The Ethylene is one of the most important products of the petrochemical industry, as a monomer to produce many other compounds such as polymers. Nowadays, to overcome the dependence from oil and fossil fuels, other strategies are investigated from renewable feedstocks. In the case of ethylene bioethanol is the most important alternative following a dehydration reaction.

The aim of this thesis is to simulate an industrial plant to produce ethylene from bioethanol, using a kinetic equation to size the reaction section in Aspen Plus and, thus, simulate the purification of the crude ethylene to obtain a high purity grade material. The reaction considered in the kinetic model and the relative kinetic parameters, are reported below:

$C_2H_5OH \rightleftarrows C_2H_4 + H_2O$ (1)

$2\ C_2H_5OH \rightleftarrows C_2H_5OC_2H_5 + H_2O$ (2)

$C_2H_5OH \rightleftarrows CH_3CHO + H_2$ (3)

$C_2H_5OC_2H_5 \rightleftarrows 2C_2H_4 + H_2O$ (4)

$2C_2H_4 \rightleftarrows C_4H_8$ (5)

$CH_3CH_2OH \rightarrow CO + CH_4 + H_2$ (6)

$CH_3CH_2OH + H_2O \rightarrow CO_2 + CH_4 + H_2$ (7)

	Kinetic constant	Activation energy (kJ/mol)
Reaction 1	454	133
Reaction 2	0.643	80.2
Reaction 3	2.19×10^{6}	143
Reaction 4	2390	107
Reaction 5	0.00685	132
Reaction 6	1.13×10^{-7}	122.9
Reaction 7	3.06×10^{-7}	195.5

The simulation is done using a combination of thermodynamic models, in almost all plant Redlich-Kwong-Soave Equation of state (EoS) for gaseous phase or at high pressure, Non-Random Two Liquids/ Redlich-Kwong EoS for mixed phases at low pressure and Henry constants with respect to water for supercritical components (as ethylene, hydrogen, etc.). In some section the thermodynamic model must be changed, in order to fit the different physical condition.

The reaction sections are simulated rigorously, foreseeing also a recycle of unreacted ethanol and the possibility to work with a huge amount of water, so avoiding a purification of the feedstock to use diluted bioethanol directly.

