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School of Industrial and Information Engineering

Department of Chemistry, Materials and Chemical Engineering” Giulio Natta”  
Master of Science in Chemical Engineering

### ***Process Systems Engineering A***

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## **Conceptual Design and Economic Feasibility of Hydrodealkylation of Toluene Plant**

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# 1. Introduction

Hydrodealkylation of Toluene represents a pivotal chemical process in organic chemistry, particularly within the industrial sector, for synthesizing various high-value chemical products. This process involves removing an alkyl group from Toluene and adding a hydrogen atom, forming Benzene. Two main reactions are occurring in this plant:



Since Benzene is the principal product of the plant, reaction 1.2 is considered an undesired reaction.

The main goal of this study is to simulate the hydrodealkylation of the Toluene plant using MATLAB and Aspen HYSYS. Then, an economic assessment and feasibility analysis, using the hierarchical approach, is conducted to calculate the plant's profitability during an operating year. In terms of economic feasibility, there are five levels of economic potential evaluation:

1. Batch Operation versus Continuous Operation
2. Input-Output Structure of Flowsheet
3. Recycle Structure of the Flowsheet
4. General Structure of the Separation System
5. Heat Exchange Network<sup>1</sup>

In this study, the fifth level of economic potential is neglected.

## 2. Process Scheme

This section will show and describe the HDA<sup>2</sup> process's process diagrams. Then, the main process specifications will be mentioned.

### 2.1 Process Diagrams

Before studying any chemical process, looking at the process diagrams is necessary to clarify and understand the process types of equipment. Many types of process diagrams exist, but there are three common types of process diagrams:

1. *Block Flow Diagram*<sup>3</sup>: This diagram Simplifies the representation of a process by using blocks to represent unit operations. This diagram is required in the early stages of process design for a high-level overview.

The block flow diagram of the HDA process is shown in the Figure below:

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<sup>1</sup> Referred to Pinch Technology

<sup>2</sup> Hydroalkylation

<sup>3</sup> BFD

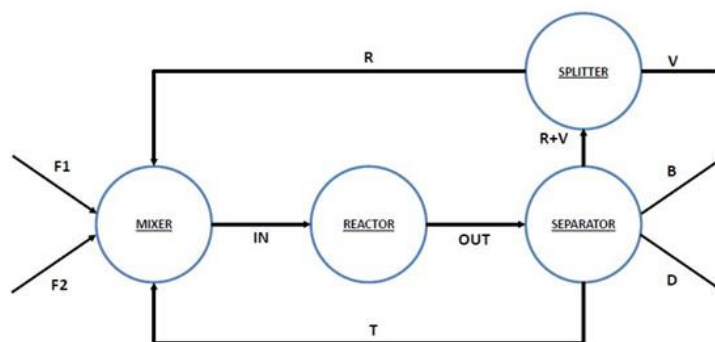


Figure 1 - BFD of Process

Note that the names of streams will be used in future calculations as variables.

2. *Process Flow Diagram*<sup>4</sup>: This diagram is More detailed than BFD and shows significant equipment, process flow, and operating conditions. It is used for design and operational analysis, showing the relationships between major components in a system.

The process flow diagram of the HDA process is shown in the Figure below:

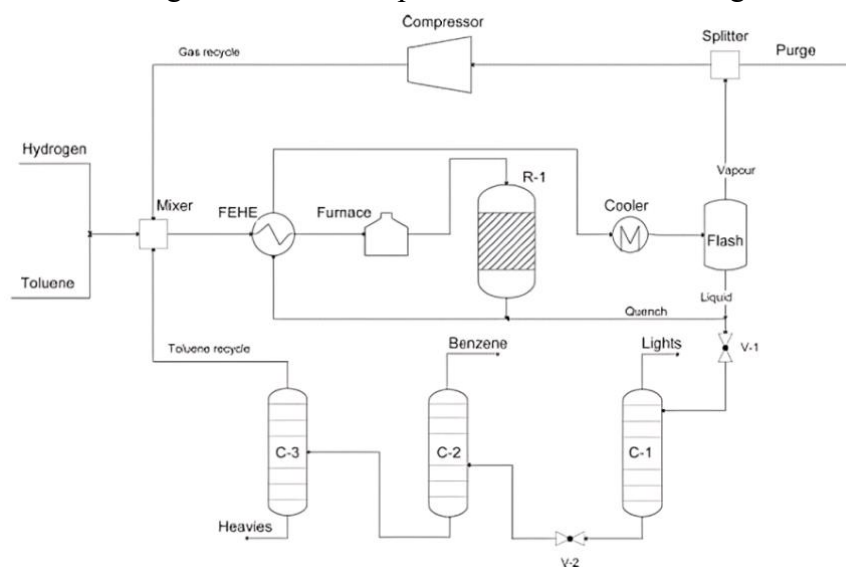


Figure 2 - PFD of Process

3. *Piping and Instrumentation Diagram*<sup>5</sup>: This detailed diagram shows piping, instrumentation, and control devices for detailed engineering design, operation, and maintenance. It consists of all process equipment, piping, valves, and instrumentation.

<sup>4</sup> PFD<sup>5</sup> P&ID

Due to the simplification of the study, the P&ID diagram is not considered. Therefore, readers do not expect to see any detailed engineering design in this study.

## 2.2 Process Specifications

To organize the given data, it is necessary to list them and make some assumptions besides.

1. The provided feedstock is at ambient temperature (25 °C).
2. The inlet stream to the mixer (F1) consists of 95% hydrogen and 5% methane. Pure Toluene makes up the other inlet stream to the mixer (F2).
3. The selectivity should be at least 96% in order to make the plant feasible.
4. To avoid the coking phenomena in the reactor, the H<sub>2</sub> to C<sub>7</sub>H<sub>18</sub> (HTR) ratio should be greater than 5. This effort leads to limiting coke formation.
5. The scheduled production capacity of the plant equals  $265 \frac{kmol}{h}$ .

In addition, here are the operating conditions of the plant:

1. The optimal pressure is 34 bar. Pressure higher than this will increase the compression cost while reducing the size of the equipment.
2. Another operating condition is temperature. Since the temperature is one of the degrees of freedom<sup>6</sup>, it is considered a manipulated variable. It is better to know the behavior of reactions to temperature increases. The primary reaction is exothermic ( $\Delta H^{rxn} < 0$ ), and the side reaction is endothermic ( $\Delta H^{rxn} > 0$ ). The temperature varies from 600°C to 750°C for controlling the set of reactions.

## 2.3 EP1 - Reactor Selection

One of the fundamental steps for designing a plant is to select a suitable reactor. In the case of time-dependency operations, chemical reactors are divided into continuous reactors and discontinuous reactors. There is a heuristic rule to determine the type of reactor. If the overall plant capacity is less than  $500 \frac{ton}{year}$ , a discontinuous (batch) reactor is the best choice (Usually, seasonal plants have an annual capacity within this range). Otherwise, if the overall annual capacity of the plant is higher than  $500 \frac{ton}{year}$ , a continuous reactor is suggested.

Note that this heuristic is only intended to assist in selecting the optimal reactor and should not replace the plant designer's expertise.

According to the plant's molar capacity, the annual mass capacity can be calculated using this equation:

---

<sup>6</sup> DOF



$$Capacity = 265 \frac{kmol}{h} \cdot 78 \frac{kg}{kmol} \cdot 8000 \frac{h}{y} = 165360 \frac{t}{y} \quad 2.1$$

The annual plant capacity is significantly higher than  $500 \frac{t}{y}$ . Thus, the suitable reactor is the continuous reactor. Continuous reactors are divided into two chief categories: CSTR<sup>7</sup> and PFR<sup>8</sup>. According to the kinetics scheme of the reactions (more reactions in series) and gaseous phase of species, the more suitable choice is the PFR.

### 3. Material Balance and DOF Analysis

Before starting the calculations, it is necessary to know the composition of each component in all streams. According to the data and BFD, stream **F1** consists of 95% Hydrogen and 5% Methane. Stream **F2** has pure toluene. As a first approximation, all the other streams can be considered pure (even the recycles); this hypothesis will be removed further in the analysis. Pure Benzene comprises stream **B**, and stream **D** consists of pure Biphenyl. In addition, stream **T** has pure Toluene. The composition of the two streams, **V** (vent) and **R** (recycle), is unknown. Both streams consist of Methane and Hydrogen, and the composition of these components is identical. Thus, the only variable is Hydrogen composition ( $x_v$ ), and Methane composition is dependent on  $x_v$ , which equals  $1-x_v$ . Finally, the stream composition table is shown as follows:

Table 1 - Stream Composition

	<b>H<sub>2</sub></b>	<b>CH<sub>4</sub></b>	<b>C<sub>6</sub>H<sub>6</sub></b>	<b>C<sub>7</sub>H<sub>8</sub></b>	<b>C<sub>12</sub>H<sub>10</sub></b>
<b>F1</b>	0.95	0.05	0	0	0
<b>F2</b>	0	0	0	1	0
<b>B</b>	0	0	1	0	0
<b>D</b>	0	0	0	0	1
<b>V</b>	$x_v$	$1-x_v$	0	0	0
<b>R</b>	$x_v$	$1-x_v$	0	0	0
<b>T</b>	0	0	0	1	0

The general form of material balance can be written as:

$$\text{Input} - \text{Output} + \text{Generation} - \text{Consumption} = \text{Accumulation}$$

The term of accumulation will equal zero in case of continuous operation ( $\frac{dm}{dt} = 0$ ).

