

GAS TREATMENT

The pretreatment process consists of four main stages. First, CO₂ and H₂S removal stage which is constructed to assure that CO₂ would not exceed 50 ppm in the natural gas feed. If the composition of CO₂ exceeded that limit it would freeze in the liquefaction process pipelines. This stage is directed more to CO₂ removal since the Bolivian natural gas contains no sulfur in it. There are two available methods to remove CO₂ from the natural gas. The first method is using sulfinol, which used to be one of the famous methods for gas CO₂ removal in most industrial applications but it started to vanish and few pretreatment plants use sulfinol any more. The reason is that sulfinol does not work well with rich natural gas (rich with heavy hydrocarbons) because it tends to attract or attach to heavy hydrocarbons and then it drags the heavies to the sulfinol pump or circulation which leads to allowing the heavy hydrocarbons to vent into the air. That usually leads to a decrease in the quality and heat content of the natural gas in the feed and according to the new EPA (Environmental Protection Agency) rules heavy hydrocarbons can not be vented to the atmosphere because it would lead to an increase in the air pollution level in the surroundings significantly. So EPA regulations will be followed in Bolivia to serve ethics purposes. Another method to remove CO₂ is using DEA (Diethyl Amine) but since DEA alone can not remove CO₂ to a ppm (particle per million) level, it is activated by injecting a chemical called Piperzine which activates the DEA to MDEA (Methyl Diethyl Amine). MDEA is also used for this pretreatment stage versus sulfinol because MDEA is cheaper to install and it has less utility since it requires less rate of solvent circulation compared to sulfinol. Therefore, this pretreatment stage is named the amine wash section.

The second stage is dehydration. Water is removed from the natural gas also to avoid freezing in the pipeline of the liquefaction process. The natural gas feed should be completely dry, even from the smallest traces of water molecules (<0.01Microgram/m³), before entering the heavy duty cooling section of the liquefaction process. TEG (Triethylene Glycol) is the primary solvent used in gas processing industry to dehydrate gases. Dry TEG contacts the moist natural gas and absorbs the water from it in a contactor tower. The tower contains a structured packing bed to maximize the mixing between the gas and TEG and to increase the contact time between the two substances. The TEG and water mixture is then sent to a TEG recycling system where TEG is separated from water by filtering then heating. The recycled TEG is then sent back to the contactor tower. Although TEG removes H₂O significantly from the natural gas, small amount of water traces still escape this process; so to insure that these traces do not accompany the natural gas feed, molecular sieves are used to serve this purpose. In average, two sieves are needed for every train. Despite all of this, in some processes H₂O in a molecular level still escapes with the natural gas in the feed. A third safety step is taken in the liquefaction process where molecules of water, which accompany the natural gas in the feed, are condensed and flashed in the stage of natural gas pre-cooling. This step will be explained in detail in the liquefaction section of this report.

The third stage is the Hg removal. Although the Bolivian natural gas has no Hg in it, this step is still taken as a precaution since the natural gas feed might contain molecular amount of Hg which is enough to cause corrosion in the expensive Aluminum LNG heat exchangers used in the liquefaction process. 10 ng/m³ (nano gram per m³) is enough to cause such a catastrophe. The process of Hg removal is also inexpensive since the activated bed filter that is used in the Hg filtration is inexpensive and it is replaced on an average of once every four years. So having

this stage in the pretreatment of the Bolivian natural gas eliminates the risk of having Hg traces in the natural gas feed that might ruin the expensive heat exchangers.

The fourth and last step is the installation of a Duster in the Pretreatment process outlet to insure that the natural gas feed is free from small solid particles which might cause a clog in the pipes of the liquefaction process or damage the heat exchangers. The figure below shows the overall process flow.

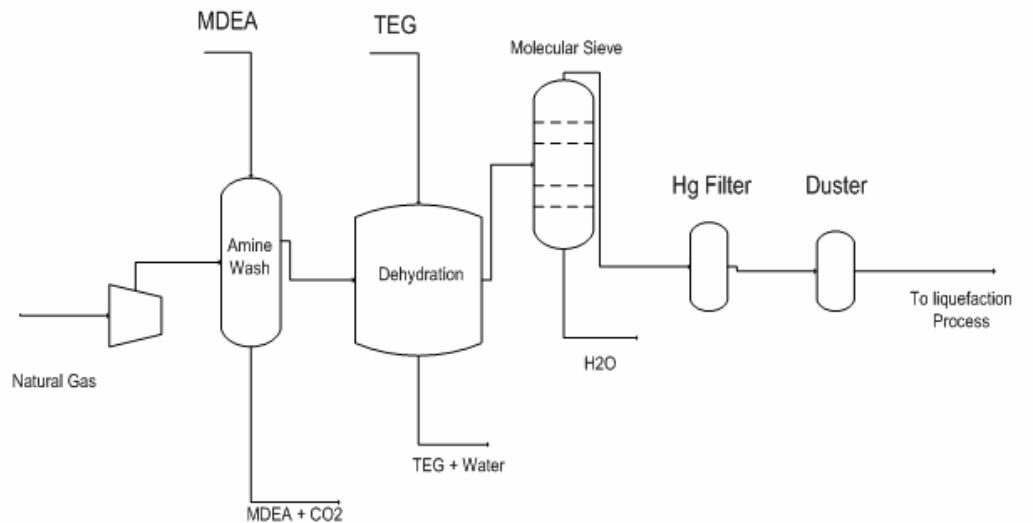


Figure 4-1: *Pretreatment schematic*

Gas Dehydration

The purpose here is to remove water. We first start determining what is the maximum content of water in a gas. Consider the following exercise

Exercise 4-1:

Consider a gas with the following composition:

| | |
|-----------------------|------------|
| 1 - CO ₂ | 0.0136 |
| 2 - HYSULFID | 0.0170 |
| 3 - METHANE | 0.8801 |
| 4 - ETHANE | 0.0640 |
| 5 - PROPANE | 0.0171 |
| 6 - IBUTANE | 1.8074E-03 |
| 7 - BUTANE | 2.3965E-03 |
| 8 - IPENTANE | 6.8899E-04 |
| 9 - PENTANE | 7.0896E-04 |
| 10 - HEXANE | 5.3921E-04 |
| 11 - HEPTANE | 6.0911E-04 |
| 12 - H ₂ O | 1.4512E-03 |

Set up a stream in Pro II and determine the dew point.

The screenshot shows the Pro II software interface. The main window is titled "PRO/II with PROVISION - Dew point Temperature Calculation - [Flowsheet]". A "Stream Data" dialog box is open, showing the following settings:

- Stream: 1
- To Unit: (Product Stream)
- Stream Type: Composition Defined
- Thermal Condition: First Specification: Pressure (720.00 psig), Second Specification: Dew Point
- Thermodynamic System: Determined From Connectivity

A "Programmer's File Editor" window is also open, displaying the following data for "STREAM '1'":

| | TOTAL | VAPOR |
|----------------------------|-----------|-----------|
| RATE, KG-MOL/HR | 5.4189 | 5.4189 |
| TEMPERATURE, C | -4.25 | -4.25 |
| PRESSURE, PSIG | 720.00 | 720.00 |
| MOLECULAR WEIGHT | 18.4541 | 18.4541 |
| FRACTION | 1.0000 | 1.0000 |
| ENTHALPY, KJ/KG-MOL | 2886.8850 | 2886.8850 |
| CP, KJ/KG-C | 2.6510 | 2.6510 |
| MOLAR FLOWRATES, KG-MOL/HR | | |
| 1 - CO ₂ | 0.0737 | 0.0737 |
| 2 - HYSULFID | 0.0921 | 0.0921 |
| 3 - METHANE | 4.7740 | 4.7740 |
| 4 - ETHANE | 0.3473 | 0.3473 |

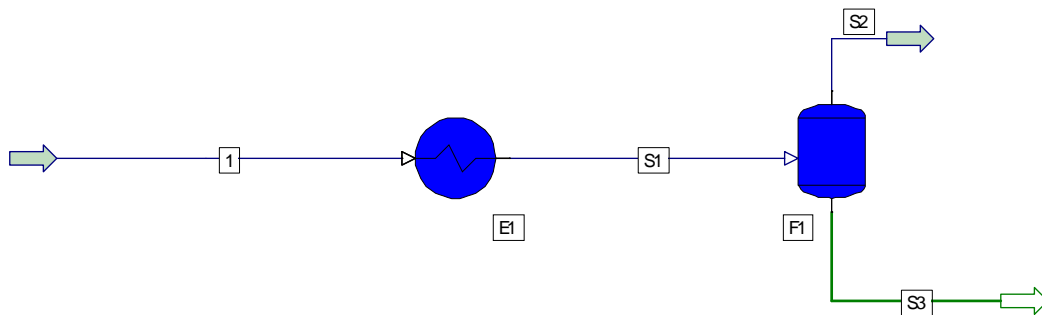
In addition, find the dew pressure.