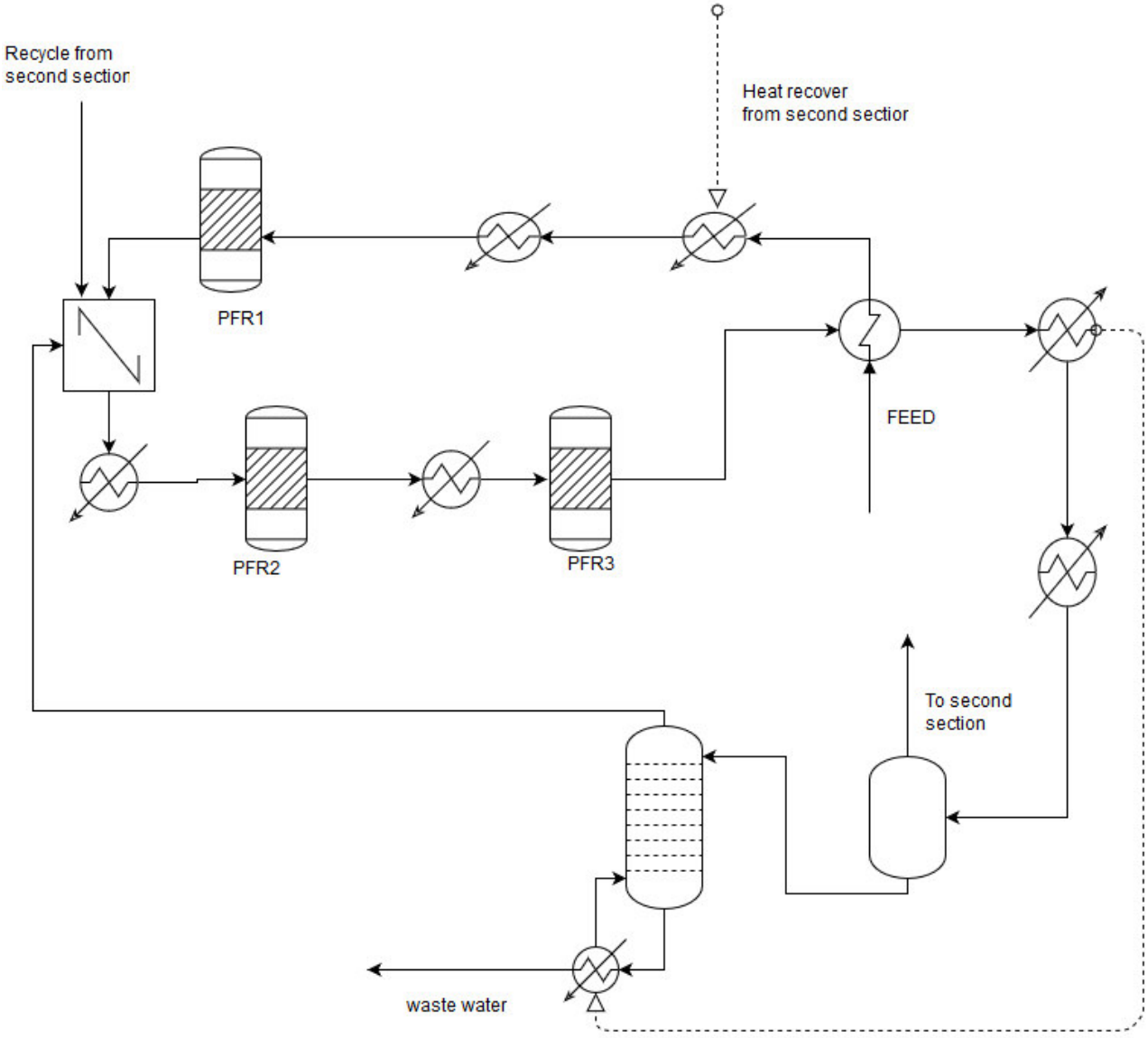

Figure 1: Reactor section with first purification and ethanol recycle.

An attempt is done also using just one bigger and more complex column, instead the previous configuration with one flash followed by one column. Nevertheless, this choice turns out to be less convenient from the energetic and economic point of view, therefore the first configuration is preferred and has been used to complete the plant.

