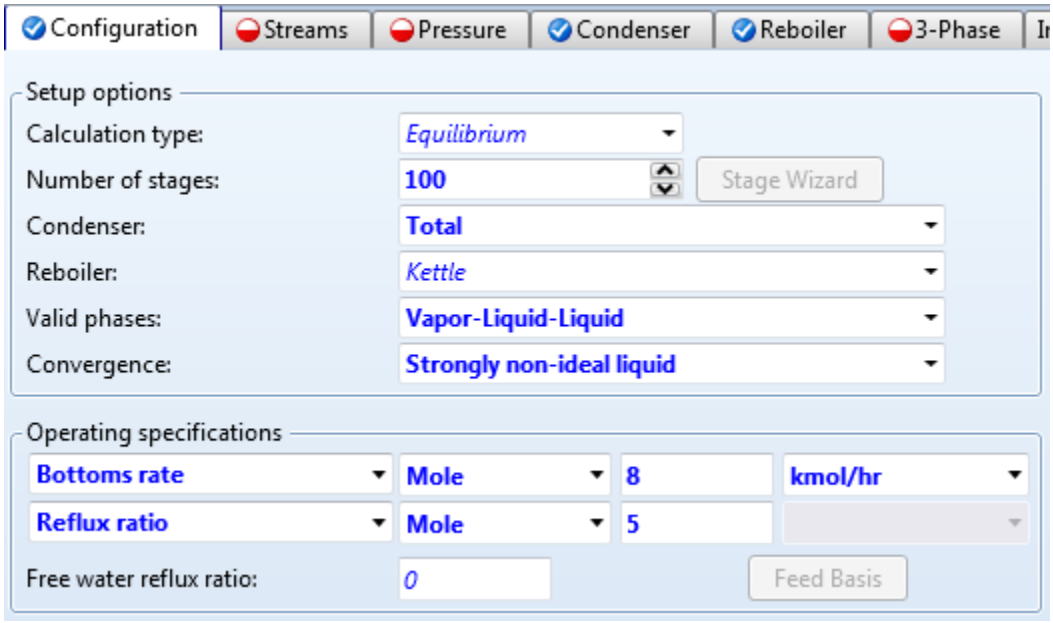


4.21. Go to the **Blocks | COL-MAIN | Specifications | Setup | 3-Phase** sheet. Enter **1** for **Starting stage** and **62** for **Ending stage**. Specify **WATER** as **Key components** in the **Key components to identify 2nd liquid phase** frame. This tells Aspen Plus that we expect the second liquid phase to be predominantly water, and since we do not know exactly which stages of the column will contain two liquid phases, we will ask Aspen Plus to check every stage.

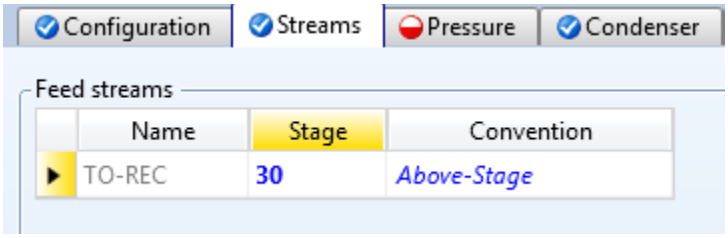


4.22. Go to the **Blocks | COL-MAIN | Convergence | Convergence | Basic** sheet. Increase **Maximum iterations** from **25** to **200**.

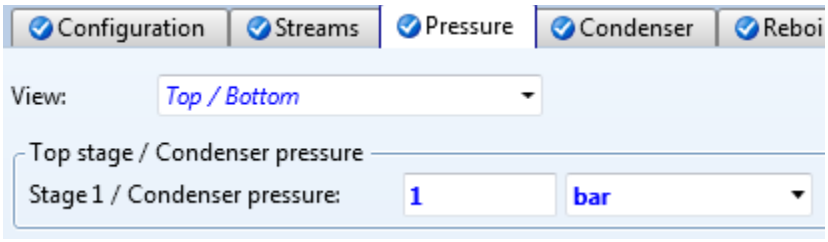
4.23. Go to the **Blocks | COL-REC | Specifications | Setup | Configuration** sheet. Enter **100** for **Number of stages.** Select **Total** for **Condenser**, **Vapor-Liquid-Liquid** for **Valid phases** and **Strongly non-ideal** for **Convergence**. In the **Operating specifications** frame, enter **5** for **Reflux ratio**. Then, select **Bottoms rate** as the other specification and enter **8** for **Bottoms rate**. Note that the value for Bottoms rate is an initial guess and it will be varied to meet the product purity specification. **Blocks | COL-REC | Specifications | Setup | Configuration** sheet should look like this.



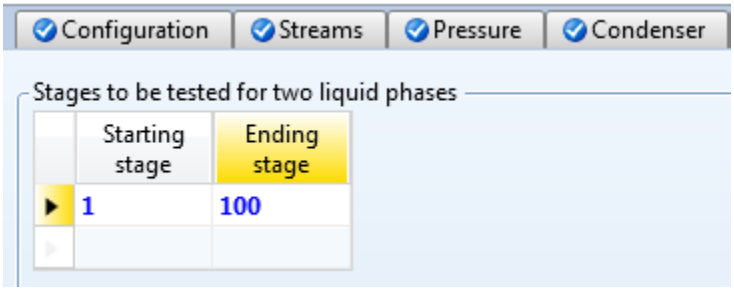
4.24. Go to the **Blocks | COL-REC | Specifications | Setup | Streams** sheet. In the **Feed streams** frame, enter **30** for **Stage** as shown below.



4.25. Go to the **Blocks | COL- REC | Specifications | Setup | Pressure** sheet. Enter **1** for **Stage 1 / Condenser pressure**.

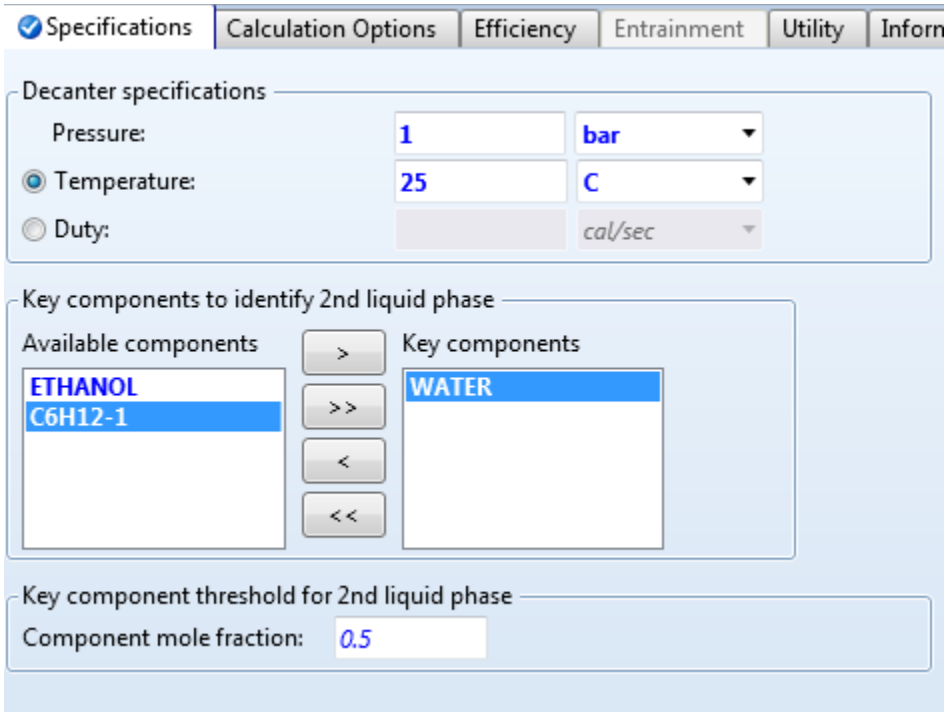


4.26. Go to the **Blocks | COL-REC | Specifications | Setup | 3-Phase** sheet. Enter **1** for **Starting stage** and **100** for **Ending stage**. Specify **WATER** as **Key components** in the **Key components to identify 2nd liquid phase** frame. This tells Aspen Plus that we expect the second liquid phase to be predominantly water, and since we do not know exactly which stages of the column will contain two liquid phases, we will ask Aspen Plus to check every stage.



4.27. Go to the **Blocks | COL-REC | Convergence | Convergence | Basic** sheet. Increase **Maximum iterations** from **25** to **200**.

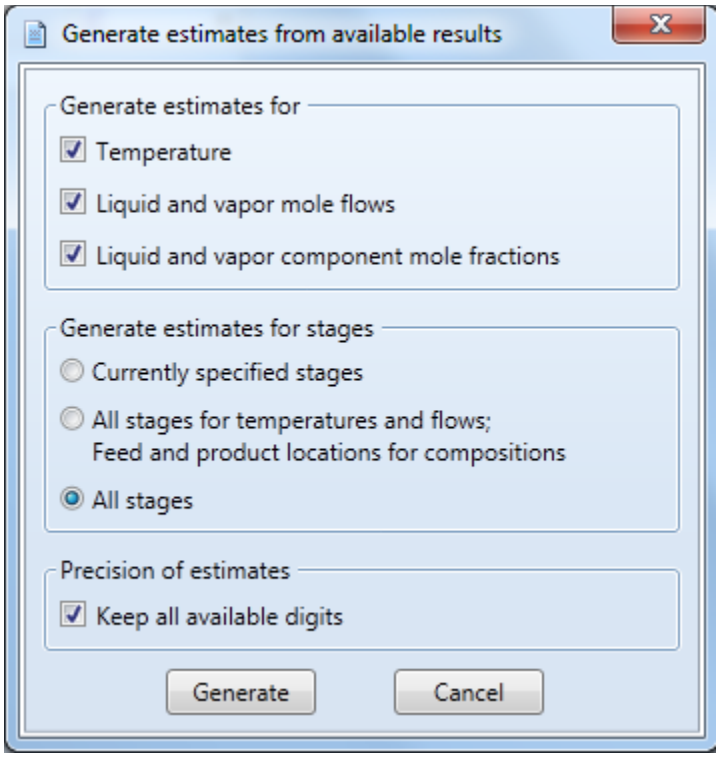
4.28. Go to the **Blocks | DECANTER | Input | Specifications** sheet. Enter **1** for **Pressure** and **25** for **Temperature**. In **Key components to identify 2nd liquid phase** frame, move **WATER** to Key components list. The **Blocks | DECANTER | Input | Specifications** sheet look like this:



4.29. Press the **F5** key to run the simulation and the simulation should complete without any error or warning.

4.30. Make the two columns numerically more robust. Go to the **Blocks | COL-MAIN | Specifications | Setup | Configuration** sheet. Change **Convergence** to **Custom**.

4.31. Go to the **Blocks | COL-MAIN | Convergence | Estimates | Temperature** sheet. Click the **Generate Estimates…** button. In the popup dialog box, select options to generate the most estimates as shown below. Then click **Generate** button and wait for estimate generation to complete.