Conversely, give a certain temperature; determine how much water will condense.

One method to remove water is to simply reduce the temperature and later use a flash drum to separate the water.

Exercise 4-2:

Take the gas of exercise 4-1, pass it through a cooler and later through a flash to separate water.



Determine the composition of the liquid obtained.

Tri/Tetra-Ethylene Glycol (TEG) Systems: These units are designed to put a liquid that has the ability to dissolve water in contact with gas. These units are called absorbers and they are depicted in the next figure: The column has gas entering from below and passing through trays that contain the liquid absorbent. These trays are either “sieve trays” (Just a tray with holes in it) or more complex valve or bubble cup arrangements. The picture below has bubble cups. The liquid, in turn, flows down from one tray to the next in downcomers. Water free TEG is put in contact with gas that has already been dehydrated. Thus, the TEG keeps increasing water concentration as it moves downwards. Similarly, the gas is reducing its water content as it flows upwards, transmitting it to the TEG.

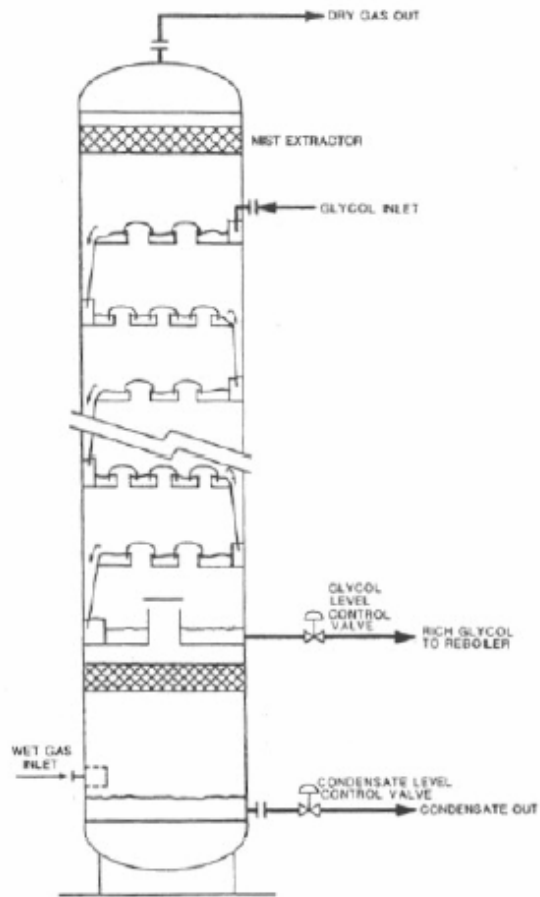
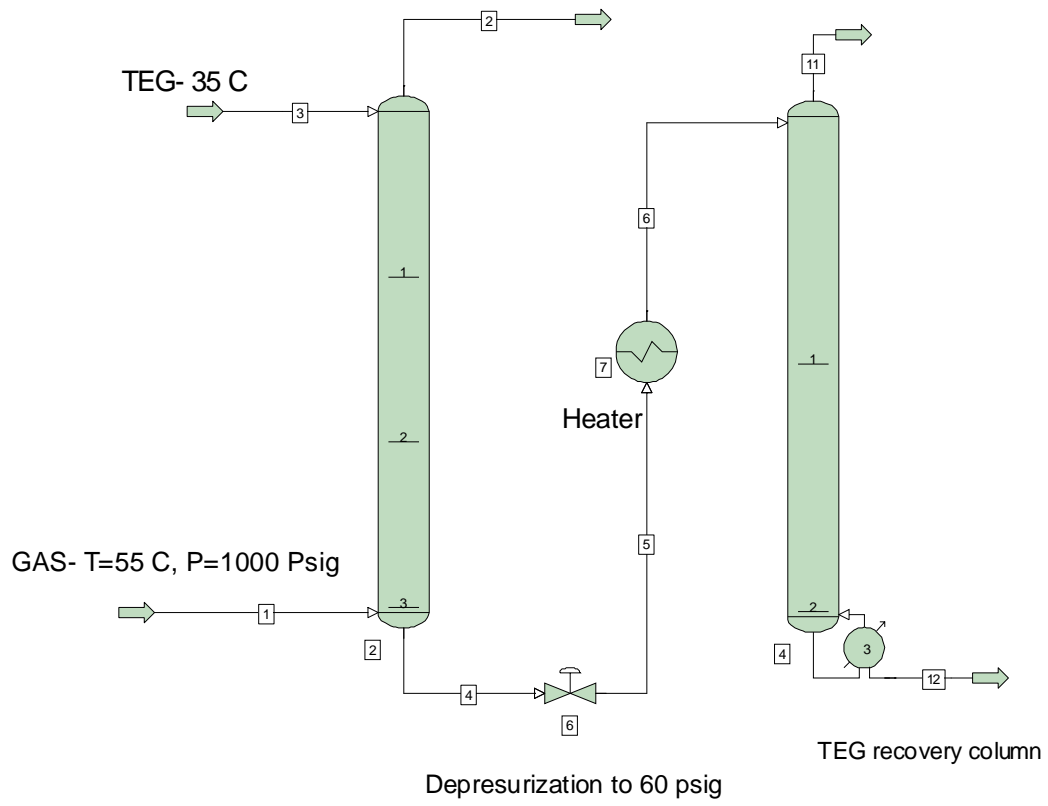


Figure 4-2: *TEG Contactor*

The water-rich TEG needs to be regenerated. Thus, it is first depressurized and later heated up. This basically removes water from the liquid phase already. It is later sent to a TEG recovery column. This column has a reboiler and allows water to be removed. Thus by heating the mixture in the bottom of the column to close to the boiling point of TEG, one should be able to remove it.



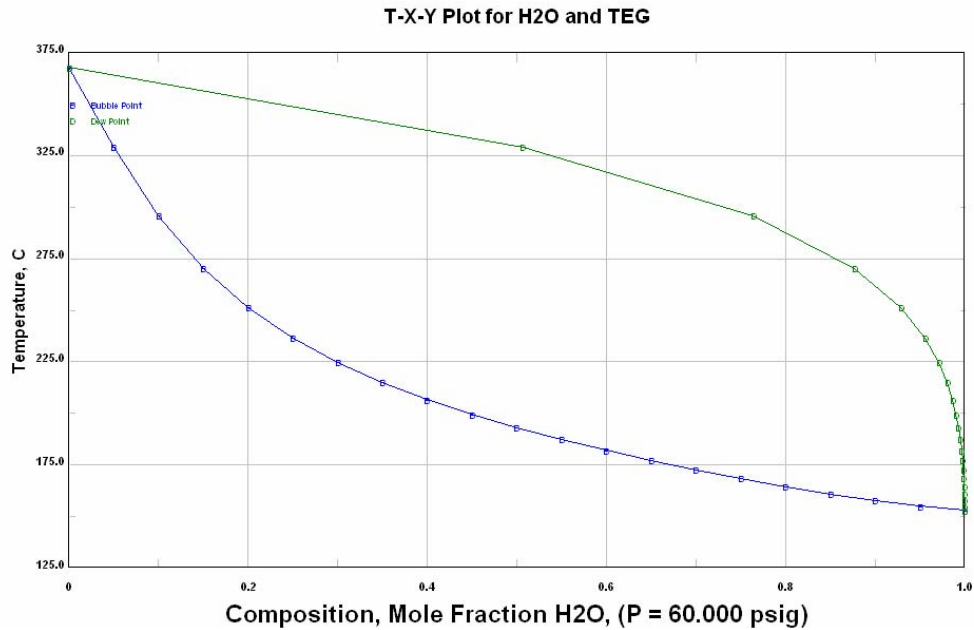


Figure 4-4: TEG –Water Temperature composition diagram.