In the following subsections, the material balance for each piece of equipment will be written down and described.

<sup>7</sup> Continuous Stirred Tank Reactor

<sup>8</sup> Plug Flow Reactor

Table 2 - Index Guide

Name	Chemical Formula	Index
Hydrogen	H <sub>2</sub>	h
Methane	CH <sub>4</sub>	m
Benzene	C <sub>6</sub> H <sub>6</sub>	b
Toluene	C <sub>7</sub> H <sub>8</sub>	t
Biphenyl	C <sub>12</sub> H <sub>10</sub>	d

### 3.1 Material balance for the mixer

The material balance around the mixer can be written as follows:

$$IN_h = F1_h + R_h \quad 3.1$$

$$IN_m = F1_m + R_m \quad 3.2$$

$$IN_t = F2_t + T_t \quad 3.3$$

### 3.2 Material balance for the reactor

The material balance around the reactor can be written as follows:

$$OUT_h = IN_h + \int (-R_1 + R_2) dV \quad 3.4$$

$$OUT_m = IN_m + \int R_1 dV \quad 3.5$$

$$OUT_t = IN_t + \int -R_1 dV \quad 3.6$$

$$OUT_b = \int (R_1 + 2R_2) dV \quad 3.7$$

$$OUT_d = \int R_2 dV \quad 3.8$$

### 3.3 Material balance for the separator

The material balance around the separator can be written as follows:

$$B_b = OUT_b \quad 3.9$$

$$D_d = OUT_d \quad 3.10$$

$$T_t = OUT_t \quad 3.11$$

$$(R + V)_h = OUT_h \quad 3.12$$

$$(R + V)_m = OUT_m \quad 3.13$$

### 3.4 Material balance for the splitter

Before writing the material balance equations, it is necessary to define a variable called Split Factor, which is expressed as the ratio between the flow rate of the vent stream and the total overall flow rate entering the separator and written as follows:

$$SF = \frac{V}{V+R} \quad 3.14$$

Hence, the material balance around the splitter can be written as follows:

$$V_h = (R + V)_h \cdot SF \quad 3.15$$

$$V_m = (R + V)_m \cdot SF \quad 3.16$$

$$R_h = (R + V)_h - V_h \quad 3.17$$

$$R_m = (R + V)_m - V_m \quad 3.18$$

### 3.5 Degree of Freedom Analysis

Degrees of freedom refers to the number of independent values that can vary in an analysis without violating constraints. For DOF<sup>9</sup> analysis, the number of equations must be subtracted from the number of independent unknown variables. The value of DOF determines how many variables should be set to have a unique solution for the set of equations. DOF is expressed as follows:

$$\text{DOF} = \text{Number of Unknowns Variables} - \text{Number of Equations}$$

According to previous equations, the set of unknowns consists of 20 stream molar flow rate, Temperature (T), Pressure (P), Split Factor (SF), and Reactor Volume (V). Then, the number of unknown variables equals to 24. In addition to the number of written material balance equations (17 in total), some more constraints can be added to the system:

$$\frac{IN_h}{IN_t} = 5 \quad 3.19$$

$$\frac{F1_m}{F1_m + F1_h} = 0.05 \quad 3.20$$

$$B_b = 265 \frac{\text{kmol}}{\text{hr}} \quad 3.21$$

$$P = 34 \text{ bar} \quad 3.22$$

$$\zeta_{B/A} = \frac{n_B^{\text{out}} - n_B^{\text{in}}}{n_A^{\text{in}} - n_A^{\text{out}}} \cdot \left| \frac{v_A}{v_B} \right| = \frac{OUT_b}{IN_t - OUT_t} = 0.96 \quad 3.23$$

Therefore, the total number of equations and constraints equals 22. Hence, the DOF equals 2. It means that a unique answer for the system can be achieved by controlling two variables. In this case, temperature and split factors are manipulated variables.

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<sup>9</sup> Degree of Freedom

## 4. Reactor Design

The overall process scheme was analyzed in the previous section, and the overall material balances were established. Following the evaluation of EP1 and consideration of the process requirements, it was determined that a plug flow reactor is the optimal choice for achieving the desired conversion. This section investigates the impact of various temperatures on reactor efficiency, specifically in conversion, selectivity, and residence time. Initially, the central assumption is that no recycling streams enter the reactor. Furthermore, given that the primary reaction is equimolar, pressure does not influence the extent of the reaction. The schematic of the reactor is shown in the Figure below:



Figure 3 - Schematic of Tubular PFR

The reactor operating conditions are known according to section 2.2, and it is assumed that the reactor operates in isothermal conditions. The primary reaction to produce Benzene is:



The rate of reaction is expressed as:

$$R_1 = k_1[C_7H_8]\sqrt{[H_2]} \quad 4.2$$

$K_1$  represents the reaction kinetics constant,  $[C_7H_8]$  represents the concentration of Toluene, and  $[H_2]$  represents the concentration of Hydrogen. The reaction kinetics constant obeys Arrhenius's law, and the kinetics parameters are shown in the table below:

Table 3 - Arrhenius's Parameters for Benzene Production Reaction

Variable	Value	Unit
$A_1$	$3.5 \cdot 10^{10}$	$\frac{m^{1.5}}{kmol^{0.5} \cdot s}$
$E_1$	50900	$\frac{kcal}{kmol}$

The side reaction which leads to the production of Biphenyl is:



The rate of the side reaction is expressed as:

$$R_2 = k_2 [C_6H_6]^2 \quad 4.4$$

$K_2$  represents the reaction kinetics constant, and  $[C_6H_6]$  represents the concentration of Benzene. Like the primary reaction, the reaction kinetics constant obeys Arrhenius's equation in this reaction, and the kinetics parameters are shown in the table below:

Table 4 - Arrhenius's Parameters for Biphenyl Production Reaction

Variable	Value	Unit
$A_2$	$2.1 \cdot 10^{12}$	$\frac{m^3}{kmol \cdot s}$
$E_2$	60500	$\frac{kcal}{kmol}$

In both tables, the variable  $A_i$  represents the pre-exponential factor, and  $E_i$  represents the activation energy of the reaction. Note that the unit of measurement of the reaction rate is  $\frac{kmol}{m^3 \cdot s}$ , and the unit of kinetics constant is the same as the unit of the pre-exponential factor.

The Arrhenius's equation is expressed as:

$$k_i = A_i \cdot \exp\left(-\frac{E_i}{R \cdot T}\right) \quad 4.5$$

$A_i$  represents the pre-exponential factor,  $E_i$  represents the activation energy of the reaction,  $R$  represents the gas universal constant<sup>10</sup>, and  $T$  represents the absolute temperature in K.

## 4.1 Governing Equations

The material balance for a tubular PFR is an ODE<sup>11</sup> and is written as follows:

$$\frac{dF_i}{dV} = r_i \quad 4.6$$

$$r_i = \sum_{j=1}^{NR} v_{j,i} R_j \quad 4.7$$

According to the general mass balances in section 3, the equations can be rewritten as:

$$\frac{dF_h}{dV} = -R_1 + R_2 \quad 4.8$$

$$\frac{dF_m}{dV} = R_1 \quad 4.9$$

<sup>10</sup> Which equals to  $8.314 \frac{J}{mol \cdot K}$

<sup>11</sup> Ordinary Differential Equation

$$\frac{dF_b}{dV} = R_1 - 2R_2 \quad 4.10$$

$$\frac{dF_t}{dV} = -R_1 \quad 4.11$$

$$\frac{dF_d}{dV} = R_2 \quad 4.12$$

The set of ODEs is defined in MATLAB as a function called *kinetics* ( $y, F, T$ ). The variable  $y$  represents the reaction volume,  $T$  represents the reactor's absolute temperature, and  $F$  represents the reactor feed, which consists of the molar flow rate of each component. The function statement involves the material balances, Arrhenius's equations, and kinetics rates. The set of ODEs will be solved using the `ode45` command, with the mentioned initial molar flows and a volume range from 0 to  $V^{12}$ .

The toluene conversion term is expressed as:

$$X = \frac{F_{tin} - F_{tout}}{F_{tin}} \quad 4.13$$

The selectivity term is expressed as:

$$\sigma = \frac{F_b}{F_{tin} - F_{tout}} \quad 4.14$$

Due to the isothermal assumption, the energy balance equations are neglected in this study.

---

<sup>12</sup> Reactor Total Volume: just for the kinetics study, it was considered a generic very large reactor (10000 m<sup>3</sup>).