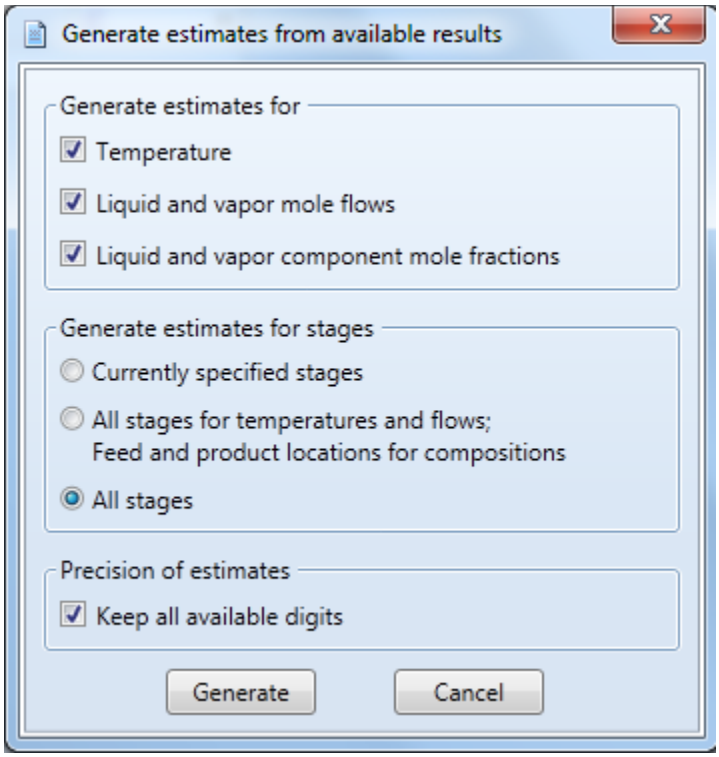


4.32. Go to the **Blocks | COL-MAIN | Convergence | Convergence | Basic** sheet. Select **Newton** for **Algorithm**.

4.33. Go to the **Blocks | COL-MAIN | Convergence | Convergence | Advanced** sheet and select **Dogleg strategy** for **Stable-Meth**.

4.34. Now, we do the same for **COL-REC**. Go to the **Blocks | COL- REC | Specifications | Setup | Configuration** sheet. Change **Convergence** to **Custom**.

4.35. Go to the **Blocks | COL- REC | Convergence | Estimates | Temperature** sheet. Click the **Generate Estimates…** button. In the popup dialog box, select options to generate the most estimates as shown below. Then click **Generate** button and wait for estimate generation to complete.

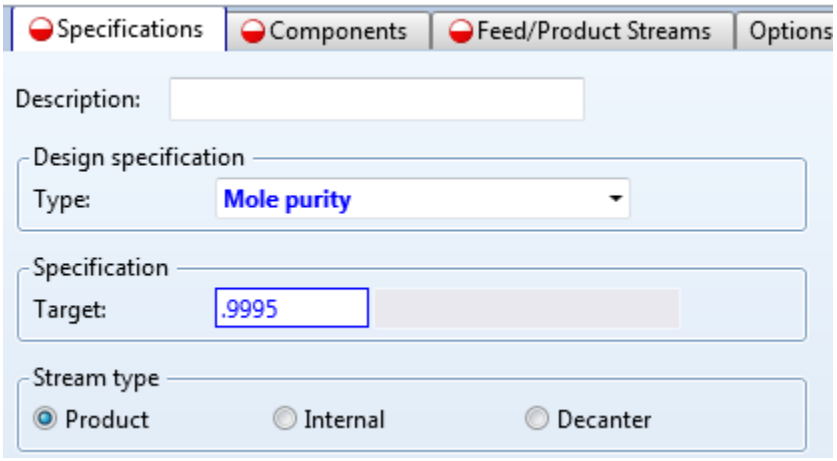


4.36. Go to the **Blocks | COL- REC | Convergence | Convergence | Basic** sheet. Select **Newton** for **Algorithm**.

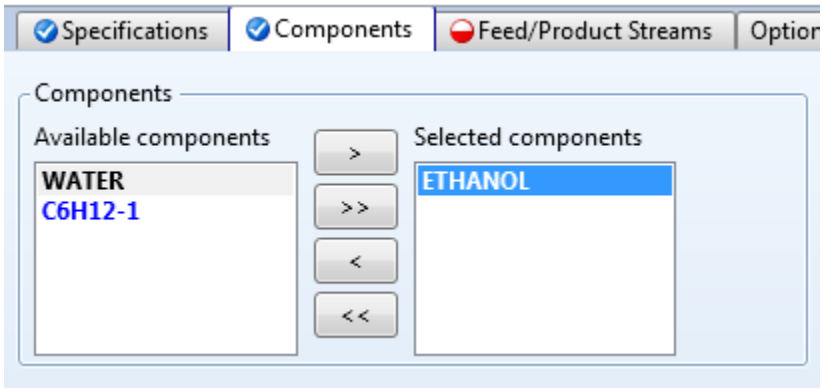
4.37. Go to the **Blocks | COL- REC | Convergence | Convergence | Advanced** sheet and select **Dogleg strategy** for **Stable-Meth**.

4.38. Now, we use **Design-Specs / Vary** to achieve the desired product purity. Go to the **Blocks | COL-MAIN | Specifications | Design Specifications** form in the navigation pane. The object manager for **Design Specifications** is displayed. Click the **New…** button to create a new **Design Specification** called **1**.

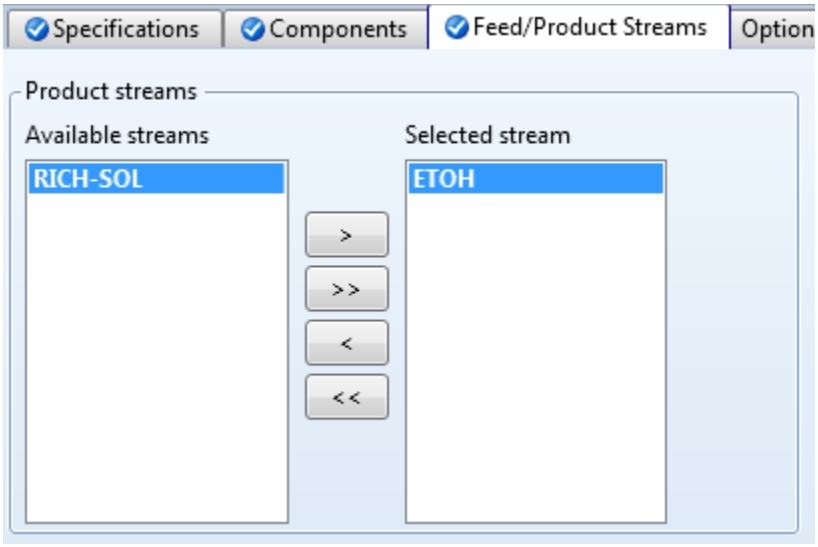
4.39. Go to the **Blocks | COL-MAIN | Specifications | Design Specifications | 1 | Specifications** sheet. Select **Mole purity** for **Type** and enter **0.9995** for **Target**.



4.40. Go to the **Blocks | COL-MAIN | Specifications | Design Specifications | 1 | Components** sheet. In the **Components** frame, move **ETHANOL** to the **Selected components** list as shown below.

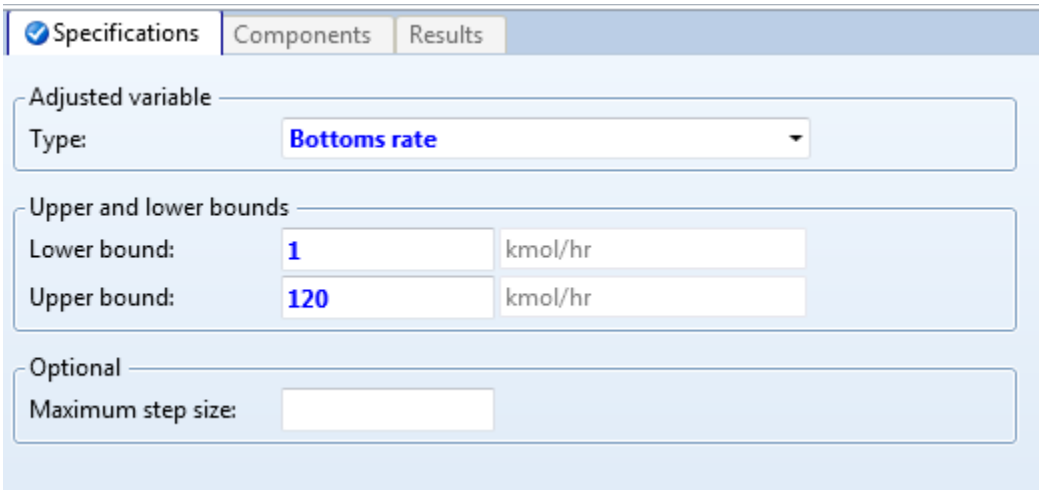


4.41. Go to the **Blocks | COL-MAIN | Specifications | Design Specifications | 1 | Feed/Product Streams** sheet. In the **Product streams** frame, move **ETOH** to the **Selected stream** list as shown below.



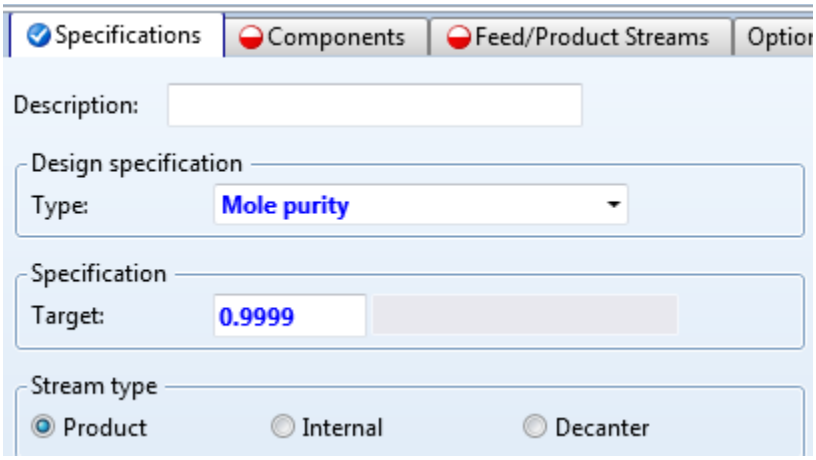
4.42. In the navigation pane, select **Blocks | COL-MAIN | Specifications | Vary**. The object manager for **Vary** is displayed. Click the **New...** button to create a new **Vary** called **1**.

4.43. Go to the **Blocks | COL-MAIN | Specifications | Vary | 1 | Specifications** sheet. Select **Bottoms rate** for **Type**. Enter **1** for **Lower bound** and **120** for **Upper bound**.