We will attempt to simulate this system. However, we need to learn how to set up distillation and absorption columns in Pro II.

Degrees of Freedom in Distillation

Degrees of Freedom in distillation

To perform a simulation of a distillation column, a set of specifications needs to be provided. To do this, one needs to understand the concept of degree of freedom. This is defined as

$$\text{Degree of Freedom} = \text{Number of unknowns} - \text{Number of equations} \quad (4- 1)$$

Consider a column with N_T trays and N_C components, total condenser and total reboiler (Figure 4-1). In the case of crude, one can consider the components to be the pseudo-components that are usually generated.

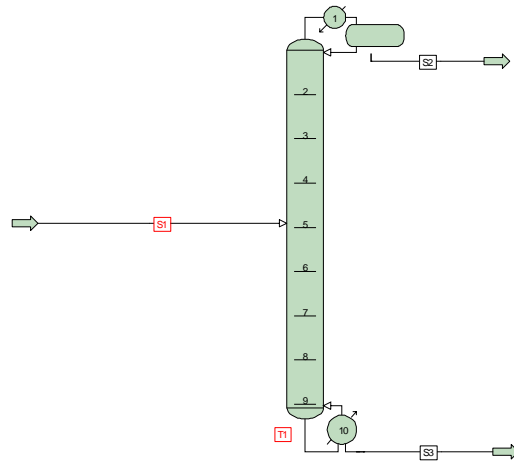


Figure 2-1: Single one-feed two product column with reboiler and condenser

VARIABLES

1) For each tray (excluding condenser and reboiler):

$$T_j, L_j, V_j, x_{j,i}, y_{j,i}$$

$$\text{Variables} = 3 N_T + 2 N_T N_C$$

L = Liquid rates

V = Vapor rates

x = liquid compositions

y = vapor compositions

T = Tray temperatures

2) For the condenser (temperature, flows, compositions and duty)

$$T_C, L_0, D, x_{C,i}, Q_C$$

$$\text{Variables} = N_C + 4$$

D = Product Rate

Q_C = Condenser heat duty

3) For the reboiler (temperature, flows, compositions and duty)

$$T_R, V_{N_T+1}, B, x_{R,i}, Q_R$$

$$\text{Variables} = N_C + 4$$

B = Product Rate

Q_R = Condenser heat duty

Total number of Variables: $N_T(3+2N_C)+8+2N_C$

EQUATIONS:

1) Steady state mass balances for all components in all trays

$$L_{j-1} x_{j-1,i} - [L_j x_{j,i} + V_j y_{j,i}] + V_{j+1} y_{j+1,i} + F_j z_i = 0 \quad i=1, \dots, N_C \quad j=1, \dots, N_T$$

Equations: $N_C N_T$

z_i = feed composition

F_j = Feed rate to tray j (here we consider only one).

2) Steady state mass balances for all components the condenser

$$y_{1,i} = x_{C,i} \quad i=1, \dots, N_C \quad \text{Equations: } N_C$$

$$V_1 - (L_0 + D) = 0 \quad \text{Equations: } 1$$

3) Steady state mass balances for all components the Reboiler

$$y_{N_T+1,i} = x_{R,i} \quad i=1, \dots, N_C \quad \text{Equations: } N_C$$

$$L_{N_T} - (V_{N_T+1} + B) = 0 \quad \text{Equations: } 1$$

4) Equilibrium Relations

$$y_{j,i} = K_{j,i}(x_{j,i}, T_j, P_j) x_{j,i} \quad i=1, \dots, N_C \quad j=1, \dots, N_T \quad \text{Equations: } N_T N_C$$

P_j = pressures (assumed given)

5) Summation equations

$$\sum_{i=1}^{N_C} x_{j,i} = 1 \quad j=1, \dots, N_T$$

$$\sum_{i=1}^{N_C} x_{C,i} = 1 \quad (\text{Condenser})$$

$$\sum_{i=1}^{N_C} y_{j,i} = 1 \quad j=1, \dots, N_T$$

$$\sum_{i=1}^{N_C} y_{NT+1,i} = 1 \quad (\text{Reboiler})$$

6) Enthalpy balance in each tray

$$L_{j-1} h_{j-1} - [L_j h_j + V_j H_j] + V_{j+1} H_{j+1} + F_j H_{F,j} = 0 \quad j=1, \dots, N_T$$

h : liquid enthalpy

H : Vapor enthalpy

H_F : Enthalpy of feed

All enthalpies are functions of composition and temperature.

7) Enthalpy balance in condenser and reboiler

$$V_1 H_1 - (L_0 + D) h_0 = Q_C \quad \text{Equations: } 1$$

$$(L_{NT} - B) h_{NT} - V_{NT+1} H_{NT+1} = Q_R \quad \text{Equations: } 1$$

Total number of equations: $N_T(3+2N_C)+2N_C+6$

Degree of Freedom: Unknowns- Equations = 2

Consider now the case of a column with a total condenser and steam injection, like the one in Figure 4-2.

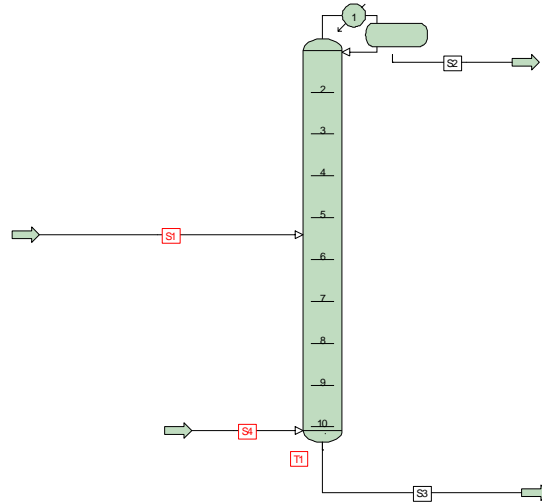


Figure 2-2: Single one-feed two product column with reboiler and condenser

Since there is no reboiler, there is N_C+4 variables less (T_R , V_{N+1} , x_{Ri} , B and Q_R). Therefore,

Total number of equations: $N_T(3+2N_C)+N_C+4$

The number of equations is reduced by N_C+3 ($N_C + 1$ material balances, one summation of compositions, one energy balance). Thus,

Total number of equations: $N_T(3+2N_C)+ N_C+3$

Degree of Freedom: Unknowns- Equations = 1

EXERCISE 4-3: Determine the degrees of freedom of a column with a partial condenser and a total reboiler.

