1. Lesson Objectives

- Aspen Plus property analysis
- RadFrac distillation modeling
- Design Specs
- NQ Curves
- Tear streams
- Understand and overcome azeotrope
- Select pressures for pressure swing distillation
- Back-of-the-envelope sizing for technically feasible design

2. Prerequisites

- Aspen Plus V8.0
- Microsoft Excel
- Some experience building flowsheets in Aspen Plus
- Working knowledge of vapor-liquid equilibrium and distillation

3. Background

Basics on Azeotropic Distillation

An azeotrope occurs when the liquid and vapor mole fractions of each component are the same. On a y-x plot, an azeotrope is shown by a line which passes through the x = y line. This presents challenges to separation processes and needs to be accounted for in process design and operation.
No further enrichment can occur in either phase when the system reaches the azeotrope constraint because the driving force is eliminated. A mixture will separate towards a pure component and the azeotropic mixture. The component which is purified depends on which side of the crossover the initial mixture is. To purify the minority component, you must first cross the azeotrope. This can be done by adding an entrainer, another chemical which breaks the azeotrope. This creates the need for additional separation and usually material recycle with a purge stream. Alternatively, the composition of the azeotrope is dependent on pressure, which can be exploited to get the mixture across the azeotrope. This is called pressure swing distillation.

Ethanol and water form an azeotrope at approximately 95.5 mol-% ethanol at 1 atm. This is a low-boiling point (or positive) azeotrope. The boiling point of the mixture is lower than either of the pure components, so the azeotropic mixture exit from the top of the column regardless of which compound is being enriched in the bottoms.
Back-of-the-Envelope Column Sizing

This column sizing will be done by creating N* RR vs N curves, where the product of number of stages and the reflux ratio required for the specified separation is plotted against the number of stages in the system. There is a minimum number of stages for a given separation, the use of which would require infinite reflux. There is a minimum reflux ratio for a given separation, the implementations of which would require an infinite number of stages. Between these extrema, there is a roughly exponential decrease in reflux ratio (RR) with increasing number of stages (N). When the y-axis is N*RR instead of RR, the points will form a curve which has a distinct minimum.

Increasing the number of stages increases the capital cost of the column. Increasing the reflux ratio increases the operating costs of the column because more material is recycled to be heated in the reboiler and condensed again in the condenser. Consequently, there is a tradeoff: larger columns have a larger upfront cost but lower operating costs, while smaller columns have smaller capital costs but are more expensive to operate. It turns out that the economic optimum between these tradeoffs often occurs around the minimum of the N*RR vs. N curve. This basic heuristic essentially puts equal weight on the number of stages and reflux ratio.

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

A feed of 24,000 kg/h of 20mol-% ethanol and 80 mol-% water must be separated. The required product stream is 99 mol-% ethanol at a flowrate of at least 7,500 kg/h. This separation will be achieved by using pressure swing distillation.

We begin by creating a technically feasible design for a two-column separation train. We will report for each column: operating pressure, number of stages, reflux ratio, and the purity and recovery specifications. Also report a stream table with the flowrates and compositions of relevant streams. Material recycle will be necessary to achieve these results.
Component and Property Package Selection

4.01. Create a **New, Blank** simulation. Enter the components as shown below.

![Component Selection Table]

- **ETOH** (ETHANOL, C2H5O-2)
- **WATER** (WATER, H2O)

4.02. Select the **Methods** button.

Under the **Method filter**, choose **CHEMICAL**. Then select the **Base method** of **NRTL-RK**. The non-random, two liquid (NRTL) model works well for very non ideal liquid systems which is important because of the hydrogen bonding present. The Redlich-Kwong equation model works much better at high pressures than the ideal gas assumption.
To populate the binary interaction parameters, open the following from the navigation pane on the left: Methods | Parameters | Binary Interaction | NRTL. Clicking on NRTL-1 populates the fields; you do not need to enter any other numbers.

Investigate Pressures

In the Analysis section of the Home ribbon, select Binary.

On the Binary Analysis window that opens, you should be able to leave most of the selections. Make sure Component 1 is ethanol and take into account that the lighter component should be entered in the component list first. In the pressure section, use the List of values option to generate data at 0.1, 1, 10, and 100 bar.
Click the **Run analysis** button. This creates a T-xy plot. Close that tab, and select y-x from the **Plot** section now available on the **Home** ribbon.