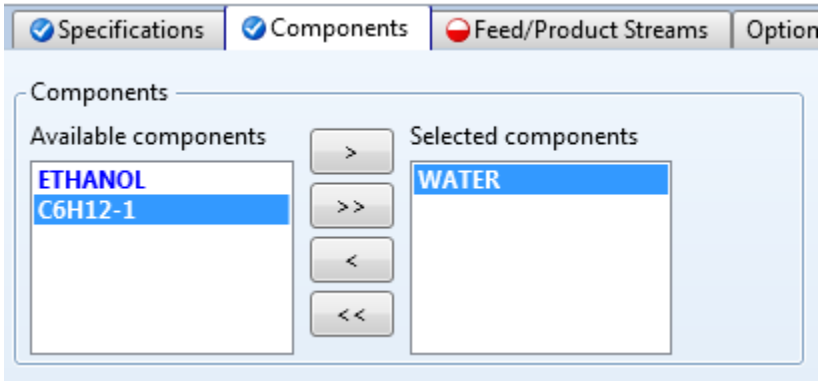


4.44. Now, we create Design Specs for **COL-REC**. In the navigation pane, select **Blocks | COL-REC Specifications | Design Specifications**. The object manager for **Design Specs** is displayed. Click the **New…** button to create a new **Design Specs** called **1.**

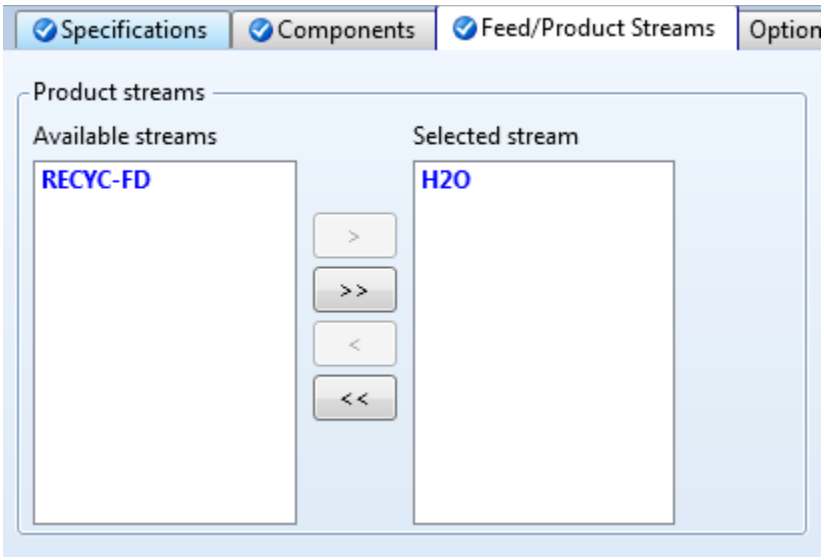
4.45. Go to the **Blocks | COL-REC | Specifications | Design Specifications | 1 | Specifications** sheet. Select **Mole purity** for **Type** and enter **0.9999** for **Target.**



4.46. Go to the **Blocks | COL-REC | Specifications | Design Specifications | 1 | Components** sheet. In the **Components** frame, move **WATER** to the **Selected components** as shown below.

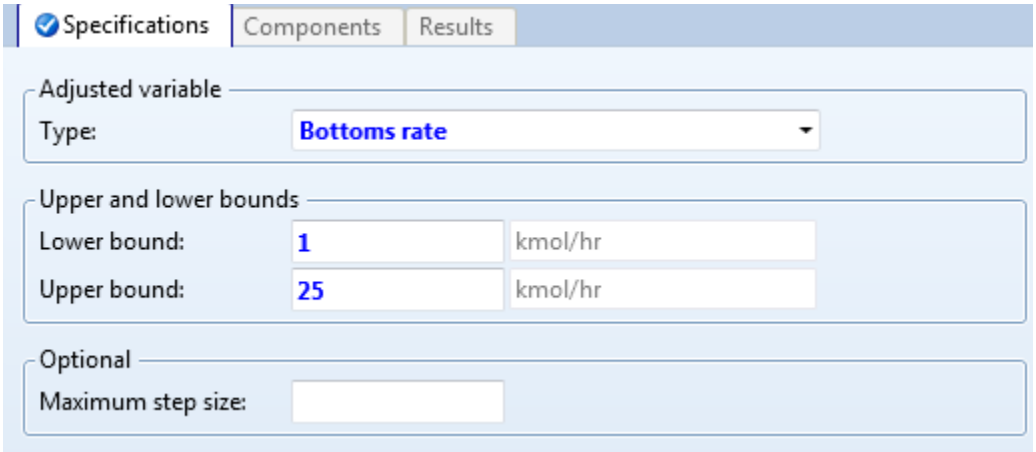


4.47. Go to the **Blocks | COL-REC | Specifications | Design Specifications | 1 | Feed/Product Streams** sheet. In the **Product streams** frame, move **H2O** to the **Selected stream** list as shown below.



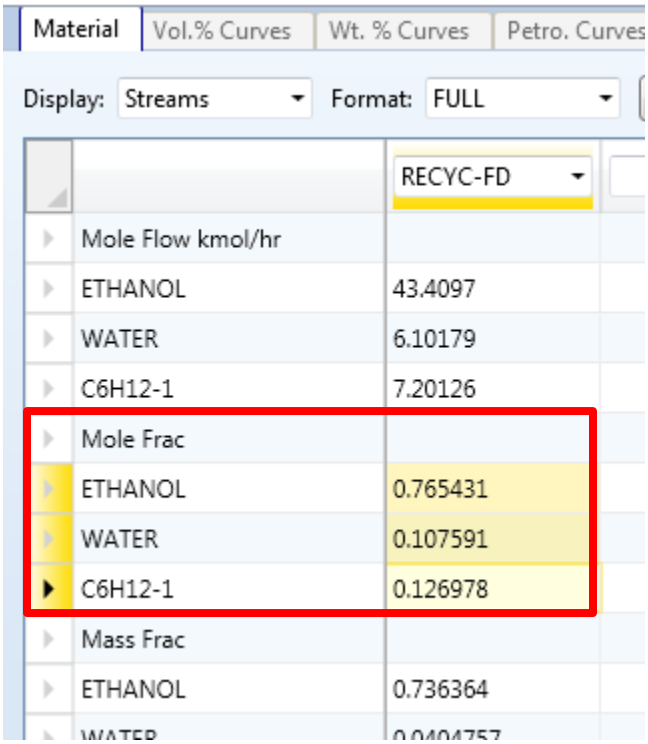
4.48. In the navigation pane, select **Blocks | COL-REC | Specifications | Vary**. The object manager for **Vary** is displayed. Click the **New…** button to create a new **Vary** called **1.**

4.49. Go to the **Blocks | COL-REC | Specifications | Vary | 1 | Specifications** sheet. Select **Bottoms rate** for **Type**. Enter **1** for **Lower bound** and **25** for **Upper bound**.

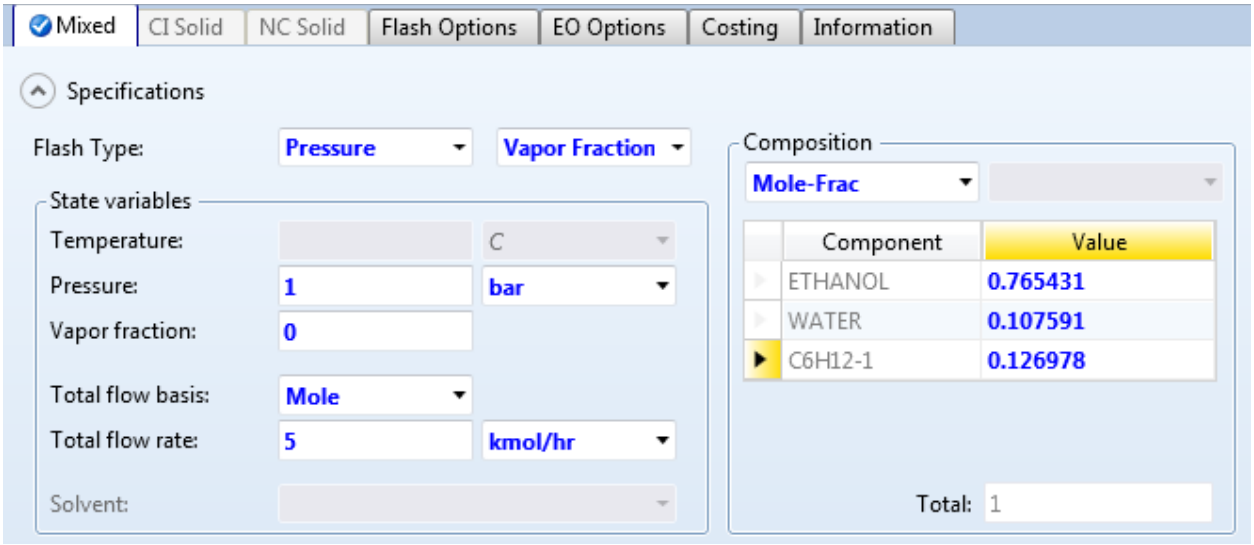


4.50. Press the **F5** key to run the simulation and the simulation should complete without any error or warning.

4.51. Before the recycle loops can be closed, the open-loop simulation should approximate the closed-loop solution. Go to the **Streams | RECYC-FD | Results | Material** sheet. Copy the mole-based composition of the **RECYC-FD** stream.



4.52. Paste the mole fractions into the **Composition** field on **Streams | DUM-FEED | Input | Mixed** sheet. Increase the **Total flow rate** to **5 kmol/hr**.