EXERCISE 4-4: Determine the degrees of freedom of an absorber (no condenser or reboiler) shown in Figure 4-3

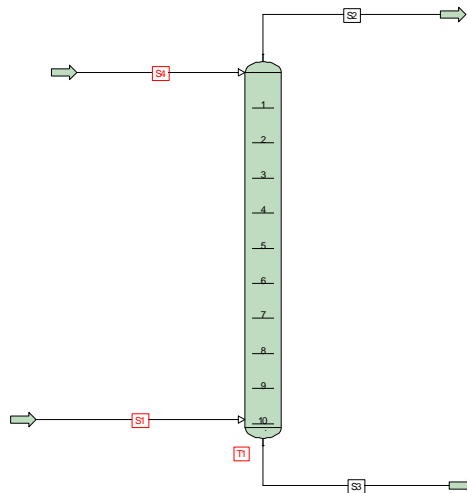


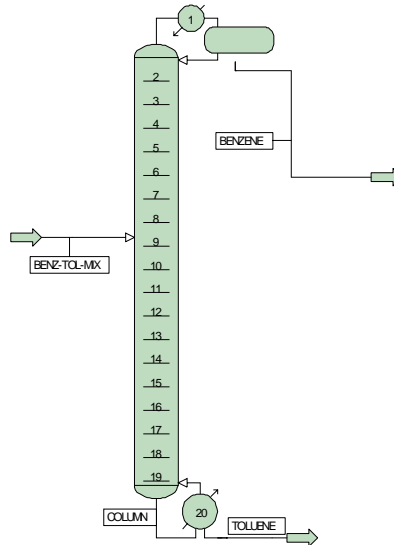
Figure 2-3: Absorber

Specifying a Distillation Column Simulation

When a particular system has a degree of freedom different from zero, multiple solutions are expected. To reduce the degree of freedom, one needs to fix the value of some unknown variables or add more equations to the system. For example, in the case of the column with reboiler and condenser, two specifications are needed. These are obtained either through fixing some values of variables or by adding some equations. For example, one can fix two flowrates (products are usually chosen), two compositions (also usually products), etc. One can also add equations. For example, the most common is to fix the reflux ratio R . The corresponding equation one is adding is $R=L_0/D$. One can also add some recovery ratio. For example, one can say that one wants in the overhead to recover 99% of component one (or any other) in the feed. The corresponding equation is: $D x_{C,1}=0.99 F z_1$.

EXAMPLE 4-1: Set up the distillation of a benzene/toluene separation unit. The instructor will show all the set up steps, one by one.

We start by building a column and connecting the streams



We continue by defining the inlet stream

PRO/II - Stream Data

UDM Flange Help Top Overview Status Notes

Stream: **BENZ-TOL-MIX** Description: _____

To Unit: COLUMN

Stream Type

- Composition Defined** (Flowrate and Composition...)
- Petroleum Assay (Stream Solids Data...)
- Referenced to Stream (Stream Polymer Data...)
- Solids Only Stream

Thermal Condition

First Specification: Temperature 35.00 F

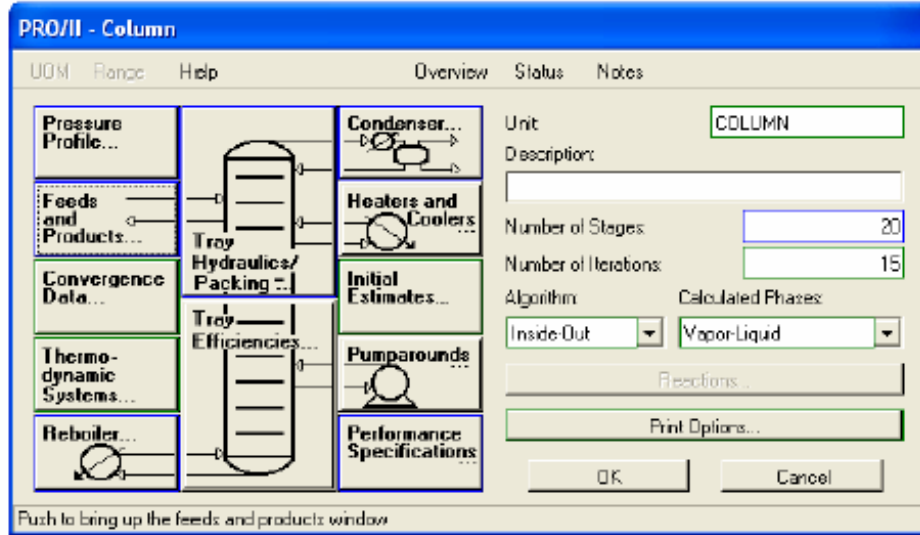
Second Specification: Pressure 14.700 psia

Thermodynamic System: Determined From Connectivity

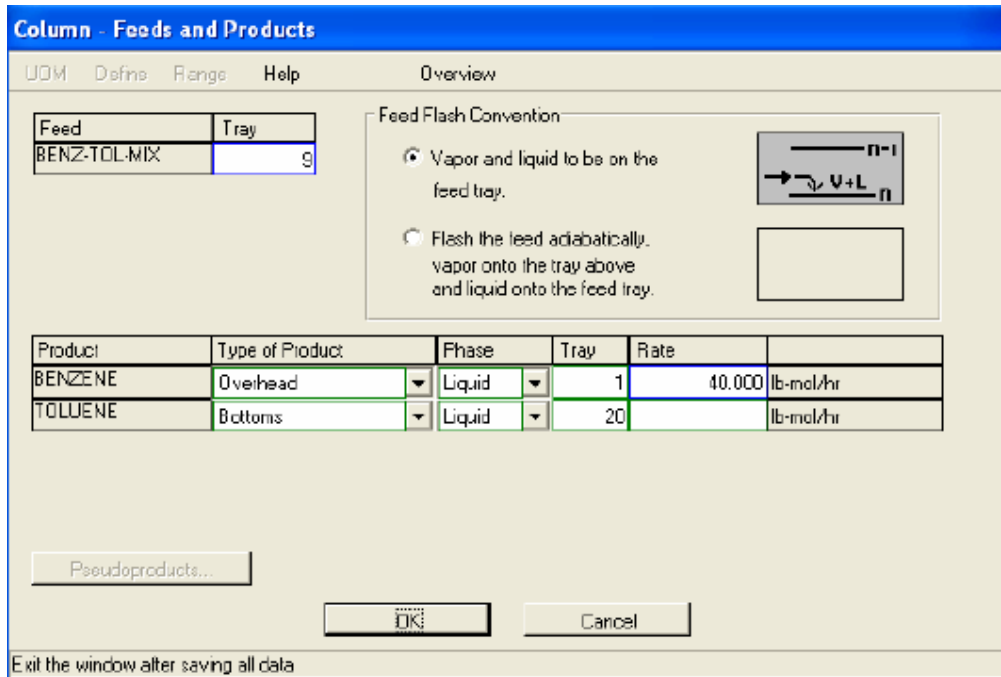
OK Cancel

Exit the window after saving all data

We enter a composition of 40% benzene and a flowrate of a 1000 lb-mol/hr. Open the column and choose the number of trays



Click on Feeds and Products and enter feed tray as well and estimates on products



Click on condenser and reboiler and pick a bubble point condenser and a kettle reboiler

Column - Condenser

UDM Define Range Help Overview

Column with Condenser

Condenser Type

- Partial
- Bubble Temperature
- Subcooled, Fixed Temperature
- Subcooled, Fixed Temperature Drop

Condenser Data

Pressure: psia

Temperature Estimate: F

Fixed Temperature: F

Degrees Subcooled: F

Duty: x 10⁶ BTU/hr

Subcooled Reflux Only

- Fixed Temperature
- Fixed Temperature Drop

Exit the window after saving all data

Column - Reboiler

UDM Define Range Help Overview

Column with Reboiler

Reboiler Type

- Kettle (Conventional)
- Thermosiphon without Baffles
- Thermosiphon with Baffles

Thermosiphon Reboiler Specification

- Return Liquid: Mole fraction
- Return Vapor: Mole fraction
- Temperature: F
- Temperature Change: F
- Rate: lb-mol/hr

