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

$$\text{Degree of Freedom} = \text{Number of unknowns} - \text{Number of equations} \qquad (2\text{-}1)$$

Consider a column with N_T trays and N_C components, total condenser and total reboiler (Figure 2-1). In the case of crude, one can consider the components to be the pseudo-components that are usually generated.
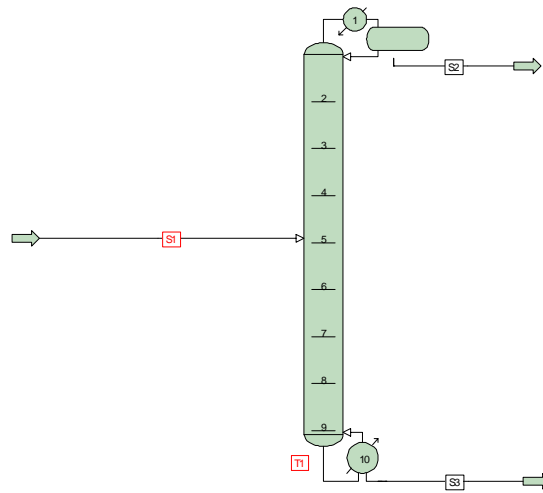

Figure 2-1: Single one-feed two product column with reboiler and condenser

VARIABLES

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

$$T_j \; , \; L_j \; , \; V_j \; , \; x_{j,i} \; , \; y_{j,i} \qquad\qquad \text{Variables} = 3\,N_T + 2\,N_T N_C$$

$L=$ Liquid rates $\qquad\qquad$ $V=$ Vapor rates
$x=$ liquid compositions $\qquad\qquad$ $y=$ vapor compositions
$T=$ Tray temperatures

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

$$T_C \; , \; L_0 \, , \, D \; , \; x_{C,i} \; , \, Q_C \qquad\qquad \text{Variables} = N_C + 4$$

D= Product Rate $\qquad\qquad\qquad\qquad$ Q_C = Condenser heat duty

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

$\qquad$ T_R , V_{NT+1} , B , x_{Ri} , Q_R $\qquad\qquad$ Variables= N_C +4

B= Product Rate $\qquad\qquad\qquad\qquad$ 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

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

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ Equations: $N_C N_T$

z= feed composition $\qquad\qquad$ F_j= Feed rate to tray j (here we consider only one).

2) Steady state mass balances for all components the condenser

$y_{1,i}=x_{Ci}$ $\qquad\qquad\qquad$ $i=1,..,N_C$ $\qquad\qquad$ Equations: N_C

V_1 -(L_0+ D)=0 $\qquad\qquad\qquad\qquad\qquad\qquad$ Equations: 1

3) Steady state mass balances for all components the Reboiler

$y_{NT+1,i}=x_{Ri}$ $\qquad\qquad\qquad\qquad$ $i=1,..,N_C$ $\qquad\qquad$ Equations: N_C

L_{NT} -(V_{NT+1} + B)=0 $\qquad\qquad\qquad\qquad\qquad$ Equations: 1

4) Equilibrium Relations

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

P_j= pressures (assumed given)

5) Summation equations

$$\sum_{i=1}^{N_C} x_{j,i} = 1 \qquad\qquad\qquad j=1,..., N_T$$

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

$$\sum_{i=1}^{N_C} y_{j,i} = 1 \qquad\qquad\qquad j=1,..., N_T$$

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

6) Enthalpy balance in each tray

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

h: liquid enthalpy $\qquad\qquad\qquad\qquad$ H: Vapor enthalpy
H_F: Enthalpy of feed
All enthalpies are functions of composition and temperature.