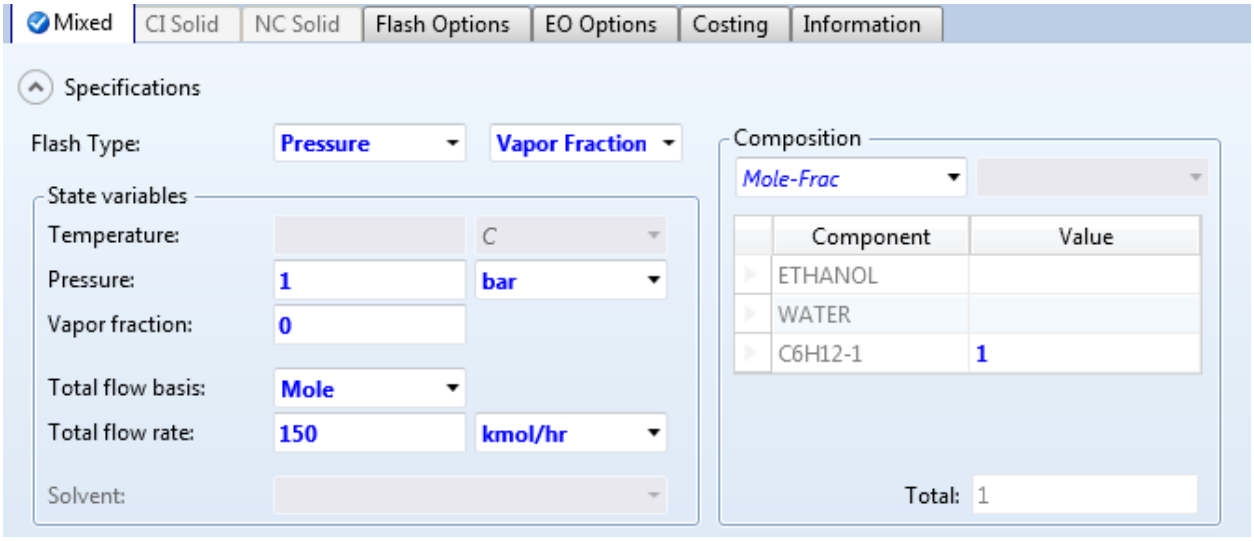


4.53. Run the simulation without reinitializing.

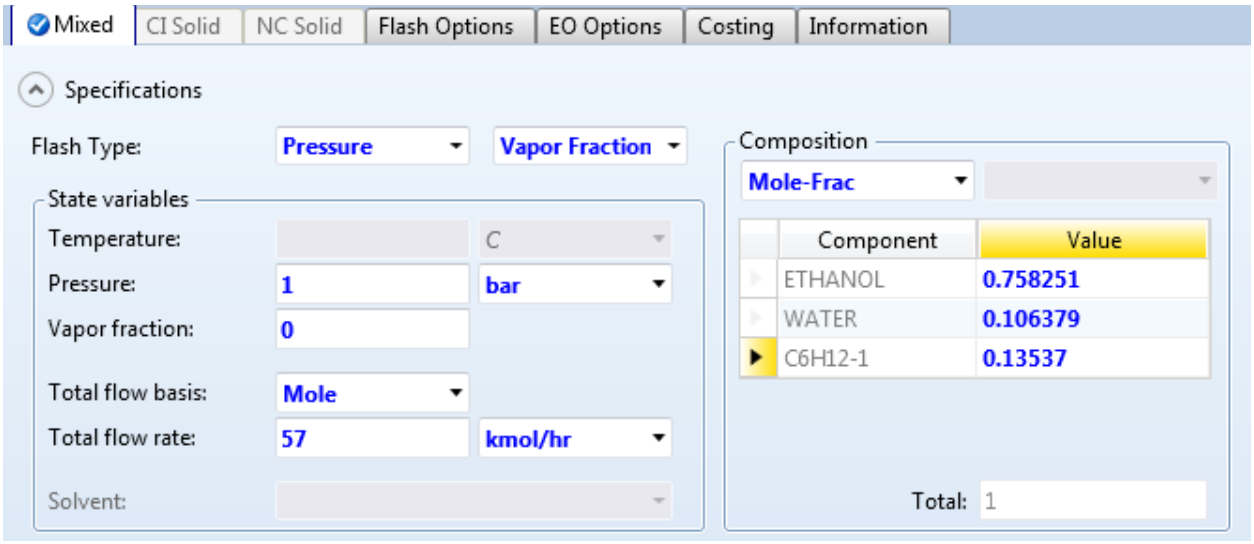
4.54. Because the RadFrac blocks are using Newton's method to converge, large changes in the feed conditions can create errors in the simulation. Change the **Total flow rate** of **DUM-FEED** to each of the values in the table below and run the simulation after each change of the flow rate.

7	**kmol/hr**
9	**kmol/hr**
15	**kmol/hr**
25	**kmol/hr**
35	**kmol/hr**
57	**kmol/hr**

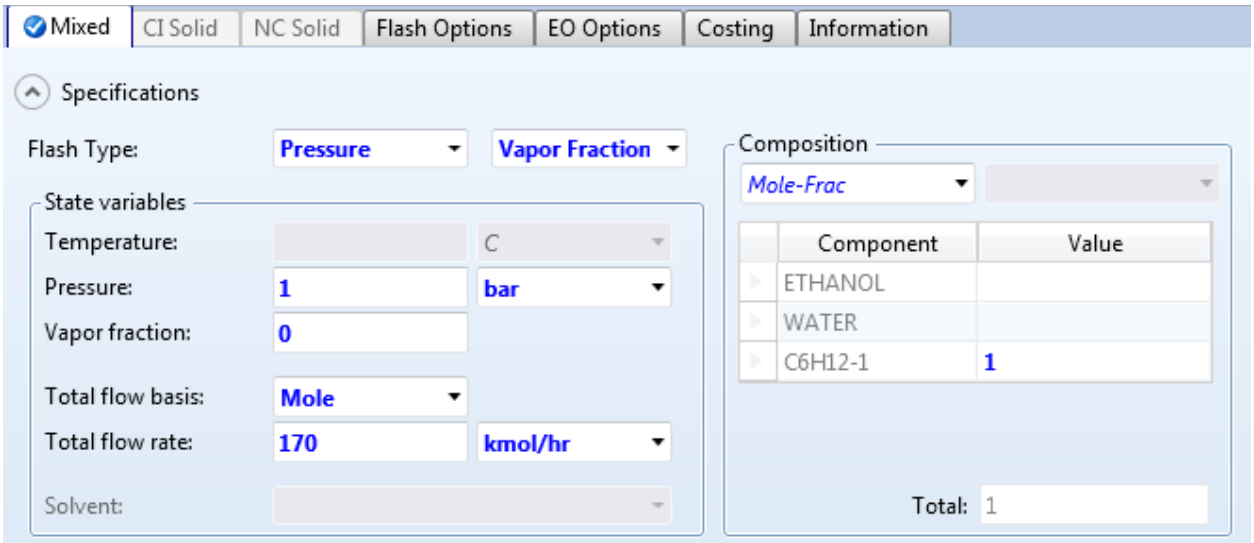
4.55. Because the flow rate of **DUM-FEED** has been increased, the flow rate of **SOLVENT** must be increased so that the column operates within the same distillation region. Change the **Total flow rate** to **150 kmol/hr** and run the simulation.



4.56. Copy the composition of **RECYC-FD** and paste it into **DUM-FEED** again. Increase the **Total flow rate** to **76 kmol/hr**.



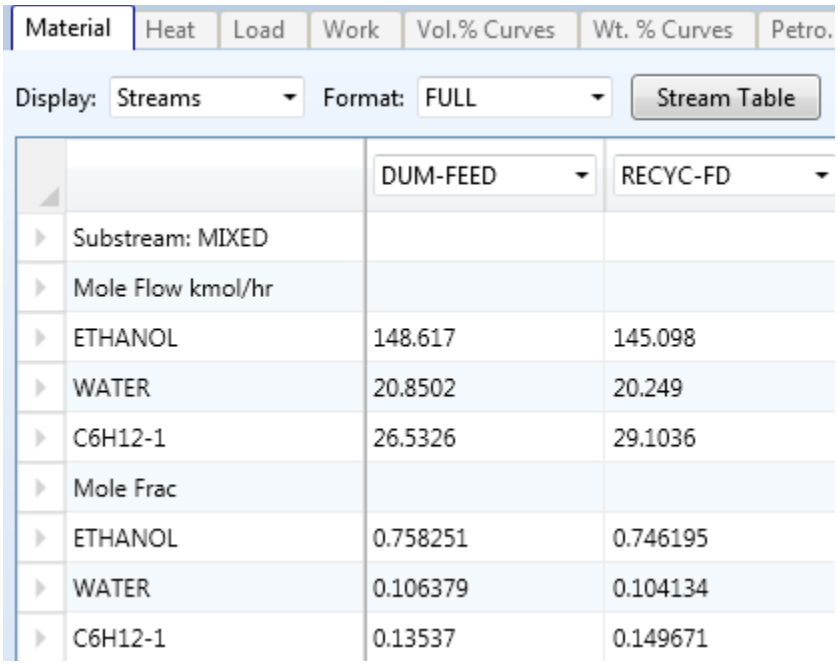
4.57. Increase the **Total flow rate** of **SOLVENT** to **170 kmol/hr** as well. Run the simulation.



4.58. Change the **Total flow rate** of **DUM-FEED** and **SOLVENT** to match the rows in the table below. Each time after changing both flow rates, run the simulation.

DUM-FEED Total flow rate		SOLVENT Total flow rate	
96	**kmol/hr**	**190**	**kmol/hr**
116	**kmol/hr**	**210**	**kmol/hr**
136	**kmol/hr**	**230**	**kmol/hr**
156	**kmol/hr**	**250**	**kmol/hr**
176	**kmol/hr**	**270**	**kmol/hr**
196	**kmol/hr**	**290**	**kmol/hr**

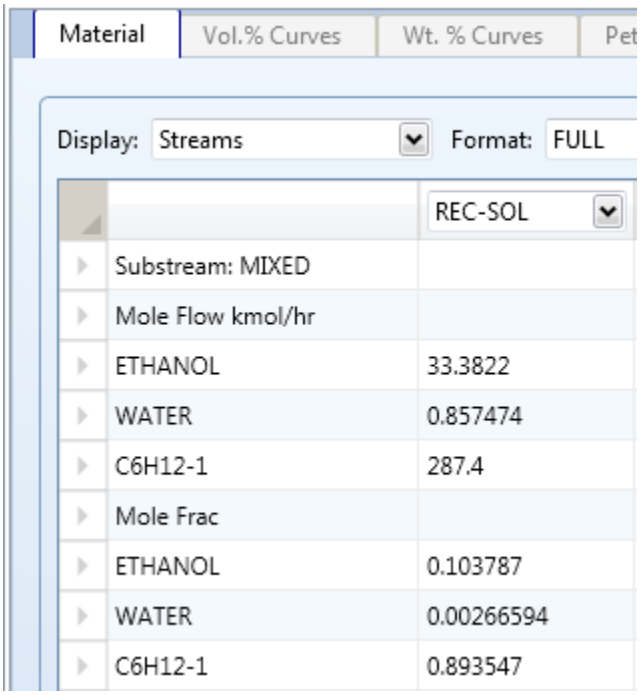
4.59. At this point, the dummy feed stream has composition and flow rate very similar to the top of the second column. Go to the **Results Summary | Streams | Materials** sheet. You should be able to see the following if you change the second stream to be **RECYC-FD**.