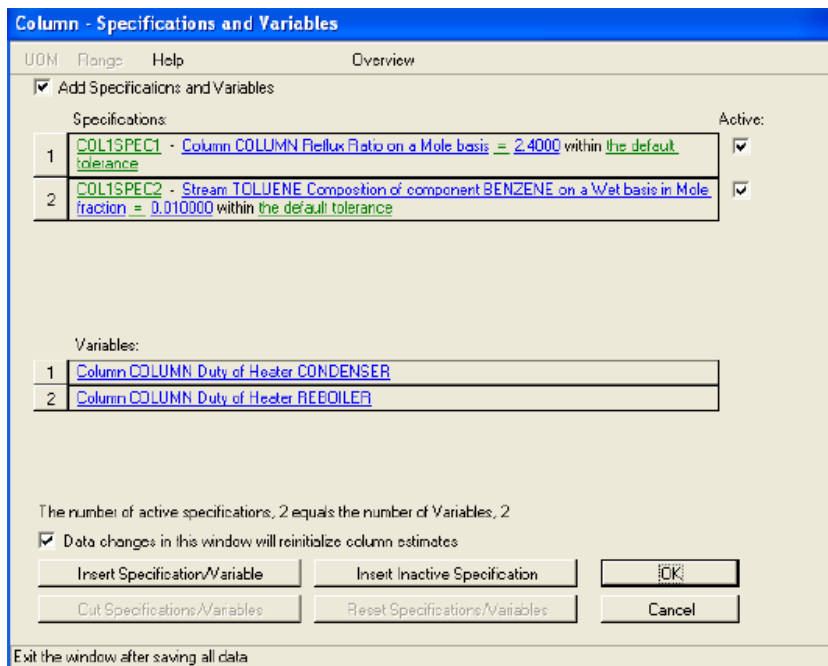
Molar Estimate

- Return Vapor: Mole Fraction
- Rate: lb-mol/hr

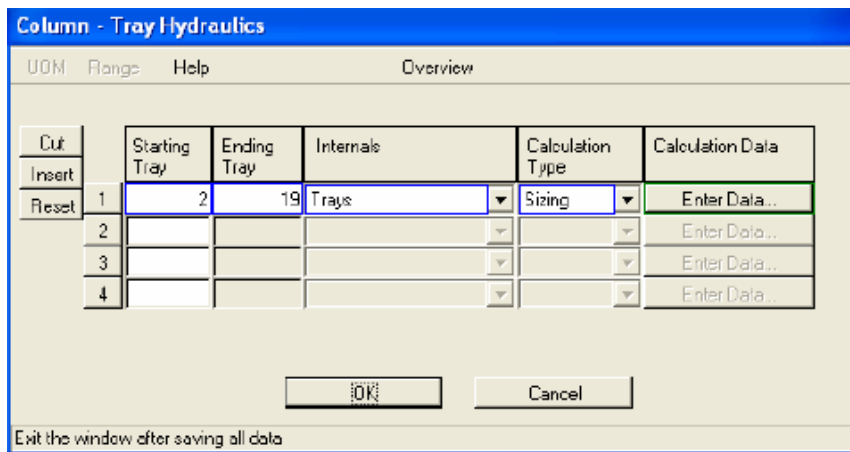
Duty: x 10⁶ BTU/hr

Exit the window after saving all data

Now go to the specifications (You need two) and enter a reflux ratio plus a desired composition in the top



Now enter the hydraulics part. Request sieve trays and sizing mode



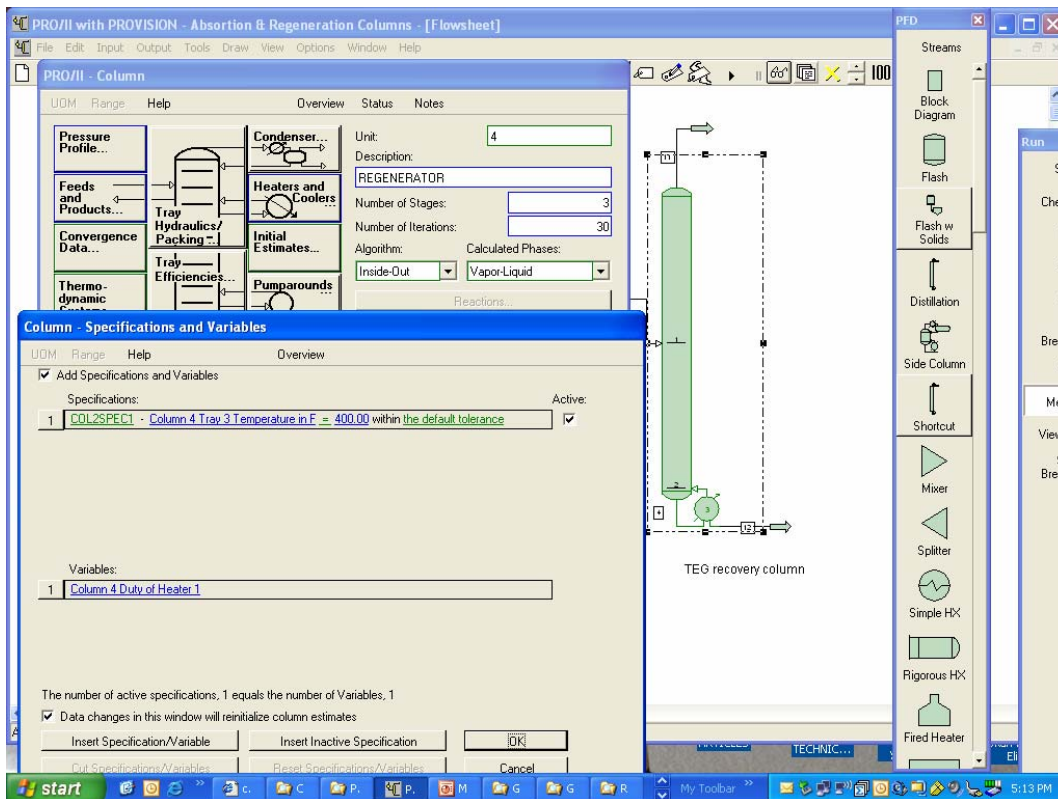
Rerun the column and generate the report by using the output menu in the top. The instructor will show how to obtain results from the screen and how to go over the output and show you where to find the column diameter.

EXERCISE 4-5: Set up a column to separate a mixture of pentane and hexane. Use Peng Robinson and SRK thermodynamic methods and compare the results for the same set of specifications. You are free to choose any. This will be discussed in class.

Simulation of a TEG System

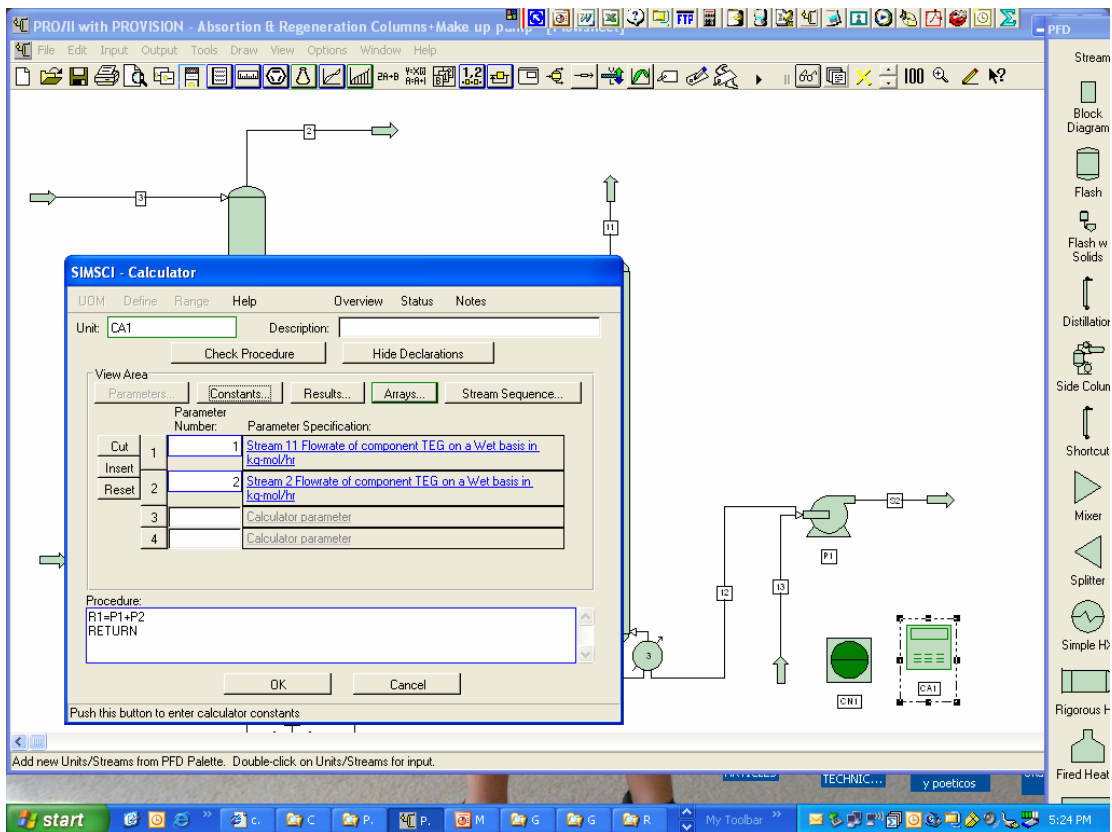
We start setting up a column and a regenerator as in the figure above. We recommend starting with 3 trays in each column. The gas is at 1000 psig, so it may need to be dewatered first. Consider first that you would not do that.

