

# Aspen Tutorials

Plant Design Group, Aalto University  
Oliwer Sliczniuk

October 12, 2023



# Preface

The research in Plant Design focuses on a process feasibility study, synthesis, design, operation, integration, simulation and optimization, inherent safety, occupational health, pollution prevention and industrial risk. The key theme is the development of systematic methodologies to identify optimum, sustainable and creative strategies that lead to process intensification, yield improvement, debottlenecking, costing, safety, pollution prevention and energy conservation. Fundamental chemical engineering principles are coupled with systems engineering approaches to develop methods and computer-aided tools applicable in all chemical process industry areas. Any plant design work includes preliminary process design, process synthesis, cost engineering, process simulation and environmental and safety aspects of design. This knowledge can be used for developing new processes, engineering new plants and improving existing ones in the chemical, petrochemical, biofuel, pulp and paper, minerals, food and biotech and pharmaceutical industries.

These lecture notes are a collection of simulations the Plant Design group uses while teaching master students.



# Contents

|          |  |           |
|----------|--|-----------|
| <b>1</b> | <b>Thermochemical processes</b>                      | <b>1</b>  |
| 1.1      | Production of synthetic gas from a biomass . . . . . | 1         |
| 1.2      | The fast pyrolysis of the biomass . . . . .          | 6         |
| <b>2</b> | <b>Process analysis</b>                              | <b>11</b> |
| 2.1      | Initial simulation . . . . .                         | 11        |
| 2.2      | Heat Exchangers . . . . .                            | 13        |
| 2.3      | Sensitivity Analysis . . . . .                       | 13        |
| 2.4      | Design-spec . . . . .                                | 15        |
| 2.5      | Column Internals . . . . .                           | 17        |
| <b>3</b> | <b>Economic Analysis</b>                             | <b>19</b> |
| 3.1      | Acetic anhydride production . . . . .                | 19        |
| 3.2      | Economic analysis steps . . . . .                    | 20        |
| 3.3      | Investment indicators . . . . .                      | 24        |
| 3.4      | APEA without process simulation . . . . .            | 27        |
|          | <b>Bibliography</b>                                  | <b>29</b> |



# Chapter 1

## Thermochemical processes

### 1.1 Production of synthetic gas from a biomass

The task is to simulate the production of synthetic gas from biomass. One way to do it is to develop an Aspen model. The model is divided into the biomass decomposition, gasification and separation units where the solids and syngas are separated. In the simulation, the gasifier is in an isothermal steady state. Decomposition products are estimated based on the ultimate biomass analysis. The model does not consider tars, but ashes are described as non-conventional solids. Biomass is pine sawdust, which is a common waste product of the forest industry. Figure 1.1 presents the process flow diagram.

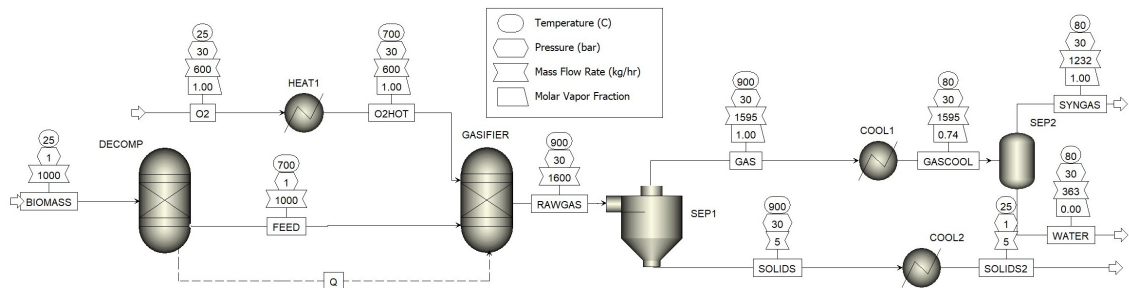


Figure 1.1: Gasification production plant

Add all simulation's components can be found in the table 1.1.

The next step is to select a thermodynamic model. The chosen property method is the Redlich-Kwong-Soave cubic equation of state with Boston-Mathias alpha function ( $RKS - BM$ ). This method is suitable for non-polar or slightly polar mixtures like hydrocarbons and light gases. The database of Aspen contains only conventional components, which means that the properties of the biomass and the coal needs to be specified manually. In the software, the properties of the non-conventional components can be specified in the "Method/NC Props" tab. HCOAL-GEN and DCOALIGT models can estimate biomass and ash properties. HCOAL-GEN and DCOALIGT models are used to calculate the enthalpy and density of non-conventional components, respectively. The HCOALGEN model requires these three component attributes for non-conventional components: proximate analysis results (denoted as PROXANAL in Aspen Plus), ultimate analysis results (denoted as

| Component ID | Type            | Component name   | Alias  |
|--------------|-----------------|------------------|--------|
| BIOMASS      | Nonconventional |                  |        |
| ASH          | Nonconventional |                  |        |
| $H_2$        | Conventional    | HYDROGEN         | $H_2$  |
| $O_2$        | Conventional    | OXYGEN           | $O_2$  |
| $N_2$        | Conventional    | NITROGEN         | $N_2$  |
| $CO$         | Conventional    | CARBON-MONOXIDE  | $CO$   |
| $CO_2$       | Conventional    | CARBON-DIOXIDE   | $CO_2$ |
| METHA-01     | Conventional    | METHANE          | $CH_4$ |
| CARBOGRA     | Solid           | CARBON-GRAPHITE  | $C$    |
| $S$          | Conventional    | SULFUR           | $S$    |
| $H_2S$       | Conventional    | HYDROGEN-SULFIDE | $H_2S$ |
| $H_3N$       | Conventional    | AMMONIA          | $H_3N$ |

**Table 1.1:** Simulation component

as ULTANAL in Aspen Plus), and sulfur analysis results (denoted as SULFANAL in Aspen Plus). The proximate analysis gives moisture, fixed carbon, volatile matter and ash weight content. The ultimate analysis gives the weight composition of coal in terms of ash, carbon, hydrogen, nitrogen, chlorine, sulfur, and oxygen. The sulfur analysis divides the sulfur content into pyritic, sulfate, and organic sulfur. The DCOALIGT model requires only the two-component attributes ULTANAL and SULFANAL. In Aspen Plus, multiple correlations have been predefined to calculate the enthalpy. The HCOALGEN option codes are shown in table 1.2.

| Option Code Value              | Calculation Method Parameter         | Names Component | Attributes                |
|--------------------------------|--------------------------------------|-----------------|---------------------------|
| 1 - Heat of Combustion         |                                      |                 |                           |
| 1                              | Boie correlation                     | BOIEC           | ULTANAL/SULFANAL/PROXANAL |
| 2                              | Dulong correlation                   | DLNGC           | ULTANAL/SULFANAL/PROXANAL |
| 3                              | Grummel and Davis correlation        | GMLDC           | ULTANAL/SULFANAL/PROXANAL |
| 4                              | Mott and Spooner correlation         | MTSPC           | ULTANAL/SULFANAL/PROXANAL |
| 5                              | IGT correlation                      | CIGTC           | ULTANAL/PROXANAL          |
| 6                              | User input value                     | HCOMB           | ULTANAL/PROXANAL          |
| 2 - Standard Heat of Formation |                                      |                 |                           |
| 1                              | Heat-of-combustion based correlation | -               | ULTANAL/SULFANAL          |
| 2                              | Direct correlation                   | HFC             | ULTANAL/SULFANAL/PROXANAL |
| 3 - Heat Capacity              |                                      |                 |                           |
| 1                              | Kirov correlation                    | CP1C            | PROXANAL                  |
| 2                              | Cubic temperature equation           | CP2C            | -                         |
| 4 - Enthalpy Basis             |                                      |                 |                           |
| 1                              | Elements at 298.15K and 1 atm        | -               | -                         |
| 2                              | Component at 298.15 K                | -               | -                         |

**Table 1.2:** HCOALGEN Option Codes

Default = 1 for each option code. In the exercise, the HCOALGEN codes for the ash are [1 1 1 1], which means default values. In biomass, the codes [6 1 1 1] mean that the heat of combustion will be specified. The heat of combustion can be introduced by implementing a new non-conventional parameter in the "Pure Components" section. Choose the biomass from the list and select the HCMOB option to introduce a  $18.4[MJ/kg]$  value.

As multiple parameters need to be evaluated, select the option "Estimate all missing parameters" from the "Estimation" tab.

Each simulation starts by defining an inlet stream. Specify the biomass feed to



be 1000[ $kg/h$ ] at 25°C] and 1[ $bar$ ]. Enter its Component attribute in table 1.1. Add proximate, ultimate and sulphur analysis data of biomass feed in NC Solid.

| Group              | Components           | w-%   |
|--------------------|----------------------|-------|
| Moisture content   | $H_2O$               | 8     |
| Proximate analysis |                      |       |
|                    | Volatile matter (VM) | 82.29 |
|                    | Fixed carbon (FC)    | 17.16 |
|                    | Ash                  | 0.55  |
| Ultimate analysis  |                      |       |
|                    | C                    | 50.54 |
|                    | H                    | 7.08  |
|                    | O                    | 41.11 |
|                    | N                    | 0.15  |
|                    | S                    | 0.57  |
|                    | Ash                  | 0.55  |
| Sulfur analysis    |                      |       |
|                    | Pyritic              | 0     |
|                    | Sulfate              | 0.057 |
|                    | Organic              | 0.513 |

**Table 1.3:** Characteristics of Biomass (pine sawdust)

The biomass is defined as a non-conventional solid in Aspen Plus and the ash present in the biomass. The presence of non-conventional components in the simulation needs the stream class MIXINC, which is for models where both conventional solids (carbon) and non-conventional solids are present and when particle size distribution is unknown (go to Simulation-> set up-> specification-> Global setting stream class).

When the simulation parameters are defined, the operational blocks can be introduced. The first operational unit is the decomposer. The solid biomass is decomposed at into gaseous products, which can follow further processing. For the decomposition of biomass, the DECOMP module is Aspen *RYield* reactor where the biomass is decomposed into  $H_2$ ,  $O_2$ ,  $N_2$ ,  $H_2O$ ,  $S$ ,  $C$  and ash according to the biomass ultimate analysis data at 700[°C] and 1[ $bar$ ]. The RYield decomposes the biomass into the constituents shown in table 1.4.

| Component         | Carbon   | Hydrogen | Oxygen | Nitrogen | Sulfur   | Ash     | Water |
|-------------------|----------|----------|--------|----------|----------|---------|-------|
| Yield (in mass %) | 0.464968 | 0.065138 | 0.3782 | 0.00138  | 0.005244 | 0.00507 | 0.08  |

**Table 1.4:** Yields for the RYIELD reactor

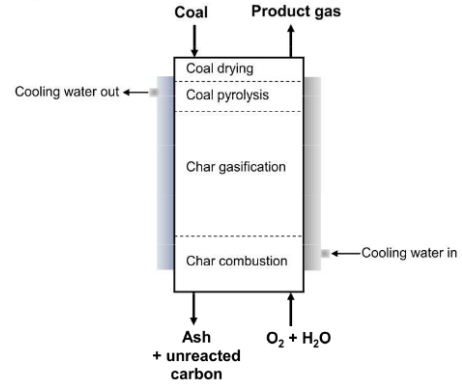
The next operation unit is the gasifier (presented in figure 1.2). For that purpose, let's use the Gibbs Reactor will produce an outlet in which the Gibbs free energy of the mixture is minimised. A set of reactions can be suggested in the reactor model. However, it is important to note that the suggested reaction might not be included in the simulation as free energy minimisation will be the dominant method. An exception to this rule is the stoichiometry of the reaction set. Without

a set, stoichiometry will not be considered in the simulation; however, with an attached reaction set with stoichiometric parameters, the simulation will account for them, and the outlet conditions can change. However, if a set is attached, only the components specified in the set will reach an equilibrium point; other components will be neglected. The Gibbs Reactor can be very useful if the user does not possess any data pertinent to the reaction or desires only a simulation of the equilibrium state. At the very least, the Gibbs Reactor can provide simulation estimates as a starting point for a more rigorous simulation through another reactor type.