## 4.2 Visualization – Molar Flow Through the Reactor

After solving the set of ODEs, the molar flow profile rate through the tube reactor for each component is illustrated in the figures below:

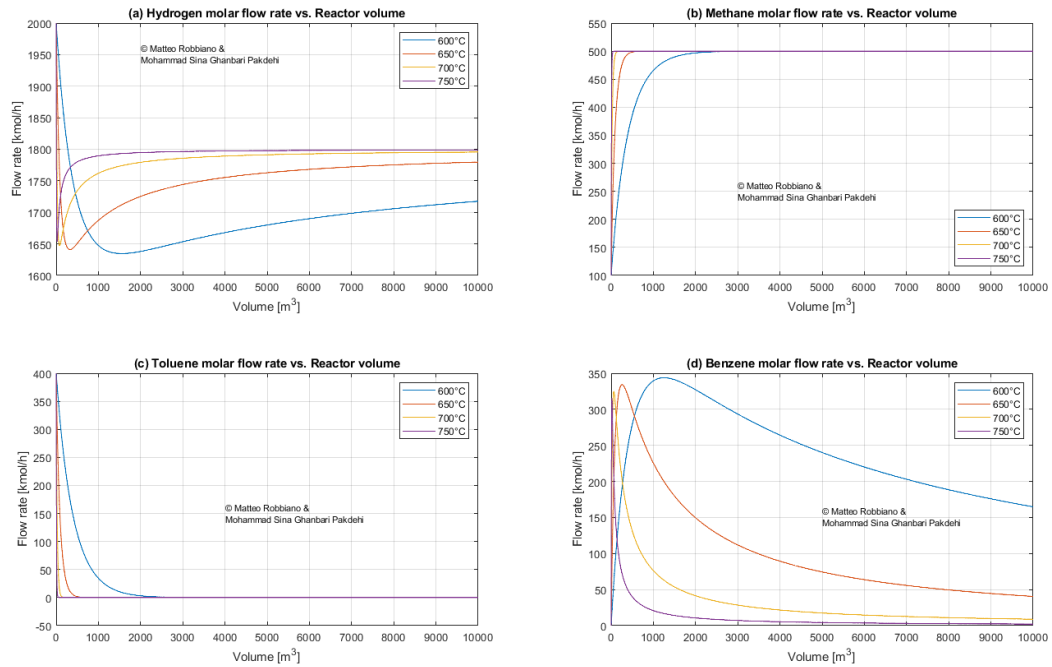


Figure 4 - Molar flow of reaction components through the tubular PFR - (a) Hydrogen (b) Methane (c) Toluene (d) Benzene

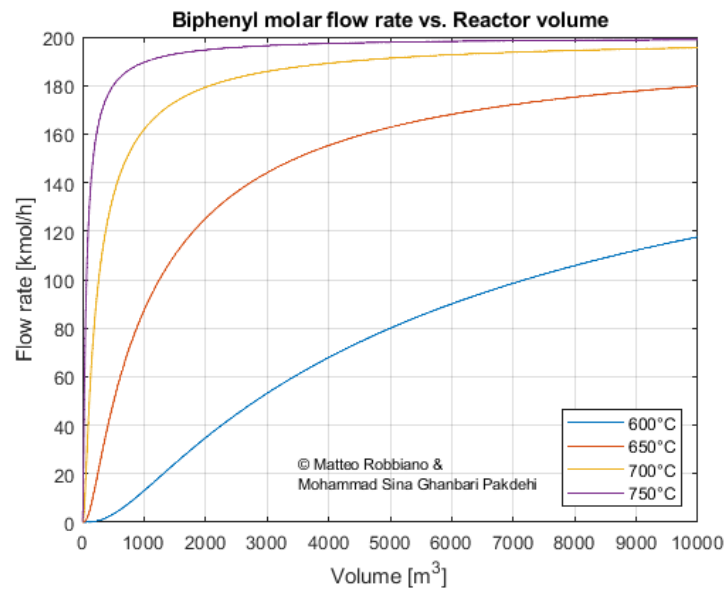


Figure 5 - Molar flow of Biphenyl through the tubular PFR

It can be observed that with increasing the temperature, all curves shift to the left, which means that the reaction occurs in the lower reactor volume (lower residence time), which leads to savings on the manufacturing costs of the reactor. Since Benzene is the primary product of this plant, its molar flow rate approaches zero by increasing the temperature, and it is not desirable. On the other hand, Benzene production has an inverse relationship with increasing temperature, and this is a trade-off between these variables.

Conversion of Toluene versus reactor volume is shown in the Figure below:

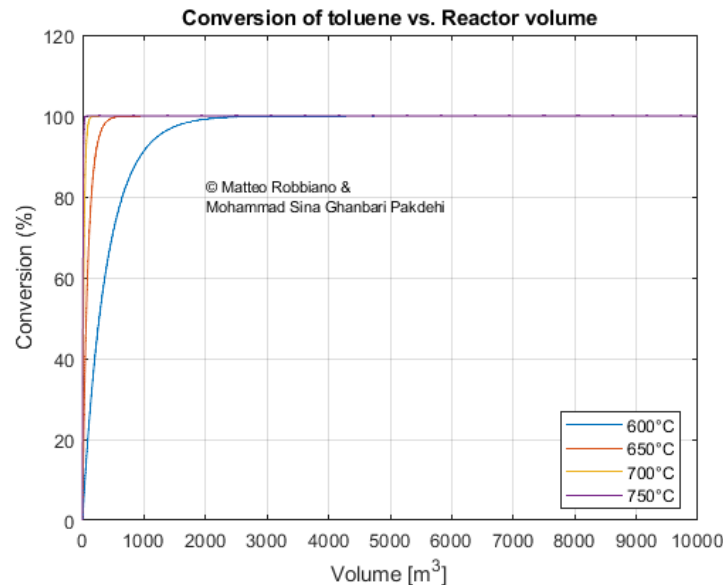


Figure 6 - Conversion of Toluene versus Reactor Volume

Without illustrating the conversion of toluene versus reactor volume, according to Figure 4, it is evident that with increasing temperature, the complete conversion occurs in lower reactor volume, which leads to lower residence time.



The selectivity of the reaction versus reactor volume in different temperatures is shown in the Figure below:

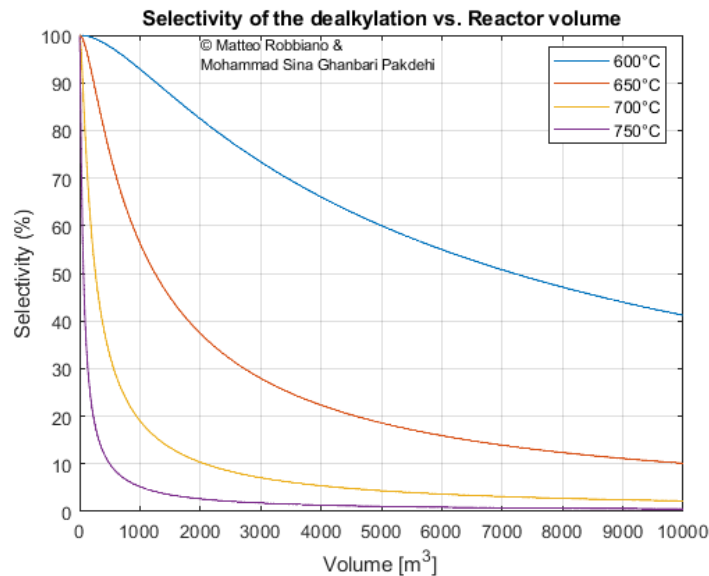


Figure 7 - Selectivity of the Reaction versus Reactor Volume

It can be observed that with increasing the temperature, the selectivity decreases significantly in the same reactor volume. Thus, it is necessary to choose a temperature that less affects selectivity.

In Figures 6 and 7, the sharp descent of selectivity or conversion in higher temperatures is due to the exponential term in Arrhenius's equation.

The selectivity of the reaction versus conversion in different temperatures is shown in the Figure below:

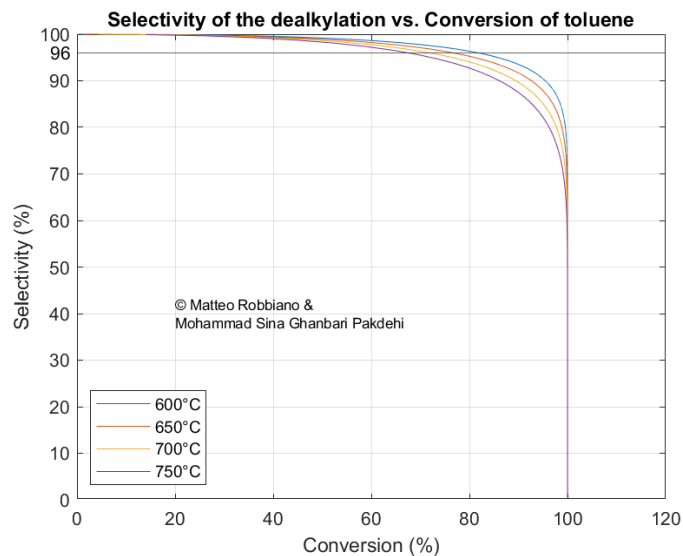


Figure 8 - Selectivity of Reaction versus Conversion

As can be seen, with increasing temperature, the selectivity of the reaction will be lower at the same temperature. There is a smooth change in higher temperatures, and it is because of the exponential change of both axes with respect to temperature changes.