The contactor does not have condenser or reboiler, so it does not need specifications. The regenerator has only a reboiler, so it needs one specification. We choose to specify the temperature. Finally, we need a special thermodynamic package for TEG.

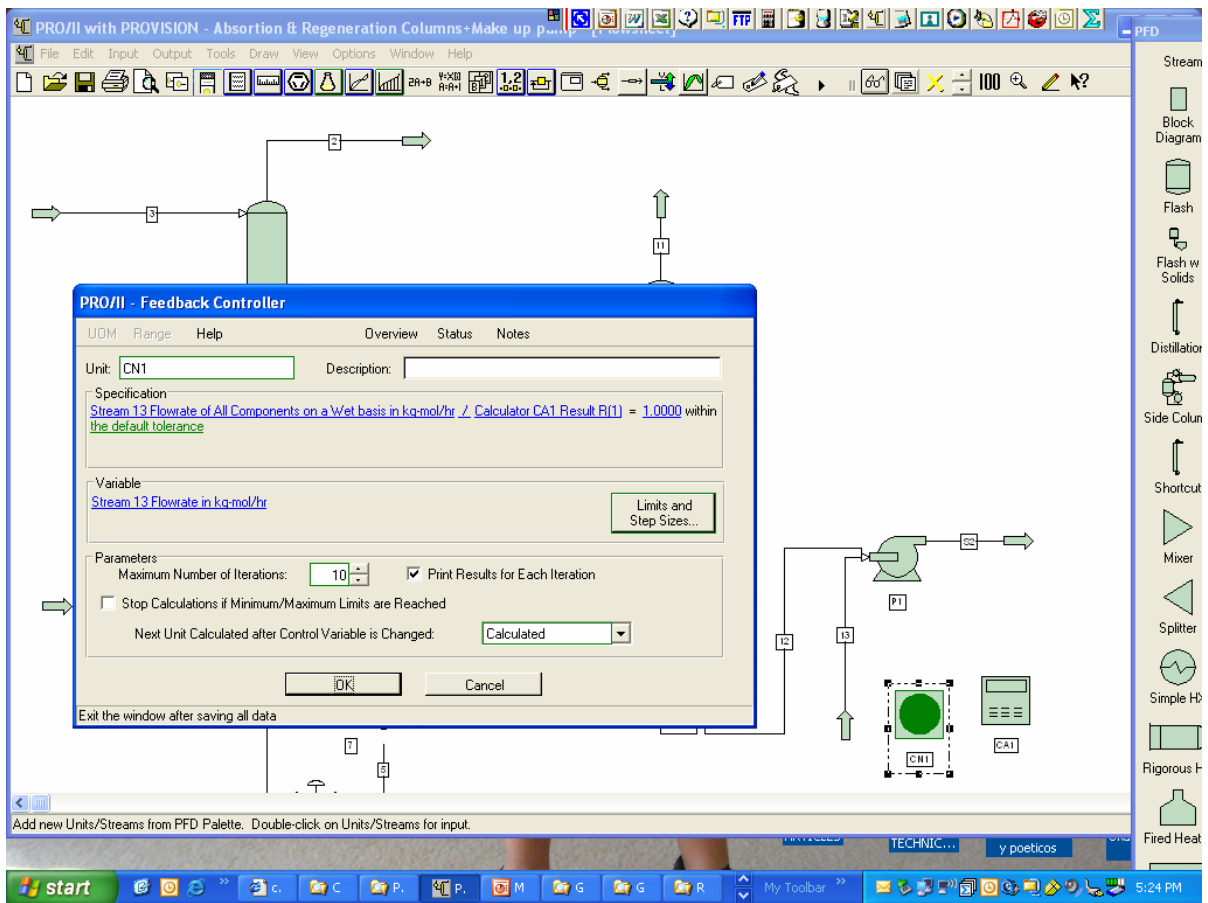


EXERCISE 4-6: Play around with the number of trays and the operating conditions in both contactor and regenerator until you reach conditions that are acceptable. For example, change the temperature of the incoming TEG, change the pressure of the regenerator, the flowrate of TEG.

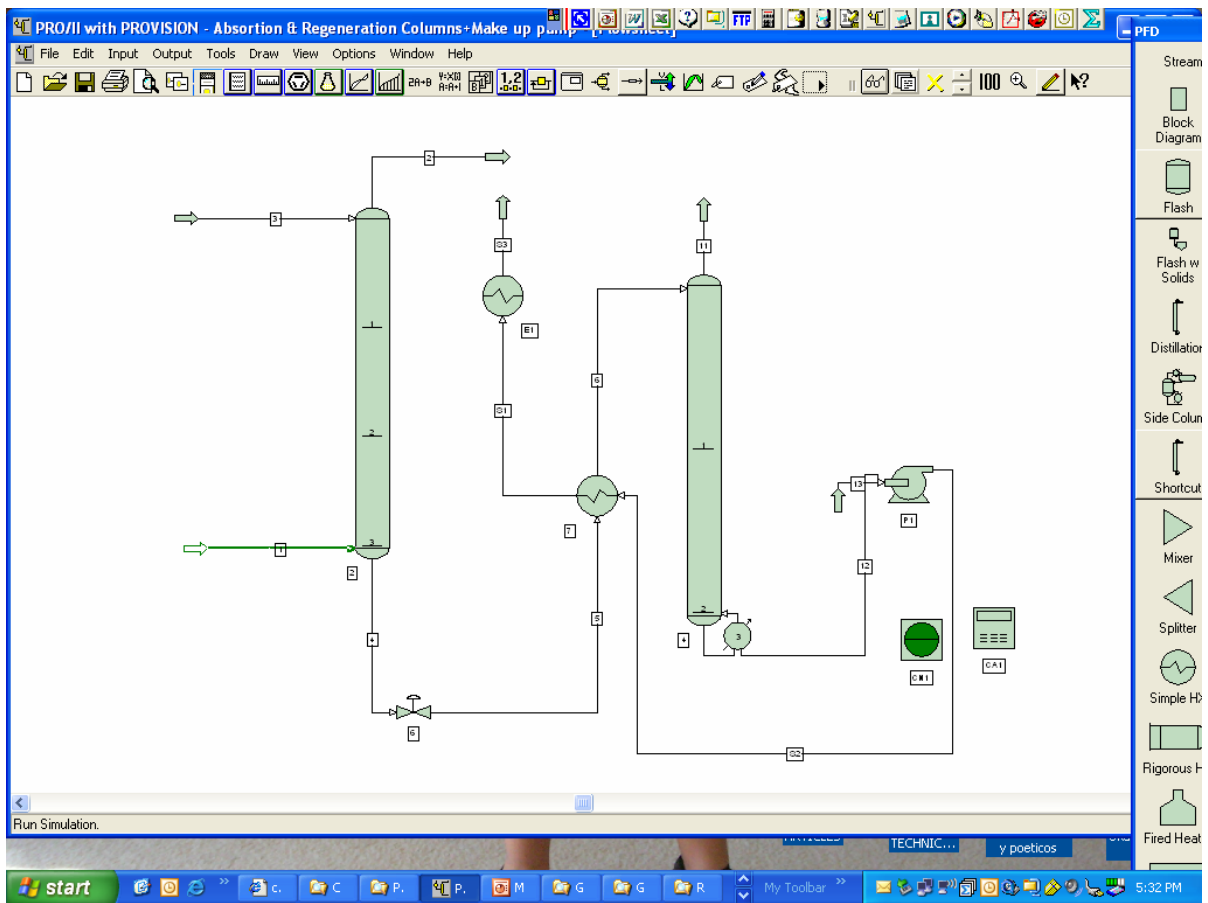
We now find a way of adding make up TEG to the system by setting up a calculator that will count how much TEG is being lost (with the gas and with the water) at the top of both columns. These are streams 2 and 11.



