

Process Systems Engineering

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Exercise 5

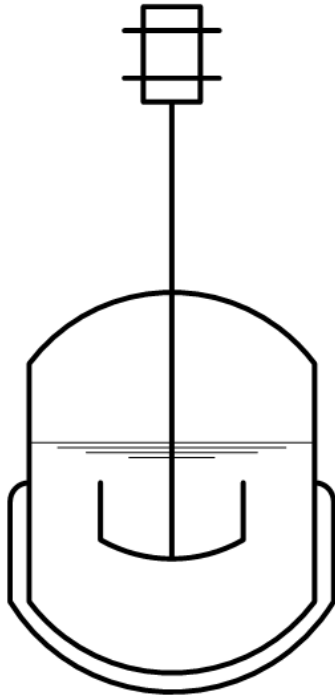
Simulation of HDA plant in UniSim[®]

Lab assistant: Adriana Savoca

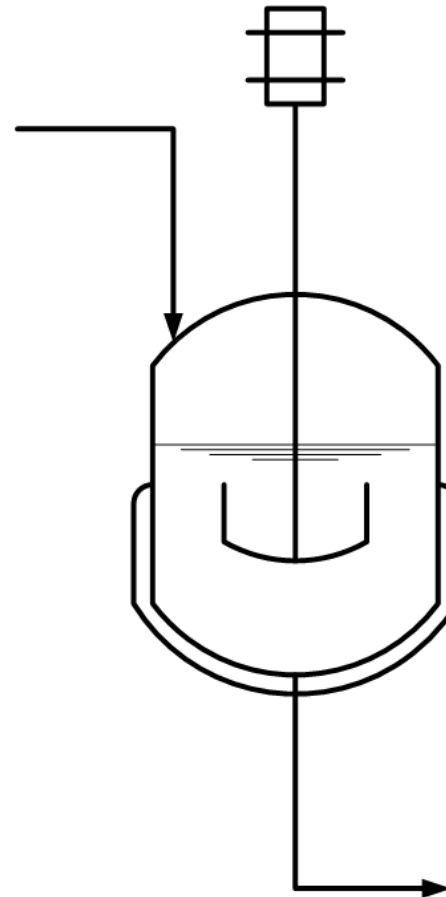


Level 1

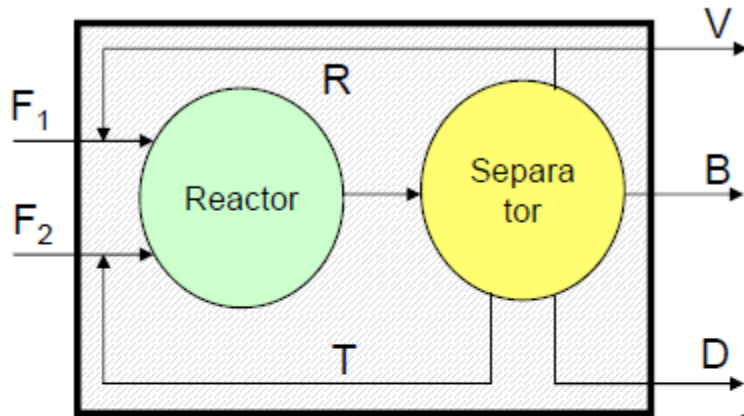
BATCH PROCESS



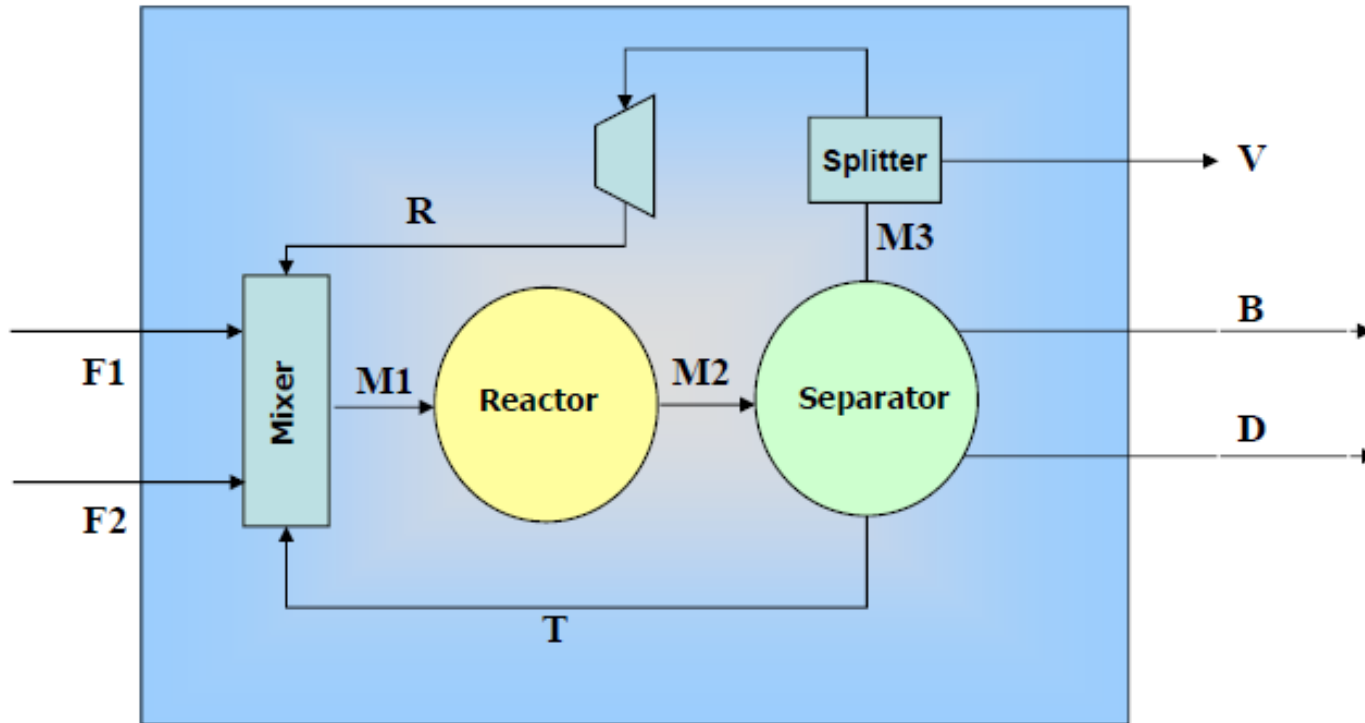
CONTINUOUS PROCESS



Level 2



Level 3



Defining EP_4

The economic potential of the fourth level is defined as:

$$EP_4 = EP_3 - \text{€}_{\text{separation section}}$$

with EP_4 in [M€/y].

- If the potential of the fourth level is greater than zero, the process may be economically attractive; *vice versa*, the process is definitely not economically interesting.
- **Remarks:** The cost of the flash is considered to be negligible, because it is much lower than that of a distillation column. Thus, it is not to be considered within the costs of the separation section.



Cost

Equipment costs are the sum of two contributions:

- the fixed costs of investment;
- operating costs.

In the calculation of EP4, the cost of columns and heat exchangers (*i.e.* reboilers and condensers, but also the furnace and other important process to process heat exchangers) is taken into account.

For the sake of simplicity, we will assume the same depreciation period for all the process units which is the one assumed for the EP3 assessment that it is 5 years.

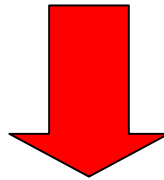
The investment costs are the sum of the physical costs of the material used for the construction of the equipment and processing costs (*i.e.* welds, ...).

The operating costs are dependent on the operating conditions, by the consumption of electrical energy and utilities (*i.e.* compressed air, oil, ...).



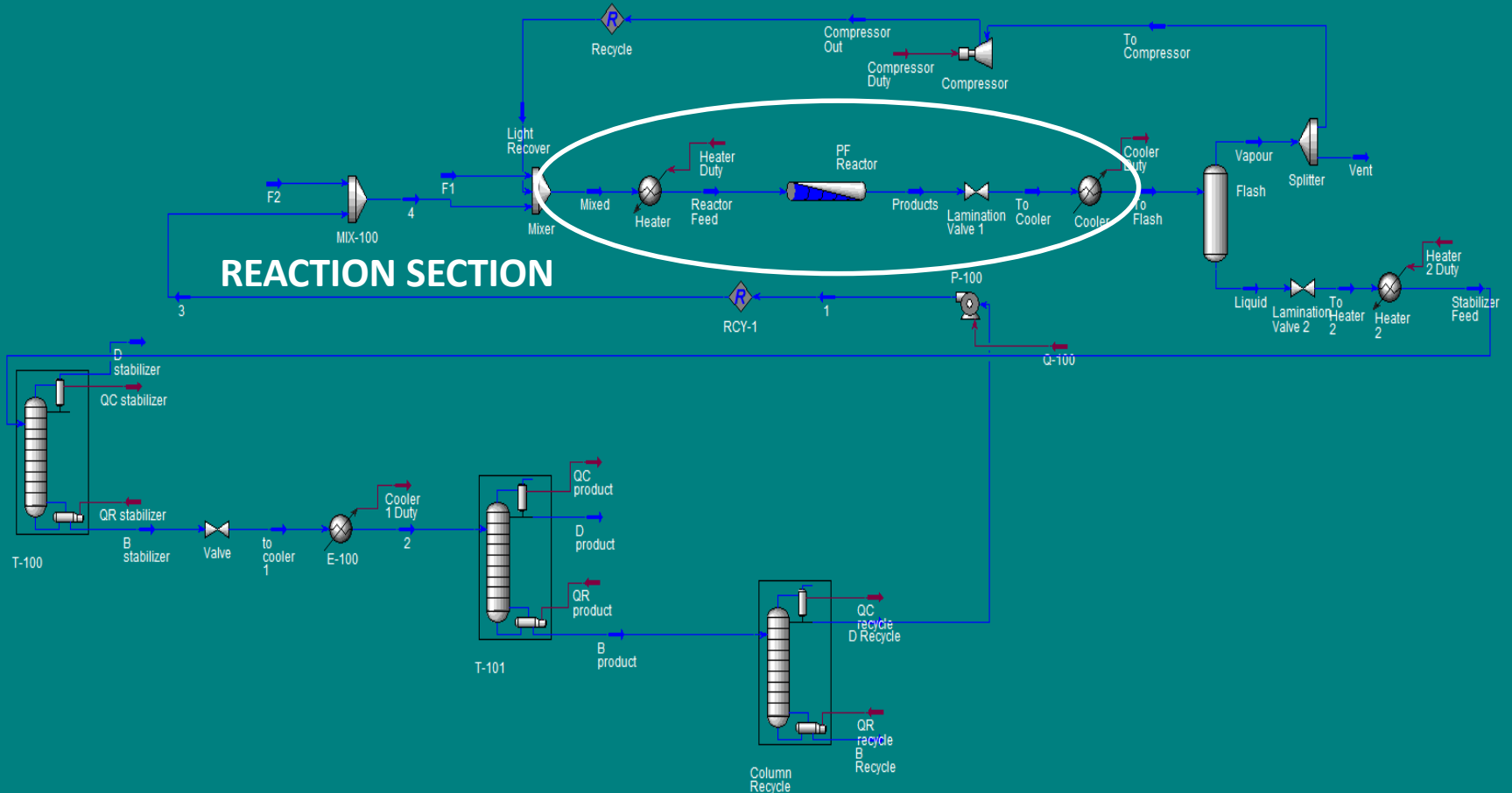
Problem!