7) Enthalpy balance in condenser and reboiler

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

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

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

Degree of Freedom: Unknowns- Equations = 2

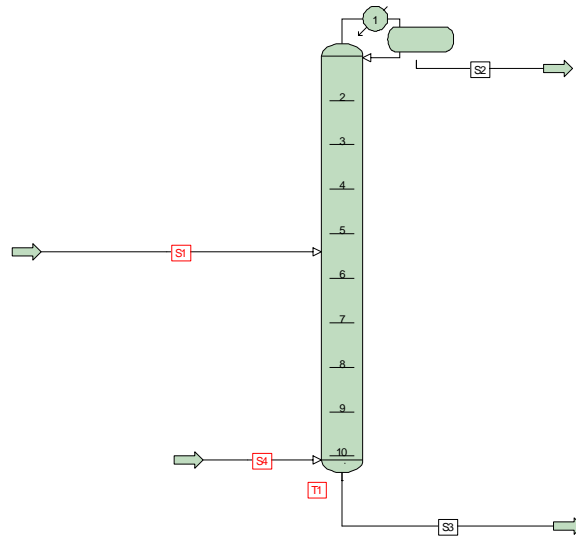Consider now the case of a column with a total condenser and steam injection, like the one in Figure 2-2.

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 2-1: Determine the degrees of freedom of a column with a partial condenser and a total reboiler.

EXERCISE 2-2: Determine the degrees of freedom of an absorber (no condenser or reboiler) shown in Figure 2-3.
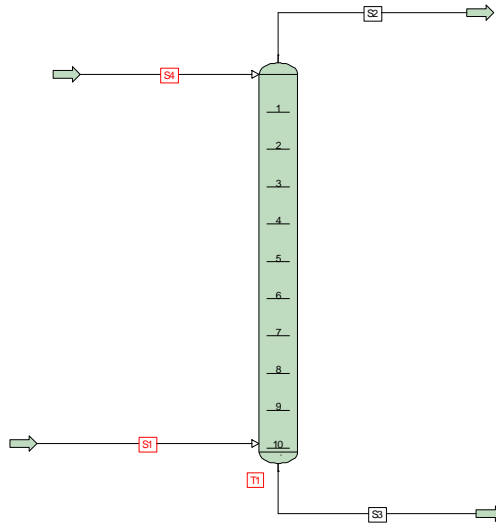

Figure 2-3: Absorber

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 2-1

Consider setting a pre-fractionation column with condenser and reboiler and the following TBP and light-end data.

TABLE 2-1: TBP Data

Vol %	TBP
5	113 $^{\circ}$F
10	179 $^{\circ}$F
30	366 $^{\circ}$F
50	537 $^{\circ}$F
70	720 $^{\circ}$F
90	1026 $^{\circ}$F