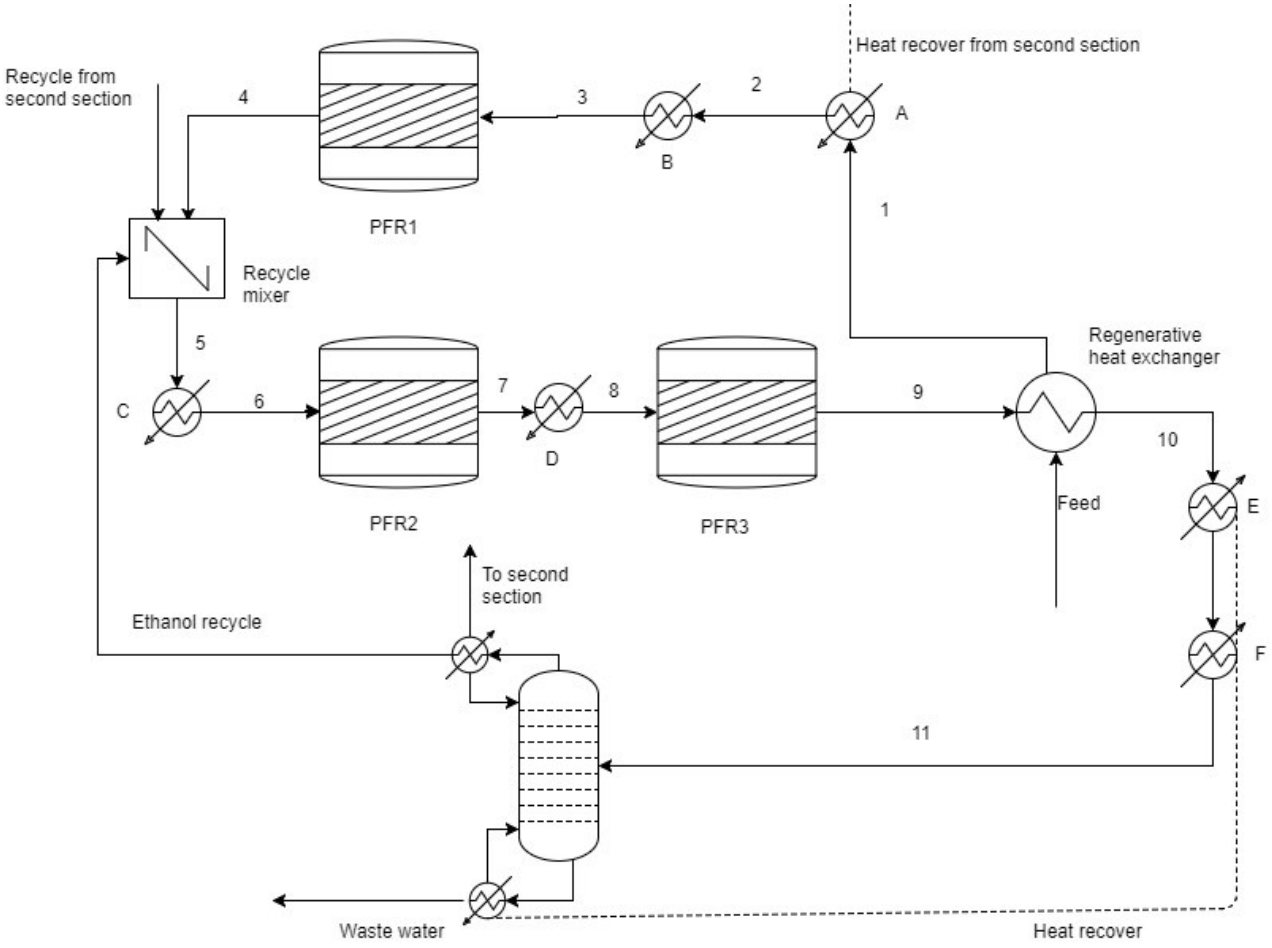

Figure 2: Flowsheet of the reactor section (alternative solution, only one column)

After the reaction section the purification of ethylene is simulated, following the strategy that is already implemented in some industrial plants that are already present worldwide. Due to the pressure increase in the second section of our flowsheet, experimental data were necessary to validate the consistency of the previsions given by Aspen Plus. However, in literature we found data collected at much higher pressure than needed, so the thermodynamic method, NRTL-RK, has been chosen because it allowed us to correctly simulate the separation of water and ethanol from the low boiling point compounds and because these results were in accordance with those find in the literature, using the same cycle to remove as much as possible water from the ethylene stream

So, the greater amount of water is removed by a cycle of compression, cooling and flash in the second section of the plant, to remove water as much as possible from the ethylene stream.