Conversion of Toluene versus temperature with a selectivity of 96% is shown in the Figure below:

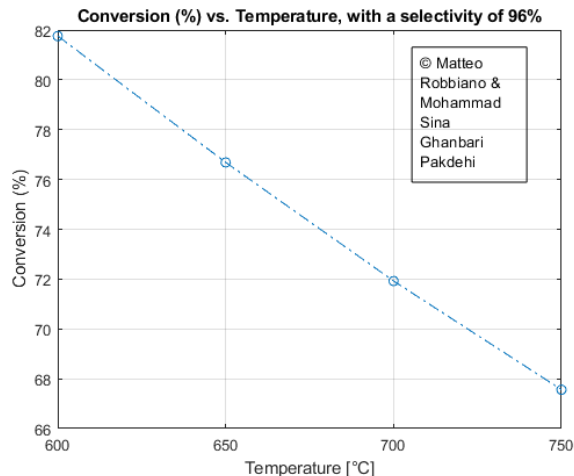


Figure 9 - Percentage of Conversion versus Temperature with a Selectivity of 96%

It can be observed that with the increase in temperature, the conversion of the Toluene decreases because the exponential coefficient for the temperature in the side reaction has a higher value than the primary reaction.

Reactor volume versus temperature with a selectivity of 96% is shown in the Figure below:

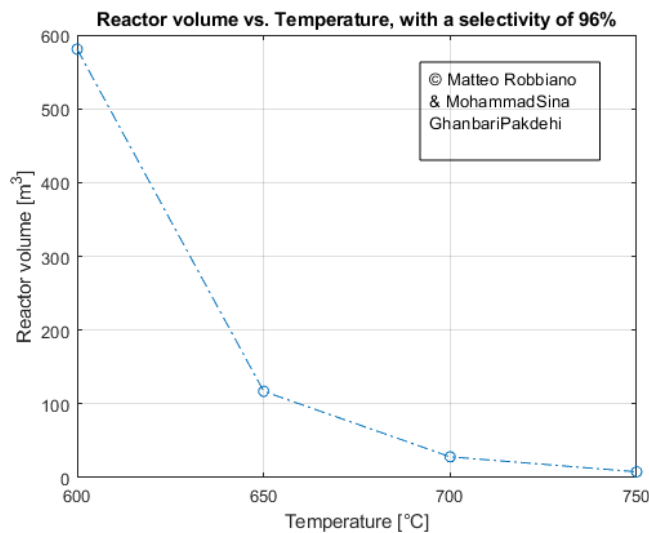


Figure 10 - Reactor Volume versus Temperature

As can be seen, the reactor volume has sharply decreased due to the increase in temperature because of the exponential change of reaction kinetics due to Arrhenius's law.

### 4.3 Adiabatic Temperature Difference Evaluation

It is necessary to evaluate the adiabatic temperature difference to validate the isothermal assumption of the employed reactor. With the neglect of heat flow through the reactor, the adiabatic temperature difference can be expressed as follows:

$$\Delta T = -\frac{\lambda \cdot \Delta H^\circ}{n_{in} \cdot C_{p_{mix}}} \quad 4.15$$

$$\Delta H^\circ = H_{out}T_{out} - H_{in}T_{in} \quad 4.16$$

Where  $\lambda$  is the extent of reaction in mol,  $\Delta H^\circ$  is the formation enthalpy in  $\frac{kJ}{kmol}$ , and  $C_{p_{mix}}$  is the mixture's heat capacity in  $\frac{kJ}{kmol.K}$  that depends on the reaction temperature. With the neglect of the effect of temperature on the heat capacity coefficient of each component, the heat capacity of each component as a function of temperature is expressed as follows:

$$C_p(T) = a + bT + cT^2 + dT^3 + eT^4 \quad 4.17$$

The coefficients for each component are extracted from the NIST webbook and shown in the table below:

Table 5 - Heat Capacity Coefficients for Reaction Components

	a	b	c	d	e
H <sub>2</sub>	25.399	2.0178·10 <sup>-2</sup>	3.8549·10 <sup>-2</sup>	3.188·10 <sup>-8</sup>	-8.7585·10 <sup>-2</sup>
CH <sub>4</sub>	34.942	-3.996·10 <sup>-2</sup>	1.9184·10 <sup>-4</sup>	-1.530·10 <sup>-7</sup>	3.9321·10 <sup>-11</sup>
C <sub>6</sub> H <sub>6</sub>	-31.368	4.746·10 <sup>-1</sup>	-3.1137·10 <sup>-4</sup>	8.524·10 <sup>-8</sup>	-5.052·10 <sup>-12</sup>
C <sub>7</sub> H <sub>8</sub>	-24.097	5.2187·10 <sup>-1</sup>	-2.9827·10 <sup>-4</sup>	6.122·10 <sup>-8</sup>	1.2576·10 <sup>-12</sup>
C <sub>12</sub> H <sub>10</sub>	-29.153	7.6716·10 <sup>-1</sup>	-3.4341·10 <sup>-4</sup>	-3.772·10 <sup>-8</sup>	4.6179·10 <sup>-11</sup>

In addition, the value of  $\Delta H^\circ$  for each component at standard conditions<sup>13</sup> has been extracted from the NIST webbook and is shown in the Figure below:

Table 6 - Formation Enthalpy of Reaction Components

Component	$\Delta H^\circ \left( \frac{kJ}{kmol} \right)$
H <sub>2</sub>	0
CH <sub>4</sub>	-74.85
C <sub>6</sub> H <sub>6</sub>	50.00
C <sub>7</sub> H <sub>8</sub>	82.93
C <sub>12</sub> H <sub>10</sub>	182.09

<sup>13</sup> 1 atm and 25°C

The adiabatic temperature difference versus reactor temperature with a selectivity of 96% is shown in the Figure below:

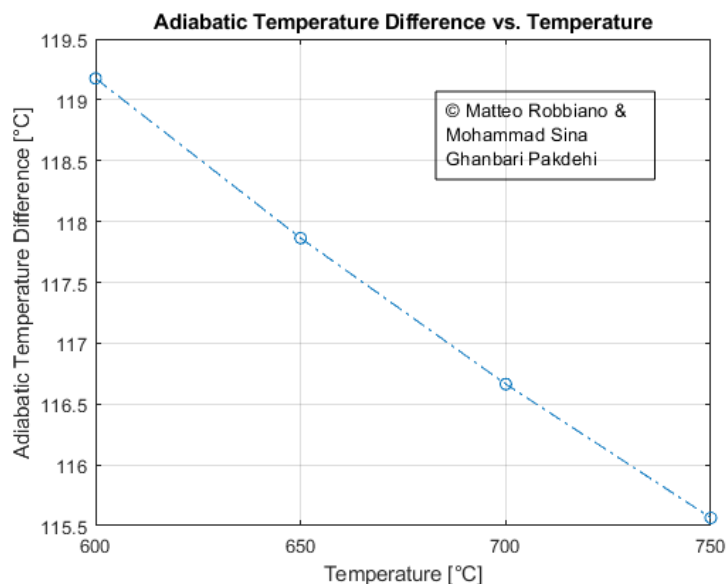


Figure 11 - Adiabatic Temperature Difference versus Temperature with Selectivity 96%

The exact values of adiabatic temperature difference in each temperature are shown in the table below:

Temperature (°C)	600	650	700	750
Adiabatic $\Delta T$ (°C)	119.1759	117.8634	116.6637	115.5646

It can be observed that the adiabatic temperature difference is within 117 °C, which is significantly higher than the recommended value in Perry’s handbook to consider the reactor as isothermal (60 °C). Although the isothermal condition is not a valid assumption, it can still be applied in some real-world cases, such as shutting down the coolant jacket or isolation from the environment.

## 5. EP2 Analysis

In the second level of economic potential analysis, the calculations are just based on the cost of raw materials and revenue of products, which can be sold as raw materials or reused internally to produce energy. The plant is considered a black box to highlight the importance of the input-output structure of the system. This level of economic potential can be responsible for 30% to 80% of the overall cost of the process.

In general, the second level of economic potential in  $\frac{M\text{€}}{y}$  can be expressed as:

$$EP2 = (\text{Main Products} + \text{By-products}) - (\text{Raw Materials})$$

In mathematical terms, it is expressed as:

$$EP2 = \sum_{j=1}^{NP} \epsilon_{P,j} \cdot F_j - \sum_{i=1}^{NR} \epsilon_{R,i} \cdot F_i \quad 5.1$$

Where  $\epsilon_{P,j}$  represents the value of products (or by-products),  $\epsilon_{R,i}$  represents the value of raw material,  $F_j$  represents the molar flow rate of the products (or by-products),  $F_i$  represents the molar flow rate of the raw materials, NP represents the number of products and by-products, and NR represents the number of raw materials. According to section 2, the plant's annual operating time equals 8000 hours. The cost of raw materials is shown in the table below:

Table 7 - Cost of Raw Materials

Material	Cost $\left(\frac{\text{€}}{\text{kmol}}\right)$
Benzene	12.5
Toluene	8.8
Hydrogen	2.1
Biphenyl	7.4

There are two existing scenarios in order to calculate EP2:

- **Sell:** In this case, the output of Hydrogen and Methane is burned, but Biphenyl is sold. The weak market demand for these materials causes the burning of Hydrogen and methane.
- **Burn:** This case is like the previous one, but Biphenyl is also burned. In order to gain profit from burning materials, it is necessary to convert them into energy, which costs 4€ per MBtu of generated energy.