TABLE 2-2: Light ends Data

Component	Liq Vol %
C2	0.13
C3	0.78
IC4	0.49
NC4	1.36
IC5	1.05
NC5	1.3

Open the simulation file *prefractionation-column.prz.* It consists of a desalter, a couple of heaters representing a heat exchanger network and the pre-fractionation column. The instructor will show you how the flowsheet is constructed.
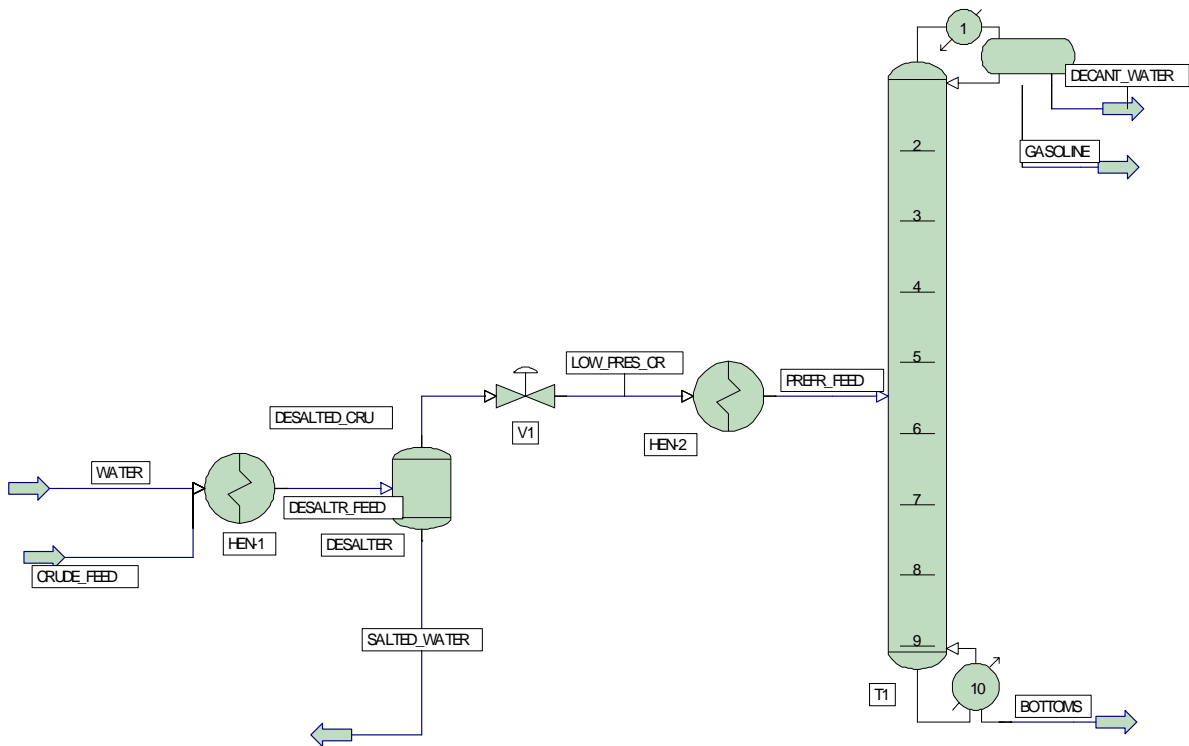

Figure 2-4: Pre-fractionation flowsheet

The number of pseudo components is set at 30, 28 of them being below 800 ^{o}F. Then the specs for the different equipments are reviewed. In the case of the column, an estimate of the products rate is entered and the specs are set at a reflux ratio of 3 and a 350 ^{o}F D86 5% point of the bottoms. The instructor will show you how to retrieve the assay data of the products.

EXERCISE 2-3: Change the reflux ratio to R=1, R=2, and to R=4. Report the 95% D86 ASTM point for the gasoline and the corresponding reboiler duty. What is the amount of lights that goes in the bottom (count all that has a vol % below 5%)

EXERCISE 2-4: Change the specification of the reflux ratio back to R=3 and change the D86 5% specification on the bottom stream to 370 ^{o}F. Report the changes on the gasoline and the duties.

EXERCISE 2-5: With the aid of the instructor, remove the reboiler and add a stream composed of steam (low pressure, 50 psig , overheated 500 ^{o}F) with a flowrate of 5000 lb/hr. Keep the reflux ratio at R=3 and remove the second specification (why?). Run the simulation and check the rate and 95% D86 temperature of the Gasoline. Increase the steam rate to 6000 lb/hr. Report the difference in the gasoline. Change the reflux ratio to 2 and to 1 until you get a comparable gasoline to the case with reboiler. Calculate the duty of the steam (~enthalpy × rate) and compare it with the duty of the pre-fractionator with a reboiler. Comment on the comparison.

Degrees of Freedom of Crude Columns

We now analyze the degrees of freedom of columns having side draw streams. In this case we add N_{LD} liquid side draws and N_{VD} vapor side draws.

This means that the new number of variables is increased by (N_{LD} +N_{VD}). In turn, no new equations are needed, but some of the equations are modified:

The new steady state mass balances for all components in all trays are:

$$L_{j-1} \ x_{j-1,i} - [(L_j + LD_j) \ x_{j,i} + (V_j + VD_j) \ y_{j,i}] + V_{j+1} \ y_{j+1,i} + F_j z_i = 0 \qquad i=1,..,N_C \quad j=1,...,N_T$$

where

LD= Liquid Draw rates $\qquad\qquad\qquad$ VD= Vapor Draw rates

The enthalpy balance in each tray becomes

$$L_{j-1} \ h_{j-1} - [(L_j + LD_j) \ h_j + (V_j + VD_j)H_j] + V_{j+1}H_{j+1} + F_j H_{F,j} = 0 \qquad j=1,..., N_T$$

Therefore:
Degree of Freedom: Unknowns- Equations = 2+ (N_{LD} +N_{VD}).