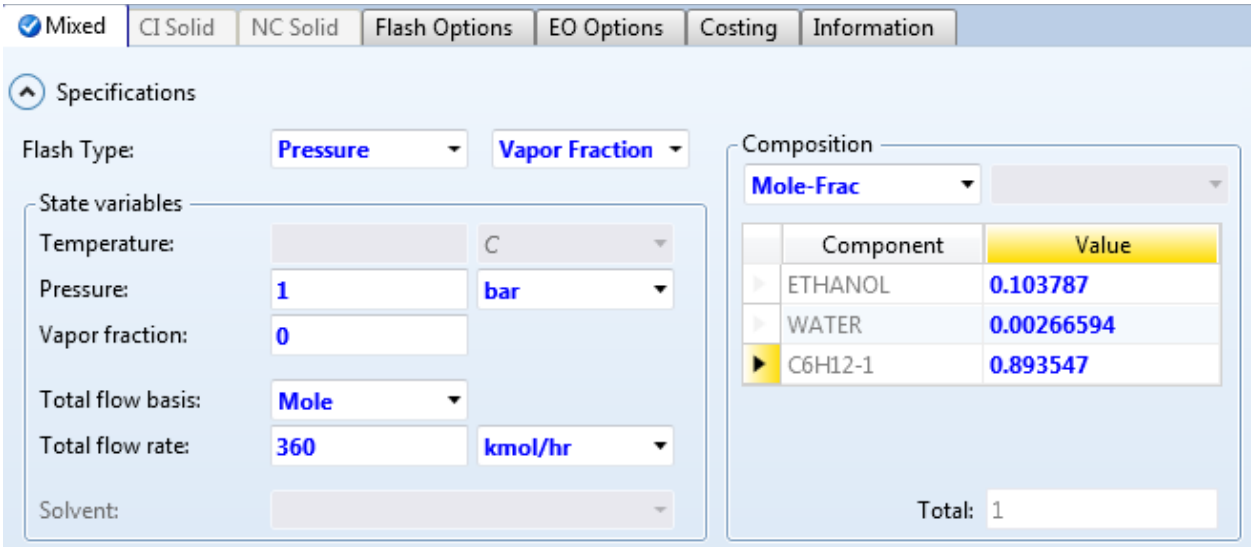
	DUM-FEED	RECYC-FD
Substream: MIXED		
Mole Flow kmol/hr		
ETHANOL	148.617	145.098
WATER	20.8502	20.249
C6H12-1	26.5326	29.1036
Mole Frac		
ETHANOL	0.758251	0.746195
WATER	0.106379	0.104134
C6H12-1	0.13537	0.149671

4.60. Re-generate all estimates for **COL-MAIN** and **COL-REC**. Re-initialize and re-run the simulation. The simulation should converge.

4.61. Go to the **Streams | REC-SOL | Results | Material** sheet. Copy the composition of the **REC-SOL** stream from the stream results.

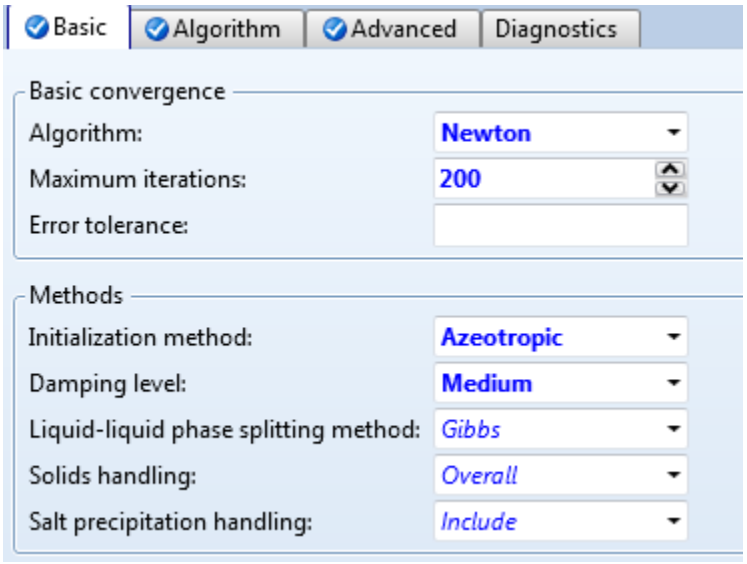


4.62. Paste the compositions into the **SOLVENT | Input | Mixed** sheet. Increase the **Total flow rate** to **360 kmol/hr**.



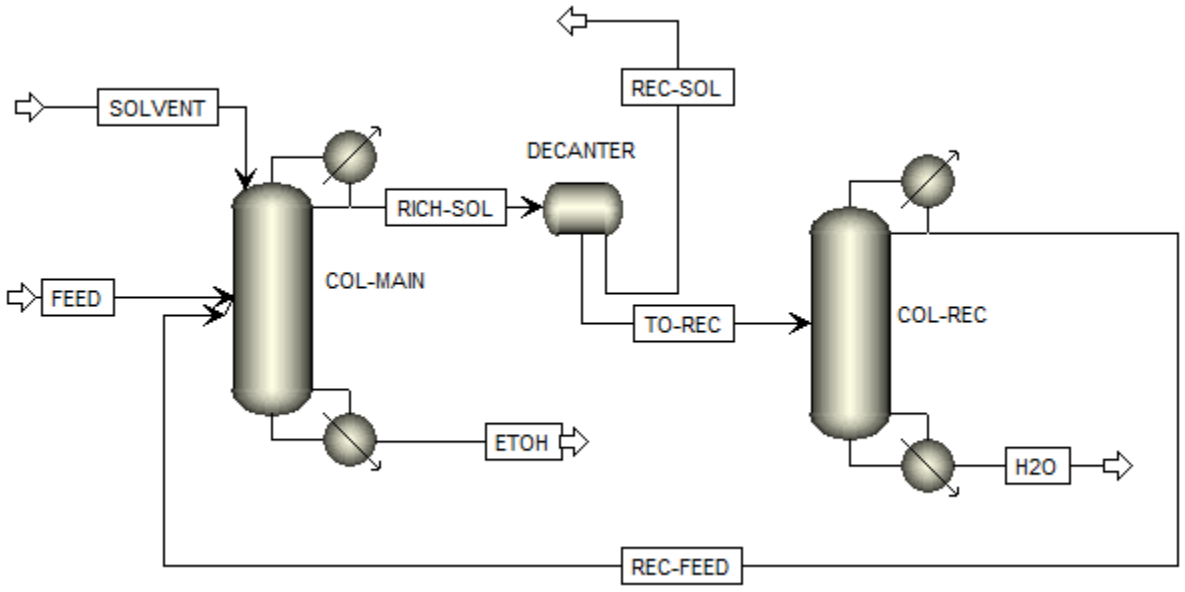
4.63. Run the simulation. There should be no errors. Re-generate all estimates again for both **COL-MAIN** and **COL-REC** according to instructions in step 4.31.

4.64. Go to the **Blocks | COL-MAIN | Convergence | Convergence** form. Change the **Initialization method** to **Azeotropic** and select **Medium** for **Damping level**.

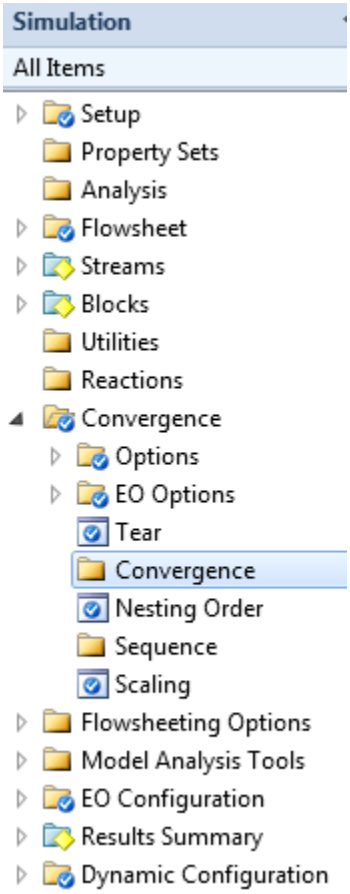


4.65. Make the same change for **COL-REC**. This increases the robustness of the convergence in these blocks.

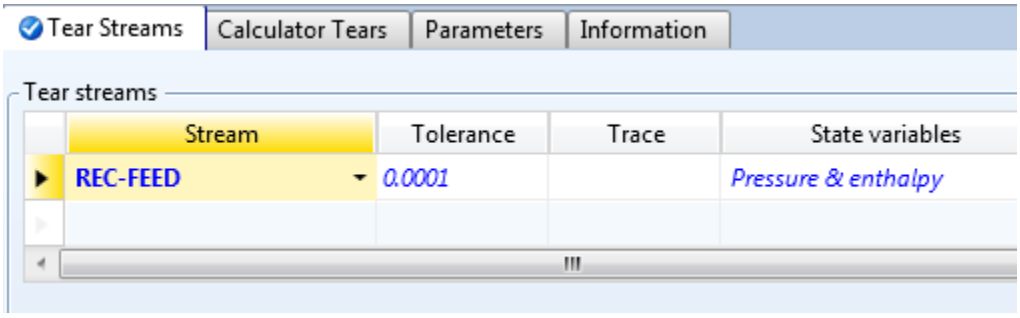
4.66. Select both **DUM-FEED** and **RECYC-FD**. Right-click one of them and select **Join Streams**. Rename the stream **REC-FEED**. The connectivity is shown below.



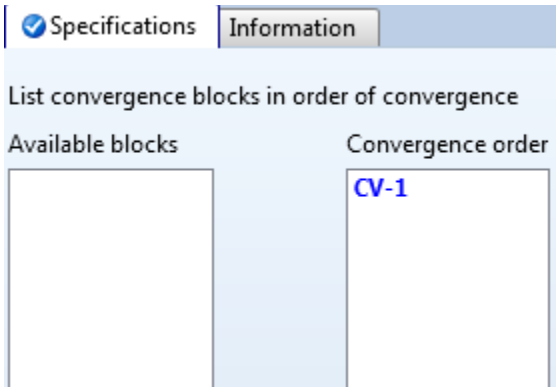
4.67. In the navigation pane, click **Convergence | Convergence**.



4.68. Click the **New** button. Let Aspen Plus name it **CV-1** and select **Wegstein** as the **Type**. Select **REC-FEED** as the **Stream**.

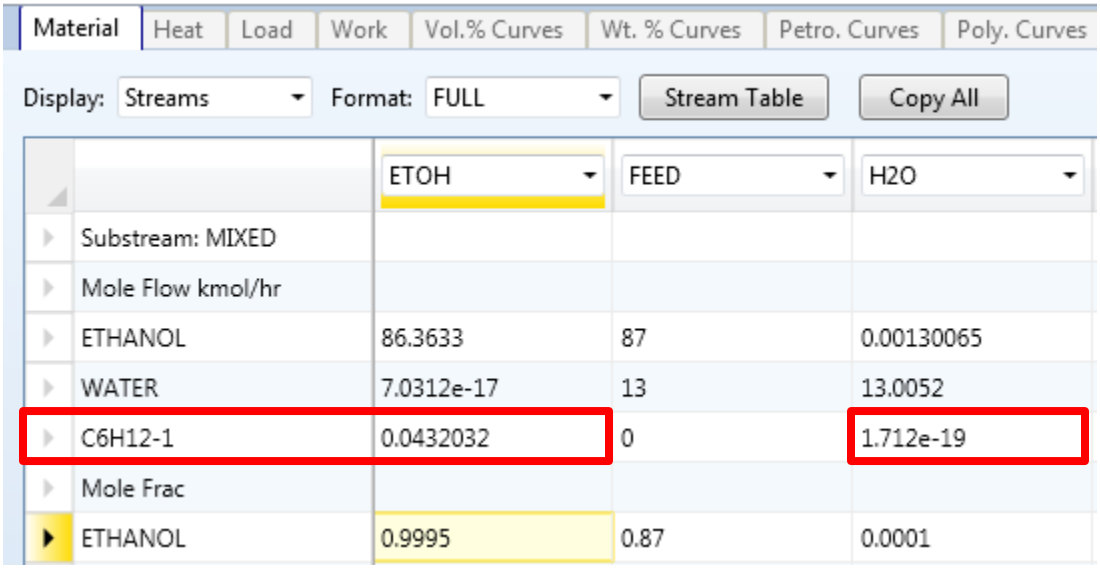


4.69. In the navigation pane, go to the **Convergence | Nesting Order | Specifications** sheet. Move **CV-1** to the **Convergence order** list as shown below.