The pressure is at 30[bar] and 900[°C], which is a typical value for real-world gasifiers. Oxygen 600[kg/h] is used as the oxidising agent, which is preheated to 700[°C]. The possible products of the gasification were predefined to be:  $H_2$ ,  $O_2$ ,  $N_2$ ,  $H_2O$ ,  $S$ ,  $C(solid)$ ,  $CO$ ,  $CO_2$ ,  $H_2S$ ,  $CH_4$ ,  $C$  and  $NH_3$ . Aspen calculated the product distributions at various conditions.

Finally, in the simulation's separation section, the solids are separated from the hot gases in SEP1, which is an Aspen SSplit. The SSPLIT assumes perfect separation of solid particles from the mainstream. The SEP2 column is a flash column used to separate the condensate. The gases are cooled to 80[°C] with heat exchanger COOL1. The product of the process is the stream SYNGAS, which contains the main syngas components  $CO$  and  $H_2$ , but also contains impurities such as  $H_2S$  and  $NH_3$ . The product of this process needs to be further purified in a separate purification facility to be helpful feedstock for other processes.

The configuration of the simulation and its results are presented below:



**Figure 1.2:** The gasifier

|                        | Units     | BIOMASS  | FEED         | GAS         | GASCOOL     | O2          | O2HOT       | RAWGAS      | SOLIDS      | SOLIDS2      | SYNGAS      | WATER        |
|------------------------|-----------|----------|--------------|-------------|-------------|-------------|-------------|-------------|-------------|--------------|-------------|--------------|
| Description            |           |          |              |             |             |             |             |             |             |              |             |              |
| From                   |           |          | DECOMP       | SEP1        | COOL1       |             | HEAT1       | GASIFIER    | SEP1        | COOL2        | SEP2        | SEP2         |
| To                     |           | DECOMP   | GASIFIER     | COOL1       | SEP2        | HEAT1       | GASIFIER    | SEP1        | COOL2       |              |             |              |
| Stream Class           |           | MIXCINC  | MIXCINC      | MIXCINC     | MIXCINC     | MIXCINC     | MIXCINC     | MIXCINC     | MIXCINC     | MIXCINC      | MIXCINC     | MIXCINC      |
| Maximum Relative Error |           |          |              |             |             |             |             |             |             |              |             |              |
| Cost Flow              | \$/hr     |          |              |             |             |             |             |             |             |              |             |              |
| - Total Stream         |           |          |              |             |             |             |             |             |             |              |             |              |
| Temperature            | C         | 25       | 700          | 900         | 80          | 25          | 700         | 900         | 900         | 25           | 80          | 80           |
| Pressure               | bar       | 1.01325  | 1.01325      | 30          | 30.3975     | 30          | 30          | 30          | 30          | 1.01325      | 30.3975     | 30.3975      |
| Mass Vapor Fraction    |           | 0        | 0.529962     | 1           | 0.772277    | 1           | 1           | 0.996831    | 0           | 0            | 1           | 0            |
| Mass Liquid Fraction   |           | 0        | 0            | 0           | 0.227723    | 0           | 0           | 0           | 0           | 0            | 0           | 1            |
| Mass Solid Fraction    |           | 1        | 0.470038     | 0           | 1.71182e-07 | 0           | 0           | 0.00316875  | 1           | 1            | 0           | 0            |
| Mass Enthalpy          | kcal/kg   | -2116.59 | 118.101      | -1265.87    | -1721.12    | -1.84382    | 162.869     | -1261.79    | 22.2112     | -191.945     | -1136.33    | -3704.33     |
| Mass Density           | kg/cum    | 1209.43  | 0.256024     | 6.40179     | 28.0242     | 39.1882     | 11.7698     | 6.4221      | 3486.88     | 3486.88      | 22.5431     | 722.435      |
| Enthalpy Flow          | Gcal/hr   | -2.11659 | 0.18101      | -2.01898    | -2.74507    | -0.00110629 | 0.0977213   | -2.01887    | 0.000112611 | -0.000973161 | -1.39965    | -1.34542     |
| Mass Flows             | kg/hr     | 1000     | 1000         | 1594.93     | 1594.93     | 600         | 600         | 1600        | 5.07        | 5.07         | 1231.73     | 363.202      |
| + Mass Fractions       |           |          |              |             |             |             |             |             |             |              |             |              |
| Volume Flow            | cum/hr    | 0.826835 | 3896.75      | 249.138     | 55.1417     | 15.3107     | 50.978      | 249.139     | 0.00145402  | 0.00145402   | 54.6389     | 0.502747     |
| - MIXED Substream      |           |          |              |             |             |             |             |             |             |              |             |              |
| Phase                  |           |          | Vapor Phase  | Vapor Phase |             | Vapor Phase | Vapor Phase | Vapor Phase |             |              | Vapor Phase | Liquid Phase |
| Temperature            | C         |          | 700          | 900         | 80          | 25          | 700         | 900         |             |              | 80          | 80           |
| Pressure               | bar       | 1.01325  | 1.01325      | 30          | 30.3975     | 30          | 30          | 30          |             | 1.01325      | 30.3975     | 30.3975      |
| Molar Vapor Fraction   |           |          | 1            | 1           | 0.736558    | 1           | 1           | 1           |             |              | 1           | 0            |
| Molar Liquid Fraction  |           |          | 0            | 0           | 0.263442    | 0           | 0           | 0           |             |              | 0           | 1            |
| Molar Solid Fraction   |           |          | 0            | 0           | 0           | 0           | 0           | 0           |             |              | 0           | 0            |
| Mass Vapor Fraction    |           |          | 1            | 1           | 0.772277    | 1           | 1           | 1           |             |              | 1           | 0            |
| Mass Liquid Fraction   |           |          | 0            | 0           | 0.227723    | 0           | 0           | 0           |             |              | 0           | 1            |
| Mass Solid Fraction    |           |          | 0            | 0           | 0           | 0           | 0           | 0           |             |              | 0           | 0            |
| Molar Enthalpy         | kcal/mol  |          | -0.0754248   | -26.5249    | -36.0642    | -0.0590001  | 5.21161     | -26.5249    |             |              | -24.9653    | -67.0958     |
| Mass Enthalpy          | kcal/kg   |          | -6.94315     | -1265.87    | -1721.12    | -1.84382    | 162.869     | -1265.87    |             |              | -1136.33    | -3704.33     |
| Molar Entropy          | cal/mol-K |          | 9.4715       | 13.3201     | -3.0995     | -6.90086    | 2.21927     | 13.3201     |             |              | 9.02204     | -36.9901     |
| Mass Entropy           | cal/gm-K  |          | 0.871889     | 0.635689    | -0.14792    | -0.21566    | 0.0693548   | 0.635689    |             |              | 0.410652    | -2.04221     |
| Molar Density          | kmol/cum  |          | 0.0125201    | 0.305518    | 1.38038     | 1.22468     | 0.36782     | 0.305518    |             |              | 1.02608     | 39.8853      |
| Mass Density           | kg/cum    |          | 0.136008     | 6.40179     | 28.0242     | 39.1882     | 11.7698     | 6.40179     |             |              | 22.5431     | 722.435      |
| Enthalpy Flow          | Gcal/hr   |          | -0.00367961  | -2.01898    | -2.74507    | -0.00110629 | 0.0977213   | -2.01898    |             |              | -1.39965    | -1.34542     |
| Average MW             |           |          | 10.8632      | 20.9539     | 20.9539     | 31.9988     | 31.9988     | 20.9539     |             |              | 21.97       | 18.1128      |
| Mole Flows             | kmol/hr   | 0        | 48.7851      | 76.1162     | 76.1162     | 18.7507     | 18.7507     | 76.1162     | 0           | 0            | 56.064      | 20.0522      |
| + Mole Fractions       |           |          |              |             |             |             |             |             |             |              |             |              |
| Mass Flows             | kg/hr     |          | 529.962      | 1594.93     | 1594.93     | 600         | 600         | 1594.93     |             |              | 1231.73     | 363.202      |
| + Mass Fractions       |           |          |              |             |             |             |             |             |             |              |             |              |
| Volume Flow            | cum/hr    |          | 3896.54      | 249.138     | 55.1417     | 15.3107     | 50.978      | 249.138     |             |              | 54.6389     | 0.502747     |
| + Vapor Phase          |           |          |              |             |             |             |             |             |             |              |             |              |
| + Liquid Phase         |           |          |              |             |             |             |             |             |             |              |             |              |
| + CISOLID Substream    |           |          |              |             |             |             |             |             |             |              |             |              |
| - NC Substream         |           |          |              |             |             |             |             |             |             |              |             |              |
| Temperature            | C         | 25       | 700          |             |             |             |             | 900         | 900         | 25           |             |              |
| Pressure               | bar       | 1.01325  | 1.01325      |             | 30.3975     | 30          | 30          | 30          | 30          | 1.01325      | 30.3975     | 30.3975      |
| Mass Enthalpy          | kcal/kg   | -2116.59 | -36.1888     |             |             |             |             | 22.2112     | 22.2112     | -191.945     |             |              |
| Mass Density           | kg/cum    | 1209.43  | 3486.88      |             |             |             |             | 3486.88     | 3486.88     | 3486.88      |             |              |
| Enthalpy Flow          | Gcal/hr   | -2.11659 | -0.000183477 |             |             |             |             | 0.000112611 | 0.000112611 | -0.000973161 |             |              |
| Mass Flows             | kg/hr     | 1000     | 5.07         | 0           | 0           | 0           | 0           | 5.07        | 5.07        | 5.07         | 0           | 0            |
| + Mass Fractions       |           |          |              |             |             |             |             |             |             |              |             |              |
| Volume Flow            | cum/hr    | 0.826835 | 0.00145402   |             |             |             |             | 0.00145402  | 0.00145402  | 0.00145402   |             |              |

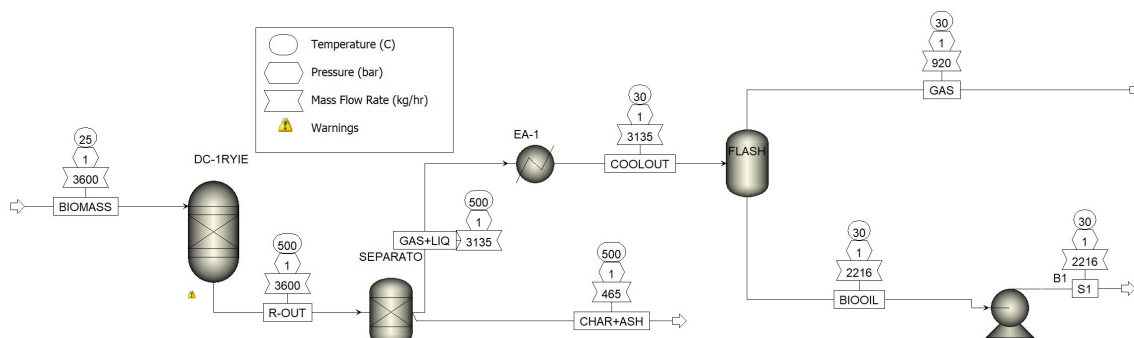
Figure 1.3: Gasification results

## 1.2 The fast pyrolysis of the biomass

Biomass fast pyrolysis is a highly non-equilibrium reaction where the main components (lignin, celluloses and hemicelluloses) are broken down into shorter molecules like acids, aldehydes, phenols, sugars and non-condensable gases. More than 200 different components have been identified in pyrolysis oil, and their share depends on the feedstock, process parameters and measurement equipment. Therefore, modelling biomass fast pyrolysis is not trivial. However, the following assumptions will allow the modelling of biomass fast pyrolysis:

- Biomass, ash, char, and lignin are defined as non-conventional components (neither molecular weight nor molecular structure can be given); Biomass attributes are computed with AspenPlus' built-in enthalpy and density models HCOALGEN and DCOALLIGT (for reference check chapter ??)
- Pyrolysis is modelled with a yield reactor where the user defines the pyrolysis products.