The more straightforward way of adding specifications to such columns is the specification of flowrates, as it is shown in the next exercise

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EXAMPLE 2-2

Consider setting a column following the pre-fractionation column as in the following figure. The corresponding file is named *prefractionation-and-column-with-draws.prz*. The desired flowrates of products are already added to the simulation.

We notice that we only put one specification in this column, because we fixed the flowrates of the draws in the estimate section of the column. We also notice that the ASTM D86 95% points of the products are: Naphtha: 369 ^{o}F, Kerosene: 571 ^{o}F, Diesel 639 ^{o}F and AGO 773 ^{o}F. The instructor will show you how to obtain these in a calculator.

If we click on the column to view it, we will find the temperature and flow profiles. It looks like the overflash ratio (volumetric flow of liquid from above the flash zone into it (tray 28's liquid rate, divided by the volumetric rate of the feed) is sufficiently low. The instructor will help you enter a calculator unit to obtain this number. In crude columns this is set to about 1-3%. We then add the specification, say 1 %, and therefore allow the flowrate of AGO to vary to meet it. As a result, the AGO flowrate entered initially will now be used as an estimate only.

It only looks like we are adding a specification, when in fact we are substituting one for another, because the flowrate of AGO is now no longer a constant. As a result, the flowrate of AGO is higher and the ASTM D86 95% point is also higher (778 ^{o}F). The instructor will indicate how one can obtain these numbers in the calculator.

If one is interested in controlling the ASTM D86 95% of the products, as it is usually the case in industry, then one can add those specs and vary the flowrates accordingly. We therefore add the following ASTM D86 95% points of the products as specifications: Naphtha: 360 ^{o}F, Kerosene: 520 ^{o}F, Diesel 620 ^{o}F. Thus, the specification on flowrate for Naphtha has to be removed and replaced by the ASTM point. We use the calculator again to obtain the flowrates of the products and we compare them with the original desired flowrates in the following table.

TABLE 2-3: Column Comparison

STREAM	Original Flowrate	Flowrate adjusted to ASTM D85 95% specs
Naphtha	1075 bph	1014 bph
Kerosene	960 bph	570 bph
Diesel	420 bph	825 bph
AGO	605 bph	670 bph

We now turn our look at the gaps. We check the ASTM D86 5% points of the products are: Kerosene: ~364 ^{o}F, Diesel ~403 ^{o}F and AGO ~479 ^{o}F. This information can also be obtained directly from a calculator unit, instead of having to browse the output report.

The 5-95 *Gaps* are: Naphtha-Kerosene: 4 ^{o}F (364 ^{o}F-360°F), Kerosene-Diesel: -117 ^{o}F (403 ^{o}F -520 ^{o}F), and Diesel-AGO: -140 ^{o}F (479 ^{o}F -620 ^{o}F). Quite clearly, these gaps are unacceptable. In other words, there are too much light components in each fraction and a better separation is required. This can only be accomplished by somehow stripping the products from light components, either by means of a reboiler or by steam injection. Steam injection has proven to be more efficient, so we will use that.

Degrees of Freedom of Crude Columns with Side-Strippers

It is easy to see that the addition of side-strippers does not add any degree of freedom. Indeed, side-strippers are like absorber columns, that is, they do not have degrees of freedom. However, one may adjust vapor rates to adjust flash points and Gaps as needed. We saw this need in the example above.

EXAMPLE 2-3

We now add side-strippers to the column build in the previous example. We leave the same specifications, now on the exit streams from the side-strippers. We rename the products as draws and the exit streams from the side-strippers as products. We fix the calculator references. We return the vapor from the side-strippers to one tray above the draw. Pressures on side-strippers are 25, 25, and 30 psig. We also add 4400 lb/h, 2250 lb/h and 3800 lb/hr to the kerosene, diesel and AGO stripper respectively. In all this process, the simulator may crash. These are beyond your control. If so happens, the instructor will provide a version of the simulation that works.