The resulting plots should look like the one below. If you go to the **Format** tab, under **Grid**, check the **Square plot** and **Diagonal line** boxes.
4.05. Return to the Analysis | BINRY-1 | Input sheet. Change the 100 bar specification to 20 bar and isolate the composition range of 50 to 100% ethanol.
Click Run Analysis, and open the y-x plot again.
From this graph, you can see that the mole fraction of ethanol at the azeotrope decreases with increasing pressure. The first column will operate at low pressure to get a high concentration of ethanol in the azeotrope. The second column will operate at high pressure so the azeotropic mixture can carry off the water and the ethanol will be purified.

![Y-x diagram for ETOH/WATER](image)

4.06. The pressures of 0.1 bar and 20 bar are chosen for the first and second column respectively. The azeotropes are at approximately 95mol-% ethanol and 77mol-% ethanol respectively. These pressures
can be chosen somewhat arbitrarily after seeing that they are feasible. The optimization of column pressures is outside the scope of this exercise.

Initial Mass Balance

Getting all the way to the azeotrope would take an infinite number of stages because of the pinch between the equilibrium line and the \( x = y \) line (which is proportional to the driving force). For that reason, specifications slightly closer to the feed composition will be required in each column. For the first column an ethanol composition of 90\% in the top of the column will be selected. The second column will have 80mol-% ethanol in the vapor stream, and 99mol-% ethanol in the bottoms. The azeotropic mixture (vapor stream) from the second column will be recycled to the first column.

(FAQ) Useful Option To Know: Improve convergence by doing preliminary mass balances

Do mass balances first. They do not have to be extremely accurate, but if you can give Aspen Plus a better initial guess, it will solve the simulation faster

4.07. This leaves one degree of freedom left in the system before the mass balance can be solved. Select a recovery value for ethanol which fulfills the product flowrate requirement of at least 7,500 kg/h. After solving for flowrates and compositions of each of the streams, you can estimate the recycle stream.

Low Pressure Column Design

Initial Guesses

4.08. Go to the simulation environment in Aspen Plus. Create a feed stream and a stream which is an initial estimate for the recycle stream. Mix these streams and put the resulting stream into a RadFrac column block. The RadFrac block is in the columns section of the model palette; it is a rigorous distillation model which can model multi-phase, very non-ideal liquids, and rate-controlled mixing in addition to modeling azeotropic mixtures. The flowsheet should look like the picture below.
4.09. Enter the conditions for the feed stream and the recycle stream estimates.
4.10. Enter the specifications of the **Mixer**.

As can be seen from the first set of y-x graphs, the split is fairly wide on the water-rich side of the azeotrope. This means a relatively easy separation so this should be achievable in ~30 stages with a reasonable reflux ratio. This kind of rough, initial estimation can be done more precisely with McCabe-Thiele diagrams.

4.11. As can be seen from the first set of y-x graphs, the split is fairly wide on the water-rich side of the azeotrope. This means a relatively easy separation so this should be achievable in ~30 stages with a reasonable reflux ratio. This kind of rough, initial estimation can be done more precisely with McCabe-Thiele diagrams.
4.12. Enter the specifications of the distillation column. Go to Blocks | COL1 in the navigation pane. The Condenser should be Partial-Vapor so the condenser acts as another equilibrium stage. Initial estimates for the Operating specifications need not be extremely accurate, as these will be set with design specifications later.

The feed is approximately 80% water, which is close to the bottoms composition, so it should be entered close to the bottom of the column (the numbering starts with the condenser as the first stage).

The operating pressure is 0.1 bar. Each stage will have some pressure drop because vapor will have to bubble through a couple inches of water-ethanol mixture at each stage.
Run the simulation. There should be no errors at this point.

4.13. Create a custom stream table. Go to Results Summary | Streams (Custom). Right-click on Default, in the top of the page and select Add New.

Right-click on the new sheet tab that you made and select Edit View.
Select the streams you want to view and the order in which you want to view them.

Click the **Property Selection** tab and select which properties you want to see and the order you want them to be reported in.
The table you have specified will be shown. This table can be saved from the Edit View window. It can be edited later to add or remove streams.

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<th>REC</th>
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<td>MIX1</td>
<td>COL1</td>
<td>COL1</td>
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</tbody>
</table>

Looking at the composition of D1, we have already met the purity spec set for the first column. However, we are throwing away a third of the ethanol in the bottoms.
Implementing the Design Specifications

4.14. To reduce the amount of wasted ethanol, you will set two design specs. Because the system is fully specified, each specification will require a parameter to vary so the system is not over-specified.