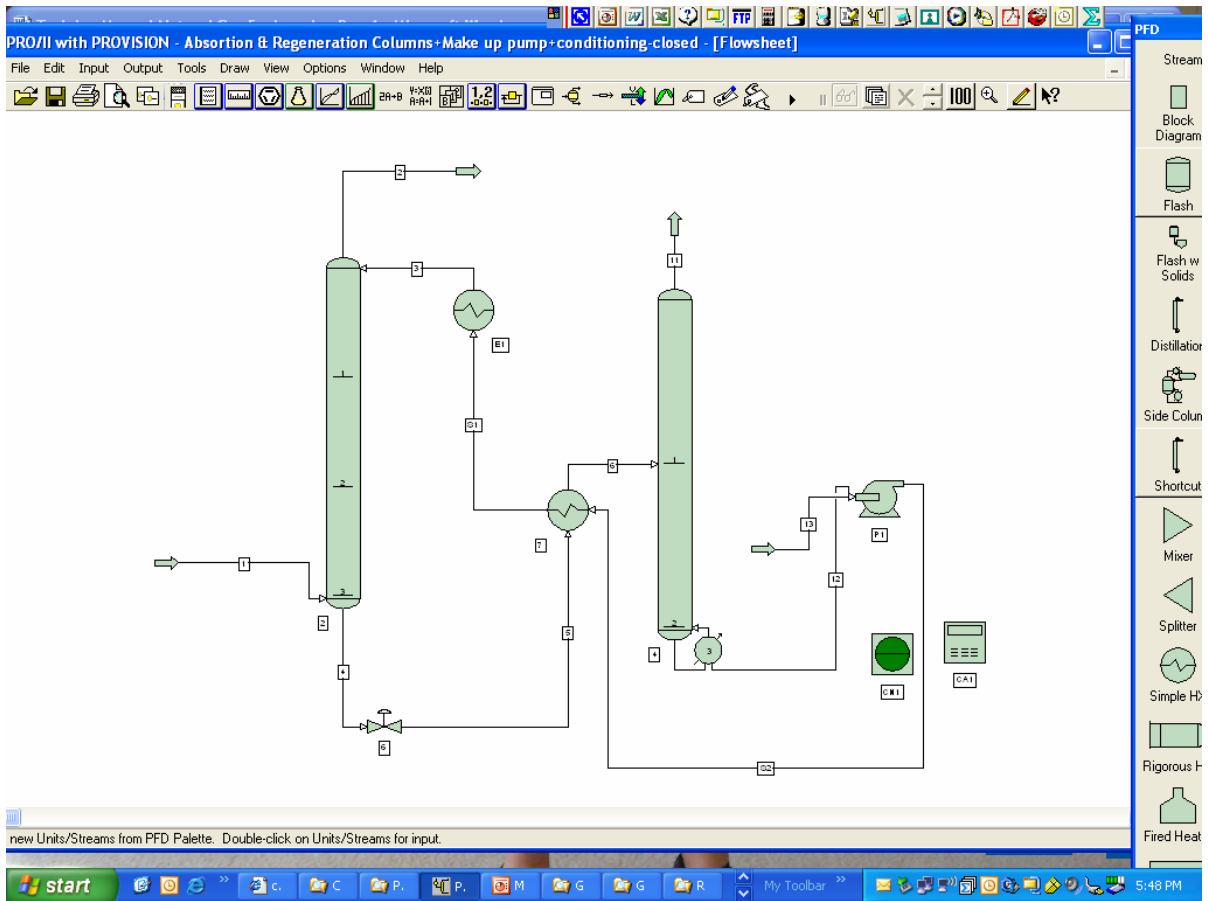
The controller, simply takes adjust the flow of TEG make up (before the pump) to be the same as the calculated loss.



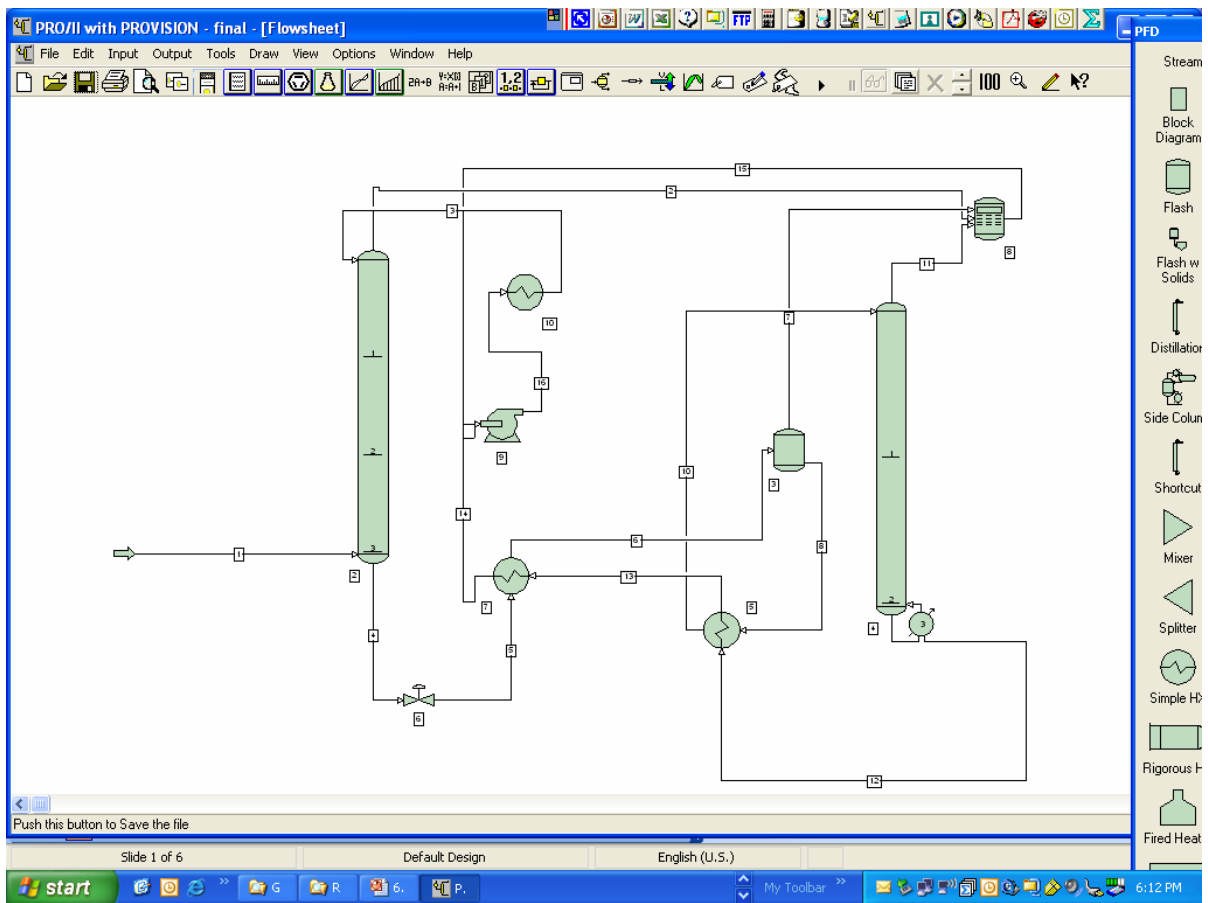
We now substitute the heater by a heat exchanger and we add a cooler for final conditioning. The instructor will show the different values of the streams.