- To calculate investment and operating costs of a column it is necessary to know the diameter and the number of trays required for the separation.
- In this phase, the hypothesis of ideal separation of the components is removed (as was introduced in the calculation of EP2). It is therefore necessary to introduce the tray efficiencies in the separator section.

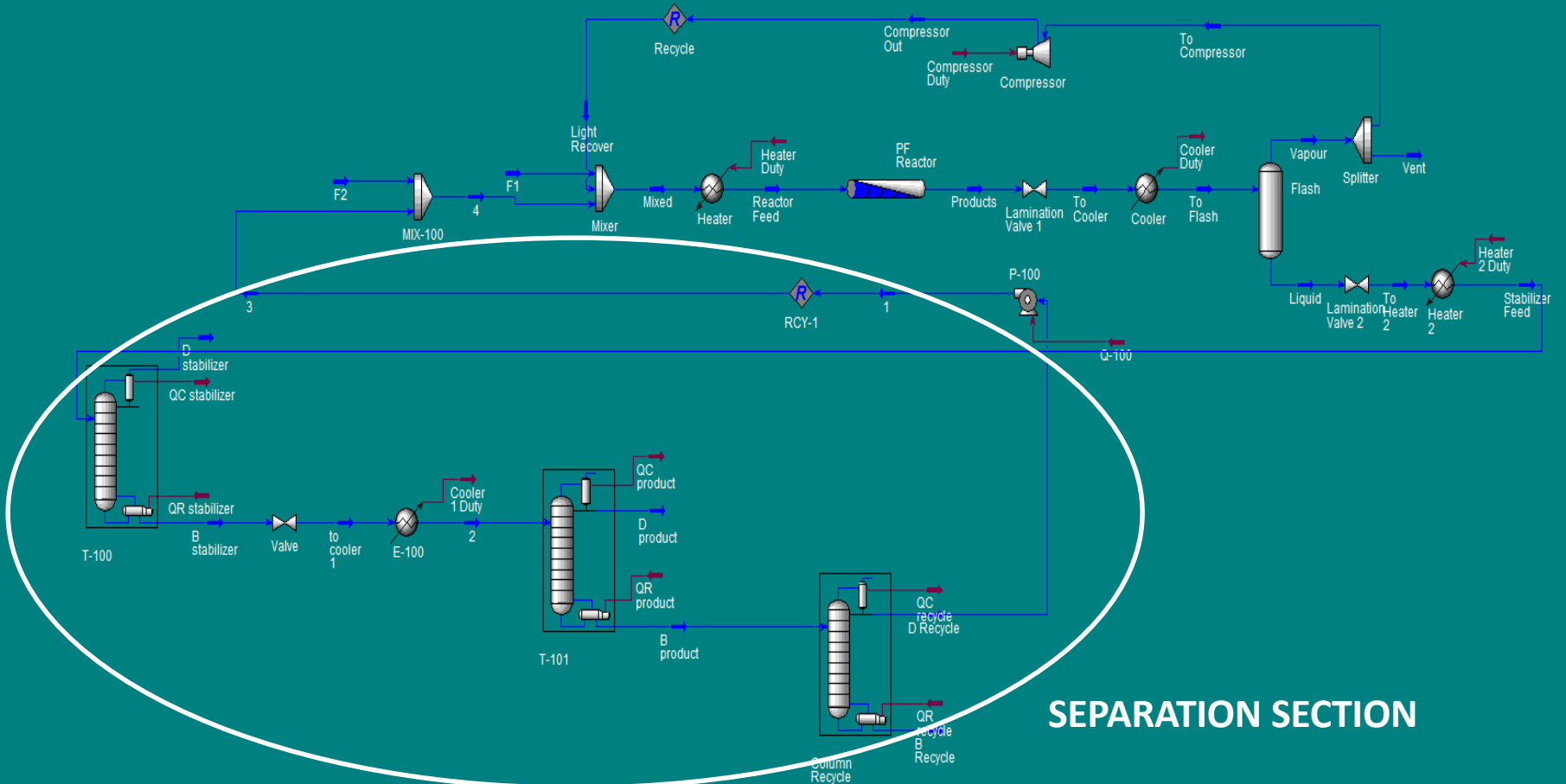


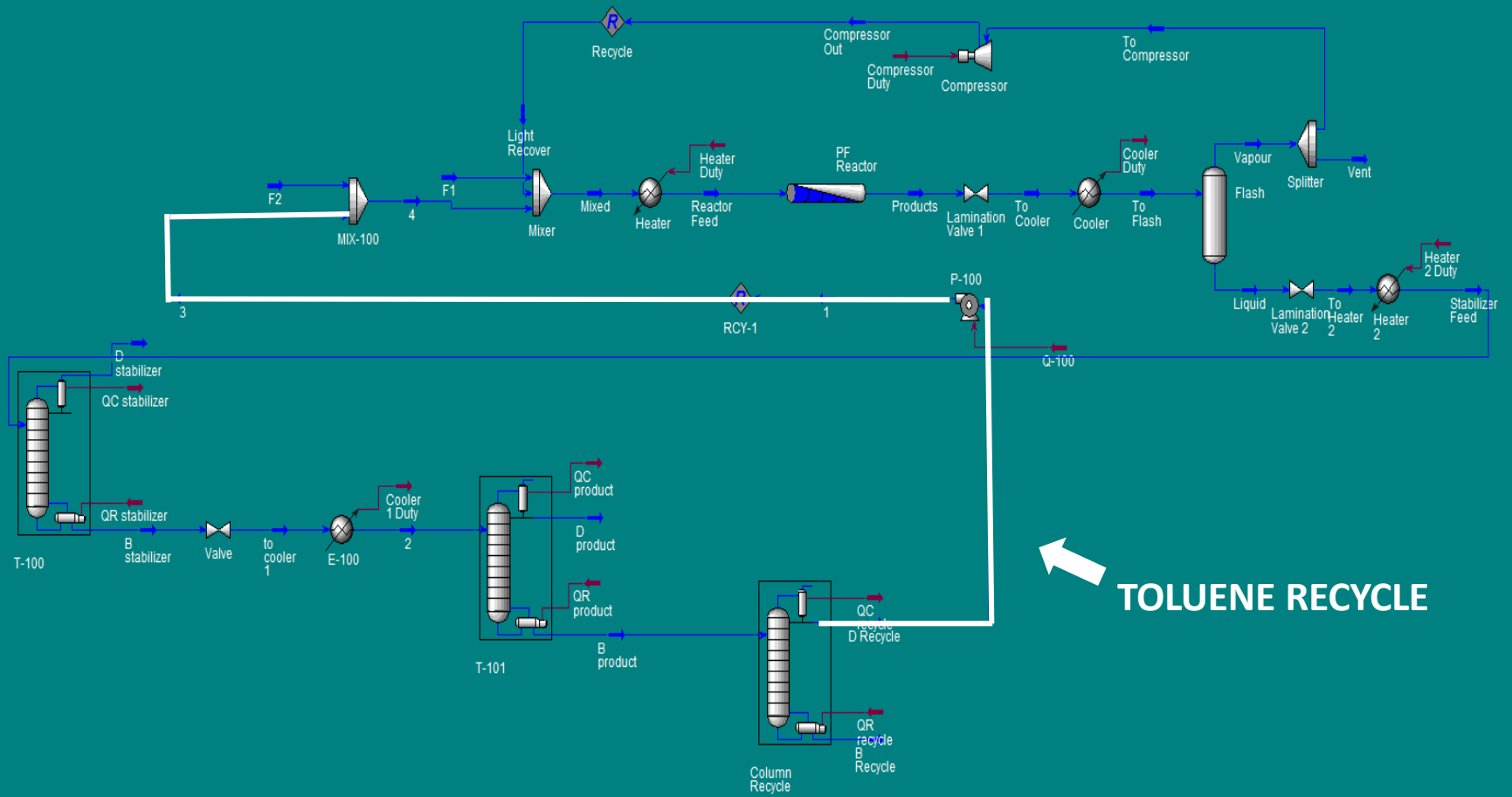
To simplify this complex operation you can simulate the system via a process simulator (UniSim®)!