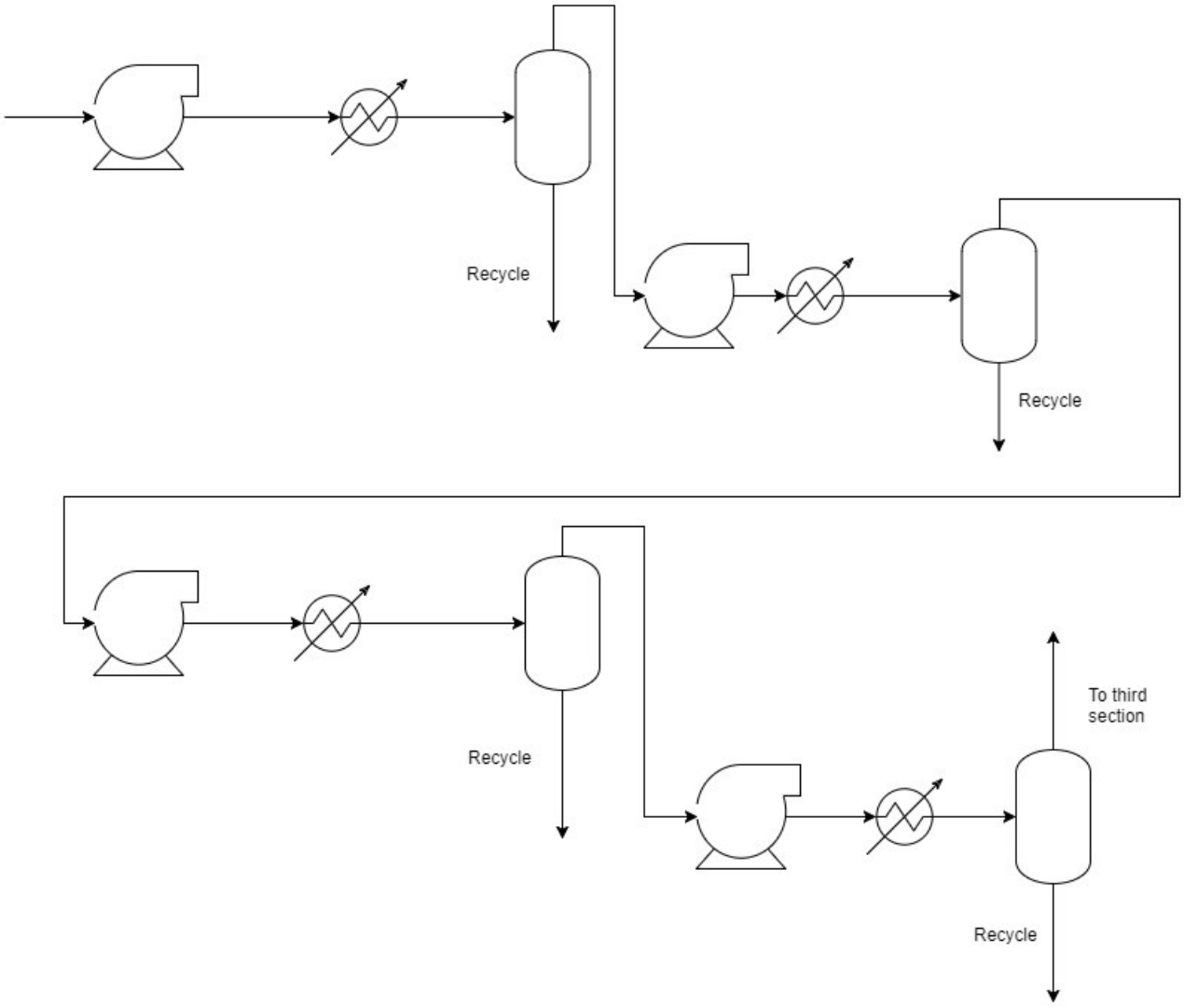

Figure 2: Second section

Then in the third section the CO_2 is removed using an innovative adsorption column with a ternary ammine (MDEA) that can be recycled, so the formation of waste can be avoided. Before the last cryogenic distillation, the water must be further removed, so a dynamic simulation of an adsorber is performed, where a zeolite bed adsorb water and then is regenerated using half part of dry ethylene that after must recycled back at the beginning of the third section.

In the Aspen Plus the equilibrium constant must be included using this equation:

lnK= A+B/T+ClnT+DT

Where K is the equilibrium constant and B, C, D are non-dimensional parameters, while A is calculated on molar fraction scale. The parameters for the reaction 8a and 8b have been calculated using the Aspen Plus data base since both are well known reaction