Double-click the column. Click on the Design Specs folder in the navigation pane under the column in the Blocks folder. Click on New. Select Mole Purity as the Type. Enter the specification of 0.9 in the Target field.

In the Components tab, select ethanol as the Component for the design spec to target.
In the Feed/Products tab, select the distillate (D1) as the target stream.

4.15. Go back the Design Spec folder and click New to create a second design specification. Select Mole recovery as the Type and enter 0.9 as the Target.

In the Components tab, select ethanol as the Selected component.
Select the distillate (D1) as the target stream. This design spec forces 90% of the moles of ethanol that enter the column to leave out the distillate stream.

4.16. Now you must include the variables which are changed to meet the design specs. Click on the Vary folder which is just below the Design Specs folder in the navigation pane. Select Reflux ratio as the Type. Enter reasonable bounds. Note that the first vary parameter will be associated with the first design specification.
Click on the Vary folder again, click on New. Select Distillate to feed ratio as the Type and enter reasonable bounds.

If the manipulated variable needs to be outside the bounds you enter to meet the design spec, you will get an error. Clicking on the Status tab of the Results page for the column will show you the reason for an error. If the reason is One or more manipulated variable lies outside user-specified bounds, click on the Results tab of your Vary pages to see which one is at the bound and change the bounds accordingly. Tighter bounds will improve convergence. Note that these varied parameters must be the same parameters you specified in the Setup sheet to avoid over specification.

Run the simulation. You should get an error saying that the Radfrac block did not converge in 25 outside loop iterations. On the control panel, you can see the error for each outside loop iteration. In this case the error is getting smaller with each iteration, which shows that this simulation might converge given more iterations. To increase the number of iterations, go to Blocks | COL1 | Convergence | Convergence. On the tab titled Basic, change the Maximum iterations to 200 and change the Damping level to Mild. The damping factor is used to stabilize convergence when oscillations are observed in the convergence behavior. Reinitialize (Shift + F5) and run the simulation. You should see on the control panel that the simulation converged in 32 iterations.

(FAQ) Useful Option To Know: Saving Checkpoints

Save ‘checkpoints’ as you go. Once you have a working section of the flowsheet, save as a new file name, so you can revert to an earlier checkpoint and a known state.
High Pressure Column Design

4.17. The second column is at a higher pressure. Before adding the column, add a **Compressor** so the system is properly pressure driven.

Double click on the compressor and select **Isentropic** as the **Type**. Enter a **Discharge pressure** of **22 bar**. Efficiencies are of no importance in this exercise because the utilities are only indirectly considered. Isentropic underestimates the temperature increase from the compression, but this precision in the energy balance is also outside the scope of this exercise.
4.18. Insert a Radfrac column after the compressor. The flowsheet should look like the following.

![Flowsheet Diagram]

Initial Guesses

4.19. The equilibrium line stays close to the $x = y$ line on the $y$-$x$ plot on the ethanol-rich side of the azeotrope. This means it is a harder separation, so it will require more stages. Double click **COL2** to specify the operating parameters. Enter 75 for **Number of stages**, select **Partial-Vapor** for **Condenser**. Enter a reasonable guess for **Distillate to feed ratio** and **Reflux ratio**.
The feed concentration for the second column is somewhere in the middle of the two specified outlet concentrations for ethanol, but the ethanol product stream is closer to the pinch-point so there will need to be more stages between the feed and the bottoms than between the feed and distillate.

Enter 20 bar as the Condenser pressure and a 2 in-water pressure drop per stage.
Run the simulation. There should be no errors.

Implementing the Design Specifications

4.20. The design specs on the second column will be similarly implemented. The two specs are 99 mol-% ethanol in the bottoms, and 80 mol-% ethanol in the distillate. The two manipulated variables are Distillate to feed ratio and Reflux ratio again. The steps are screen-captured below.

Design spec 1:
Target component is ethanol.

![Diagram showing components selection]

Target stream is B2.

4.21. Design spec 2:

![Diagram showing product streams selection]

**Description:** Mole purity of ethanol in distillate

**Type:** Mole purity

**Target:** 0.8

**Stream type:** Product
Target component is ethanol.

Target stream is the distillate.

Specify the varied parameters.
This is a harder separation, so the **Reflux ratio** may need to be higher.

Run the simulation. There should be no errors.