Level 4



Level 4

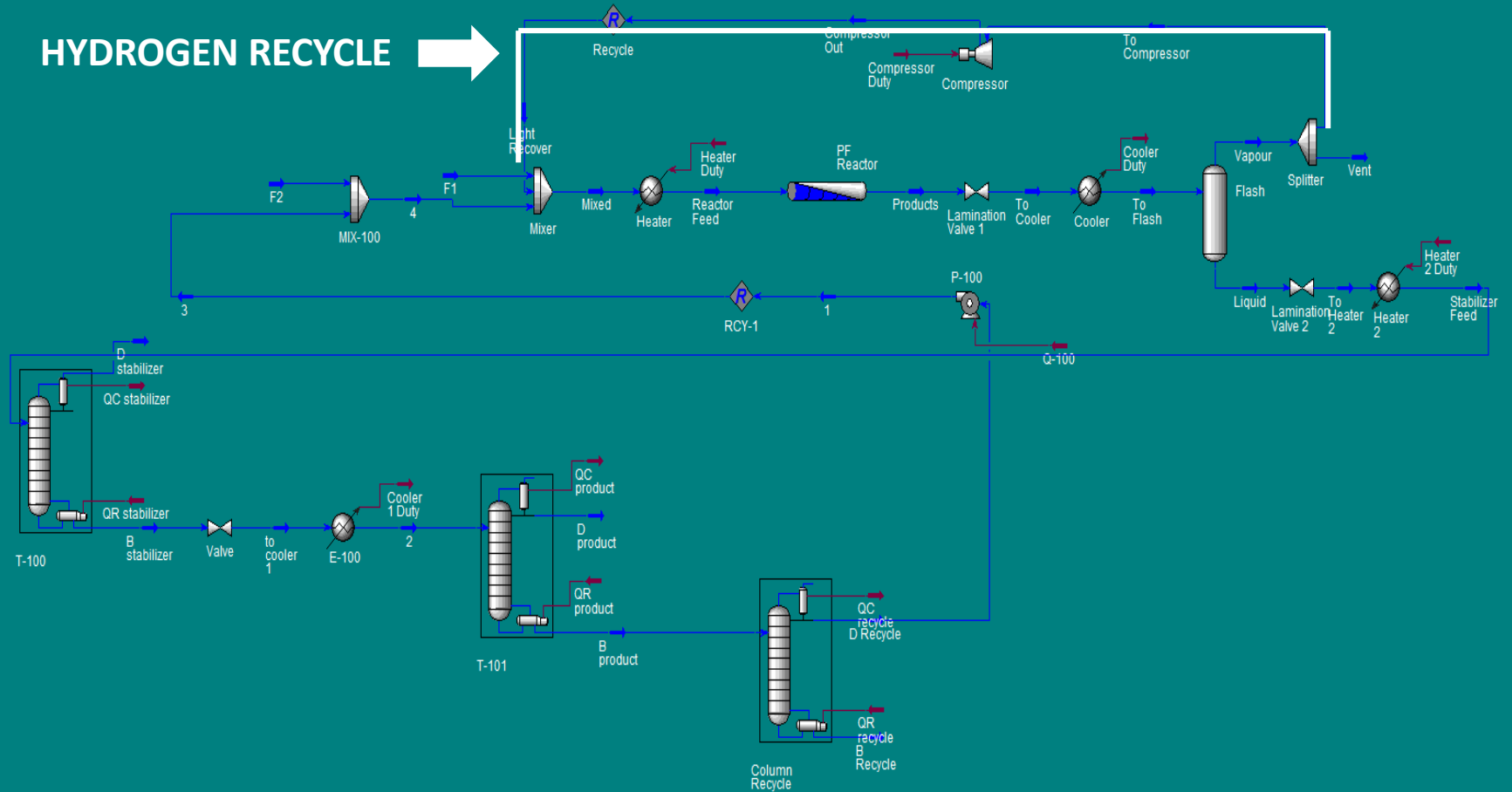




TOLUENE RECYCLE

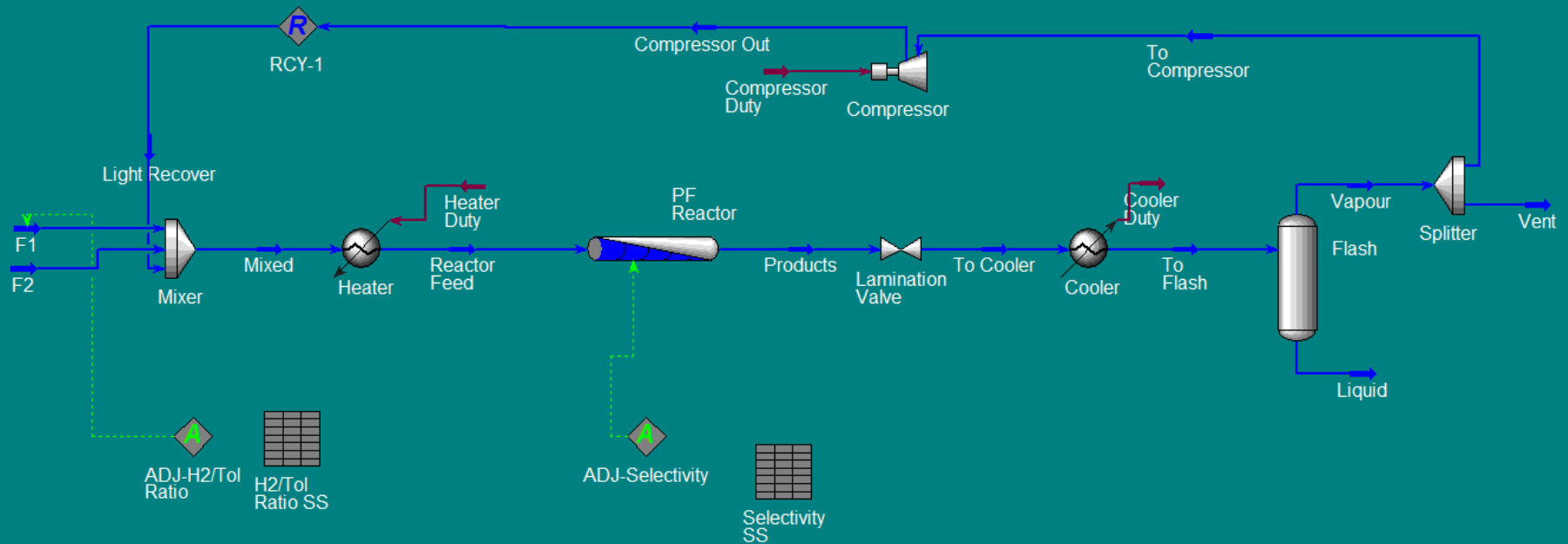


HYDROGEN RECYCLE



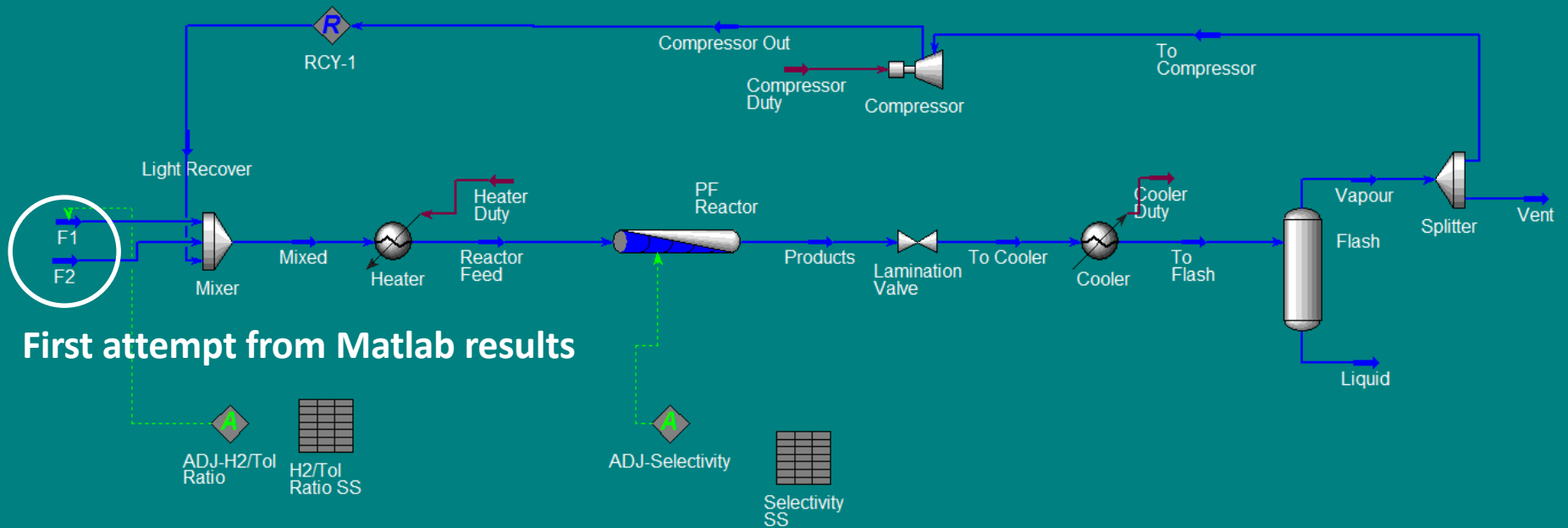
First steps

Until flash



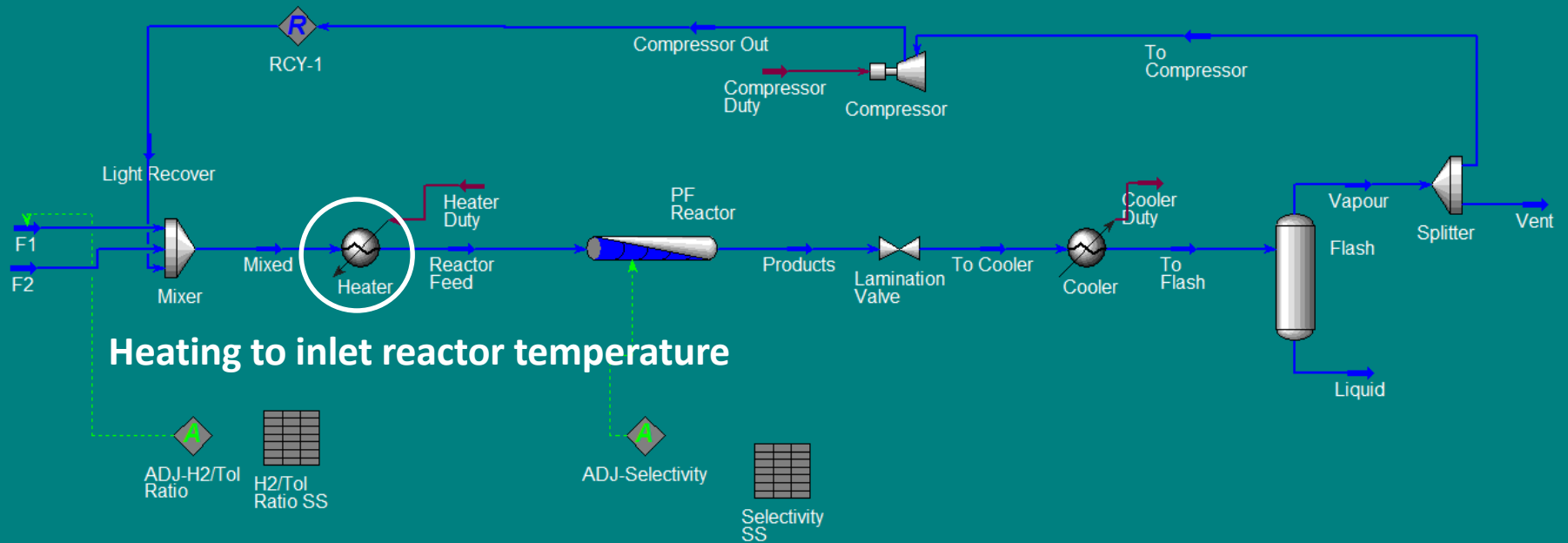
First steps

Until flash