The combustion heat of each reaction element is listed in the table below:

Table 8 - Combustion Heat of Reaction Elements

Material	$\Delta H_{\text{combustion}} \left(\frac{\text{MBtu}}{\text{kmol}}\right)$
Hydrogen	0.123
Methane	0.383
Benzene	1.41
Toluene	1.68
Biphenyl	2.688

The first scenario to calculate EP2 is to sell Biphenyl, which is expressed as follows:

$$EP2_{\text{sell}} = 8000 \cdot [\epsilon_b \cdot B + \text{burn}_{\text{CH}_4} \cdot (1 - x_v) \cdot V + \text{burn}_{\text{H}_2} \cdot x_v + \epsilon_{\text{C}_{10}\text{H}_{12}} \cdot D] - [0.95 \cdot \epsilon_{\text{H}_2} + 0.05 \cdot \epsilon_{\text{CH}_4} \cdot F_1 + \epsilon_{\text{C}_7\text{H}_8} \cdot F_2] \quad 5.2$$

The second scenario to calculate EP2 is to burn Biphenyl, which is expressed as follows:

$$EP2_{sell} = 8000 \cdot [\epsilon_b \cdot B + \text{burn}_{CH_4} \cdot (1 - x_v) \cdot V + \text{burn}_{H_2} \cdot x_v + \text{burn}_{C_{10}H_{12}} \cdot D] - [0.95 \cdot \epsilon_{H_2} + 0.05 \cdot \epsilon_{CH_4} \cdot F_1 + \epsilon_{C_7H_8} \cdot F_2] \quad 5.3$$

The molar fraction of Hydrogen in the vent stream is expressed as:

$$x_v = \frac{V_h}{V_h + V_m} \quad 5.4$$

The molar fraction of Hydrogen in the vent stream versus the split factor in different temperatures is shown in the below Figure:

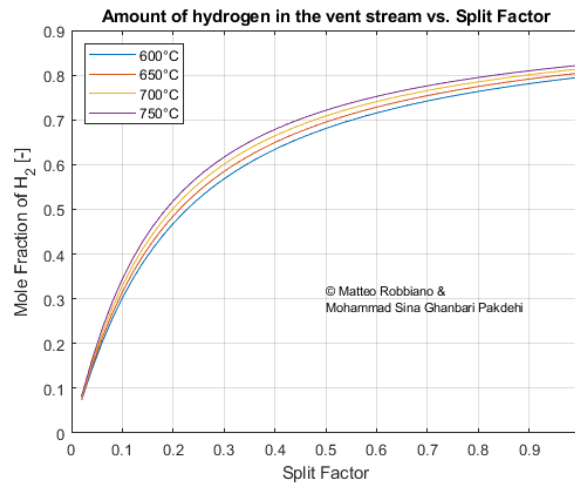


Figure 12 - Amount of Hydrogen in the Vent Stream versus Split Factor

It can be observed that with increasing split factor, the amount of Hydrogen molar fraction in the vent stream is increased dramatically.

The relation between EP2 and the molar fraction of Hydrogen in the vent stream is shown in the Figure below:

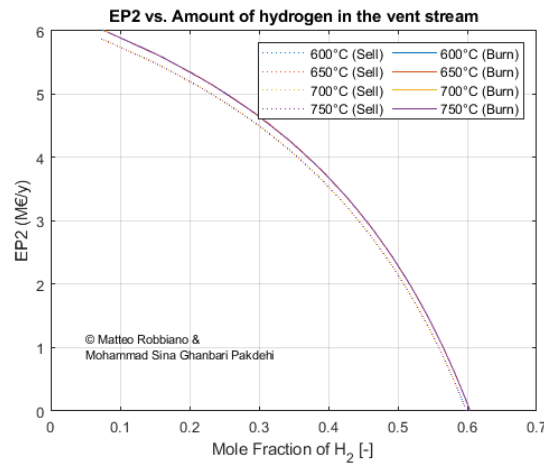


Figure 13 - EP2 versus Amount of Hydrogen in the vent stream

It can be understood that venting more Hydrogen causes a reduction in EP2, so from an economic point of view, recycling the Hydrogen in the reactor is more beneficial than purging it to burn and generate energy. This reduction in EP2 is because a lower amount of Hydrogen in the recycle stream leads the plant to consume more Hydrogen in the feed stream, which costs more money.

The relation between EP2 and the split factor is shown in the Figure below:

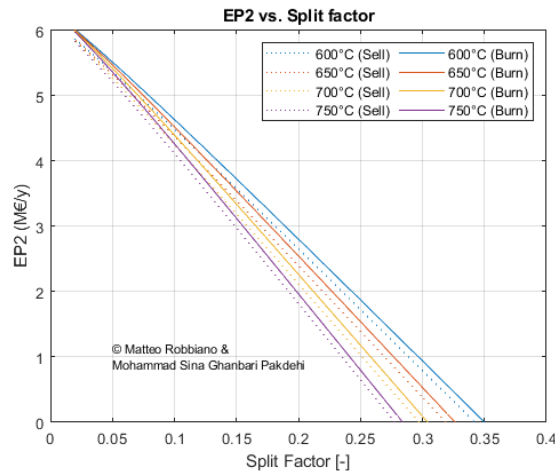


Figure 14 - EP2 versus Split Factor

By increasing the split factor, the EP2 value decreases linearly. This happens because if more gases are vented, an even higher amount of make-up gases will be needed to produce Benzene, the desired product: this causes a decrease in the revenue. Burning the Biphenyl rather than selling it also has a clear economic advantage.

The relation between EP2 and temperature with various split factors is shown in the Figure below:

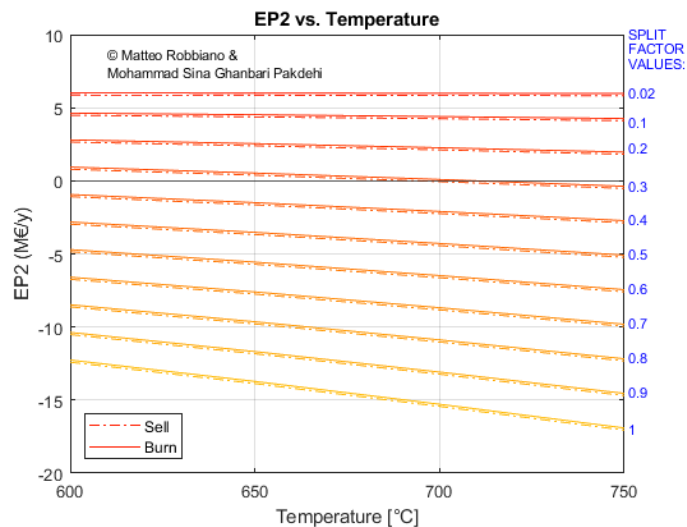


Figure 15 - EP2 versus Temperature with Different Split Factors

As can be seen, with increasing the split factor, the slope of EP2 change becomes slightly sharper negatively. The EP2 decreases with temperature because of the lower selectivity of Benzene and the higher amount of less valuable products such as Biphenyl.

The relation between EP2 and conversion with various split factors is shown in the Figure below:

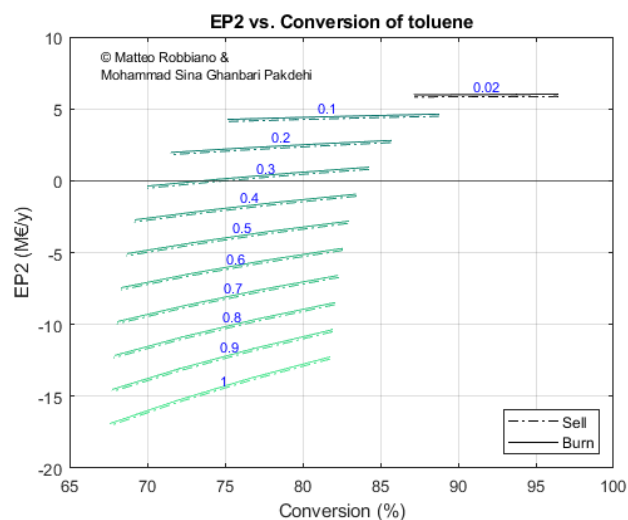


Figure 16 - EP2 versus Conversion with Different Split Factors

It can be observed that with increasing the split factor, the slope of EP2 becomes slightly sharper in a positive way. Additionally, the upper and lower bounds of conversion are shifted to the left by increasing the split factor.

## 6. EP3 Analysis

The costs related to the reactor and fluid compression can be determined in the third level of economic potential analysis. From this level and going forward, some considerations will have to be made both for the “CapEx” and the “OpEx”: the term “CapEx” means “Capital expenditures” and is the sum of the costs related to the purchase of the equipment itself, such as the construction, transportation, and installation costs; the term “OpEx” means “Operational Expenditures” and is the sum of all the costs related to the usage of said equipment over time, such as the cost related to the electricity consumption or the cost related to utilities (steam, cooling water, air...) usage.

In this report, while the CapEx will be expressed in millions of euros (M€), the OpEx will be expressed in millions of euros per year (M€/y): the various EPs need to account for both terms, so the CapEx must be “normalized” to a specific depreciation time. For this study, the depreciation time chosen will be five years for all the analyzed equipment.