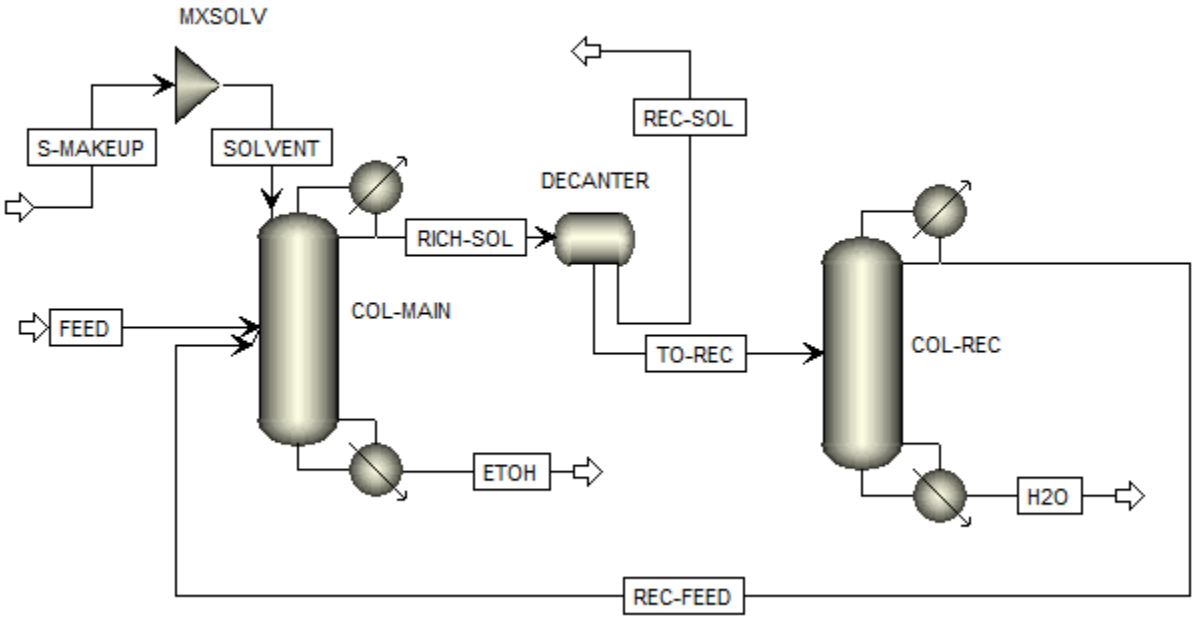
4.70. Run the simulation. There should be no errors.

4.71. Now, let us check solvent loss to **ETOH** and **H2O**. Go to the **Results Summary | Streams | Material** sheet. Select **ETOH** and **H2O**. We lose **0.0432032 kmol/hr** of **cyclohexane** to stream **ETOH**. Therefore, we need to create a solvent makeup stream.

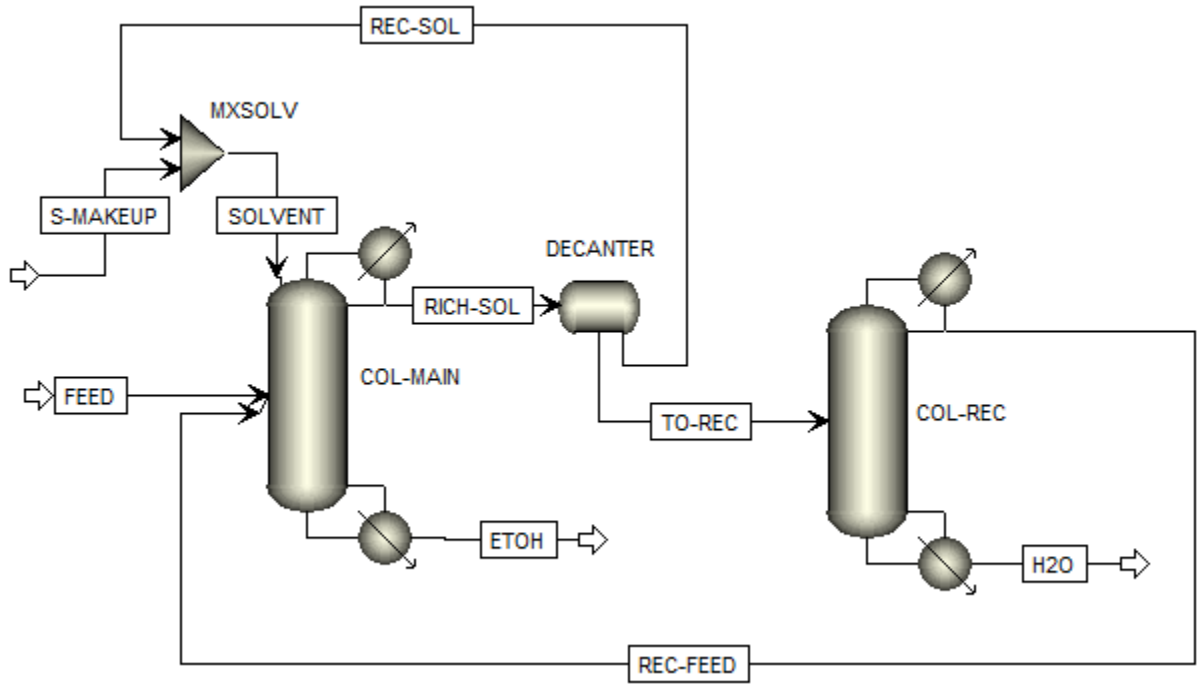


	ETOH	FEED	H2O
Substream: MIXED			
Mole Flow kmol/hr			
ETHANOL	86.3633	87	0.00130065
WATER	7.0312e-17	13	13.0052
C6H12-1	0.0432032	0	1.712e-19
Mole Frac			
ETHANOL	0.9995	0.87	0.0001

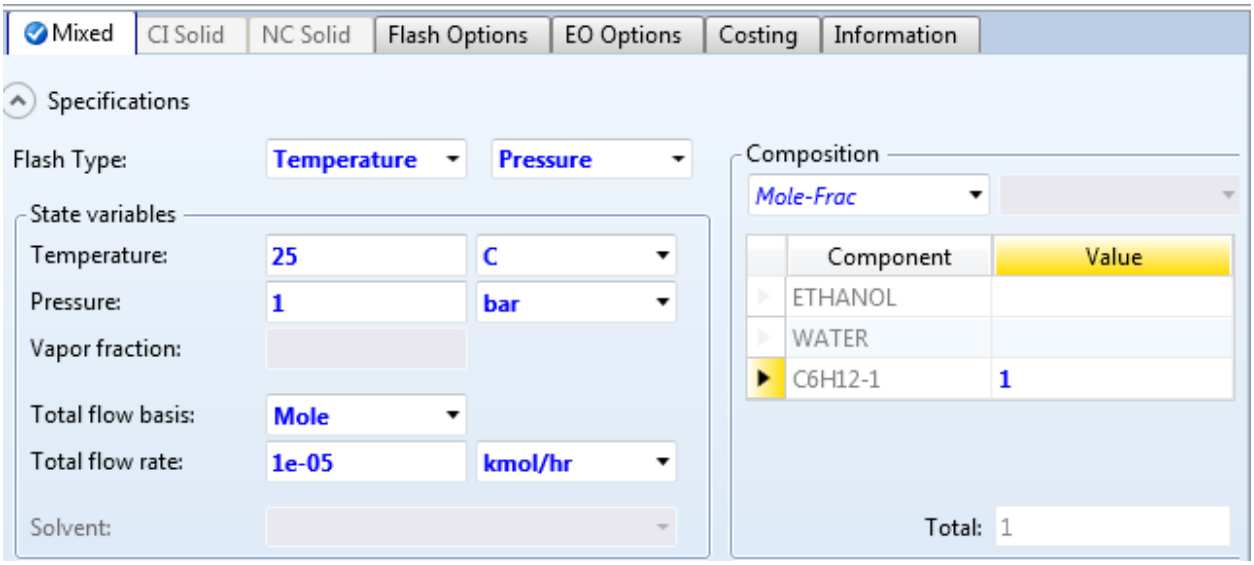
4.72. Add a **Mixer** block, **MXSOLV**, before stream **SOLVENT** and add a solvent make-up stream, **S-MAKEUP**. The flowsheet should look like the screenshot below.



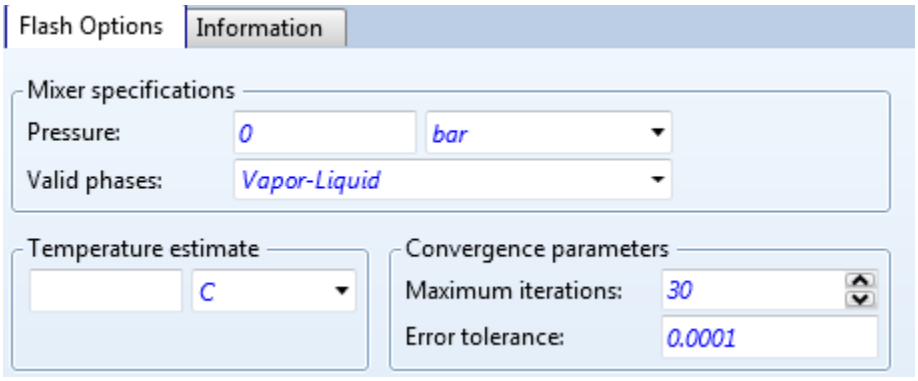
4.73. Close the second recycle loop. In the **Main Flowsheet** window, right click stream **REC-SOL** and select **Reconnect Destination** on the context menu. Move the mouse cursor over the inlet port icon of **MXSOLV** and click the inlet port icon. The flowsheet should look like the screenshot below.