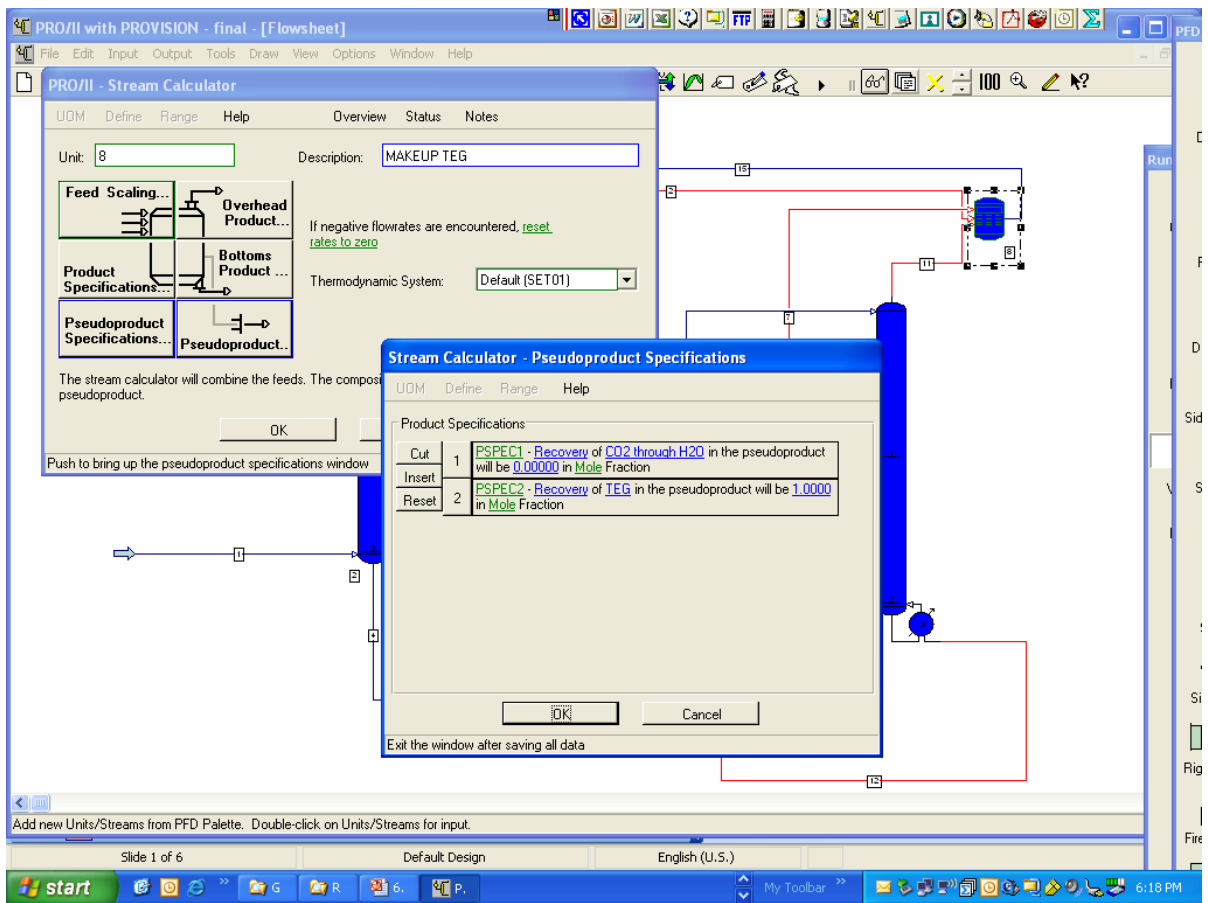
Once we get the conditions of the input close to the conditions of the output, we can connect the streams.



Finally, one can use a flash drum to separate the gas before sending into the regenerator and a stream calculator to simulate the recovery all the TEG as follows:



The stream calculator input is shown next

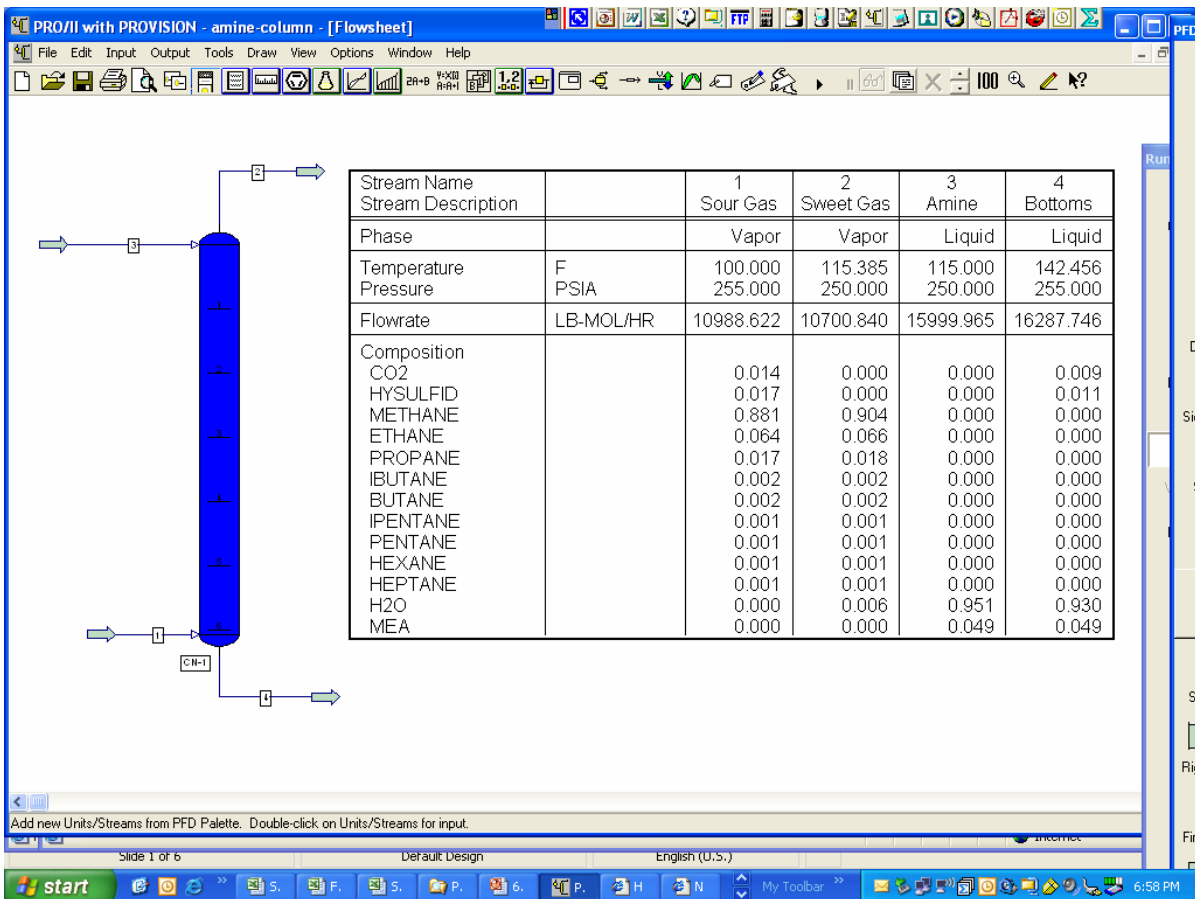


EXERCISE 4-7: Once that you connected the streams evaluate the system. Determine the loss of hydrocarbon and the loss of TEG.

Amine Sweetening

The purpose of amine sweetening is to remove CO₂ and H₂S from gas. As, mentioned above, to do this Monoethanol-amine (MEA) is used.

We set up an absorption column with the conditions listed below (we use a special package for amines that is available in Pro II).



We now also go through the same sequence of steps as in the case of TEG dehydration to make use of a regenerator and close the loop.

EXERCISE 4-8: With the aid of the instructor, set up an amine regeneration column and connect the loop to verify the system performance. Note that in this case, a distillation column with a condenser is needed.