## 6.1 Reactor Costs

The reactor used for the hydrodealkylation of Toluene is very simple: it does not involve a catalyst, and because of the isothermal reactor assumption, it does not require heating or cooling systems. Therefore, it can be considered as adiabatic. In addition, since the reactor is a PFR, no stirring is needed. Consequently, the reactor has no OpEx and can be treated as a simple pressure vessel for the CapEx evaluation, which will heavily influence several design choices for the reactor itself.

For calculating the reactor CapEx, a correlation that considers the reactor dimensions and its construction material properties was chosen, and it is called Guthrie's formula:

$$CapEx_{reactor} = 1.15 \cdot \frac{M\&S}{280} \cdot 101.9 \cdot D^{1.066} \cdot H^{0.802} \cdot (2.18 + F_p \cdot F_m) \quad 6.1$$

the coefficient of 1.15 was added to the original correlation to account for the fact that the reactor needs to be thermally insulated to make the final cost more significant. M&S is the Marshall and Swift cost index worth 1110 for all the examined equipment.  $F_p$  is a parameter that takes into account the fact that the construction material needs to resist a certain amount of pressure: the reactor operates at 34 bar, or 493 psi, very close to the value of 500 psi, for which a value of 1.45 for  $F_p$  is recommended.  $F_m$  is a parameter dedicated to the construction material: the reactor flowrate contains a considerable amount of Hydrogen, a known cause of corrosion in the chemical industry, especially at high temperatures. For this reason, the chosen material is stainless steel AISI 316, which has a  $F_m$  equal to 3.67. The correlation above gives the CapEx value in €; D and H are expressed in ft. While the reactor diameter and height are unknown, the reactor volume was previously calculated by solving the DAE system. By considering the reactor as a cylinder and using a recommended H/D ratio of 10, it is then possible to calculate the reactor dimensions from the volume:

$$V = \frac{\pi}{4} \cdot D^2 \cdot H \Rightarrow V = \frac{\pi}{4} \cdot D^2 \cdot \frac{D}{D} \cdot H \Rightarrow V = \frac{\pi}{4} \cdot D^3 \cdot H/D \Rightarrow D = \sqrt[3]{\frac{4 \cdot V}{\pi \cdot H/D}} \quad 6.2$$

$$H = H/D \cdot D \quad 6.3$$

A value of both D and H can be calculated for each reactor volume.

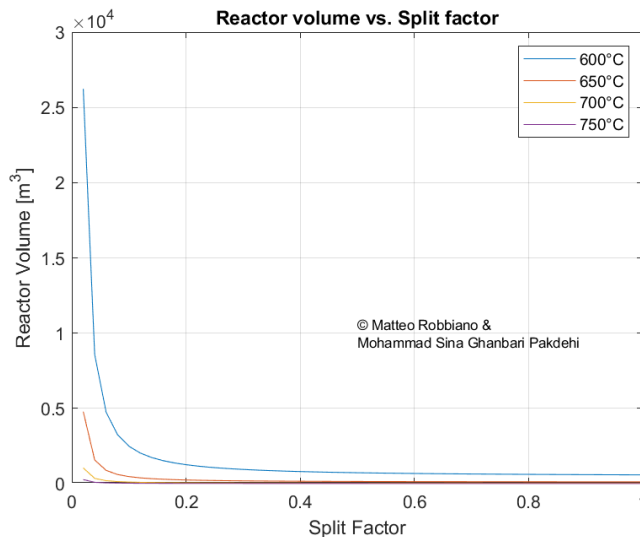


Figure 17 - Reactor volume versus Split factor at different temperatures

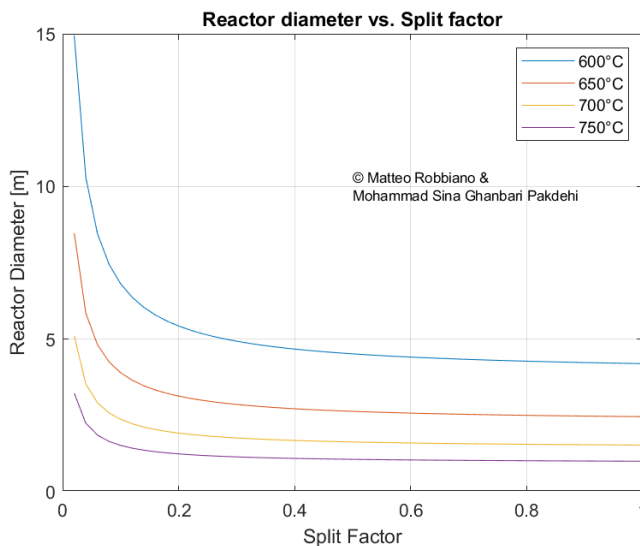


Figure 18- Reactor diameter versus Split factor at different temperatures

The trend in both graphs clearly shows that for a higher split factor, the reactor volume (and diameter) will be lower: this is because the higher the split factor is, the smaller the gases recycle stream will be, thus resulting in a lower total flowrate being processed by the reactor and, therefore, a smaller reactor volume. In addition, for a particular split factor, the reactor volume decreases with the temperature (and so does the diameter) because the reaction kinetics are faster at higher temperatures. Therefore, a smaller reactor is needed.

The two parameters share the same trend since the volume is directly proportional to the diameter. Since the reactor CapEx is directly related to the reactor diameter, we can expect a similar trend.

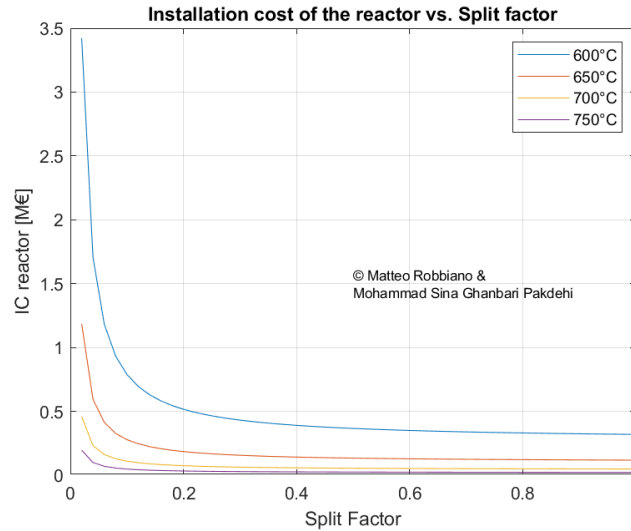


Figure 19- Reactor Capex versus Split factor at different temperatures

## 6.2 Compression Costs

This plant uses two machines to transport fluids: a pump for the Toluene recycle stream, and a centrifugal compressor for the gases recycle stream, which at this stage of the analysis can be considered only Hydrogen and methane. Since pumps are usually mass-produced and the compression cost of liquids is meager with respect to gases, the cost of the pump will be neglected. Thus, this report will only focus on the costs of the compressor.

Another Guthrie's formula can calculate the compressor Capex:

$$CapEx_{compressor} = \frac{M\&S}{280} \cdot 517.5 \cdot bhp^{0.82} \cdot (2.18 + F_c) \quad 6.4$$

where  $F_c$  is equal to 1. The term  $bhp$  refers to the power of the motor shaft, which powers the compressor and is expressed in British horsepower. The correlation gives the CapEx value in €.

It is assumed that the total amount of pressure drops between the reactor and compressor is 6 atm, equally distributed between the two pieces of equipment. The compression duty can be calculated considering an ideal compression as a reference.

$$\tilde{l} = R \cdot T \cdot \frac{\beta^{\gamma_{mix}} - 1}{\gamma_{mix}} \quad 6.5$$

where  $\tilde{l}$  is expressed in J/mol;  $\beta$  is the compression ratio between downstream and upstream of the compressor;  $R$  is the gas constant expressed in J/mol/K;  $T$  is the inlet temperature and is 35 °C (308 K);  $\gamma_{mix}$  is the specific heat ratio of the mixture and is the result of a weighted average of the specific heat ratios of the single components of the stream (Hydrogen and methane):

$$\gamma_{mix} = \sum_{i=1}^{NC} x_i \cdot \gamma_i \quad 6.6$$

Table 9- Specific heat ratio of gas recycle stream components

Component	$\gamma$
Hydrogen	0.29
Methane	0.23

The duty is finally calculated because both the compressor and the motor shaft are not ideal but have a non-unitary efficiency  $\eta$ :

Table 10- Efficiency of the gas compression equipment

Equipment	$\eta$
Compressor	0.9
Motor shaft	0.9

$$bhp = \frac{1.341}{1000} \cdot \frac{\dot{I}}{\eta_{comp} \cdot \eta_{motor}} \cdot R_{TOT} \cdot \frac{1000}{3600} \quad 6.7$$

where  $R_{TOT}$  is the sum of  $R_m$  and  $R_{m'}$ , which are the hydrogen and methane flowrates in the gas recycle stream, computed by solving the DAE system and expressed in kmol/h. These flow rates are expected to diminish when the split factor gets higher: higher split factors mean higher vent streams and higher vent streams mean lower recycle streams.