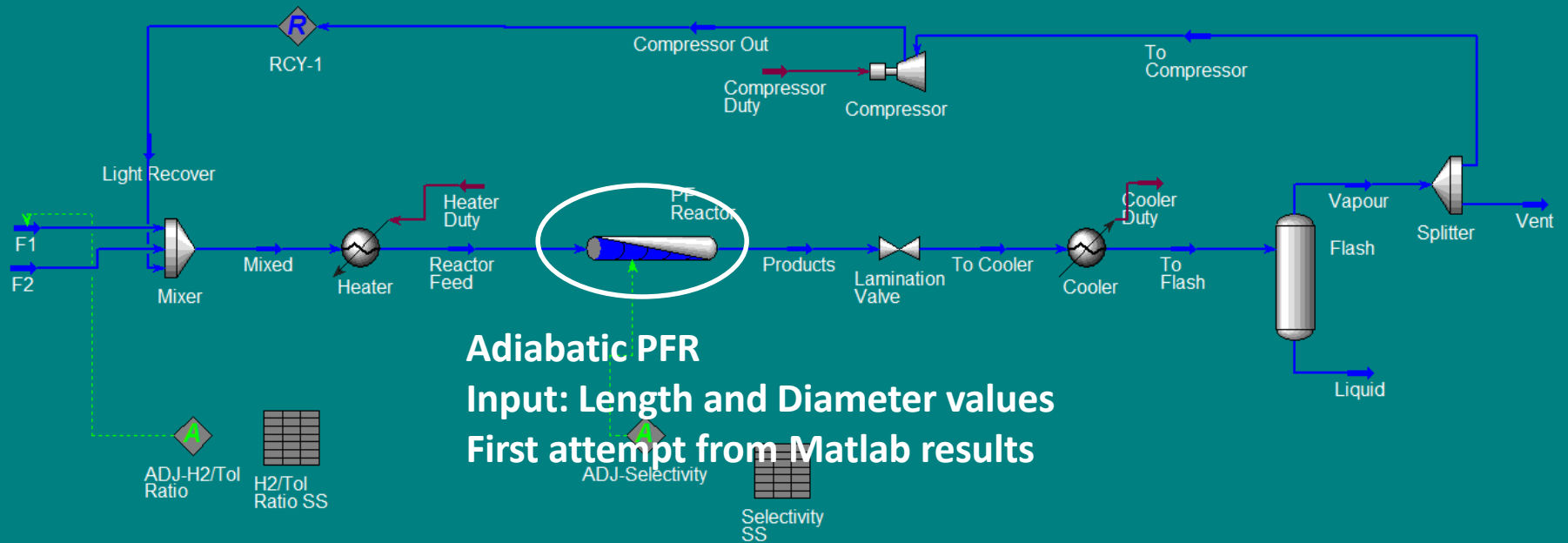
First steps

Until flash



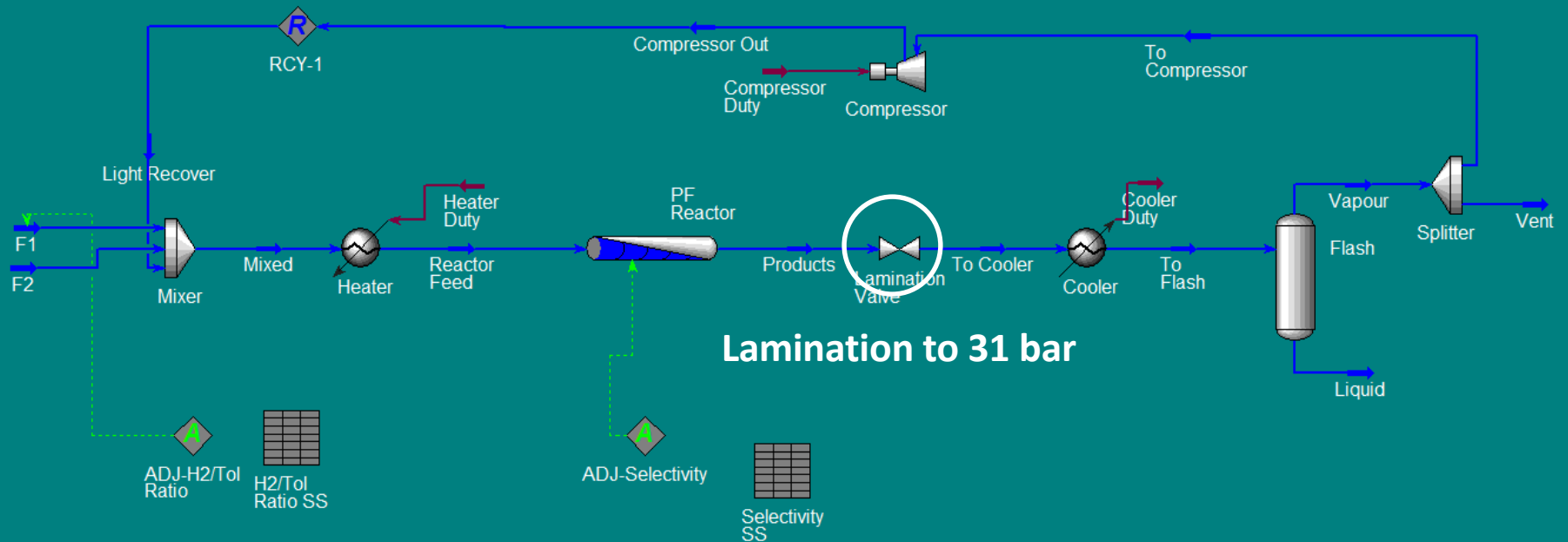
First steps

Until flash



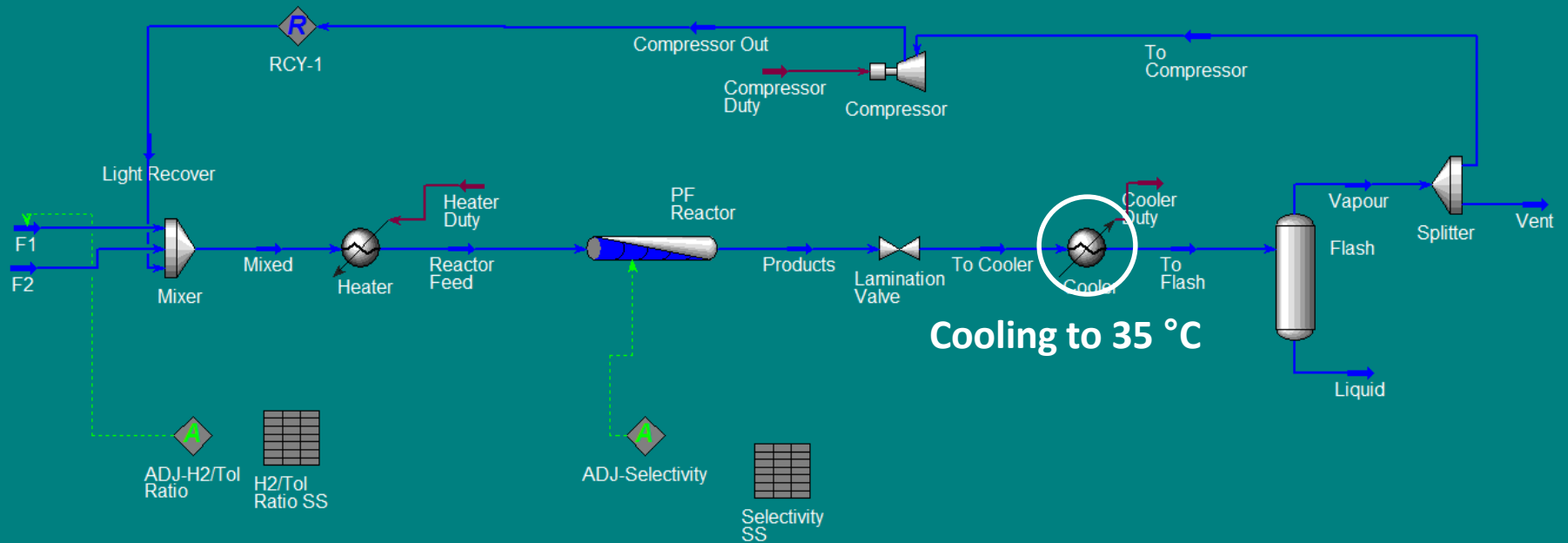
First steps

Until flash



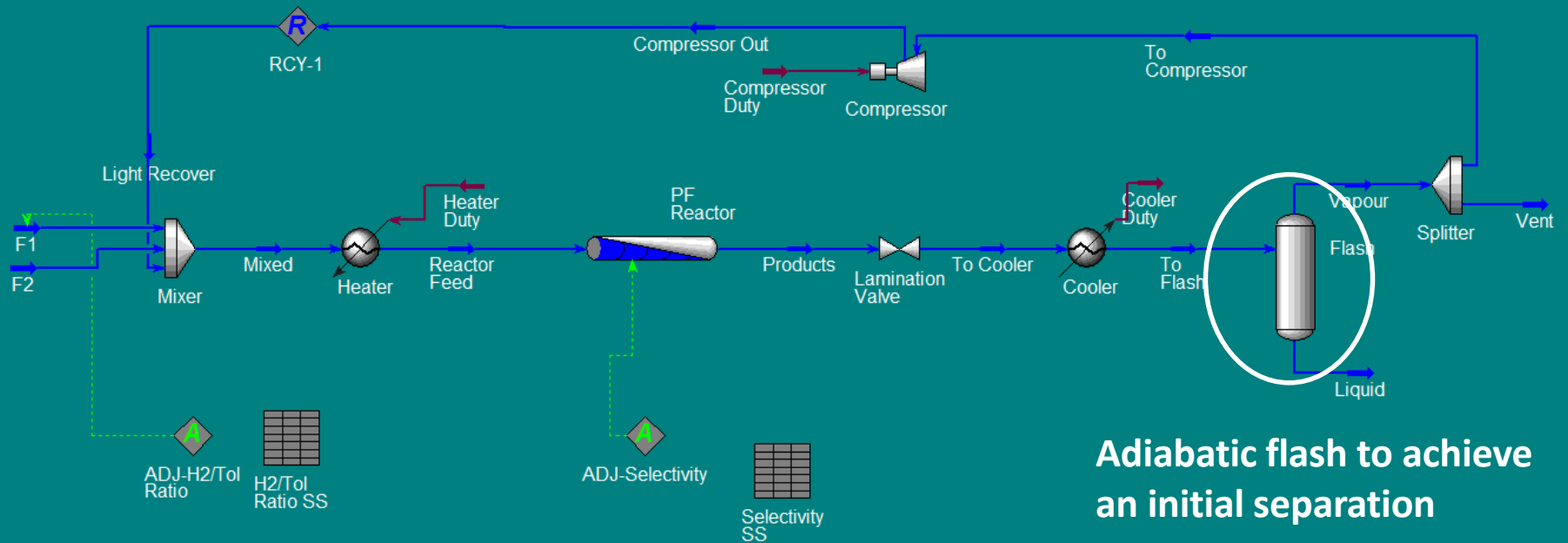
First steps

Until flash