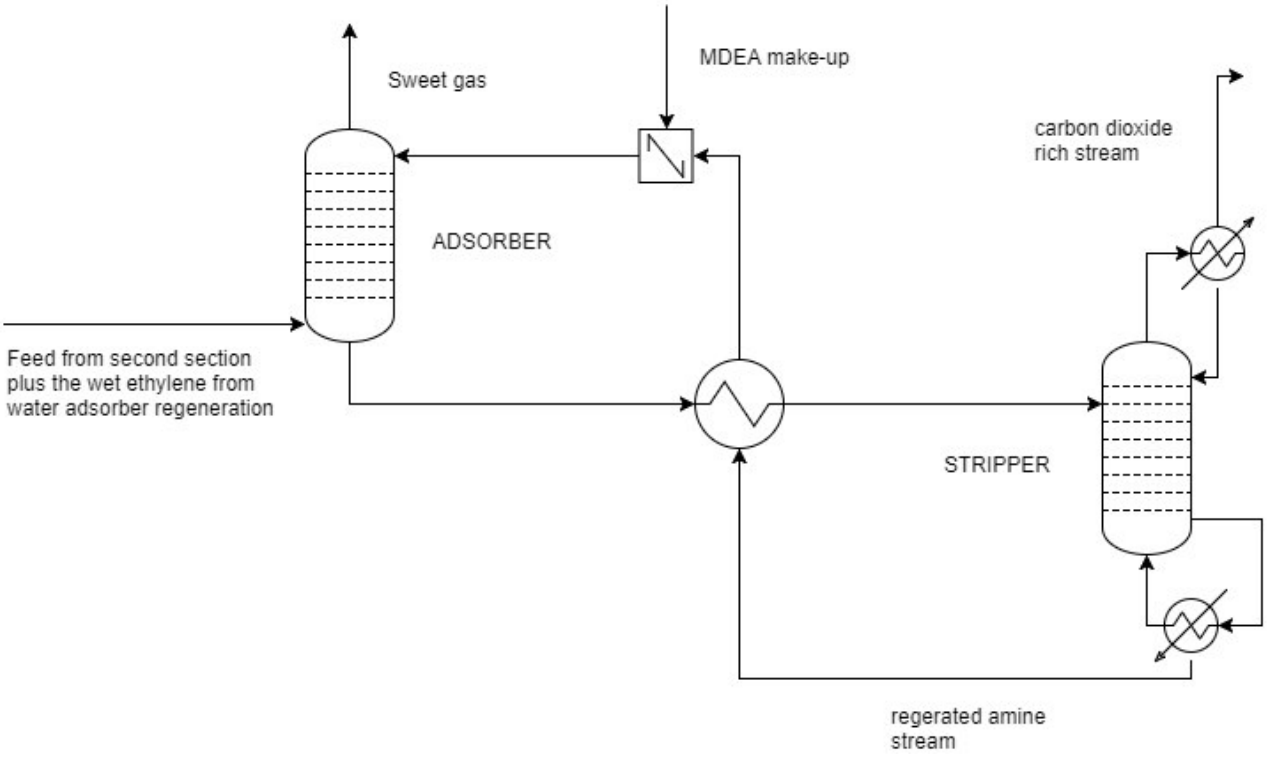

Figure 3: CO_2 adsorption and ammine recycle

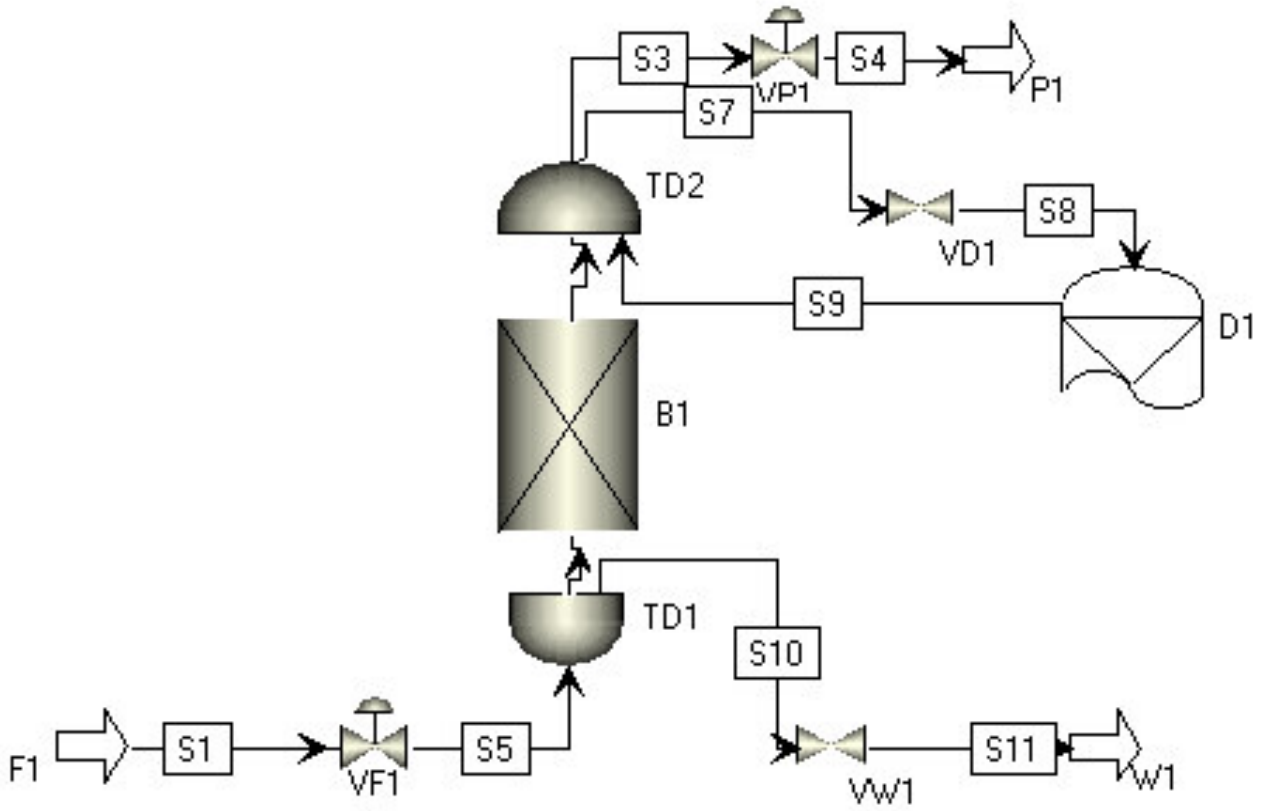

Figure 4: Water adsorption in Aspen Adsorption (dynamic simulation)

The last purification is constituted of a cryogenic column where the ethylene is separated from the heavy compounds.

The very low working temperature make necessary to check the thermodynamic method and the one that fits better the experimental data is PSRK, when the pressure is increased. Therefore, PSRK has been used to calculate the vapor liquid equilibria of the cryogenic distillation.

At the end of cryogenic distillation, a polymer-grade ethylene is obtained, with a purity higher than 99%.