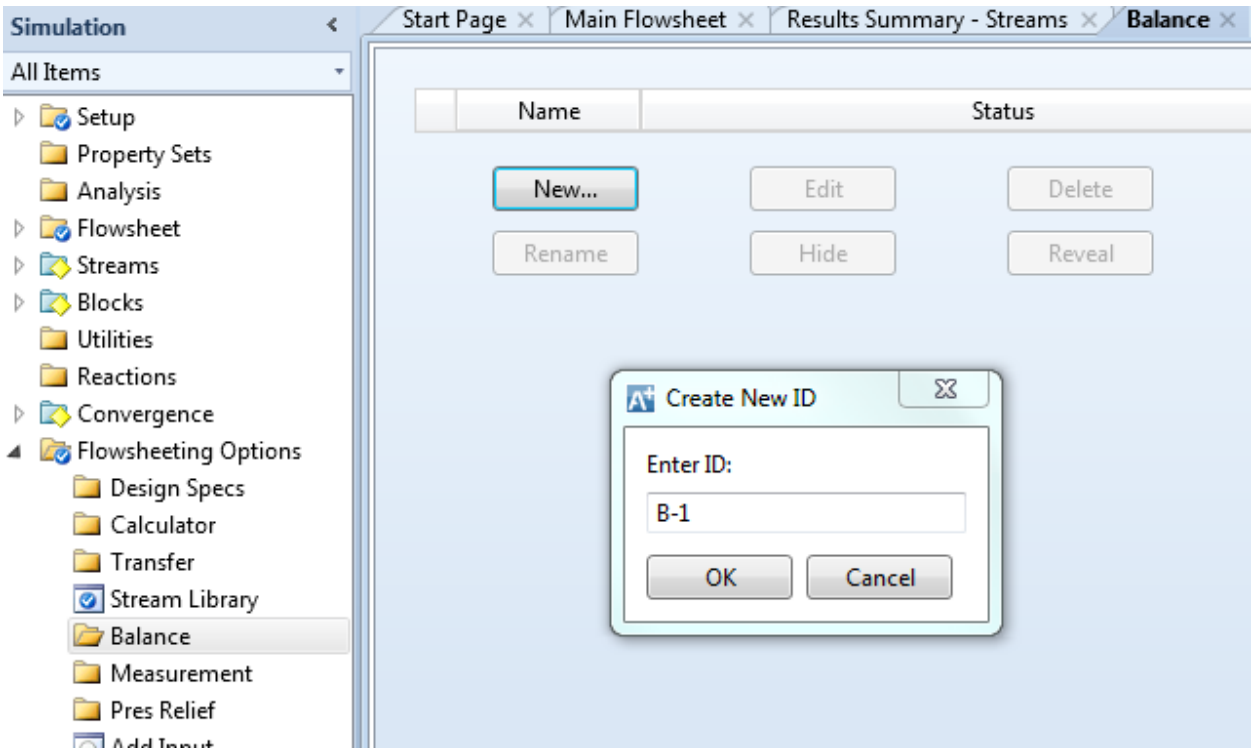
4.74. Go to the **Streams | S-MAKEUP | Input | Mixed** sheet. Enter **25** for **Temperature**, **1** for **Pressure** and **0.00001** for **Total flow rate**. In the **Composition** frame, select **Mole-Frac** and enter **1** for **C6H12-1**. For now, we just enter a tiny total flow rate for the solvent make-up stream as an estimate. Later on, we will use a **Balance** block to calculate its flowrate. Now the **Streams | S-MAKEUP | Input | Mixed** sheet should look like this.



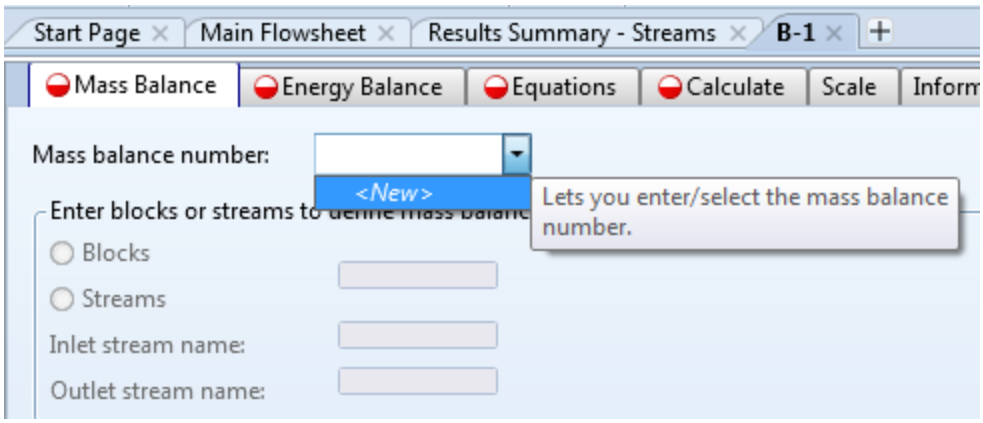
4.75. Go to the **Blocks | MXSOLV | Input | Flash Options** sheet. Note that the value for **Pressure** is **0**, indicating no pressure drop.



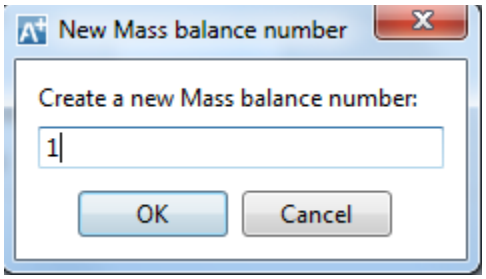
4.76. In the navigation pane, click the **Flowsheeting Options | Balance** node. The object manager for **Balance** is displayed. Click the **New...** button and click the **OK** button to create a **Balance** block called **B-1**.



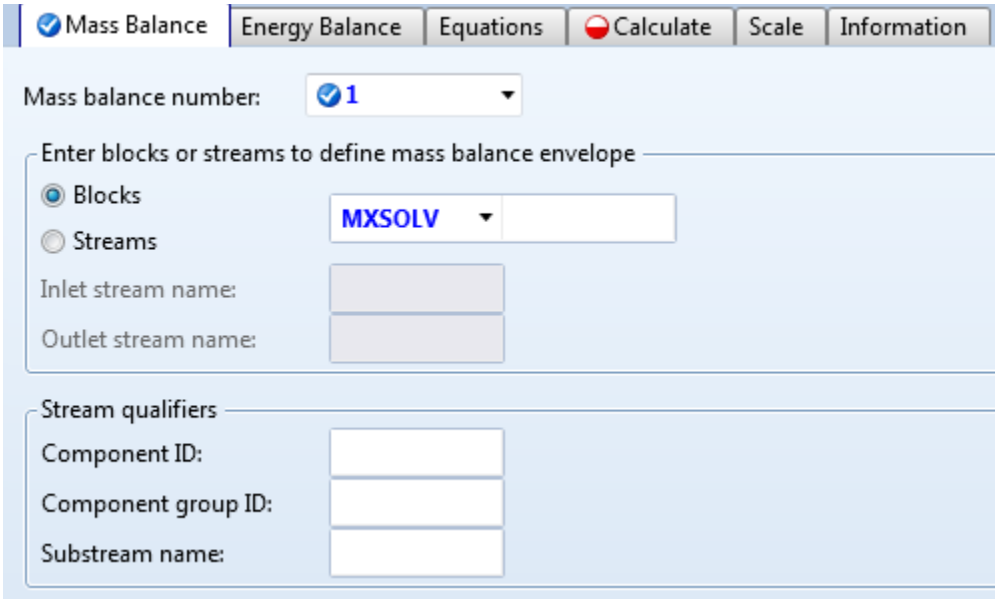
4.77. Go to the **Flowsheeting Options | Balance | B-1 | Setup | Mass Balance** sheet. Click the **Mass balance number** dropdown box and click **<New>**.



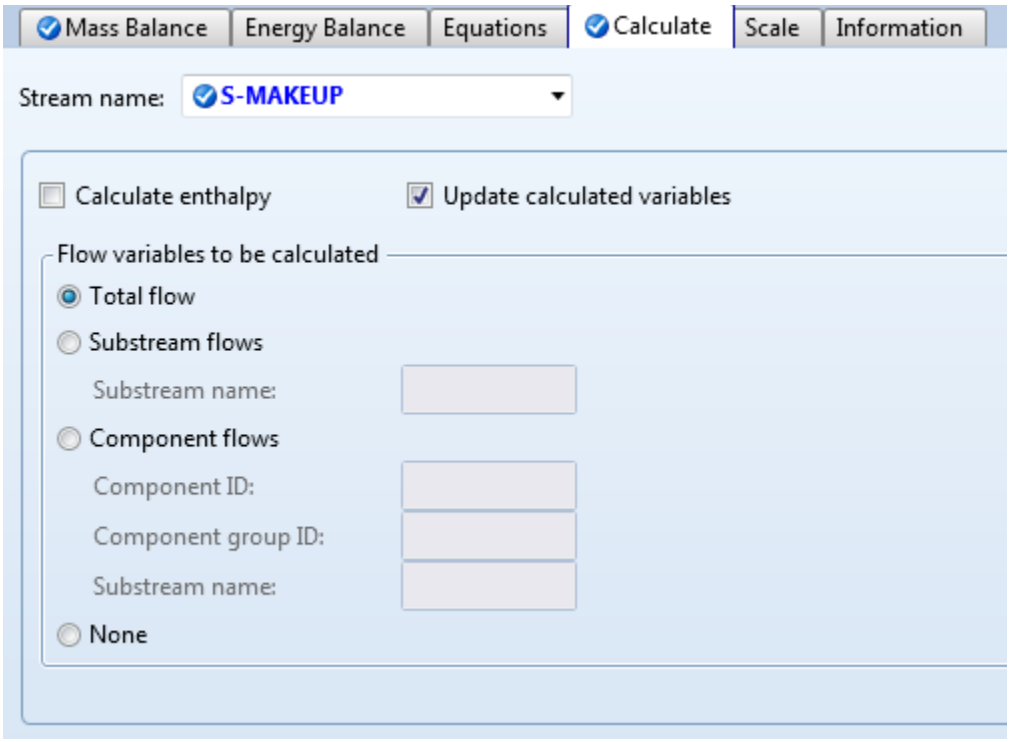
4.78. The **New Mass balance number** window pops up. Click the **OK** button.