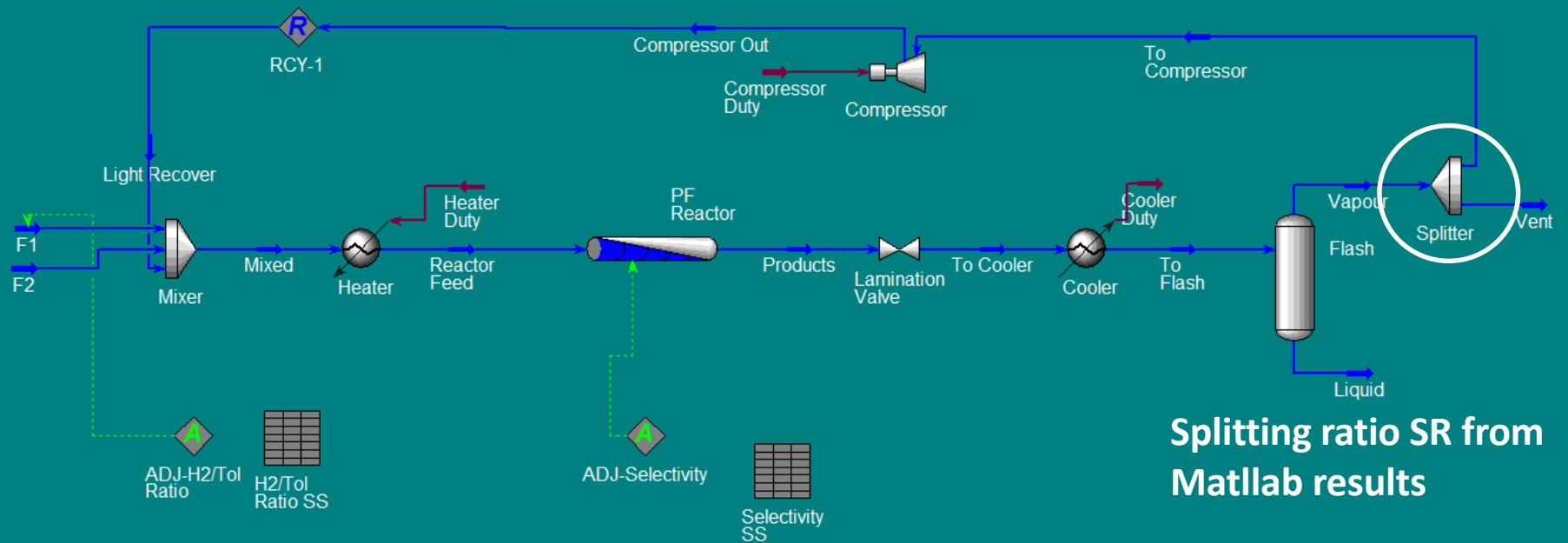
First steps

Until flash



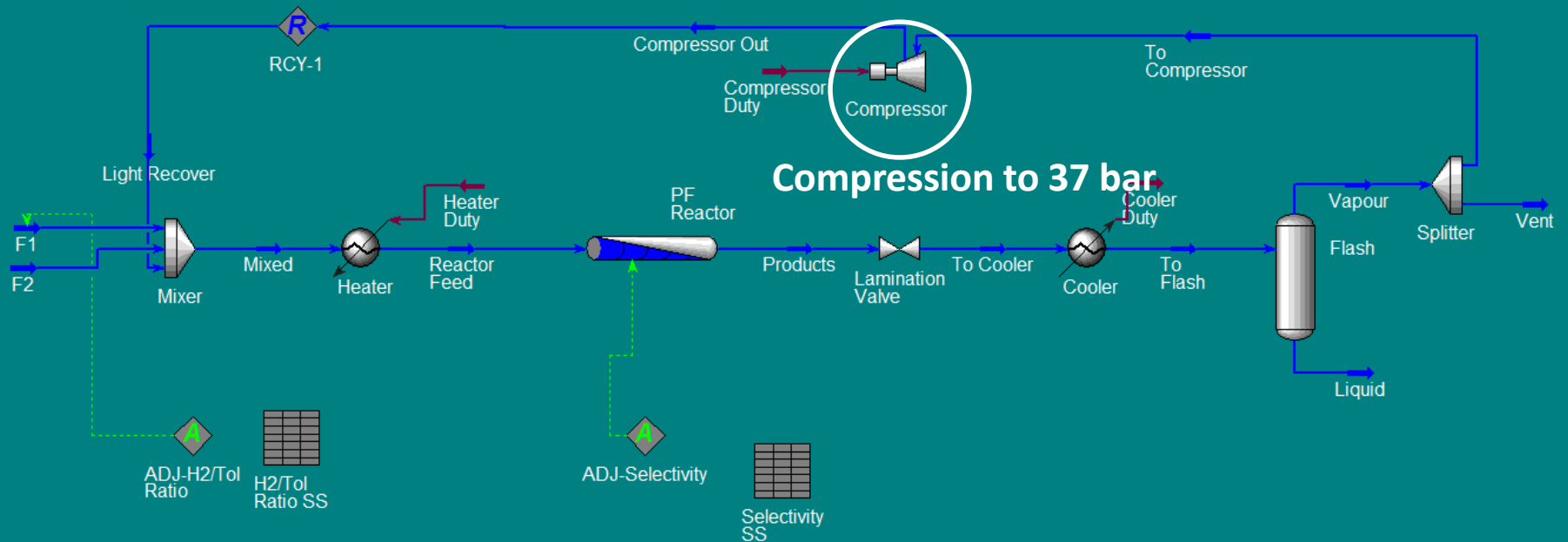
First steps

Until flash



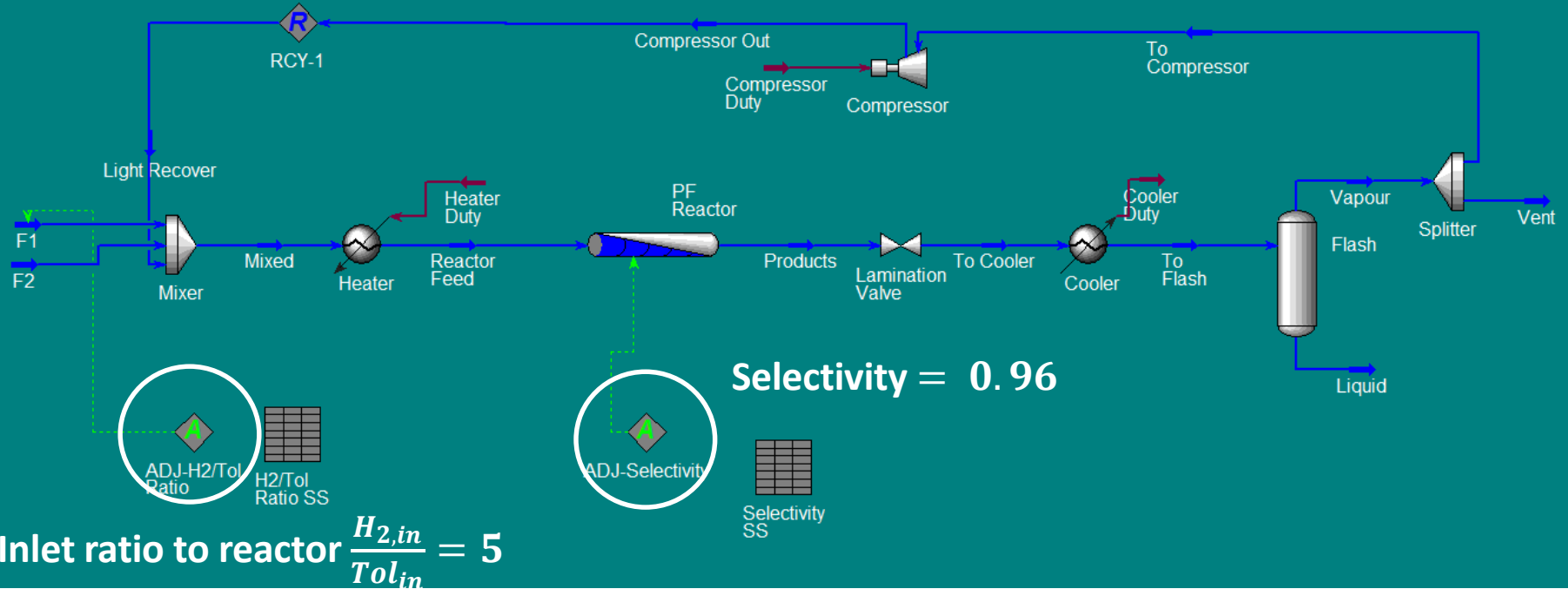
First steps

Until flash



First steps

Until flash



Data recap

Initial values of the material flows F1 and F2:

- From Matlab results corresponding to the optimal value of xv;

Heat exchanger:

- $T_{out} = 600-750^{\circ}\text{C}$;

PFR:

- Values of H, D [m] from Matlab results corresponding to the optimal value of xv;

Valve:

- $P_{out} = 31 \text{ bar}$;

Heat exchanger:

- $T_{out} = 35^{\circ}\text{C}$;

Adiabatic flash:

- The operative conditions are set by the valve and the heat exchanger; no other input is needed



Data recap

Splitter:

- Splitting ratio SR corresponding to the optimal value of xv;

Compressor:

- Pout = 37 bar;

Mixer:

- Set outlet to the lowest inlet;

Adjust 1:

- *Target variable*: Inlet ratio to the reactor
- *Adjustable variable* : F1 flow-rate

Adjust 2:

- *Target variable*: Selectivity
- *Adjustable variable*: Tube length



Some tips

- It would be better to use as first attempt the values of the process streams identified in the calculation of EP2. Thus simulating the first mixer accounting only for the fresh streams (F1 and F2), it is better accounting also for the recycling stream in the gaseous phase (R) and the recycling stream of toluene in the liquid phase (T).
- The feed ratio of 5:1 can be controlled by means of two operations: the "Spreadsheet", *i.e.* a spreadsheet where you can import the compositions of the two main components in the stream exiting the first mixer and then calculate the ratio, and the operator "Adjust", capable of acting on a dependent variable (the hydrogen feed F1), in order to reach the specified value of the target variable (the cell of the Spreadsheet where it is calculated the ratio between hydrogen and toluene).



UniSim - Setting up the simulation

To set up a simulation with UniSim® you must proceed according to the following steps:

- Select all the components involved in the simulation.
- Select the most appropriate equation of state (EoS).
- Provide information on the chemical reactions involved in the simulation.



UniSim - Chemical composition

- In the window "Simulation Basis Manager", the list of components can be entered by selecting the tab "Components". Add new components to the simulation by pressing the "View ...".
- You can search for a single component within the UniSim database in three ways:
 - Via the name in the database.
 - Via the real name of the chemical species.
 - Via the chemical formula
- Once you have selected the component of interest, press the button "*←Add Pure*".
- Once you have entered all the chemical species of interest, close the window.



UniSim - Equation of state

- In the window "Simulation Basis Manager", it is possible to select the most appropriate equation of state (EoS) by selecting the tab "Fluid Pkgs". Issues to be considered in the choice are the nature of mixture, the operating conditions, and the presence of phases splitting.
- For the simulation of the HDA plant, we recommend using the equation of state for vapor-liquid equilibrium called "RKS".



UniSim - Kinetic Scheme

- In the window "Simulation Basis Manager", by selecting the tab "Reactions", it is possible to add a set of chemical reactions.
- Using the button "Add Rxn ..." you can enter a single reaction in the kinetic scheme: at this point you need to select the typology of information to be provided (kinetics, equilibrium, conversion ...).
- Once you open the new window, in the menu "stoichiometry" insert chemical species taking part in the reaction, accompanied by their stoichiometric coefficients (note that those of the reactants are negative). Then make sure that the mass balance is satisfied.
- Within the tab "Basis" select the main component and the phase in which the reaction takes place.
- If the selection is conversion, the expression of the conversion is to be entered (note that it is in %).
- If the selection is kinetics, enter the pre-exponential term and the activation energy in the tab "Parameters".
- Once you've entered all the reactions, add the package thermodynamic by selecting the "**Add to FP**".



UniSim - Kinetic Scheme

It is possible to fit the kinetic scheme in different ways. For instance:

- **Reactions to conversion:** it is necessary to provide conversion of the reactions with respect to the main reactant (in case of the HDA, toluene and benzene respectively for the first and the second reaction) calculated by Matlab™ at 4 different temperatures. Within the simulation environment, it will be necessary to use a conversion reactor.
- **Reaction kinetics:** You must provide the kinetic parameters of the reactions. Once we are inside the simulation environment, it will be necessary to use a PFR reactor . Because of non-ideality of the reaction mixture, the conversion will be lower than that calculated by Matlab™; it will be therefore appropriate to resize the reactor to meet the specifications.



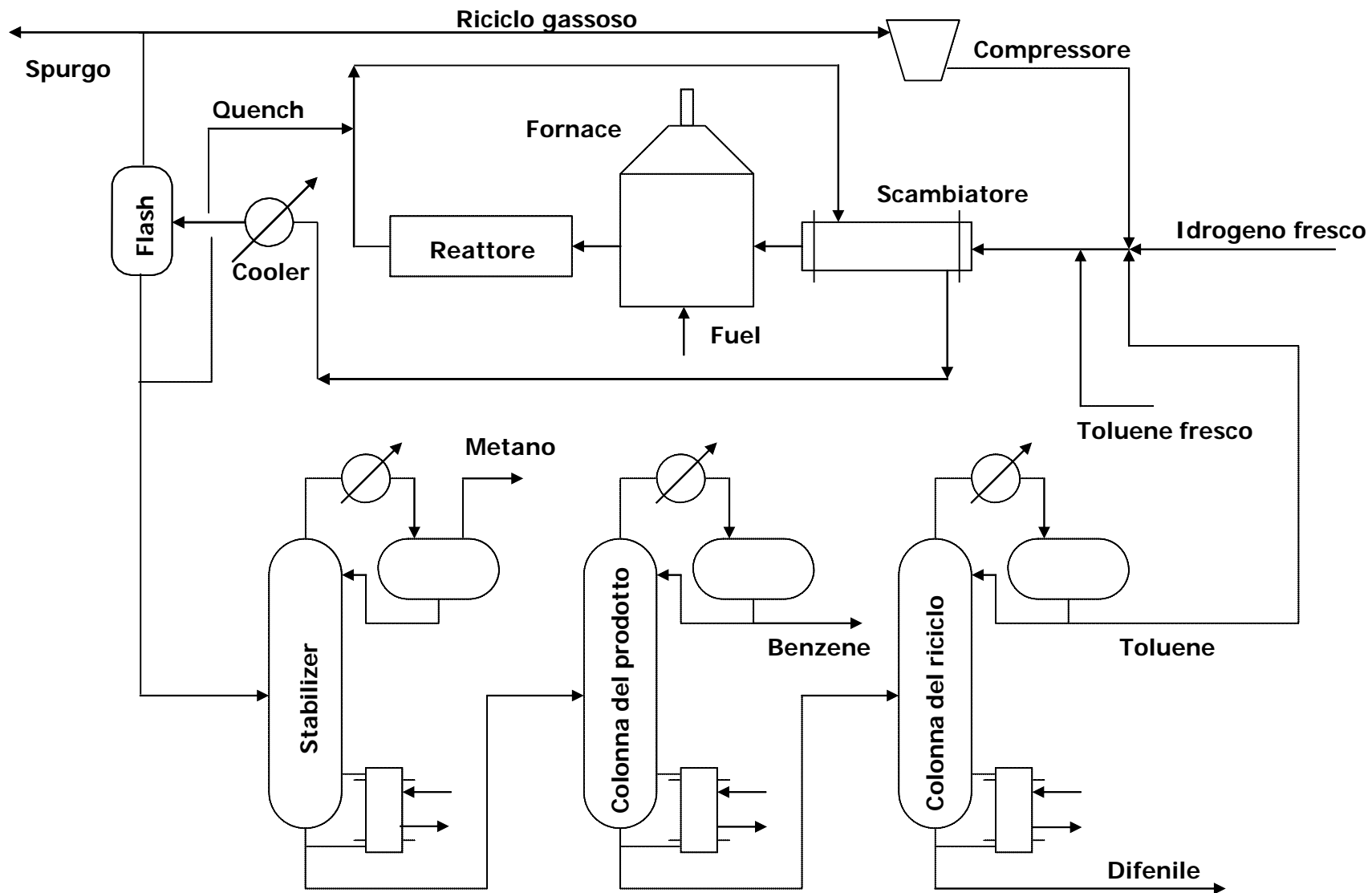
UniSim - Simulation environment

After completing all the above steps, you can enter in the simulation by pressing the "Enter Simulation Environment".

At this point it is possible to build the plant.



Flowsheet HDA (real plant)



Downstream of the Flash - Data

- Downstream of the flash, the **vapor phase** is re-circulated to the reactor after purging.
- The composition of the **liquid flow** coming out of the flash depends **ONLY** on the temperature and the molar fraction of hydrogen in the vent. This stream is heated to **$T = 93.35 \text{ }^\circ\text{C}$** and laminated to **3.6 bar** to be sent to the separation section.



Design of the separation section

Downstream of the flash, the liquid phase is sent to reach the specification on the purity of benzene (99.97% molar).

We have to design some columns to operate the separation between four different phases:

- Benzene (main product)
- light products (*i.e.* methane and hydrogen, burnt to produce energy within the plant, according to decision at level 2)
- Toluene (to be recycled to the reactor)
- Biphenyl (to be burnt to produce energy within the plant, according to decision at level 2))

You need to design a section separation, while working to minimize costs.



Design of the separation section

You need to separate four components: there are different options!

However, there are guidelines to help you select the most appropriate sequence:

1. Remove the CORROSIVE components first (this affects the selection of the material).
2. Remove components and REACTIVE MONOMERS.
3. Remove PRODUCTS streams and recycling as DISTILLATES in order to have purified streams that do not degrade the quality of the product and reactants.
4. In the case in which PRODUCTS and recycles are located at bottom of the column, it is better to vaporize them in the vapor phase and then condense them for the same reason as point 3.