Figure 1.4 presents the process flow diagram. The biomass is fed directly to the pyrolysis unit, which operates at high temperature and atmospheric pressure. Then the gaseous streams are cooled down, and the two-phase mixture is separated.



**Figure 1.4:** Fast pyrolysis plant

Add all the conventional components in the component list as given in the table 1.5 and non-conventional components BIOMASS, ASH, CHAR and LIGNIN.

The thermodynamic method used in this exercise is UNIQUAC (universal quasichemical), an activity coefficient model used to describe phase equilibria. This model belongs to a lattice model derived from a first-order approximation of interacting molecule surfaces in statistical thermodynamics. The model is, however, not fully thermodynamically consistent due to its two-liquid mixture approach. In this approach, the local concentration around one central molecule is assumed to be independent of the local composition around another type of molecule. The UNIQUAC model also serves as the basis for developing the group contribution method UNIFAC, where molecules are subdivided into functional groups. In fact, UNIQUAC is equal to UNIFAC for mixtures of molecules which are not subdivided, e.g. the binary systems water-methanol, methanol-acrylonitrile and formaldehyde-DMF.

| Group              | Component        | Formula        | CAS                 | Final yield [kg/kg biomass] |
|--------------------|------------------|----------------|---------------------|-----------------------------|
| Proximate analysis |                  |                |                     |                             |
|                    | Carbonmonoxide   | $CO$           | 630-08-0            | 0,05681                     |
|                    | Hydrogen         | $H_2$          | 1333-74-0           | 0,00813                     |
|                    | Methane          | $CH_4$         | 74-82-8             | 0,00048                     |
|                    | Carbondioxide    | $CO_2$         | 124-38-9            | 0,04693                     |
|                    | Ethane           | $C_2H_6$       | 74-84-0             | 0,00196                     |
|                    | Propane          | $C_3H_8$       | 74-98-6             | 0,00210                     |
|                    | Ammonia          | $NH_3$         | 7664-41-7           | 0,00172                     |
|                    | Hydrogensulfide  | $H_2S$         | 7783-06-4           | 0,00075                     |
| Liquid / Oil       |                  |                |                     |                             |
|                    | Phenol           | $C_6H_6O$      | 108-95-2            | 0,04201                     |
|                    | Formic Acid      | $CH_2O_2$      | 64-18-6             | 0,1001                      |
|                    | Formaldehyde     | $CH_2O$        | 50-00-0             | 0,14865                     |
|                    | Glucose          | $C_6H_{12}O_6$ | 50-99-7             | 0,05841                     |
|                    | Fluoranthene     | $C_{16}H_{10}$ | 206-44-0            | 0,08807                     |
|                    | Dihydrogenoxide  | $H_2O$         | 7732-18-5           | 0,17202                     |
|                    | Pyrolitic Lignin | $NC$           | $CH_{1.1}O_{0.3}$   | 0,14285                     |
| Solid              |                  |                |                     |                             |
|                    | Char             | NC             | $CH_{0.48}O_{0.23}$ | 0,12185                     |
|                    | Ash              | NC             | Ash                 | 0,00716                     |
| Sum                |                  |                |                     | 1                           |

**Table 1.5:** Characteristics of Biomass (pine sawdust)

The non-conventional components' properties need to be defined through values for HCOALGEN and DCOALLIGT.

In the Simulation section, Main Flowsheet, select a yield reactor and connect IN and Out streams. In the Setup sheet, set the Stream class to 'MIXNC'. This will enable the calculation of non-conventional components (go to Simulation-> set up-> specification-> Global setting stream class).

The next step is to define Biomass feed at 25 °C, 1 bar and 1 kg/s. Use Component Attribute is given in table 1.6a. The biomass stream enters the yield reactor, which represents the pyrolysis unit. The reaction works at the following conditions: 1[bar] and 500[°C]. The reaction yields are shown in table 1.6a. In the reactor block, the non-conventional product components need to be defined by their analyses according to tables 1.6b, 1.6c and 1.6d. The product compositions should be included in the "Comp. Attr." tab of the reactor unit.

The outlet stream from the reactor flows to the separator. The solid particles The SSPLIT assumes perfect separation of solid particles from the mainstream. Then the mixture of gaseous and liquid products enters the heat exchanger, which works at 30[°C] and 1[bar]. As a result, condensation occurs. The following step separates vapour from the liquid phase in a flash. The flash is assumed to be adiabatic and isobaric. The liquid stream is the main product and represents the bio-oil.

| Group              | Components           | w-%   |
|--------------------|----------------------|-------|
| Moisture content   | $H_2O$               | 10    |
| Proximate analysis |                      |       |
|                    | Volatile matter (VM) | 82.73 |
|                    | Fixed carbon (FC)    | 16.47 |
|                    | Ash                  | 0.8   |
| Ultimate analysis  |                      |       |
|                    | C                    | 50.64 |
|                    | H                    | 6.18  |
|                    | O                    | 42.22 |
|                    | N                    | 0.16  |
|                    | S                    | 0.08  |
|                    | Ash                  | 0.80  |
| Sulfur analysis    |                      |       |
|                    | Pyritic              | 0.0   |
|                    | Sulfate              | 0.0   |
|                    | Organic              | 0.08  |

**(a)** Biomass fuel analysis

| Group              | Components           | w-%   |
|--------------------|----------------------|-------|
| Moisture content   | $H_2O$               | 0     |
| Proximate analysis |                      |       |
|                    | Volatile matter (VM) | 80.00 |
|                    | Fixed carbon (FC)    | 20.00 |
|                    | Ash                  | 0.0   |
| Ultimate analysis  |                      |       |
|                    | C                    | 66.80 |
|                    | H                    | 6.18  |
|                    | O                    | 27.02 |
|                    | N                    | 0.0   |
|                    | S                    | 0.0   |
|                    | Ash                  | 0.0   |
| Sulfur analysis    |                      |       |
|                    | Pyritic              | 0.0   |
|                    | Sulfate              | 0.0   |
|                    | Organic              | 0.0   |

**(b)** The composition of lignin

| Group              | Components           | w-%   |
|--------------------|----------------------|-------|
| Moisture content   | $H_2O$               | 0     |
| Proximate analysis |                      |       |
|                    | Volatile matter (VM) | 80.00 |
|                    | Fixed carbon (FC)    | 20.00 |
|                    | Ash                  | 0.0   |
| Ultimate analysis  |                      |       |
|                    | C                    | 74.32 |
|                    | H                    | 2.99  |
|                    | O                    | 22.69 |
|                    | N                    | 0.0   |
|                    | S                    | 0.0   |
|                    | Ash                  | 0.0   |
| Sulfur analysis    |                      |       |
|                    | Pyritic              | 0.0   |
|                    | Sulfate              | 0.0   |
|                    | Organic              | 0.0   |

**(c)** The composition of char

| Group              | Components           | w-%   |
|--------------------|----------------------|-------|
| Moisture content   | $H_2O$               | 0     |
| Proximate analysis |                      |       |
|                    | Volatile matter (VM) | 0.00  |
|                    | Fixed carbon (FC)    | 0.00  |
|                    | Ash                  | 100.0 |
| Ultimate analysis  |                      |       |
|                    | C                    | 0.0   |
|                    | H                    | 0.0   |
|                    | O                    | 0.0   |
|                    | N                    | 0.0   |
|                    | S                    | 0.0   |
|                    | Ash                  | 100.0 |
| Sulfur analysis    |                      |       |
|                    | Pyritic              | 0.0   |
|                    | Sulfate              | 0.0   |
|                    | Organic              | 0.0   |