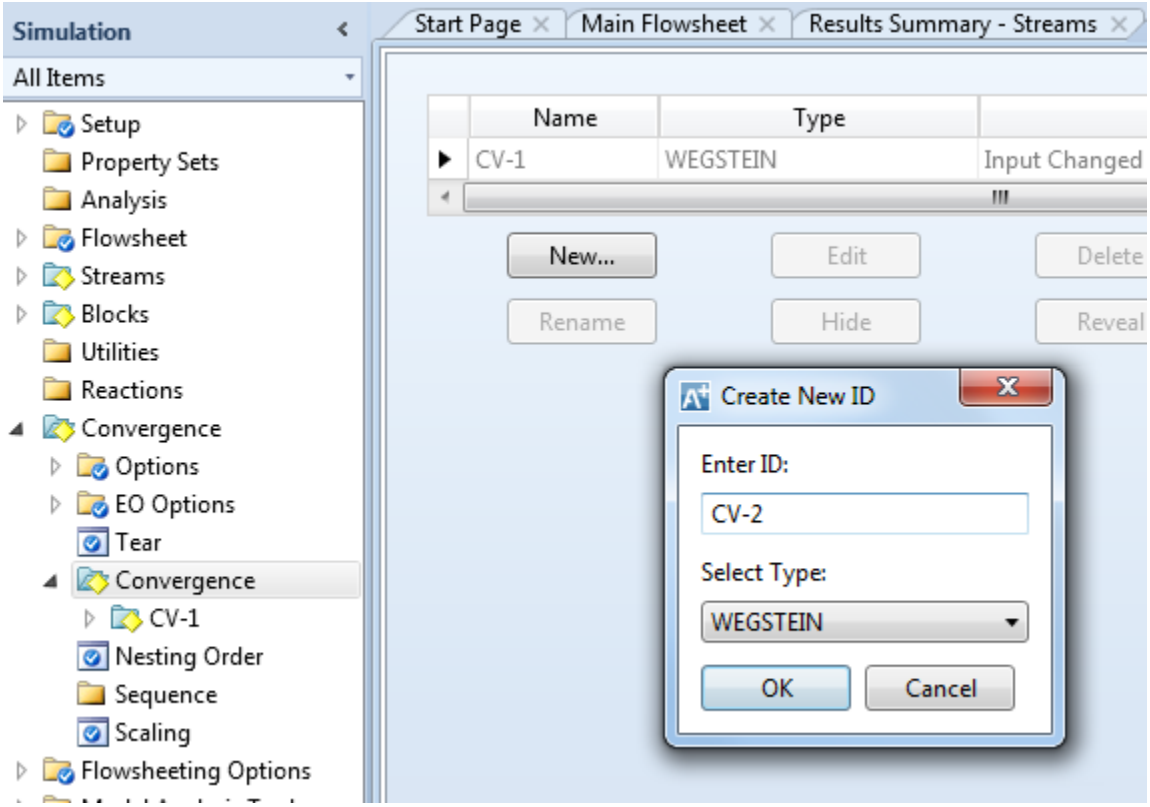
4.79. In the **Enter blocks or streams to define mass balance envelope** frame, select **MXSOLV** for **Blocks**.



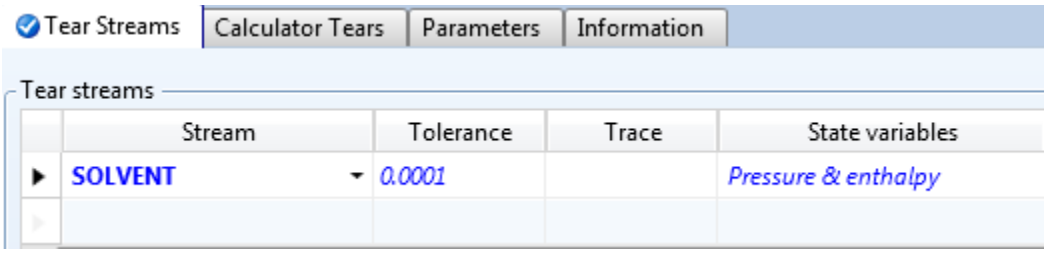
4.80. Go to the **Flowsheeting Options | Balance | B-1 | Setup | Calculate** sheet. Select **S-MAKEUP** for **Stream name**. This **B-1** balance block will calculate the flowrate of stream **S-MAKEUP**.



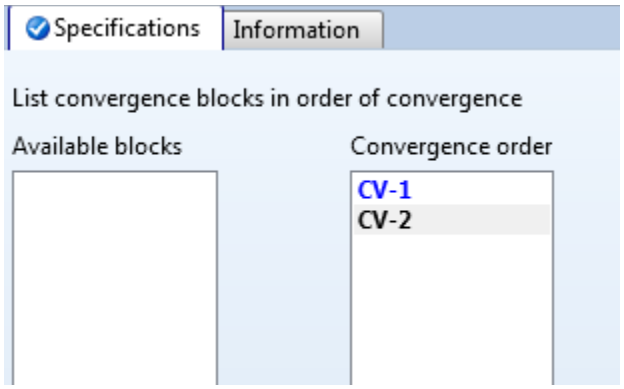
4.81. Create a convergence block for the second recycle stream. In the navigation pane, click **Convergence | Convergence**. The **Convergence** object manager is displayed. Click the **New...** button and the **Create New ID** window pops up. Select **WEGSTEIN** for **Select Type** and click the **OK** button.



4.82. On the **Convergence | Convergence | CV-2 | Input | Tear Streams** sheet, select **SOLVENT** in the first row in the **Stream** column as shown below.

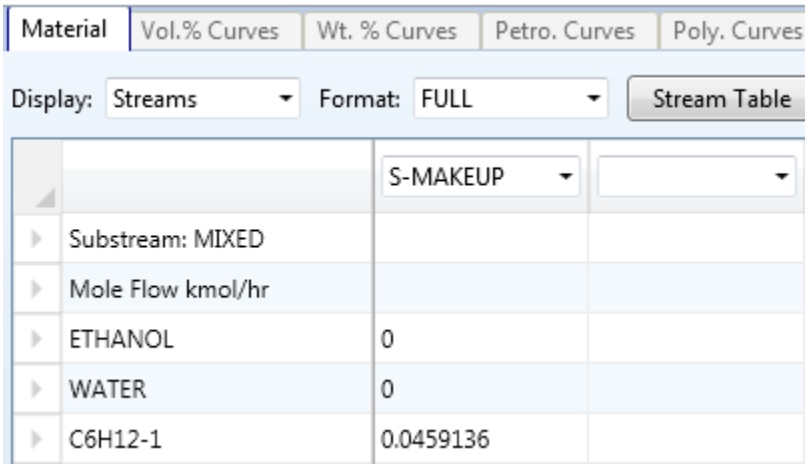


4.83. Go to the **Convergence | Nesting Order | Specifications** sheet. Move **CV-2** from the **Available blocks** list to the **Convergence order** list as shown below.

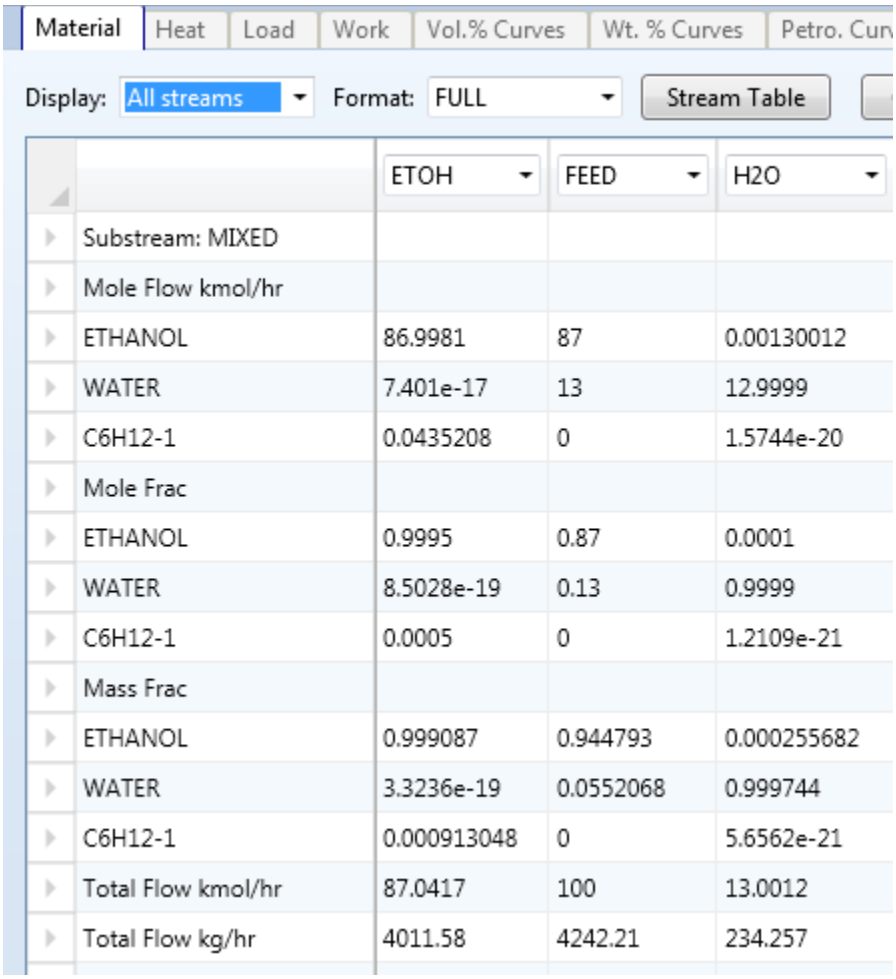


4.84. Click the button in the **Home | Run** group of the ribbon to reinitialize simulation. Then, press the **F5** key to run the simulation again. Note that the simulator reports an error when the **B-1** block is executed for the first time and there is no error or warning for subsequent executions of the **B-1** block. Therefore, this error can be safely ignored.

4.85. Go to the **Streams | S-MAKEUP | Results | Material** sheet. Note that the flowrate for **C6H12-1** is **0.459136 kmol/hr** instead of the originally entered 0.00001 kmol/hr.



4.86. Go to the **Results Summary | Streams | Material** sheet. We can find information related to the feed stream and two product streams there.



	ETOH	FEED	H2O
Substream: MIXED			
Mole Flow kmol/hr			
ETHANOL	86.9981	87	0.00130012
WATER	7.401e-17	13	12.9999
C6H12-1	0.0435208	0	1.5744e-20
Mole Frac			
ETHANOL	0.9995	0.87	0.0001
WATER	8.5028e-19	0.13	0.9999
C6H12-1	0.0005	0	1.2109e-21
Mass Frac			
ETHANOL	0.999087	0.944793	0.000255682
WATER	3.3236e-19	0.0552068	0.999744
C6H12-1	0.000913048	0	5.6562e-21
Total Flow kmol/hr	87.0417	100	13.0012
Total Flow kg/hr	4011.58	4242.21	234.257

5. Conclusions

In this example, cyclohexane is used as the entrainer to separate water and ethanol to produce anhydrous ethanol. By using the proper amount of solvent, we obtain pure ethanol from the bottom of the first column. The stream from the top of the first column is separated into two streams using a decanter: One stream contains mainly the solvent and is recycled back to the first column as solvent; the other stream is well within another distillation region so that we can use the second column to obtain pure water from the bottom of the second column. The top stream of the second column is recycled back to the first column as feed.

Please note that this process has two solutions and this example only presents one of them. Dist-016 provides details on how to obtain both solutions.

6. Copyright