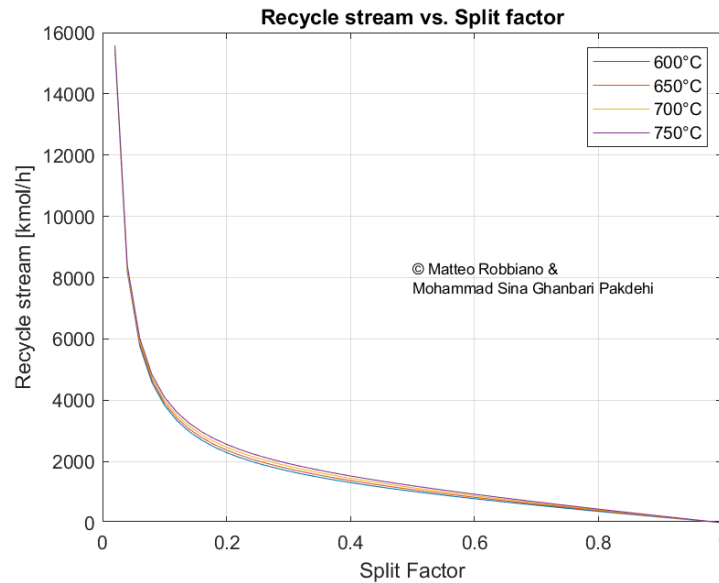


Figure 20- Recycle stream versus Split factor at different temperatures

The compressor Opex (expressed in €) can be calculated simply by multiplying the duty by the cost of electricity and the annual operating time:

$$OpEx_{compressor} = \frac{bhp}{1.341} \cdot 8000h \cdot 0.061095 \frac{\text{€}}{\text{kWh}} \quad 6.8$$

Both the Capex and the Opex of the compressor are heavily influenced by the duty  $bhp$ , which in turn is heavily influenced by the flow rate  $R_{TOT}$ , and, therefore, it can be expected that all these parameters will share a very similar trend with a varying split factor.

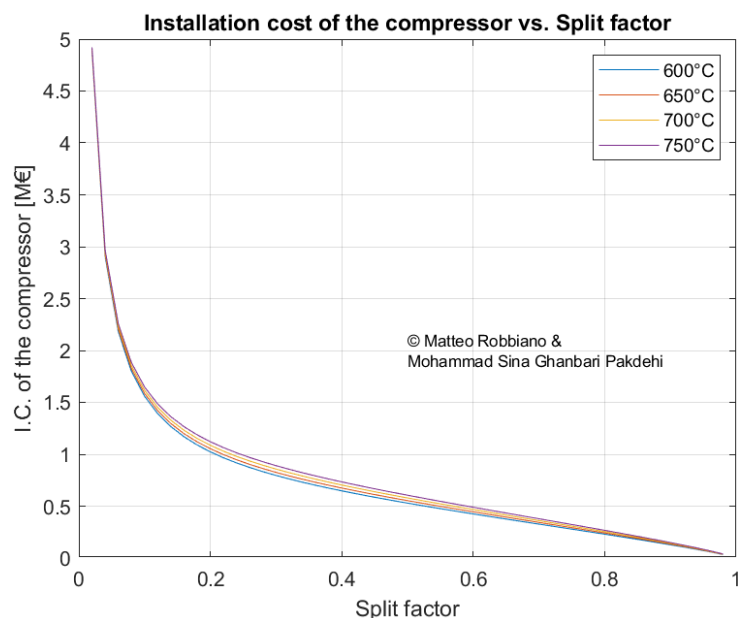


Figure 21- capex of the compressor versus Split factor at different temperatures

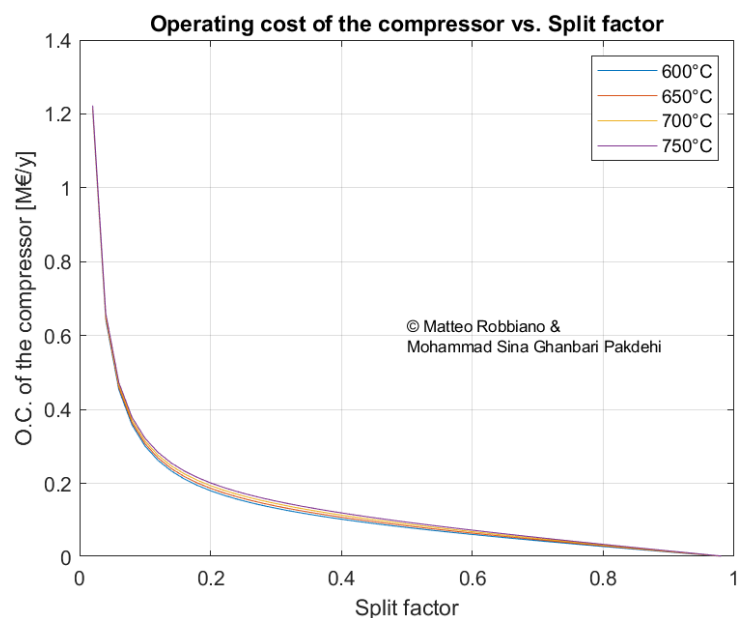


Figure 22- Opex of the compressor versus Split factor at different temperatures

With both the CapEx and OpEx of all the equipment related to this level of analysis, it is now possible to evaluate the EP3. Since the second level of analysis revealed that selling Biphenyl was generally less profitable than burning it, only the scenario in which all the produced Biphenyl is burned off will be considered.

The EP3 is calculated with its definition:

$$EP3 = EP2 - \sum \left( \frac{CapEx}{5y} + OpEx \right)_{reactor \& compressor} \quad 6.9$$

Furthermore, the result is expressed in M€/y.

With this formula, it is possible to find the EP3 for all the temperature and split factor combinations analyzed until now. The trend concerning the split factor clearly shows an “optimum.” For each temperature, a specific value of the split factor allows the maximum economic potential to be achieved. The EP2 will be high at deficient split factors, but the level-3 costs will also be very high. If the split factor increases, the level-3 costs quickly become less and less influential in the EP3 evaluation, but the EP2 decreases much more and becomes even more negative. This means there must be some split factor values for which the EP2 will still be positive, and the level-3 costs will not be very high.

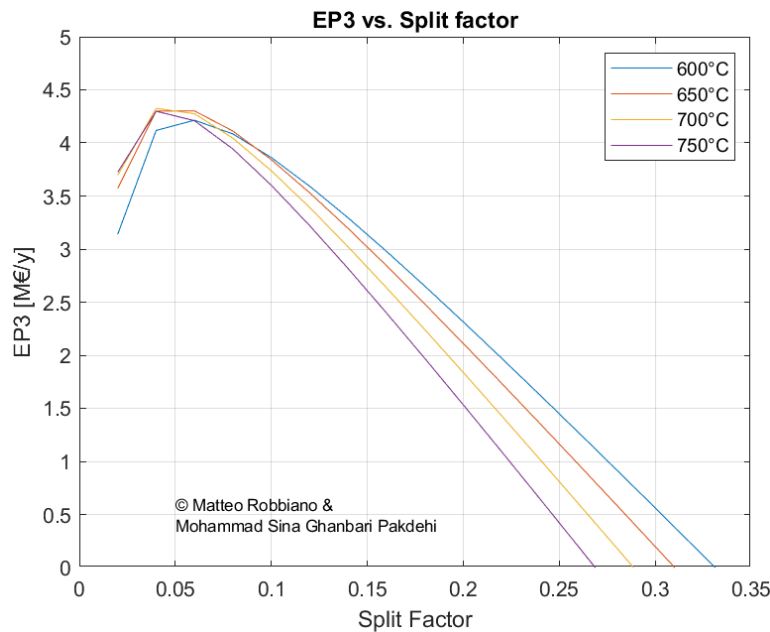


Figure 23- OpEx of the compressor versus Split factor at different temperatures

The optimal split factor values and the related parameters for each temperature are significant for evaluating the EP4, which will be discussed in the following chapter.

Table 11- Optimal values of split factor and related parameters for future analysis

Temperature [°C]	Split factor	Reactor volume [m <sup>3</sup> ]	Reactor diameter [m]	R <sub>TOT</sub> [kmol/h]	F <sub>1,TOT</sub> [kmol/h]	T [kmol/h]	F <sub>2,TOT</sub> [kmol/h]
600	0.18	1372.8	5.5912	2472.7	537.27	44.598	276.04
650	0.2	241.84	3.1343	2372.6	587.62	65.782	276.04
700	0.14	74.856	2.1202	3146.9	506.76	79.348	276.04
750	0.16	17.771	1.3128	2967.8	559.78	104.65	276.04

The values of EP3 obtained from the optimal split factor values are displayed below in the form of a graphic representation.