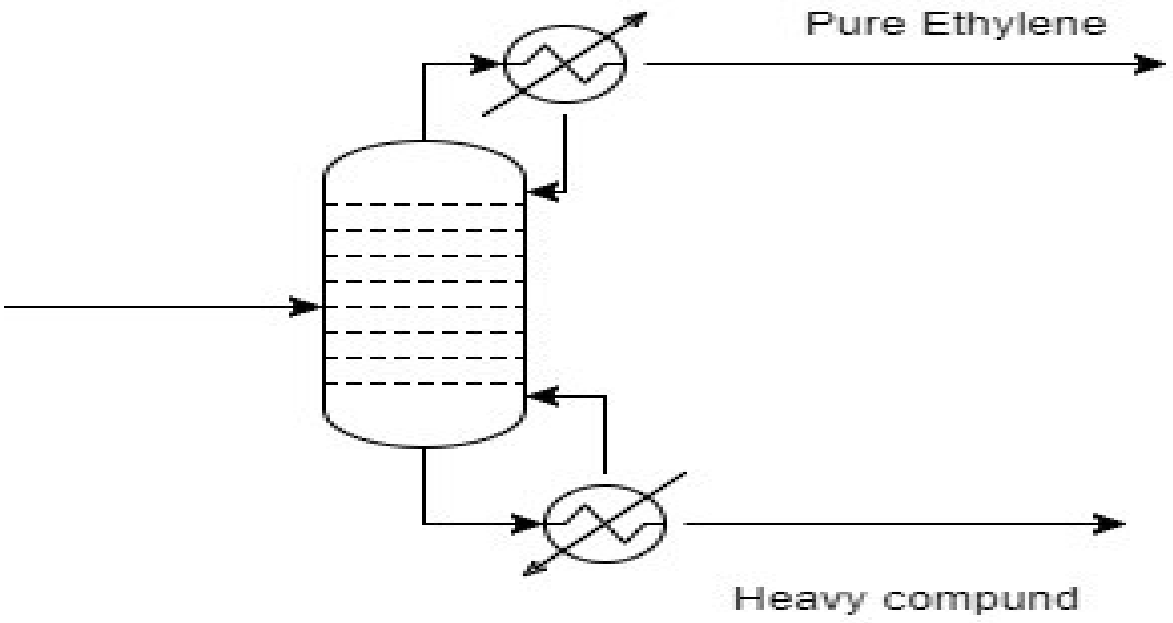

Figure 5: Final cryogenic column

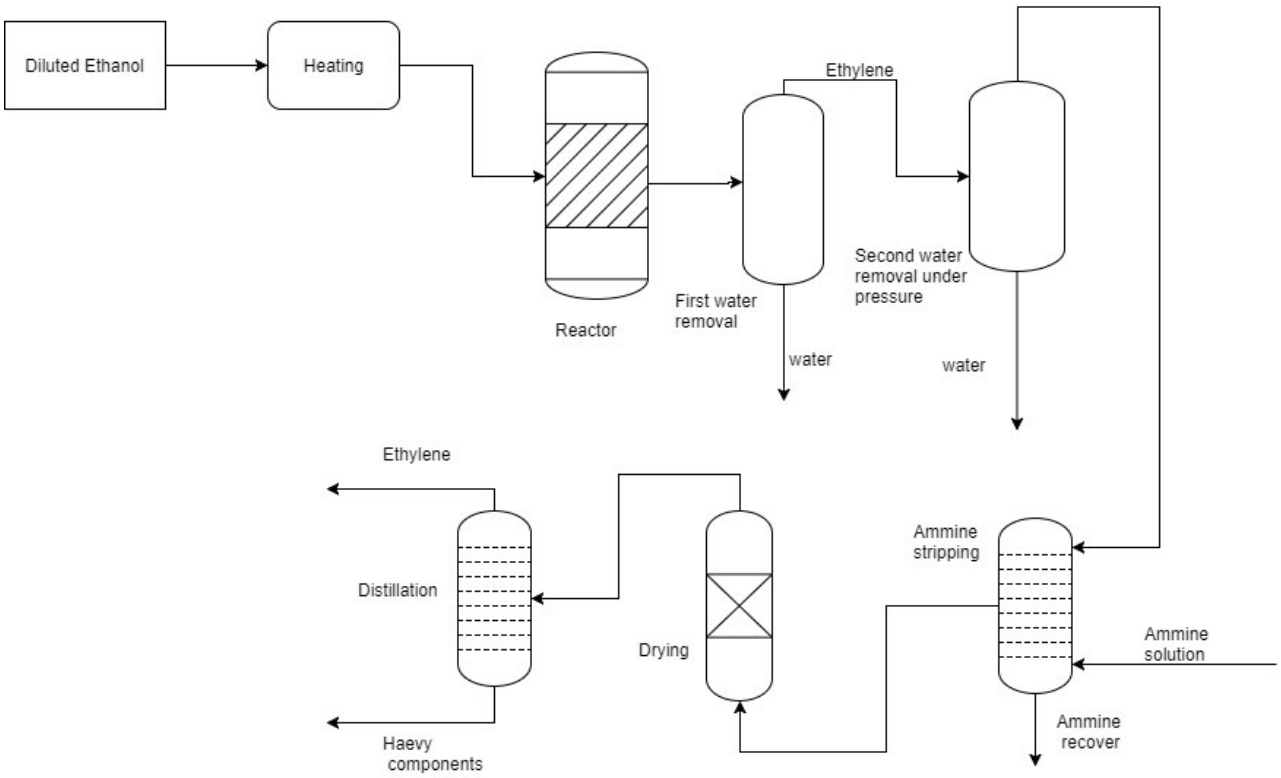

Figure 6: Simplified representation of the final flowsheet

In conclusion, the possibility to produce high quality of ethylene from diluted bioethanol is investigated, the simulation with software show that the most critical parts are:

- The kinetic model and how to implement it in Aspen Plus, to have a good representation of the reality
- The CO_2 adsorption with ammine, where equilibrium reactions and ions are involved in the adsorption and in the regeneration making the simulation more complex
- The dynamic simulation of the adsorber, the input required, the variable of time and the difficulty to get convergence make this part very complex, so this is the part on which the future efforts should be concentrate