Design of the separation section

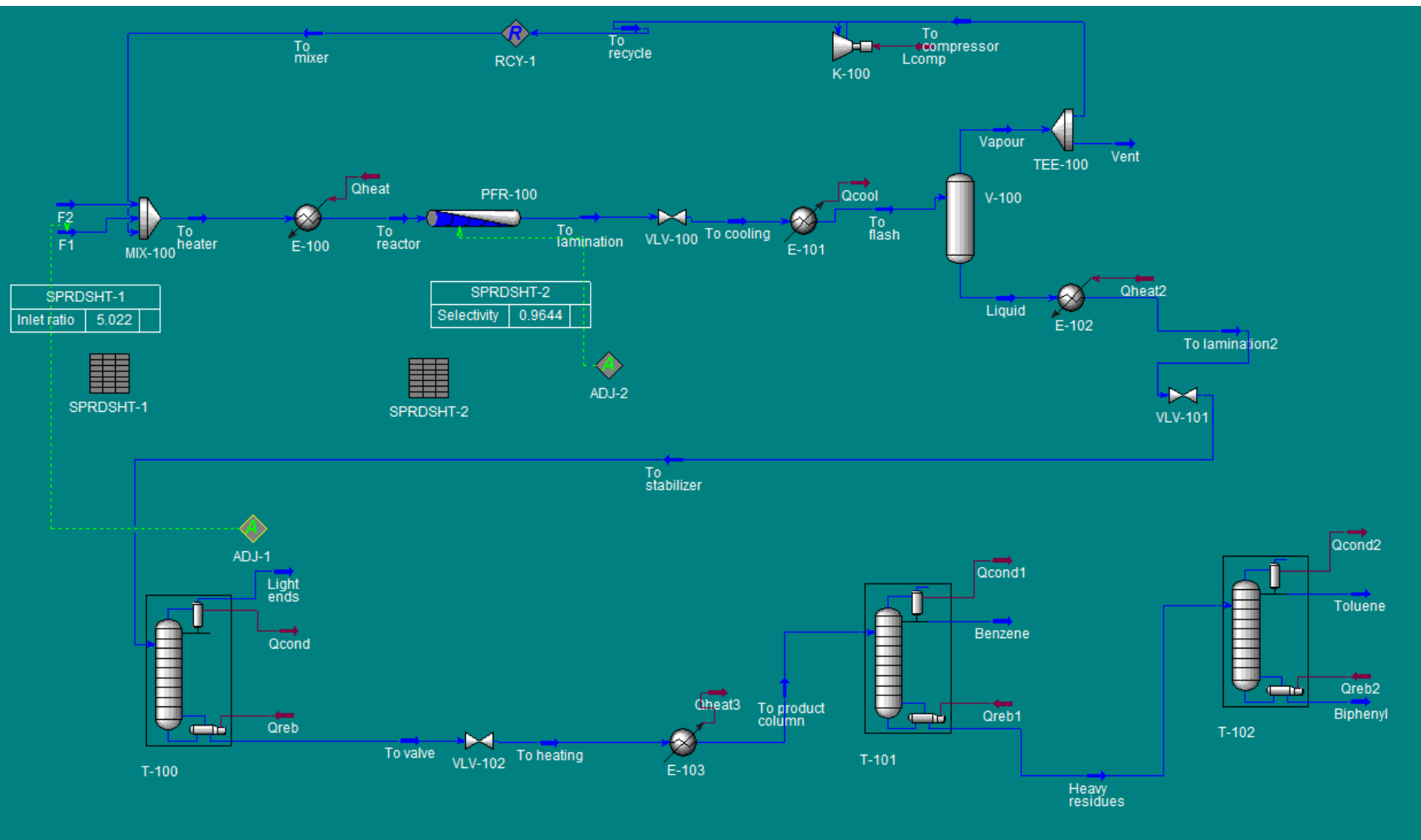
Following the guidelines, we can draw the following conclusions:

- Remove *light ends* first, by using a column (Stabilizer), also to avoid corrosion by hydrogen.
- To separate benzene, toluene, and biphenyl you can proceed in two different ways:
 1. Separate first Benzene from Toluene + Biphenyl and then from Toluene;
 2. First separate Benzene + Toluene from Biphenyl and then the Benzene from Toluene.

First option is more convenient, because Benzene is the most abundant compound. Furthermore, using the first solution, the main product (benzene) and the recycled stream to the reactor (toluene) will be separated as distillates of the columns, thus resulting streams are more likely to be purified.



Next steps: separation section



Column stabilizer

The stabilizer (full reflux) is made up of five real stages (3 trays) and its “feed stage” is 2nd. The top pressure is 3.573 bar.

The refrigerant to be used is water, as it is an economical fluid that does not create safety problems or corrosion. The inlet water temperature is 30 °C, whereas the maximum recommended output temperature is 38 °C.

Input data:

- Reflux ratio $\frac{R}{D} = 0.619$;
- Temperature of the light ends (to be calculated basing on the minimum required difference of temperature ΔT_{\min} , considering the maximum outlet water temperature);

Additional data (at T = 600 °C) (indicative, to check results):

- kettle reboiler duty = $2 \cdot 10^6$ kJ/h
- T_{bottom} estimated as 132 °C
- Light ends flowrate = 14 kmol/h

The liquid stream exiting the stabilizer is cooled to **T = 87.08°C** and laminated to **1 bar**.



Product column

For the design of the second column the **specifications** assigned at the top are:

- purity of the recovered benzene 99.97% molar;
- recovery of 99.5% with respect to benzene fed.

The column operates at atmospheric pressure ($P = 1 \text{ atm}$) and with a total condenser. For the calculation of the efficiency of the column, we use the formula:

$$E_0 = \frac{0.5}{(\mu_F \alpha)^{0.25}}$$

where μ_F is the viscosity of liquid feed to the bubble point measured in cP (centipoise - we recommend a value of 0.3 cP) and α is relative volatility of the two species to be separated.

Efficiency concept

The efficiency is related to the mass transfer, which depends on the geometry and the design of the trays by the flow rate, from the paths followed by the currents, from the composition.

You can define:

The efficiency of the column:

$$\eta = \frac{N_{id}}{N_{real}}$$

Basically you assign a unique value of efficiency to the entire column. Is it okay for a preliminary design? In fact the concept of efficiency is too articulated in order to be confined to a single parameter for the whole column.



Concept of efficiency

- The “local efficiency”: identifies the efficiency of a point on the plate, good for large diameter columns.
- The “tray efficiency” : also known as the Murphree efficiency. The calculation assumes a perfect mixing on the plate. For multi-component mixtures must be assigned an efficiency of tray for each of the components themselves.



Product column

The design of the product column should be entirely done by the student.

The column should be sized by methods **other** than McCabe and Thiele because it is not ideal (e.g. Fenske). It is possible to assume a reflux ratio 1.3 times the minimum ratio.

The choice will have to take into account that the lowering of number of trays involves an increase in the duties. Also remember to determine the optimal feed point.



Fenske-Underwood-Gilliland method

1) Selection of light-key component and heavy-key component

light-key: benzene

heavy-key: toluene

$$\alpha_B > \alpha_T > \alpha_D$$

NB. No distributed components between light-key and heavy-key components.

2) From the specifications and the following material balances we calculate the composition and flowrates at the top and the bottom of the column:

$$\begin{cases} Fz_i \cong Dx_{i,D} & i < lk \\ Fz_i \cong Dx_{i,D} + Bx_{i,B} & i = lk, hk \\ Fz_i \cong Bx_{i,B} & i > hk \end{cases}$$

NB. F and z_i come from Unisim results, but with the assumption that methane (whose fraction is in the order of 10^{-5}) is absent.



Fenske-Underwood-Gilliland method

3) Calculation of relative volatilities at the top and the bottom of the column

$$\alpha_{i,hk} = \frac{P_0(T)_i}{P_0(T)_{hk}} \quad \text{relative volatility of component } i \text{ respect to } hk$$

4) N_{min} calculation: Fenske correlation

$$\left(\frac{Dx_{i,D}}{Bx_{i,B}} \right) / \left(\frac{Dx_{hk,D}}{Bx_{hk,B}} \right) = \alpha_i^{N_{min}} \xrightarrow{i=lk} N_{min} = \frac{\ln \left(\frac{Dx_{lk,D}}{Bx_{lk,B}} \cdot \frac{Bx_{hk,B}}{Dx_{hk,D}} \right)}{\ln \alpha_{lk}}$$

$$\alpha_{average} = \sqrt[3]{\alpha_{top} \alpha_{bottom} \alpha_{feed}}$$



Fenske-Underwood-Gilliland method

5) R_{min} calculation: Underwood equations

$$1) \sum_{i=1}^{NC} \frac{\overline{\alpha}_i \cdot z_i}{\overline{\alpha}_i - \theta} = 1 - q$$
$$2) \sum_{i=1}^{NC} \frac{\overline{\alpha}_i \cdot x_{i,D}}{\overline{\alpha}_i - \theta} = R_{min} + 1$$

Enthalpy factor

$$q = \frac{h^V - h^F}{h^V - h^L}$$

NB. Molar enthalpies from Unisim.