**Open-Loop Manual Convergence**

4.22. Check results. Go to **Results Summary | Streams (Custom)**. Modify the custom stream table to show all streams.
Open-Loop Manual Convergence

4.23. Before sizing the columns, the flows must be as close to the final values as possible. Refine the estimate of the recycle stream by guessing and checking the molar flow values until REC and D2 match for a few significant digits. This process is made easier by the fact that there is a design spec which holds the composition of D2 constant. After several iterations of setting the component flow of the REC stream equal to the component flow of the D2 stream, the recycle stream had the following component mole flows. This will make convergence easier when we connect the recycle stream.

![Flash Type and State variables](image)

Column Sizing

The current flowsheet now fulfills the problem specifications. However, its feasibility is unproven. The next step in a technically feasible design is back-of-the-envelope sizing. This ensures that the equipment not only meets the flowrate and compositional (and perhaps temperature, pressure, conversion, etc.) specifications, but also that it could be constructed and implemented.

You will use the NQ Curves feature in Aspen Plus to generate N*RR vs. N curves and from these, choose the number of stages for each column. Create a Microsoft Excel document so you can copy and paste the results from the NQ Curves routine in Aspen Plus and get a graph of N*RR vs. N. To determine if a point is a minimum, you must have several points on both sides. The resulting graph should resemble the one below. A reasonable selection for technically feasible number of stages is circled. A point slightly to the right of the minimum is selected because the RadFrac model assumes complete equilibrium in each stage. In essence, the hand-waiving argument is that a real column will need slightly more stages to achieve the separation modeled in the RadFrac block in equilibrium mode because a real column cannot achieve the same efficiency as the model.
COL1 Column Sizing

4.24. Go to Blocks | COL1 | Analysis | NQ Curves. Select New to create a new NQ Curve analysis.

4.25. In the NQ Curves Specifications tab, enter a Lower limit of 19, an Upper limit of 35, and select FEED2 as the Feed stream. Note that Upper Limit can only be as high as the number of stages currently entered in the Setup page for the column. In order to enter an upper limit of 35 you must first increase the number of stages to 35 in the column setup page.

4.26. Run the simulation and check the results of the NQ Curves analysis. Go to Blocks | COL1 | Analysis | NQ Curves | 1 | Results | Basic Results. If you then copy the basic results table to excel and plot N*RR vs N, you will get the following:
The number of stages for the first column was selected to be 28 which had an optimum feed stage of 27. Change the column configuration in your open loop flowsheet to match these, and delete the NQ curves analysis.

**COL2 Column Sizing**

4.27. The same procedure will be used for the second column. Make an MS Excel file which will graph N*RR vs. N. Change the Lower and Upper limits in the NQ Curves tool so that there is a distinct minimum in the N*RR vs. N graph.

4.28. The NQ Curves specifications used are shown right below. The resulting NQ vs. N graph is also shown. Note that when you run the NQ Curves analysis you may get errors stating that the design spec could not be reached because the manipulated variable is at its bound. Simply increase the upper limit for the reflux ratio in the design spec and run the simulation again.
The number of stages for the second column was selected to be 49 which had an optimum feed stage of 22. Change the column configuration in your open loop flowsheet to match these, and delete the NQ Curves analysis.
4.29. The last thing to do is close the recycle loop. Run the simulation after updating the number of stages and feed stages for both columns. Troubleshoot any errors before closing the recycle loop. Double check that the distillate of the second column and the estimated recycle stream are the same for a few significant digits.

Select both the distillate of the second column and the estimated recycle stream by holding shift and clicking on them. Right-click either of the streams and select Join Streams. Click OK.

4.30. Reinitialize and run the simulation. There should be no warnings or errors. This flowsheet is now complete.
5. Conclusions
The azeotrope in the ethanol-water system presents a barrier to separation, but pressure swing distillation can be used to purify ethanol. A technically feasible design for purifying ethanol to 99 mol-% with pressure swing distillation can be constructed using Aspen Plus, and a first pass at size optimization can be done using NQ Curves. A column with 29 equilibrium stages and operating at 0.1 bar with a reflux ratio of 3.55 increases the ethanol composition to 90 mol-%. A second column with 59 equilibrium stages and operating at 2 bar with a reflux ratio of 11.5 increases the purity to 99 mol-%.

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<th>D1</th>
<th>FEED2</th>
<th>REC</th>
<th>FEED</th>
<th>B2</th>
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<td>COMP</td>
<td>COL</td>
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