**(d)** The composition of char

**Table 1.6:** The composition of pyrolysis products

|                        | Units     | BIOMASS  | BIOOIL       | CHAR+ASH  | COOLOUT   | GAS         | GAS+LIQ     | R-OUT       | S1           |
|------------------------|-----------|----------|--------------|-----------|-----------|-------------|-------------|-------------|--------------|
| Description            |           |          |              |           |           |             |             |             |              |
| From                   |           |          | FLASH        | SEPARATO  | EA-1      | FLASH       | SEPARATO    | DC-1RYIE    | B1           |
| To                     |           | DC-1RYIE | B1           |           | FLASH     |             | EA-1        | SEPARATO    |              |
| Stream Class           |           | MIXNC    | MIXNC        | MIXNC     | MIXNC     | MIXNC       | MIXNC       | MIXNC       | MIXNC        |
| Maximum Relative Error |           |          |              |           |           |             |             |             |              |
| Cost Flow              | \$/hr     |          |              |           |           |             |             |             |              |
| Total Stream           |           |          |              |           |           |             |             |             |              |
| Temperature            | C         | 25       | 30           | 500       | 30        | 30          | 500         | 500         | 30           |
| Pressure               | bar       | 1        | 1            | 1         | 1         | 1           | 1           | 1           | 1            |
| Mass Vapor Fraction    |           | 0        | 0            | 0         | 0.293757  | 1           | 0.835974    | 0.72805     | 0            |
| Mass Liquid Fraction   |           | 0        | 0.767749     | 0         | 0.542217  | 0           | 0           | 0           | 0.767749     |
| Mass Solid Fraction    |           | 1        | 0.232251     | 1         | 0.164026  | 0           | 0.164026    | 0.27195     | 0.232251     |
| Mass Enthalpy          | kcal/kg   | -1553.33 | -1725.08     | -268.029  | -1556.12  | -1149.93    | -1184.67    | -1066.33    | -1725.08     |
| Mass Density           | kg/cum    | 1266.25  | 1079.87      | 1518.11   | 2.85618   | 0.840595    | 0.536065    | 0.615498    | 1079.87      |
| Enthalpy Flow          | Gcal/hr   | -5.59199 | -3.81974     | -0.124569 | -4.87882  | -1.05909    | -3.71421    | -3.83878    | -3.81974     |
| Mass Flows             | kg/hr     | 3600     | 2214.24      | 464.76    | 3135.24   | 920.999     | 3135.24     | 3600        | 2214.24      |
| Mass Fractions         |           |          |              |           |           |             |             |             |              |
| Volume Flow            | cum/hr    | 2.84304  | 2.05047      | 0.306144  | 1097.7    | 1095.65     | 5848.62     | 5848.92     | 2.05047      |
| MIXED Substream        |           |          |              |           |           |             |             |             |              |
| Phase                  |           |          | Liquid Phase |           |           | Vapor Phase | Vapor Phase | Vapor Phase | Liquid Phase |
| Temperature            | C         |          | 30           |           | 30        | 30          | 500         | 500         | 30           |
| Pressure               | bar       |          | 1            | 1         | 1         | 1           | 1           | 1           | 1            |
| Molar Vapor Fraction   |           |          | 0            |           | 0.477811  | 1           | 1           | 1           | 0            |
| Molar Liquid Fraction  |           |          | 1            |           | 0.522189  | 0           | 0           | 0           | 1            |
| Molar Solid Fraction   |           |          | 0            |           | 0         | 0           | 0           | 0           | 0            |
| Mass Vapor Fraction    |           |          | 0            |           | 0.351395  | 1           | 1           | 1           | 0            |
| Mass Liquid Fraction   |           |          | 1            |           | 0.648605  | 0           | 0           | 0           | 1            |
| Mass Solid Fraction    |           |          | 0            |           | 0         | 0           | 0           | 0           | 0            |
| Molar Enthalpy         | kcal/mol  |          | -71.5735     |           | -49.0161  | -24.3637    | -37.744     | -37.744     | -71.5735     |
| Mass Enthalpy          | kcal/kg   |          | -2000.17     |           | -1701.4   | -1149.93    | -1310.13    | -1310.13    | -2000.17     |
| Molar Entropy          | cal/mol-K |          | -45.2759     |           | -21.7435  | 3.97449     | 4.6746      | 4.6746      | -45.2759     |
| Mass Entropy           | cal/gm-K  |          | -1.26527     |           | -0.754741 | 0.18759     | 0.16226     | 0.16226     | -1.26527     |
| Molar Density          | kmol/cum  |          | 28.9365      |           | 0.0829104 | 0.0396748   | 0.0155564   | 0.0155564   | 28.9365      |
| Mass Density           | kg/cum    |          | 1035.45      |           | 2.38858   | 0.840595    | 0.448168    | 0.448168    | 1035.45      |
| Enthalpy Flow          | Gcal/hr   |          | -3.40026     |           | -4.45934  | -1.05909    | -3.43383    | -3.43383    | -3.40026     |
| Average MW             |           |          | 35.7836      |           | 28.8092   | 21.1871     | 28.8092     | 28.8092     | 35.7836      |
| Mole Flows             | kmol/hr   | 0        | 47.5072      | 0         | 90.9771   | 43.4698     | 90.9771     | 90.9771     | 47.5072      |
| Mole Fractions         |           |          |              |           |           |             |             |             |              |
| Mass Flows             |           |          |              |           |           |             |             |             |              |
| CO                     | kg/hr     |          | 1699.98      |           | 2620.98   | 920.999     | 2620.98     | 2620.98     | 1699.98      |
| H2                     | kg/hr     |          | 0.210696     |           | 204.516   | 204.305     | 204.516     | 204.516     | 0.210696     |
| H2                     | kg/hr     |          | 0.00334524   |           | 29.268    | 29.2647     | 29.268      | 29.268      | 0.00334524   |
| CH4                    | kg/hr     |          | 0.00423811   |           | 1.728     | 1.72376     | 1.728       | 1.728       | 0.00423811   |
| CO2                    | kg/hr     |          | 2.08479      |           | 168.948   | 166.863     | 168.948     | 168.948     | 2.08479      |
| C2H6                   | kg/hr     |          | 0.119714     |           | 7.056     | 6.93629     | 7.056       | 7.056       | 0.119714     |
| C3H8                   | kg/hr     |          | 0.493963     |           | 7.56      | 7.06604     | 7.56        | 7.56        | 0.493963     |
| NH3                    | kg/hr     |          | 2.06668      |           | 6.192     | 4.12532     | 6.192       | 6.192       | 2.06668      |
| H2S                    | kg/hr     |          | 0.105075     |           | 2.7       | 2.59493     | 2.7         | 2.7         | 0.105075     |
| C6H6O                  | kg/hr     |          | 150.956      |           | 151.236   | 0.279673    | 151.236     | 151.236     | 150.956      |
| CH2O2                  | kg/hr     |          | 351.921      |           | 360.036   | 8.1153      | 360.036     | 360.036     | 351.921      |
| CH2O                   | kg/hr     |          | 70.7053      |           | 535.14    | 464.435     | 535.14      | 535.14      | 70.7053      |
| C6H12O6                | kg/hr     |          | 210.276      |           | 210.276   | 5.56162e-11 | 210.276     | 210.276     | 210.276      |
| H2O                    | kg/hr     |          | 593.984      |           | 619.272   | 25.2883     | 619.272     | 619.272     | 593.984      |
| C16H10                 | kg/hr     |          | 317.05       |           | 317.052   | 0.00177661  | 317.052     | 317.052     | 317.05       |
| O2                     | kg/hr     |          | 0            |           | 0         | 0           | 0           | 0           | 0            |
| N2                     | kg/hr     |          | 0            |           | 0         | 0           | 0           | 0           | 0            |
| SO2                    | kg/hr     |          | 0            |           | 0         | 0           | 0           | 0           | 0            |
| NO2                    | kg/hr     |          | 0            |           | 0         | 0           | 0           | 0           | 0            |
| C                      | kg/hr     |          | 0            |           | 0         | 0           | 0           | 0           | 0            |
| Mass Fractions         |           |          |              |           |           |             |             |             |              |
| Volume Flow            | cum/hr    |          | 1.64177      |           | 1097.29   | 1095.65     | 5848.21     | 5848.21     | 1.64177      |
| Vapor Phase            |           |          |              |           |           |             |             |             |              |
| Liquid Phase           |           |          |              |           |           |             |             |             |              |
| NC Substream           |           |          |              |           |           |             |             |             |              |
| Temperature            | C         | 25       | 30           | 500       | 30        |             | 500         | 500         | 30           |
| Pressure               | bar       | 1        | 1            | 1         | 1         | 1           | 1           | 1           | 1            |
| Mass Enthalpy          | kcal/kg   | -1553.33 | -815.699     | -268.029  | -815.699  |             | -545.207    | -413.625    | -815.699     |
| Mass Density           | kg/cum    | 1266.25  | 1258.31      | 1518.11   | 1258.31   |             | 1258.31     | 1369.57     | 1258.31      |
| Enthalpy Flow          | Gcal/hr   | -5.59199 | -0.419481    | -0.124569 | -0.419481 |             | -0.280378   | -0.404947   | -0.419481    |
| Mass Flows             | kg/hr     | 3600     | 514.26       | 464.76    | 514.26    | 0           | 514.26      | 979.02      | 514.26       |
| BIOMASS                | kg/hr     | 3600     | 0            | 0         | 0         | 0           | 0           | 0           | 0            |
| ASH                    | kg/hr     | 0        | 0            | 26.1      | 0         | 0           | 0           | 26.1        | 0            |
| CHAR                   | kg/hr     | 0        | 0            | 438.66    | 0         | 0           | 0           | 438.66      | 0            |
| LIGNIN                 | kg/hr     | 0        | 514.26       | 0         | 514.26    | 0           | 514.26      | 514.26      | 514.26       |

Figure 1.5: Fast pyrolysis results

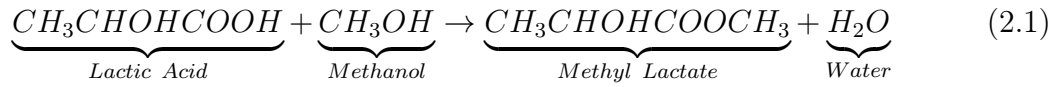




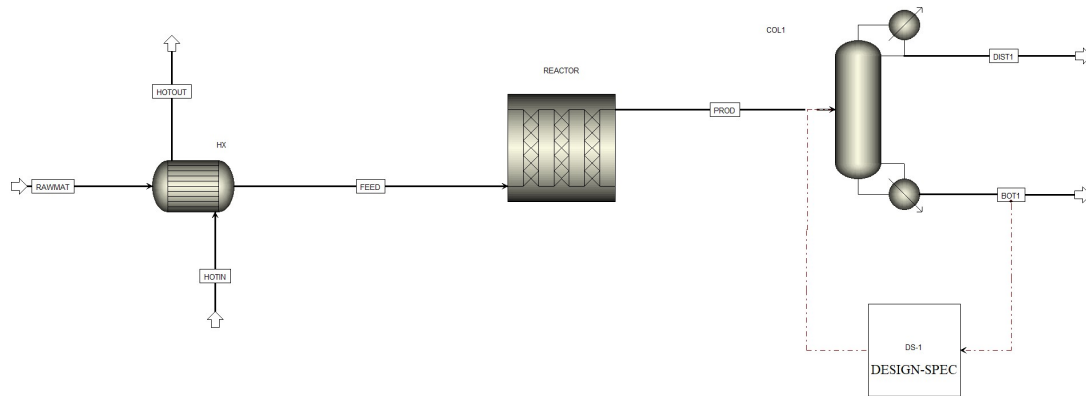
# Chapter 2

## Process analysis

Following the work of [1], let's analyse the esterification of lactic acid with methanol given by the following chemical reaction



The simplified process flow diagram, is presented on Figure 2.1.



**Figure 2.1:** Process flow diagram

The kinetic model is used to represent the reaction rate, but the effect of the reverse reaction is neglected. Thus, the reaction rate is expressed as follows:

$$r = k_1 \exp\left(\frac{-E_a}{RT}\right) a_{LACTIC}^2 a_{MeOH} \quad (2.2)$$

where  $k_1$  is equal to  $6.024 \times 10^8 \text{ [mol} \cdot \text{min}^{-1}]$ ,  $E_A$  is equal to  $56.45 \text{ [kJ} \cdot \text{mol}^{-1}]$ , and  $a_i$  is the activity of the component  $i$ .

### 2.1 Initial simulation

The thermodynamics is calculated based on the UNIFAC method. In statistical thermodynamics, the UNIFAC method (UNIQUE Functional-group Activity Coefficients) is a semi-empirical system for predicting non-electrolyte activity in non-ideal

mixtures. UNIFAC uses the functional groups present on the molecules that make up the liquid mixture to calculate activity coefficients. The activity of each of the solutions can be calculated by using interactions for each of the functional groups present on the molecules and some binary interaction coefficients. The UNIFAC correlation attempts to break down the problem of predicting interactions between molecules by describing molecular interactions based on the functional groups attached to the molecule. This is done in order to reduce the sheer number of binary interactions that would be needed to be measured to predict the state of the system.

Let's initiate the simulation by setting up the reactor block first. In this case, 100 [kmol/h] of lactic acid is allowed to enter a tubular reactor. Methanol is also fed to the reactor, with a methanol/lactic acid mole ratio of 3 : 1. The reactor operates at 340 [K] and 1 [bar]. Esterification of lactic acid occurs inside the vessel; thus, the stream leaving the equipment contains methyl lactate, water, and unreacted methanol and lactic acid. The reaction occurs in a Plug Flow Reactor (PFR). The first parameter to be decided is the characteristic of the reactor, which in this case is set to *reactor with specified temperature*, which means that the feed temperature determines the reactor's temperature. To set the initial simulation the reactor length is assumed to be 5 [m], and the diameter to be 0.1 [m].

Because the kinetic model is provided as a power law, the reaction type is selected as *POWERLAW*. The coefficients of the reactants (lactic acid and methanol) are set as -1, and the coefficients of the products (methyl lactate and water) are set as 1. The exponent is defined as 2 for lactic acid and 1 for methanol because it is the power for each component activity in the kinetic expression. The products are not involved in the kinetic model for the straight reaction. Thus, the field is left blank, which implies an exponent of 0. The values for the pre-exponential factor  $k_1$  and the activation energy  $E_a$  are known. The reference temperature  $T_0$  is not specified; the exponent n is set as 0 to allow temperature dependence to be modelled using the Arrhenius equation. Finally, the basis for concentration is selected as Mole gamma to allow the kinetic calculations to be based on the activities of the component.

The simulation results presented in Table 2.1.

|                |         | Feed | Product |
|----------------|---------|------|---------|
| Mole Flows     | kmol/hr | 400  | 400     |
| LACTI-01       | kmol/hr | 100  | 96.73   |
| METHA-01       | kmol/hr | 300  | 296.73  |
| METHY-01       | kmol/hr | 0    | 3.268   |
| WATER          | kmol/hr | 0    | 3.268   |
| Mole Fractions |         |      |         |
| LACTI-01       |         | 0.25 | 0.24    |
| METHA-01       |         | 0.75 | 0.74    |
| METHY-01       |         | 0    | 0.0082  |
| WATER          |         | 0    | 0.0082  |

**Table 2.1:** Initial simulation results

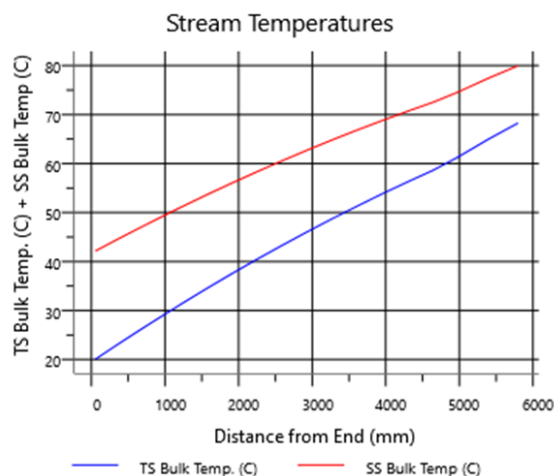
This reaction is characterized by low conversion to methyl lactate ( $\approx 3.3 \text{ mol\%}$ ). The reactor design is considered inefficient enough to convert to methyl lactate.