The flowrates of the products are:

TABLE 2-4: Column Comparison

STREAM	Original Flowrate	Flowrate adjusted to ASTM D85 95% specs	Flowrate Column with Side strippers
Naphtha	1075 bph	1014 bph	1082 bph
Kerosene	960 bph	570 bph	576 bph
Diesel	420 bph	825 bph	825 bph
AGO	605 bph	670 bph	597 bph

From the table, we notice that lights have been stripped from the heavier AGO and Diesel and therefore the production of Kerosene and Naphtha has increased. ASTM D86 5% points of the products are: Kerosene: 391 ^{o}F, Diesel 435 ^{o}F and AGO 610 ^{o}F. The 5-95 *Gaps* are: Naphtha-Kerosene: 31 ^{o}F (391 ^{o}F-360°F) (spec is $\geq$ 16.7 °C), Kerosene-Diesel: -85°F (435 ^{o}F -520 ^{o}F) (Spec is $\geq$ 0 °C), and Diesel-AGO: -10 ^{o}F (610 ^{o}F -620 ^{o}F) (spec is -5.6 °C to –11 °C). The diesel-kerosene gap is still below spec, the diesel ago is reasonably in spec and the naphtha-kerosene is all right.

Try to increase the steam to the diesel side-stripper to realize this has no fix using steam. The problem in this column is that the diesel draw should be lower. To check this we modify the draw and return trays to be 17 and 16 respectively. The new gaps are: 35 ^{o}F, 1 ^{o}F, -22 ^{o}F, which are now OK. The new flowrates of products are given below. They show the remarkable shift in flowrate between diesel and Kerosene.

TABLE 2-5: Column Comparison

STREAM	Original Flowrate	Flowrate adjusted to ASTM D85 95% specs	Flowrate Column with Side strippers (new trays)
Naphtha	1075 bph	1014 bph	1079 bph
Kerosene	960 bph	570 bph	950 bph
Diesel	420 bph	825 bph	379 bph
AGO	605 bph	670 bph	671 bph

Columns with Pump-Around Circuits

It is also easy to see that the addition of pump-around circuits add two degrees of freedom. Indeed, the rate, the heat and the return temperature are related by one equation. Thus, one needs to specify two of those. We also realize that they alter the traffic of liquid in the column, but they do not change the overall duty of all refluxes. We now show this through and example.

EXAMPLE 2-4

We start from the column with side-strippers of the previous example. The instructor will show how to add three pump around circuits between trays 4 and 2, trays 15 and 13 and trays 20 and 18. We specify the duties and return temperatures to be -40 MMBtu/hr, 220 ^{o}F, -30 MMBtu/hr, 300 ^{o}F, and -30 MMBtu/hr, 450 ^{o}F.

We now investigate the effect on the overall duty, the rates of products and the gaps. Flowrates are given in the next table. We see a deterioration of the kerosene production, which mostly goes to diesel.

TABLE 2-6: Column Comparison

STREAM	Original Flowrate	Flowrate adjusted to ASTM D85 95% specs	Flowrate Column with Side strippers (new trays)	Flowrate Column with Side strippers (new trays) and pump around circuits.
Naphtha	1075 bph	1014 bph	1079 bph	1054 bph
Kerosene	960 bph	570 bph	950 bph	953 bph
Diesel	420 bph	825 bph	379 bph	394 bph
AGO	605 bph	670 bph	671 bph	678 bph

Clearly, this is due to deterioration in Gaps. Indeed, the 5-95 *Gaps* are: Naphtha-Kerosene: 23 ^{o}F (spec is $\geq$ 16.7 °C), Kerosene-Diesel: -16 ^{o}F (Spec is $\geq$ 0 °C), and Diesel-AGO: -24 ^{o}F (spec is -5.6 °C to –11 °C). This can only be fixed with a larger steam injection. We focus on Diesel again. As we keep increasing the steam, we notice an improvement in the Kerosene-Diesel Gap. We leave this as an in-class exercise.