6) R calculation: heuristic rule

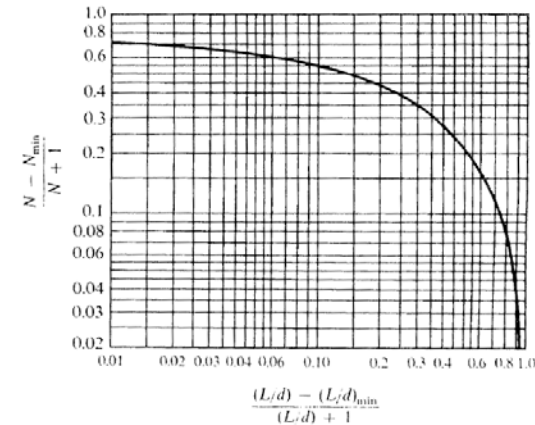
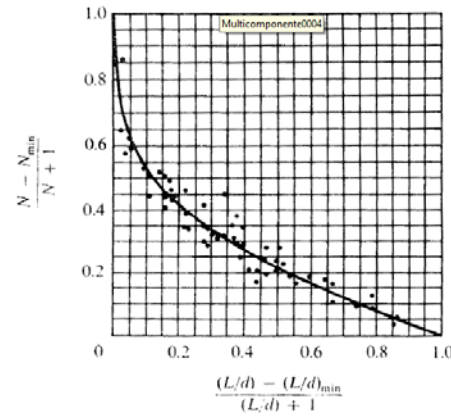
$$R_{opt} = 1.3 R_{min}$$

Fenske-Underwood-Gilliland method

7) Gilliland diagram

$$\phi(N) = \frac{N - N_{\min}}{N + 1}$$

$$F(R) = \frac{R - R_{\min}}{R + 1}$$



Gilliland correlation. (Adapted from Robinson and Gilliland, 1950, pp. 348 and 349; used by permission.)

$$\phi = 0.75 - 0.75F^{0.5668} \quad \text{Eduljee}$$

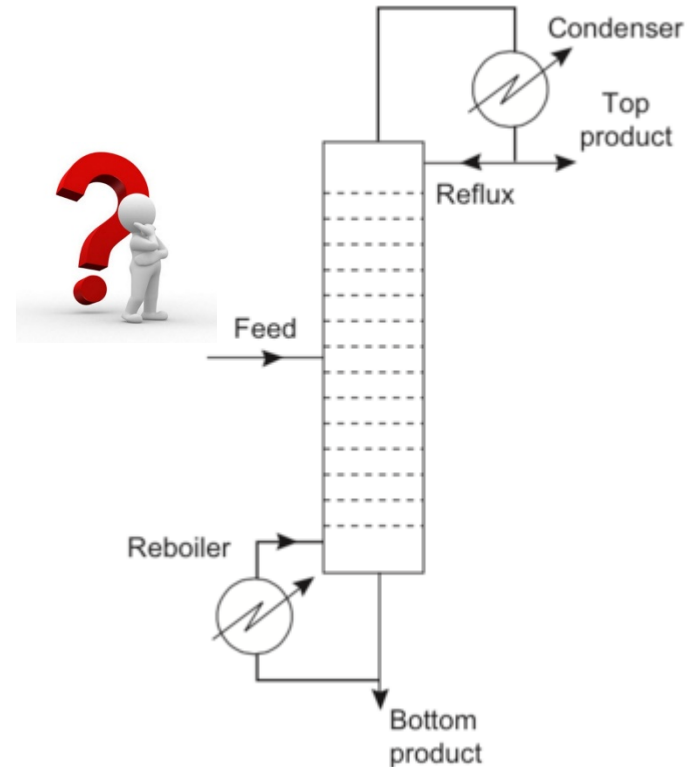
$$\phi = 1 - e^{\left(\frac{1 + 54.4F}{11 + 117.2F} \cdot \frac{F - 1}{\sqrt{F}} \right)} \quad \text{Molokanov}$$

Fenske-Underwood-Gilliland method

8) Optimal feed point: Fenske correlation

$$N_{\min, INF} = \frac{\ln \left(\frac{z_{lk} \cdot x_{hk,B}}{z_{hk} \cdot x_{lk,B}} \right)}{\ln \alpha_{lk, INF}}$$

$$\frac{N_{INF}}{N_{\min, INF}} = \frac{N}{N_{\min}}$$



Recycling column

Specifications: You are required to recover:

- Top product at 99.5% of the toluene fed;
- Bottom product at 99.5% of biphenyl fed.

The real stages are 20 (18 trays) and the “feed tray” is at 14th stage (numbered from the top). The column works at atmospheric pressure with a total condenser. The efficiency of the column is computed with the formula previously presented.

Additional data (at $T = 600\text{ °C}$) (indicative, to check results):

- Condenser duty of $1,35 \cdot 10^6$ kJ/h
- Kettle reboiler duty of $1,4 \cdot 10^6$ kJ/h
- Biphenyl flowrate = 4 kmol/h



Close toluene recycle

Pump:

- $P_{out} = 34$ bar;

Recycle operator:

- No input data₁

Adjust operator:

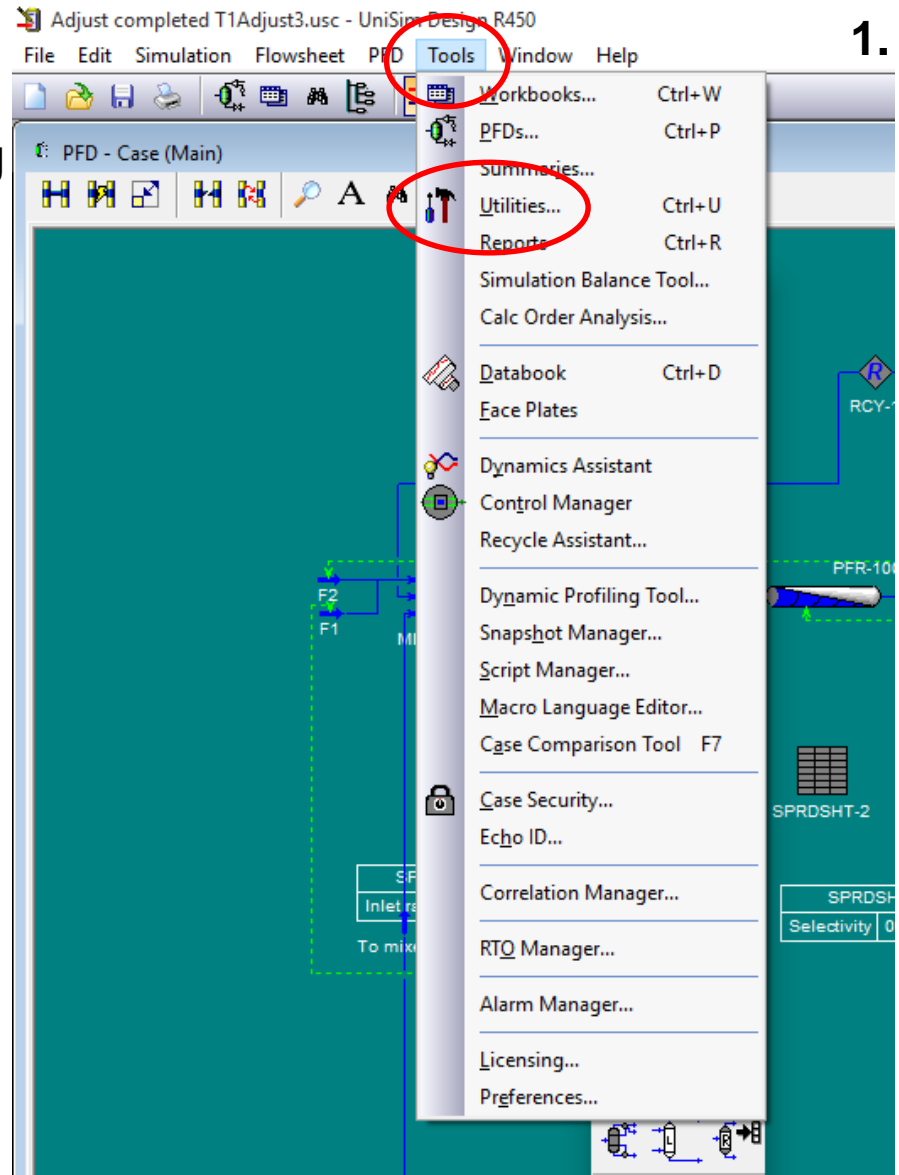
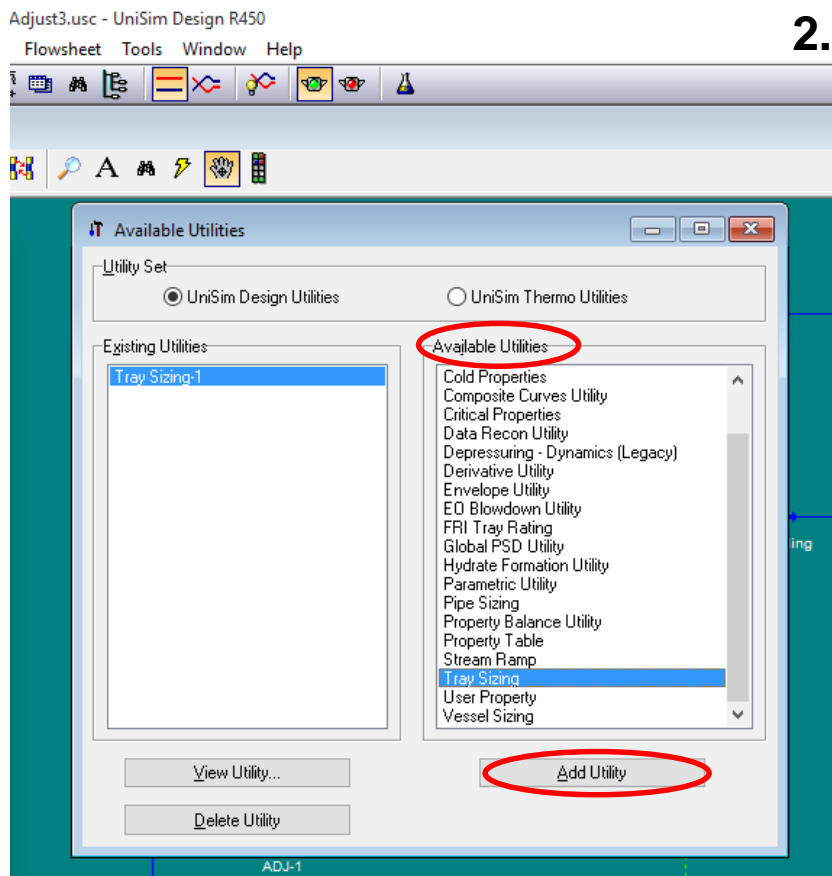
- *Target variable*: Benzene productivity (benzene flowrate in the distillate flowrate of the product column)
- *Adjustable variable* : F2 flow-rate

NB. Make sure that you “*ignore*” the two other adjust operators **before** you connect the recycle and put the adjust operator on the benzene productivity.



Tray sizing - Auto Section tool

1. **Ctrl + U** or **Tools** → **Utilities**:
2. **Available Utilities**: select **Tray Sizing** → **Add utility**



Tray sizing - Auto Section tool

3.

3. Select TS → Select Tray section

4. Auto Section

5. See Performance to visualize results and potential warnings.

4. and 5.