## 2.2 Heat Exchangers

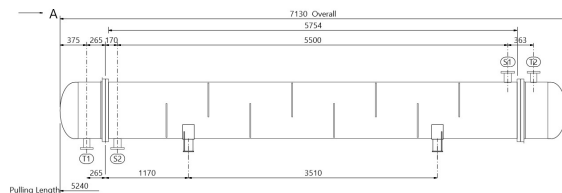
Let's assume that the reactants' temperature is not 340[K] as specified before, but 293 [K]. Therefore, a heat exchanger is needed to raise the temperature of the inlet stream. As the temperature difference is relatively low, we assume that the thermal fluid is hot water (temperature 353 [K] and flowrate equal 1000 [kmol/h]). The *HeatX* module will be used in this simulation. First, the shortcut calculations are performed to set *Cold stream outlet temperature* to be 340 [K]. Then, the *Shell & Tube* type of heat exchanger is selected to perform more detailed calculations. Remember, the more precise calculations might be characterised by lower efficiency than the shortcut calculations, for example, by considering a pressure drop. We use interactive sizing is used to find the heat exchanger geometry. Luckily, there is no error; nevertheless, some warnings are present. For simplicity, we will modify the simulation to decrease the pressure drop to a minimum (0.07 [bar]), as we do not simulate pumps in this work. However, checking if the pressure drop doesn't force a phase change is always recommended.

In non-conventional cases, each heat exchanger section might be specified by assigning a specific TEMA-type equipment.

The suggested design is a classic Shell&Tube heat exchanger with one pass. Figure 2.2 shows the final result of the heat exchanger design.



(a) Stream temperatures along the heat exchanger



(b) External dimension of the heat exchanger

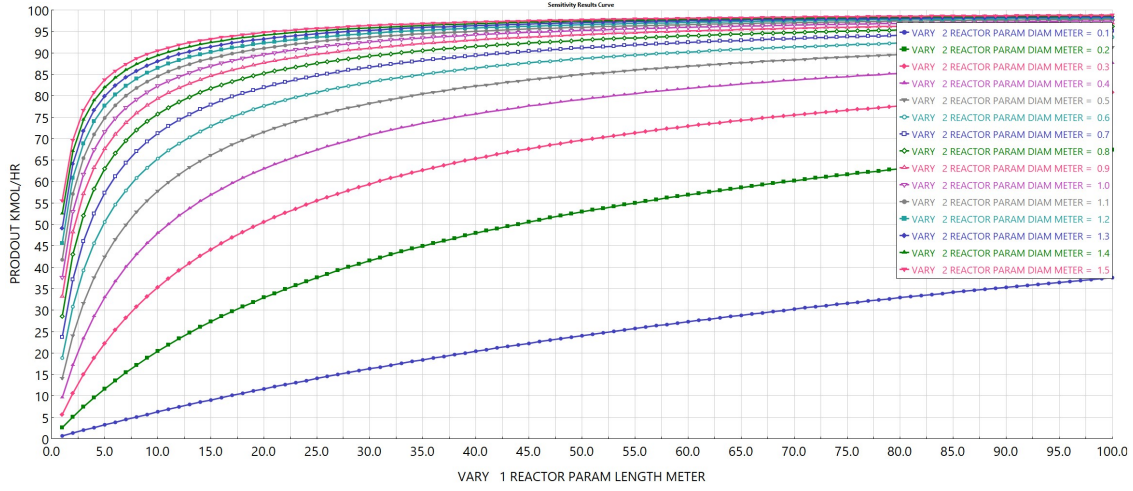
**Figure 2.2:** Results of heat exchanger design

## 2.3 Sensitivity Analysis

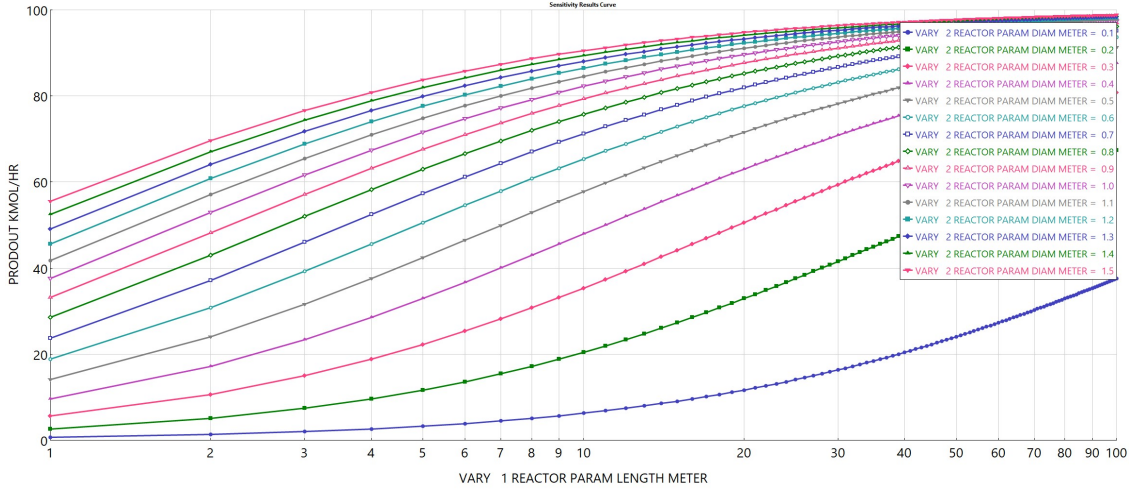
The *sensitivity analysis* allows evaluating a parameter's influence on model output. In this case, the reactor's diameter and length are selected as degrees of freedom and can be manipulated. The system output is the amount of the methyl lactate at the reactor outlet.

In *Vary* section, two variables are created: one corresponds to the length of the reactor, while the second one is the diameter of the reactor. Both variables are *Block-Var* Type. Let the length change from 1 [m] to 100 [m] every 1[m], and the diameter change from 0.1 – 1.5 [m] every 0.1 [m]. In *Define* section, model output is defined. The model output is affected by a change from *Vary* section. The output variable, in this case, is the mole flowrate of methyl lactate in the outlet stream.

The mole flowrate can be found in the *Streams* category. The sensitivity analysis results are in Figure 2.3.



(a) Sensitivity analysis - linear scale



(b) Sensitivity analysis - log scale

**Figure 2.3:** Sensitivity analysis results

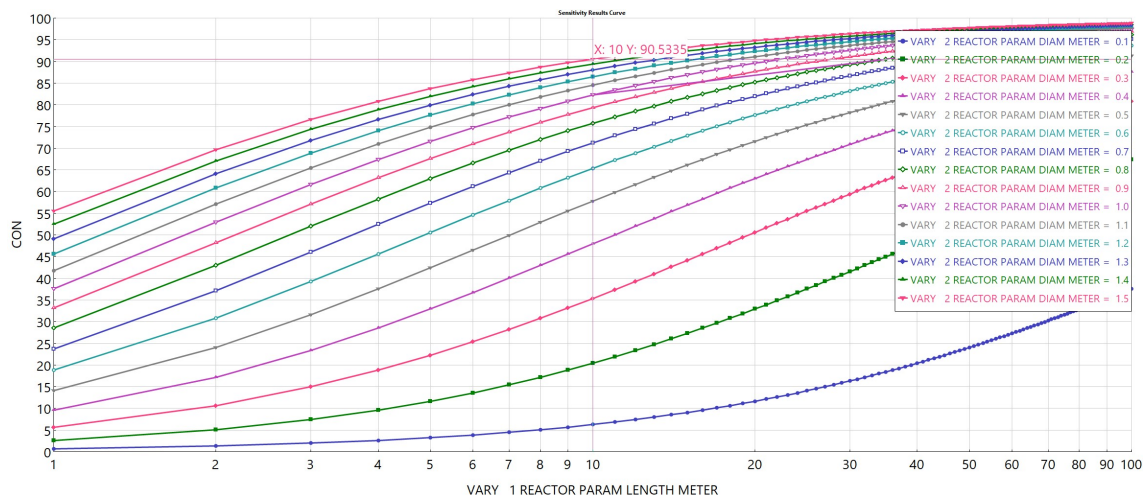
As shown in Figure 2.3, the initial value of reactors length and diameter are insufficient to obtain high conversion.

The next step is defining a local variable describing lactic acid's conversion. Three variables need to be defined in the *Define* section. Two variables describe the molar flowrate of lactic acid at the inlet and the outlet stream, and the third one describes the conversion rate. The molar flowrates can be found in the *Streams* category. The conversion is defined as *Local-Param*, but the conversion formula should be written in the *Fortran* section.

Be careful to use the symbols in the exact form as they are defined in the *Define* page. The conversion can be calculated from the following equation:

$$CON = \frac{(FEED - PRODUCT)}{FEED} \cdot 100\% \quad (2.3)$$

The results of the sensitivity analysis conducted with respect to the conversion are presented in Figure 2.4.



**Figure 2.4:** Sensitivity analysis with respect to conversion

Based on the sensitivity analysis, we select the first value, which gives us the conversion of 90%, so the length of 10 [m] and the diameter of 1.5 [m]. Any reasoning can be applied to select the reactor size. One can perform a similar analysis with respect to any indicator and use it to draw a conclusion.

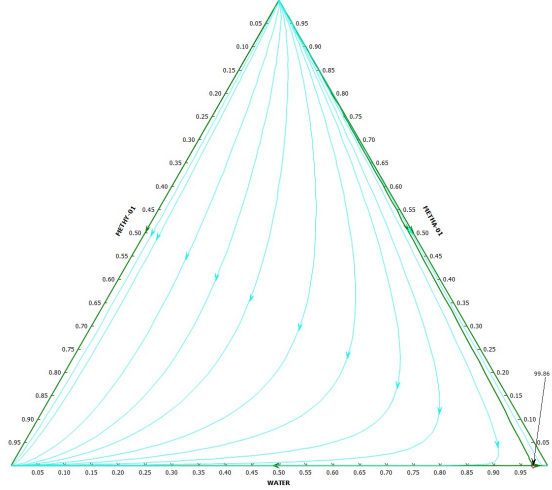
## 2.4 Design-spec

Let's investigate how to separate compounds of the stream leaving the reactor. By analysing singular points from the Distillation Synthesis Analysis (Table 2.2), it can be noticed that there is one azeotrope.

|   | Temp (C) | Classification | Type        | No. Comp. | LACTI-01 | METHA-01 | METHY-01 | WATER |
|---|----------|----------------|-------------|-----------|----------|----------|----------|-------|
| 1 | 216.627  | Stable node    | Homogeneous | 1         | 1.000    | 0.000    | 0.000    | 0.000 |
| 2 | 64.535   | Unstable node  | Homogeneous | 1         | 0.000    | 1.000    | 0.000    | 0.000 |
| 3 | 144.813  | Saddle         | Homogeneous | 1         | 0.000    | 0.000    | 1.000    | 0.000 |
| 4 | 100.018  | Saddle         | Homogeneous | 1         | 0.000    | 0.000    | 0.000    | 1.000 |
| 5 | 99.855   | Saddle         | Homogeneous | 2         | 0.000    | 0.000    | 0.027    | 0.973 |

**Table 2.2:** Singular points from the Distillation Synthesis Analysis

The same conclusion can be drawn from the ternary plot (Figure 2.5).



**Figure 2.5:** Ternary plot

In this simulation work, we are going to remove non-azeotropic components first. We start with *METHA-01*, one of the reactants with the lowest boiling point. The distillation column is modelled with *RadFrac* module. We assume the number of stages to be 30 and the feed stage to be 15. The distillation column is characterized by the Distillate rate equal to the mole flowrate of the *METHA-01*, and the molar reflux ratio equal to 1. The *Design-spec* is used to increase the bottom stream's purity. It is assumed that the number of stages, the feed stage and the distillate rate are fixed, but the reflux ratio can be manipulated. The *Design-spec* can be found in the *Flowsheeting Option* folder. First, the model output needs to be defined. In this case, the model output is the mole fraction of acetic acid in the bottom stream. In the *Spec* section, the target value of the model output is specified. We assume that the bottom stream should have the molar fraction of the acetic acid equal to  $1e-4$ , with tolerance  $1e-5$ . The next step is to define what parameter can be used to tune the model output. In this case, we used the molar reflux ratio, which can vary from 0.5 to 2. The adjusted value of the reflux ratio is 1.5524972, and simulation results can be found in Table 2.3.

|                |         | Product | Distillate | Bottom     |
|----------------|---------|---------|------------|------------|
| Mole Flows     | kmol/hr | 400     | 190.51     | 209.5      |
| LACTI-01       | kmol/hr | 9.467   | 9.467      | 4.82E-50   |
| METHA-01       | kmol/hr | 209.467 | 0.019      | 209.45     |
| METHY-01       | kmol/hr | 90.53   | 90.53      | 2.61E-16   |
| WATER          | kmol/hr | 90.53   | 90.48      | 0.053      |
| Mole Fractions |         |         |            |            |
| LACTI-01       |         | 0.023   | 0.050      | 2.30E-52   |
| METHA-01       |         | 0.523   | 0.0001     | 0.9997     |
| METHY-01       |         | 0.226   | 0.476      | 1.2450E-18 |
| WATER          |         | 0.226   | 0.475      | 0.000251   |

**Table 2.3:** Stream results of the distillation column



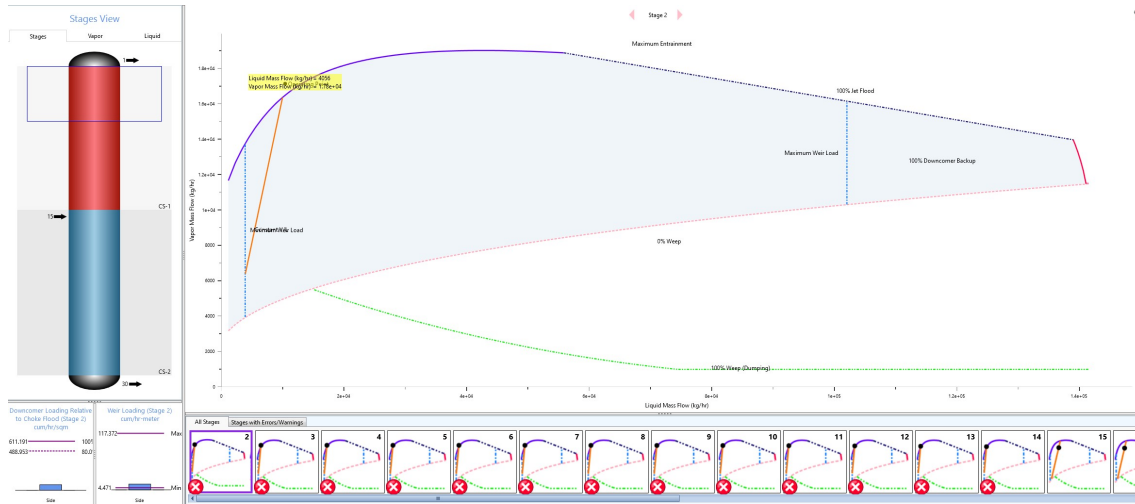
## 2.5 Column Internals

The next step is to analyse the distillation column from the hydraulic point of view. The fact that the simulation of the distillation column has converged and satisfies the mass balance doesn't mean that the hydraulics are well designed. This requires special attention and separate analysis. The analysis tools for a column hydraulic can be found in the *Column Internals* folder. One can use the *Auto Section* option to create different sections along the column. In this case, the software suggests two sections of different diameters (both with sieve trays). One section is above, and the second is below the feed stage. The results of the auto-section tool are given in Table 2.4.

| Name | Start Stage | End Stage | Mode               | Internal Type | Tray/Packing Type | Number of Passes | Tray Spacing/Section Packed Height | Dimension | Diameter | Dimension |
|------|-------------|-----------|--------------------|---------------|-------------------|------------------|------------------------------------|-----------|----------|-----------|
| CS-1 | 2           | 14        | Interactive sizing | Trayed        | SIEVE             | 1                | 0.6096                             | meter     | 1.608    | meter     |
| CS-2 | 15          | 29        | Interactive sizing | Trayed        | SIEVE             | 1                | 0.6096                             | meter     | 1.596    | meter     |

**Table 2.4:** Column design given by automatic tool

The graphical representation of the this column is presented on Figure 2.6



**Figure 2.6:** Column internals

The software returns the following error "Entrainments on Stages 2 - 14 are above the specified maximum percent liquid entrainment of 10. We recommend increasing tray spacing." First, both sections have almost the same diameter (1.6 [m]), so the whole column can be represented by one section. The error given by the software can be solved by increasing the spacing from the default value of 0.6096 [m] to 0.75 [m]. Figure 2.7 presents the corrected column hydraulic.

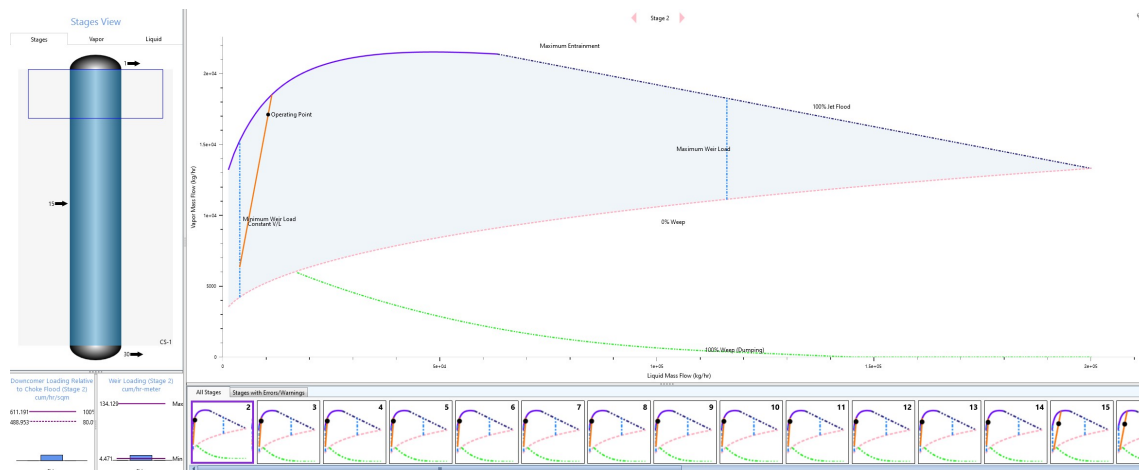


Figure 2.7: Column internals

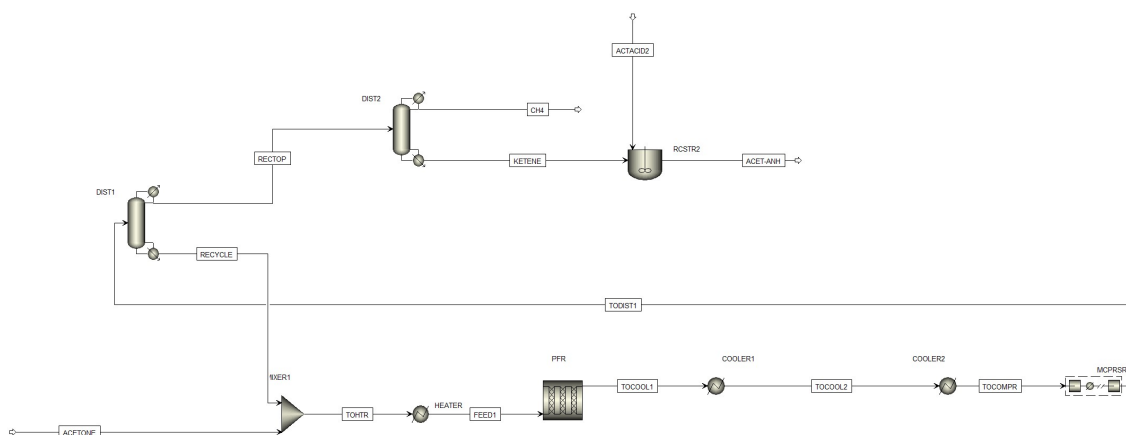


# Chapter 3

## Economic Analysis

### 3.1 Acetic anhydride production

We use the production of acetic anhydride from acetone to demonstrate how to evaluate the economic attributes of a chemical process. We are going to follow the book of [2]. The process flowsheet for acetic anhydride production is made of PFR with a recycle for the unreacted acetone, followed by two downstream separation units: rectifying and distillation column and finally, the conversion of ketene and acetic acid into acetic anhydride using CSTR. The flowsheet is presented on Figure 3.1



**Figure 3.1:** The process flowsheet for acetic anhydride production with recycling of the unreacted acetone

The methods recommended by Aspen for Carboxylic Acids are activity coefficient methods with Nothangel or Hayden-O’Connel model with vapour phase association with NRTL-HOC or WILSON-NTH. In this simulation, Wilson-NTH is chosen.

All the missing binary interaction coefficients can be estimated by the UNIFAC method, which uses information about the structure of particular components to predict their behaviour.

The reactor design in Aspen Plus depends on the reactor type the user chooses. In this exercise, the PFR and CSTR reactors are used. The first reactor is PFR. Firstly, one needs to decide on the reactor type. The adiabatic reactor is used in

this case. Then the reactor dimensions should be provided. The third step is to define the kinetics of the reaction need to be defined. The powerlaw model is used. Kinetic data can be found in [3].

The outlet stream from the reactor contains a high amount of unreacted acetone, which should be separated and recirculated. This can be done with an absorption column or distillation column.

Although, the vapour feed to the column should be compressed before the separation. The 4-stage compressor can be used for that purpose. Then the stream is fed into the column. This is an example of a rare process which belongs to the cryogenic group due to the significantly lower temperature in the condenser. The acetone is a bottom product and is recycled. The methane is separated from ketene in a distillation column in the second column. The ketene is a bottom product of the distillation and is used as a feed for the CSTR reactor. The ketene is mixed with acetic acid in the reactor. First, the information about working conditions (T and P) and the reactor's technical details (Volume) must be introduced to Aspen Plus. Then the reaction is described. The powerlaw model is used again, but the reaction type is "equilibrium", meaning that the Gibbs energy minimization algorithm is used.

The input file can be found at the end of this chapter. The results of the simulation are presented in table 3.1:

|                                  | Units   | ACET-ANH | ACETONE  | ACTACID2 | CH4       | FEED1    | KETENE   | RECTOP    | RECYCLE  | TOCOMPR  | TOCOOL1  | TOCOOL2  | TODIST1  | TOHTR    |
|----------------------------------|---------|----------|----------|----------|-----------|----------|----------|-----------|----------|----------|----------|----------|----------|----------|
| Temperature                      | C       | 7.50E+01 | 2.50E+01 | 2.50E+01 | -9.79E+01 | 7.62E+02 | 5.59E+01 | -6.05E+01 | 2.03E+02 | 9.00E+01 | 6.28E+02 | 1.40E+02 | 1.95E+02 | 7.01E+01 |
| Pressure                         | bar     | 1.50E+01 | 1.60E+00 | 1.50E+01 | 2.80E+01  | 1.60E+00 | 2.80E+01 | 2.90E+01  | 2.90E+01 | 1.60E+00 | 1.60E+00 | 1.60E+00 | 2.90E+01 | 1.60E+00 |
| Mole Flows                       | kmol/hr | 1.72E+01 | 1.72E+01 | 1.71E+01 | 1.72E+01  | 7.37E+01 | 1.72E+01 | 3.44E+01  | 5.65E+01 | 9.09E+01 | 9.09E+01 | 9.09E+01 | 9.09E+01 | 7.37E+01 |
| CH <sub>3</sub> COH <sub>3</sub> | kmol/hr | 1.22E-02 | 1.72E+01 | 0.00E+00 | 4.92E-32  | 7.37E+01 | 1.22E-02 | 1.22E-02  | 5.65E+01 | 5.65E+01 | 5.65E+01 | 5.65E+01 | 5.65E+01 | 7.37E+01 |
| C <sub>2</sub> H <sub>2</sub> O  | kmol/hr | 7.94E-02 | 0.00E+00 | 0.00E+00 | 2.82E-14  | 1.22E-02 | 1.72E+01 | 1.72E+01  | 1.22E-02 | 1.72E+01 | 1.72E+01 | 1.72E+01 | 1.72E+01 | 1.22E-02 |
| CH <sub>4</sub>                  | kmol/hr | 1.72E-02 | 0.00E+00 | 0.00E+00 | 1.72E+01  | 1.72E-12 | 1.72E-02 | 1.72E+01  | 1.72E-12 | 1.72E+01 | 1.72E+01 | 1.72E+01 | 1.72E+01 | 1.72E-12 |
| CH <sub>3</sub> COOH             | kmol/hr | 1.16E-05 | 0.00E+00 | 1.71E+01 | 0.00E+00  | 0.00E+00 | 0.00E+00 | 0.00E+00  | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 |
| ACET-ANH                         | kmol/hr | 1.71E+01 | 0.00E+00 | 0.00E+00 | 0.00E+00  | 0.00E+00 | 0.00E+00 | 0.00E+00  | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 |
| H <sub>2</sub> O                 | kmol/hr | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00  | 0.00E+00 | 0.00E+00 | 0.00E+00  | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 |
| Mole Fractions                   |         |          |          |          |           |          |          |           |          |          |          |          |          |          |
| CH <sub>3</sub> COH <sub>3</sub> |         | 7.08E-04 | 1.00E+00 | 0.00E+00 | 2.86E-33  | 1.00E+00 | 7.08E-04 | 3.54E-04  | 1.00E+00 | 6.21E-01 | 6.21E-01 | 6.21E-01 | 6.21E-01 | 1.00E+00 |
| C <sub>2</sub> H <sub>2</sub> O  |         | 4.61E-03 | 0.00E+00 | 0.00E+00 | 1.64E-15  | 1.66E-04 | 9.98E-01 | 5.00E-01  | 2.16E-04 | 1.89E-01 | 1.89E-01 | 1.89E-01 | 1.89E-01 | 1.66E-04 |
| CH <sub>4</sub>                  |         | 9.98E-04 | 0.00E+00 | 0.00E+00 | 1.00E+00  | 2.33E-14 | 9.98E-04 | 5.00E-01  | 3.04E-14 | 1.89E-01 | 1.89E-01 | 1.89E-01 | 1.89E-01 | 2.33E-14 |
| CH <sub>3</sub> COOH             |         | 6.76E-07 | 0.00E+00 | 1.00E+00 | 0.00E+00  | 0.00E+00 | 0.00E+00 | 0.00E+00  | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 |
| ACET-ANH                         |         | 9.94E-01 | 0.00E+00 | 0.00E+00 | 0.00E+00  | 0.00E+00 | 0.00E+00 | 0.00E+00  | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 |
| H <sub>2</sub> O                 |         | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00  | 0.00E+00 | 0.00E+00 | 0.00E+00  | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 |

**Table 3.1:** Simulation result of the acetic anhydride production

## 3.2 Economic analysis steps

If we have the process simulation ready and stable, we can move to the economic analysis of the process. The economic analysis requires defining feed and product stream prices, defining utilities in terms of pricing, and associating them with equipment such as a pump, compressor, condenser, reboiler, and heater. The economic analysis consists of several steps.

### Step 1: Investment options

In "Navigation" panel, let us go to "Setup" | "Costing Options" | "Costing options" tab form to specify "operating life of plant", "length of plant startup" and "start of basic engineering".

### Step 2: Feed, product and utility prices

In the "Setup" | "Stream Price" | "Input" form, the price per unit of the feed or product stream can be specified. In the "Utilities" folder, each utility used in the simulation is characterized. Each pre-defined utility has its own "purchase price" or "energy price". The price of a utility can be modified by entering detailed information about that utility. The prices used in this exercise are shown in table 3.2, and the utility prices have default values suggested by the software.

| Stream ID | Source | Destination | Basis | Price | Unit     |
|-----------|--------|-------------|-------|-------|----------|
| ACET-ANH  | RCSTR2 |             | Mass  | 1000  | \$/tonne |
| ACTACID2  |        | RCSTR2      | Mass  | 600   | \$/tonne |
| ACETONE   |        | MIXER1      | Mass  | 1200  | \$/tonne |
| CH4       | DIST2  |             | Mass  | 6150  | \$/tonne |

**Table 3.2:** Feed and product prices

### Step 3: Activation of the economical module

There are two routs to perform economic analysis with Aspen environment. First one is to use the economic module, which is incorporated in the Aspen Plus software. The second one is to use stand-alone module called "Aspen Economic Analyzer" (APEA). We are going to focus on the second method as it is more comprehensive and give more flexibility.

Nevertheless which method is used, the general steps are the same: "Mapping", "Sizing" (Step 4) and "Evaluation" (Step 6). Details on each step will be covered in the following text.

The first step is to send the process simulation to the APEA. It can be done with "Send to APEA" button in the "Economics". Next, a new project needs to be created. Then the simulation data can be loaded, but special attention needs to be paid to check if correct fluid are associated to each utility. In this case, "AIR" utility should associated with air fluid, "FH100" utility with high-temperature hot oil, and "REFRIG4" with refrigerant ethane.

The details of the economic variables can be found in the "Project Basis View". The list of equipment is located in the "Process View" section. In case of need, more pieces of equipment can be added in this section directly (so it is not needed to go back to the process simulation).

### Step 4: Mapping and sizing

The "Map option" can be activated with the "Map simulator Items" button at the top of the page. The "Size equipment" should be marked, while "Custom sizing" can be left unmarked. The "Customize sizing" option interferes with equipment sizing details and allows to use of custom sizing models. In the "Map Preview" window, all the flowsheet objects are mapped with APEA built-in objects. For example, we are going to use the following mapping:

- (a) COOLER1 is "Floating headshell and tube exchanger" because of a significant temperature difference between the hot and cold stream.

- (b) COOLER2 is "Air cooler" to reflect that "AIR" utility is used.
- (c) DST1(RADFRAC) and DST2(RADFRAC); The distillation columns consist of the sets of equipment, and each should be specified.
  - Tower type is "Multiple diameters, trayed or packed tower".
  - Condenser type is "Bare pipe immersion coil".
  - Condenser drum is a "Horizontal drum".
  - Reflux pump type is "Centrifugal single or multi-stage pump".
- (d) Heater type is "Box type process furnace".
- (e) Mixer can be represented as "Agitated tank – enclosed".
- (f) The compressor type is "Centrifugal compressor - horizontal".
- (g) PFR is "Packed tower".
- (h) CSTR is "Agitated tank – enclosed, jacketed".

The mapping and sizing are performed automatically.

#### Step 5: Debugging

The next step would be to evaluate the project by clicking the "Evaluate Project" button. If things go smoothly, you will reach the final executive summary for costs without hassles, and you can go to the [Step 6](#). However, you may get a warning or error message during the evaluation step regarding sizing or missing input data for some pieces of equipment. To check for issues, you can look at the generated report to find that APEA reports errors due to improper entry, such as the type of construction material or a property value that is out of range. On the other hand, the warning message alarms the user that an error might be incurred in the user's selected mapped object specifications.

- HEATER

*ERROR> 'FU - 5' STRESS FOR MATERIAL A 214 IS ZERO AT A TEMPERATURE OF 791.85 SYSTEM MAY NOT CONTAIN STRESS VALUES FOR THE MATERIAL.*

This means that construction A214 (Carbon Steel) material is unsuitable for a high-temperature heater. However, the default Carbon steel A214 can be replaced with S347.

Each piece of equipment can be modified in the "Project View" section. Right-click on an item and select modify to access the details of each piece of equipment. After changes, the inner "Evaluate" use a button to evaluate only a selected item.

- PFR

*Component Item Description: PFR User Tag Number: PFR \*Component Ref #: 2 WARN > 'TW - 2' PACKING TYPE ' ' AND/OR VOLUME INCORRECT.*

If we use "1.0 CRR Ceramic raschig ring" as the "Packing type".

- COOLER 1

*Component Item Description: COOLER1 User Tag Number: COOLER1  
\*Component Ref #: 17 WARN > 'HE - 17' DESIGN TEMPERATURE  
TOO HIGH FOR VACUUM OR EXTERNAL PRESSURE DESIGN*

COOLER1 material can be specified as "347S" and "SS347" for both tube and shell construction.

**Step 6:** Project evaluation

Clicking on "Capital Costs" o generate a full-fledge report s that includes all cost-based technical project details, including design, equipment, civil, structural, piping, mechanical, steel, instrumental, electrical, insulation, paint, labor, management, and the project metrics, such as Independent Project Analysis (IPA) metrics and Project Evaluation System (PES) summary and cost check.

The investment analysis of the project is summarized in table [3.3](#).

The summary of the overall cost obtained from the economic analysis can be found in table [3.4](#).

Remember that total operating cost includes:

- |                            |                           |
|----------------------------|---------------------------|
| • Total raw materials cost | • Operating charges       |
| • Total utilities cost     | • Plant overhead          |
| • Operating labor cost     | • Subtotal operating cost |
| • Maintenance cost         | • General and admin cost  |

| ITEM  | UNITS          |               |
|---|----------------|---------------|
| TW (Number of Weeks per Period)                                 | Weeks/period   | 52            |
| T (Number of Periods for Analysis)                              | Period         | 20            |
| DTEPC (Duration of EPC Phase)                                   | Period         | 0.75          |
| DT (Duration of EPC Phase and Startup)                          | Period         | 1.13462       |
| WORKP (Working Capital Percentage)                              | Percent/period | 5             |
| OPCHG (Operating Charges)                                       | Percent/period | 25            |
| PLANTOVH (Plant Overhead)                                       | Percent/period | 50            |
| CAPT (Total Project Cost)                                       | Cost           | 1.35E+07      |
| RAWT (Total Raw Material Cost)                                  | Cost/period    | 1.45E+07      |
| PRODT (Total Product Sales)                                     | Cost/period    | 2.76E+07      |
| OPMT (Total Operating Labor and Maintenance Cost)               | Cost/period    | 1.36E+06      |
| UTILT (Total Utilities Cost)                                    | Cost/period    | 547531        |
| ROR (Desired Rate of Return/Interest Rate)                      | Percent/period | 20            |
| AF (ROR Annuity Factor)   |                | 5             |
| TAXR (Tax Rate)   | Percent/period | 40            |
| IF (ROR Interest Factor)  |                | 1.2           |
| ECONLIFE (Economic Life of Project)                             | Period         | 10            |
| SALVAL (Salvage Value (Percent of Initial Capital Cost))        | Percent        | 20            |
| DEPMETH (Depreciation Method)                                   |                | Straight Line |
| DEPMETHN (Depreciation Method Id)                               |                | 1             |
| ESCAP (Project Capital Escalation)                              | Percent/period | 5             |
| ESPROD (Products Escalation)                                    | Percent/period | 5             |
| ESRAW (Raw Material Escalation)                                 | Percent/period | 3.5           |
| ESLAB (Operating and Maintenance Labor Escalation)              | Percent/period | 3             |
| ESUT (Utilities Escalation)                                     | Percent/period | 3             |
| START (Start Period for Plant Startup)                          | Period         | 1             |
| PODE (Desired Payout Period (excluding EPC and Startup Phases)) | Period         |               |
| POD (Desired Payout Period)                                     | Period         |               |
| DESRET (Desired Return on Project for Sales Forecasting)        | Percent/Period | 10.5          |
| END (End Period for Economic Life of Project)                   | Period         | 10            |
| GA (G and A Expenses)   | Percent/Period | 8             |
| DTEP (Duration of EP Phase before Start of Construction)        | Period         | 0.480769      |
| OP (Total Operating Labor Cost)                                 | Cost/period    | 1.24E+06      |
| MT (Total Maintenance Cost)                                     | Cost/period    | 115000        |

**Table 3.3:** Summery of the investment analysis

| INVESTMENT:                |               |                 |
|----------------------------|---------------|-----------------|
| Currency Conversion Rate   | 1.00          | USD/U.S. DOLLAR |
| Total Project Capital Cost | 13'450'400.00 | USD             |
| Total Operating Cost       | 18'820'400.00 | USD/Year        |
| Total Raw Materials Cost   | 14'536'300.00 | USD/Year        |
| Total Utilities Cost       | 547'531.00    | USD/Year        |
| Total Product Sales        | 27'587'800.00 | USD/Year        |
| Desired Rate of Return     | 20.00         | Percent/'Year   |
| P.O. Period                | 5.83          | Year            |

**Table 3.4:** Overall costs of the acetic anhydride production

### 3.3 Investment indicators

An economy of an arbitrary process can be analysed based on different indicators. The most popular indicator is the **Net Present Value (NPV)**, which applies to

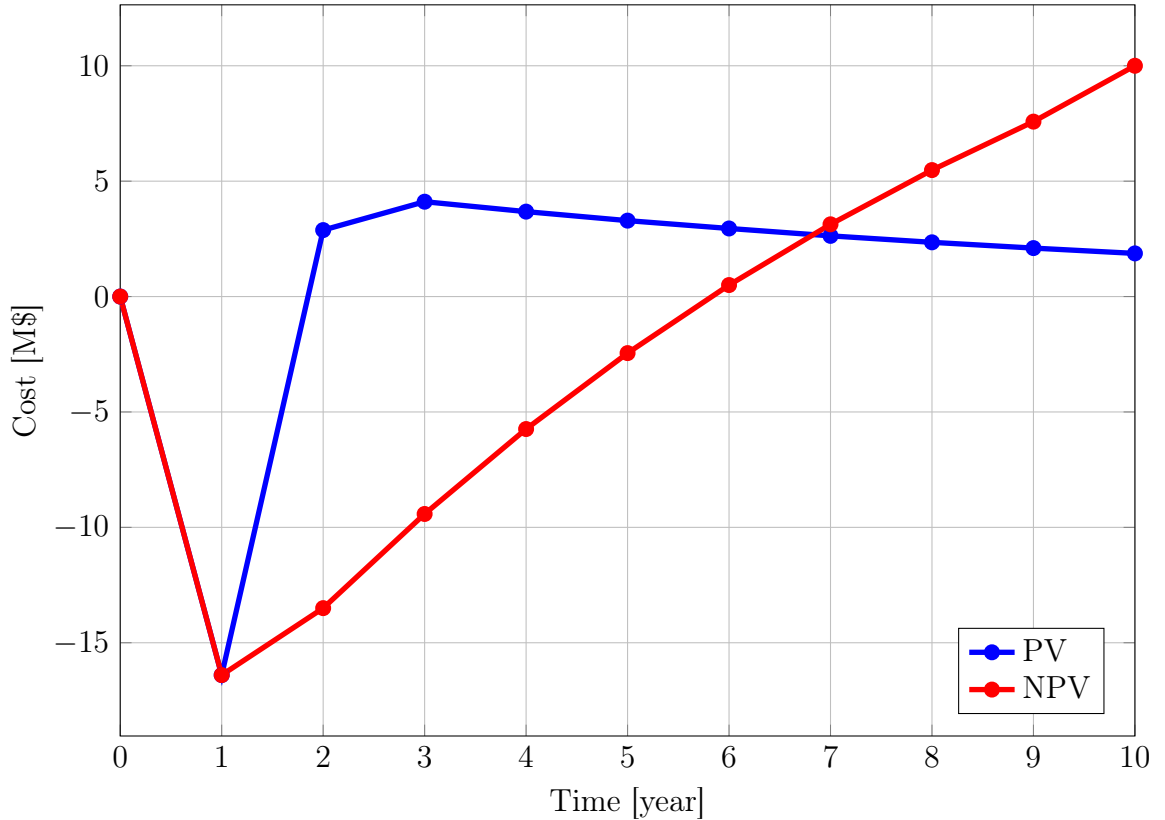
a series of cash flows occurring at different times and accounts for the "time value of money". NPV is determined by calculating the costs (negative cash flows) and benefits (positive cash flows) for each period of an investment. After the cash flow for each period is calculated, the present value (PV) of each one is achieved by discounting its future value (see equation 3.1) at a periodic rate of return (the rate of return dictated by the market). NPV is the sum of all the discounted future cash flows, as given by equation 3.2.

$$PV = \frac{R_t}{(1 + r)^t} \quad (3.1)$$

$$NPV = \sum_{i=0}^N \frac{R_t}{(1 + i)^t} = \sum_{i=0}^N PV \quad (3.2)$$

where  $t$  is the time of the cash flow,  $r$  is the discount rate, i.e. the return that could be earned per unit of time on investment with similar risk, and  $R_t$  is the net cash flow, i.e. cash inflow – cash outflow, at time  $t$  and  $N$  is the number of time intervals.

Based on the project evaluation performed in Step 6, the PV and NPV are found. The PV and NPV curves are presented in Figure 3.2.



**Figure 3.2:** Cash flow

NPV is negative for the first six years and becomes positive afterwards, meaning the project appears profitable from year seven onward.

The second indicator is the **discounted payout period (DPP)**, which is described by equation 3.3

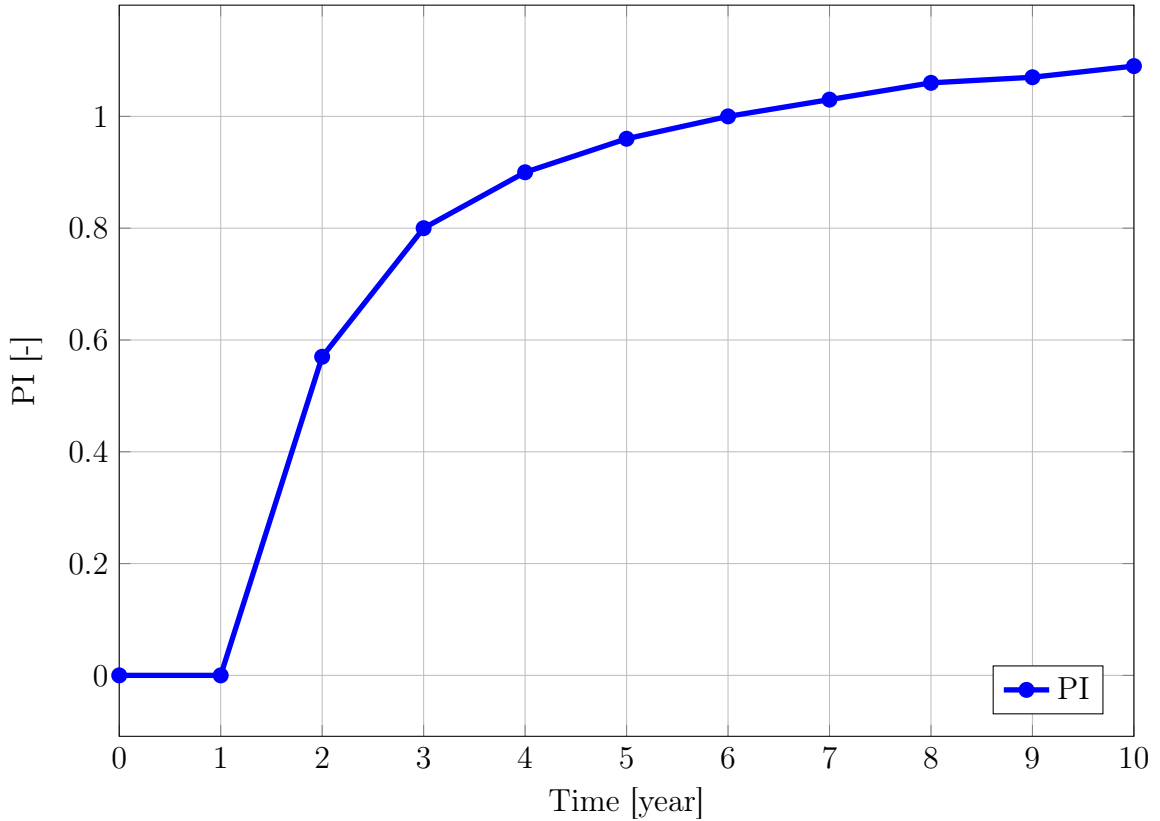
$$DPP = \text{Years with negative NPV} + \frac{|\text{NPV}|}{\text{PV}} = 5 + \frac{|-2.45E+06|}{2.95E+06} = 5.83 \text{ years} \quad (3.3)$$

DPP represents the length of time required to recover the cost of an investment. The payout (or, payback) period of a given investment project is an important determinant of whether to undertake the project, as longer payback periods are typically not desirable for investment projects. Notice that the payout period indicator ignores any benefits that occur after the payback period and, therefore, does not measure profitability. In addition, it ignores the time value of money.

The third indicator is the **profitability index (PI)** that shows the present value of the benefits relative to the present value of the costs. The PI is defined as given by equation 3.4

$$PI = \frac{\text{Present Value of the Cumulative Cash Inflows (PVI)}}{\text{Present Value of the Cumulative Cash Outflows (PVO)}} \quad (3.4)$$

If the profitability index is greater than one, then the project appears to be profitable. If this index is less than one, the project appears unprofitable. If this number equals one, the project incurs no losses or gains (break-even point). PI's time evolution is shown in Figure 3.3.



**Figure 3.3:** Profitability index



The fourth indicator is the **internal rate of return (IRR)**. The internal rate of return (IRR) is the discount rate at which the net present value of an investment becomes zero. In more specific terms, the IRR of an investment is the discount rate at which the net present value of costs (negative cash flows) of the investment equals the net present value of the benefits (positive cash flows) of the investment. In this case, the  $IRR = 34.27\%$ . A project should only be accepted if its IRR is NOT less than the target internal rate of return. When comparing two or more mutually exclusive projects, the project with the highest value of IRR should be considered.

The fifth indicator is the **modified internal rate of return (MIRR)**. IRR assumes that positive cash flows are reinvested at the same rate of return as the investments (i.e., the project which generates them). This assumption is questionable as funds are reinvested at a rate that reflects the organization's cost of capital or returns on cash. Consequently, if we stick with the assumption of an equal rate for both negative and positive cash flow, IRR gives an optimistic (i.e., overestimated) rate of return for the cash flows. In addition, more than one IRR may be found for projects with alternating positive and negative cash flows, leading to confusion. Two interest rates are needed to use MIRR: The reinvestment rate for the positive cash flow (PV) and the finance rate for the negative cash flow (NV). The MIRR is given by equation 3.5.

$$MIRR(\%) = \left[ \left[ \frac{FV}{-PV} \right]^{\frac{1}{EPELP}} - 1 \right] \times 100\% \quad (3.5)$$

where EPELP is the "End Period for Economic Life of Project" (i.e., EPELP=10 years, by default),  $PV$  is the sum of cash flows (brought to the beginning of the first period), and  $FV$  is the sum of positive cash flows (brought to the end of the last period).

The MIRR value was found to be 21.03%, which is less than IRR.

### 3.4 APEA without process simulation

It is not always possible to simulate a whole production process, in particular in case of bio-based processes. The APEA can be used to estimate an equipment price, based on limited amount of informations. To use the APEA without the process simulation, piece of equipment from the *Process equipment* section. *Process equipment* section is usually located in the top-right corner in the *Components* tab. Then, an analysed equipment needs to be added in the *list* section by drag-and-drop. The selection of an equipment from *Process equipment* section corresponds to the mapping procedure, which was discussed before. The drag-and-drop will cause the opening of a new windows called *New Component information*, where the name of analysed machine needs to be assign. After acceptance of the equipment name, a new windows with technical sheet will open. Depending on the equipment, different information about the equipment size are required to evaluate the cost. The necessary information are highlighted. In case of a vessel, a necessary information

is its radius and height. If a heat exchanger is discussed, then a heat transfer area needs to be known a priori.

# Bibliography

- [1] Juan Gabriel Segovia-Hernández and Fernando Israel Gómez-Castro. Stochastic Process Optimization using Aspen Plus®. CRC Press, 2020. ISBN 9780367573096.
- [2] Kamal I. M. Al-Malah. Aspen Plus Chemical Engineering Applications. Wiley & Sons, Incorporated, John, 2016. ISBN 9781119293620.
- [3] H. Scott Fogler. The elements of chemical kinetics and reactor calculations (a self-paced approach). Prentice-Hall, 1974. ISBN 0132634422.