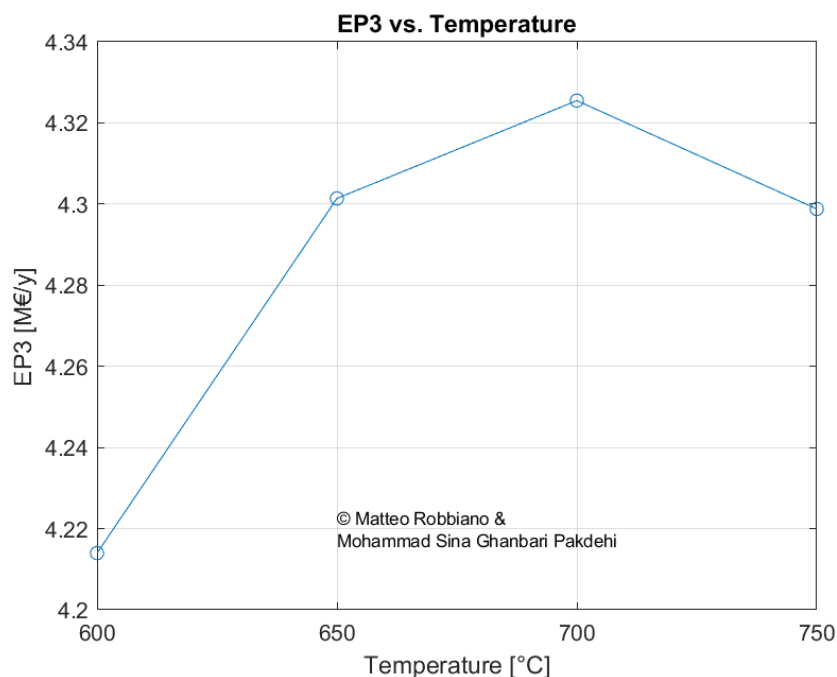


Figure 24- Economic potential of level-3 (EP3) at different temperatures

At this level of analysis, it seems that the most economically convenient temperature for conducting the process would be 700°C. However, this conclusion can easily be deemed no longer valid if a more thorough analysis is carried out; such will be the case for the EP4.

## 7. EP4 Analysis

In the fourth level of economic potential analysis, the costs related to the purification and separation of the various compounds are evaluated. At this level, it is no longer possible to study and simulate the plant just with MATLAB: a proper process simulator is needed to assess the complex behavior of the various unit operations present in the plant. In addition, several decisions need to be made to design the separation section, such as the order of separation of the components or the tray spacing of the various distillation columns.

### 7.1 Design of the Separation Train

The first thing to decide is the order in which the components get separated from the mixture: this is important because a particular order of separation can imply a less expensive separation section than any other possibility. In order to choose a proper order of separation, some recommendations well-established in the chemical industry will be followed. In particular:

- Corrosive components need to be removed as soon as possible: in this way, less equipment will have to be built with special (and more expensive) materials.
- Monomers and reactive components need to be removed as soon as possible in order to prevent undesired reactions or fouling from occurring.
- The most abundant component should be removed as soon as possible: in this way, the downstream equipment can be smaller and, therefore, less expensive.
- Product and recycle streams must be separated as distillates to better control their purity.

Following these recommendations, the following process design decisions have been made:

- The first components to be separated will be the so-called “light ends,” a mixture of mostly Hydrogen and methane because both can be reactive. In addition, Hydrogen is a corrosive substance (as explained in Chapter 6.1). The light ends will be separated with an adiabatic flash unit and a small distillation column called a “Stabilizer.”
- The second separate component will be Benzene, the final product of the entire process and the most abundant component in the mixture. Benzene will be separated as a distillate with the “Product Column,” the second column of the distillation train.
- The last distillation column, the “Recycle Column,” will separate Toluene (to be recycled at the reactor) as a distillate. In contrast, Biphenyl will be separated at the bottom and sent to a burner.

Unlike in EP2 and EP3, in EP4, the separation is not considered ideal: all the streams exiting the separation section are not pure but mixtures of at least two or more components.

## **7.2 Simulation with Aspen HYSYS**

For this analysis, the software Aspen HYSYS V7.3 was used. A dedicated simulation is conducted for each investigated temperature using the optimal split factor and the related parameters listed in Table 10. The Redlich-Kwong-Soave equation of state was chosen for all the process fluids in the plant. The only chemical reactions occurring in the entire plant are the dealkylation of Toluene to give Benzene and Methane and the formation of Biphenyl. No coking or fouling is occurring. The reactor is still considered adiabatic.

The PFD of the simulated plant is shown below: it has been simplified by removing the quench streams previously shown in Figure 2.

The light ends, exiting both the flash and the stabilizer, and is sent to the splitter to be either recycled back to the reactor or vented and then burned off.



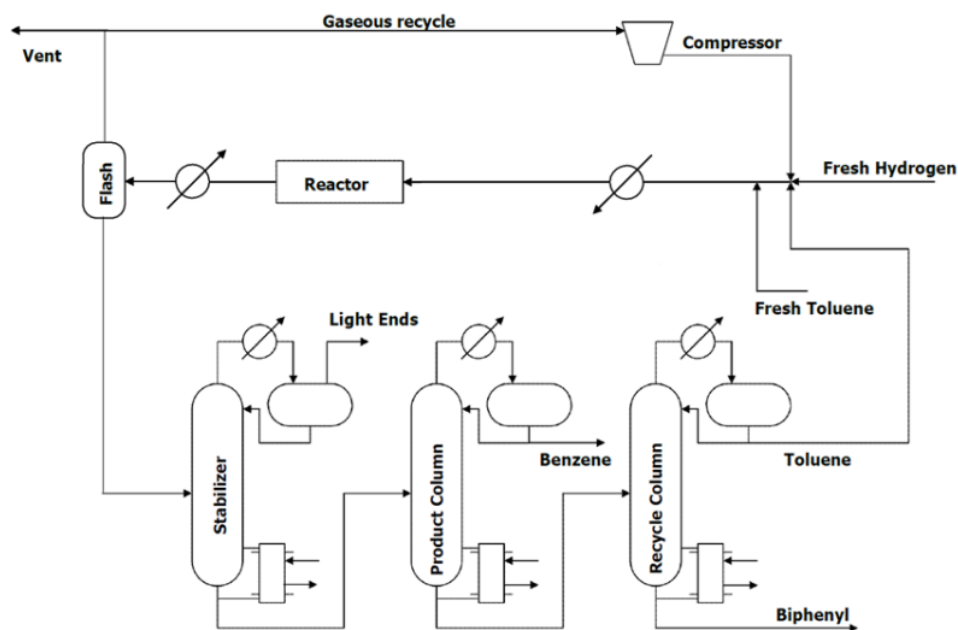


Figure 25- Simplified PFD of the process

The first distillation column is the stabilizer: it has five stages (3 actual trays, with the second being the feed tray) with unitary efficiency. There are no pressure drops in the column, and all the stages have a pressure of 3.573 bar. The condenser operates with full reflux, meaning the condensed liquid is sent back to the column while the gases are sent to the splitter. The reflux ratio  $R/D$  (in this case, the ratio between the liquid and vapor streams exiting the condenser) is fixed at 0.619; since the condenser is operated with water as a coolant, its inlet temperature is fixed at 30°C, while the outlet temperature is fixed at 38°C: this value is fixed because it is not legally possible to discharge in the environment water that is warmer than a specific maximum value. In order to properly operate, it is recommended that the light ends exit the condenser with a temperature at least 10°C higher than the inlet temperature of the coolant: this means that both the light ends. The liquid reflux exits the condenser at 40°C.

The second distillation column is the Product Column. It operates at 1 bar and with a total condenser: no vapor phase exits as distillate. There are no pressure drops in the column. The chosen reflux ratio  $R/D$  is 1.3 times the minimal one. The column operates with two specifications related to Benzene: the distillate must have a purity of 99.97% (molar), and the recovery efficiency of the Benzene fed to the column needs to be 99.5% (molar). Since this is a multi-component distillation, the number of trays has to be evaluated by a proper method, such as the Fenske-Underwood-Gilliland method or FUG method: Benzene and Toluene have been chosen as light-key and heavy-key components, respectively; the presence of Hydrogen and methane is neglected. The Molokanov equation was used to evaluate the number of ideal trays, while the feed tray was determined using the Fenske correlation. The column efficiency is calculated with the O'Connell correlation (where the dynamic viscosity of the inlet stream is 0.3 cP): the result is then applied to every tray in the column in the simulation environment.

The third and final column of the distillation train is the Recycle Column: like the previous one, it operates at 1 bar and with a total condenser. The column operates with two specifications related to Toluene: the distillate needs to have a purity of 99.5% (molar), and the Toluene's recovery efficiency needs to be 99.5% (molar). The chosen reflux ratio is 1.3 times the minimal one. The column efficiency is assumed to be 0.24 for all the trays in the column. The column design is done with the “Short-Cut Distillation Column” tool available in the Aspen HYSYS software, and the obtained result is used to simulate the actual Recycle Column with the “Modified (HYSYM) Inside-Out” solver.

Once all the columns are correctly designed, all the loops and recycles in the process can be closed. There are two recycle loops in the process: the Toluene distilled in the Recycle Column is sent back to the reactor, the light ends are sent to the splitter, and a part of them is compressed to be sent back to the reactor. Three “Adjust” (ADJ) tools are added to the simulation, one for each of the three specifications of the plant:

- The HTR needs to be 5.000, which is obtained in the simulation by manipulating the variable F1 (the hydrogen and methane make-up) with ADJ-1;
- The reactor selectivity of Benzene needs to be 0.96, which is obtained in the simulation by manipulating the reactor diameter with ADJ-2;
- The benzene productivity needs to be 265 kmol/h, which is obtained in the product column by manipulating the variable F2 (the toluene make-up) with ADJ-3.

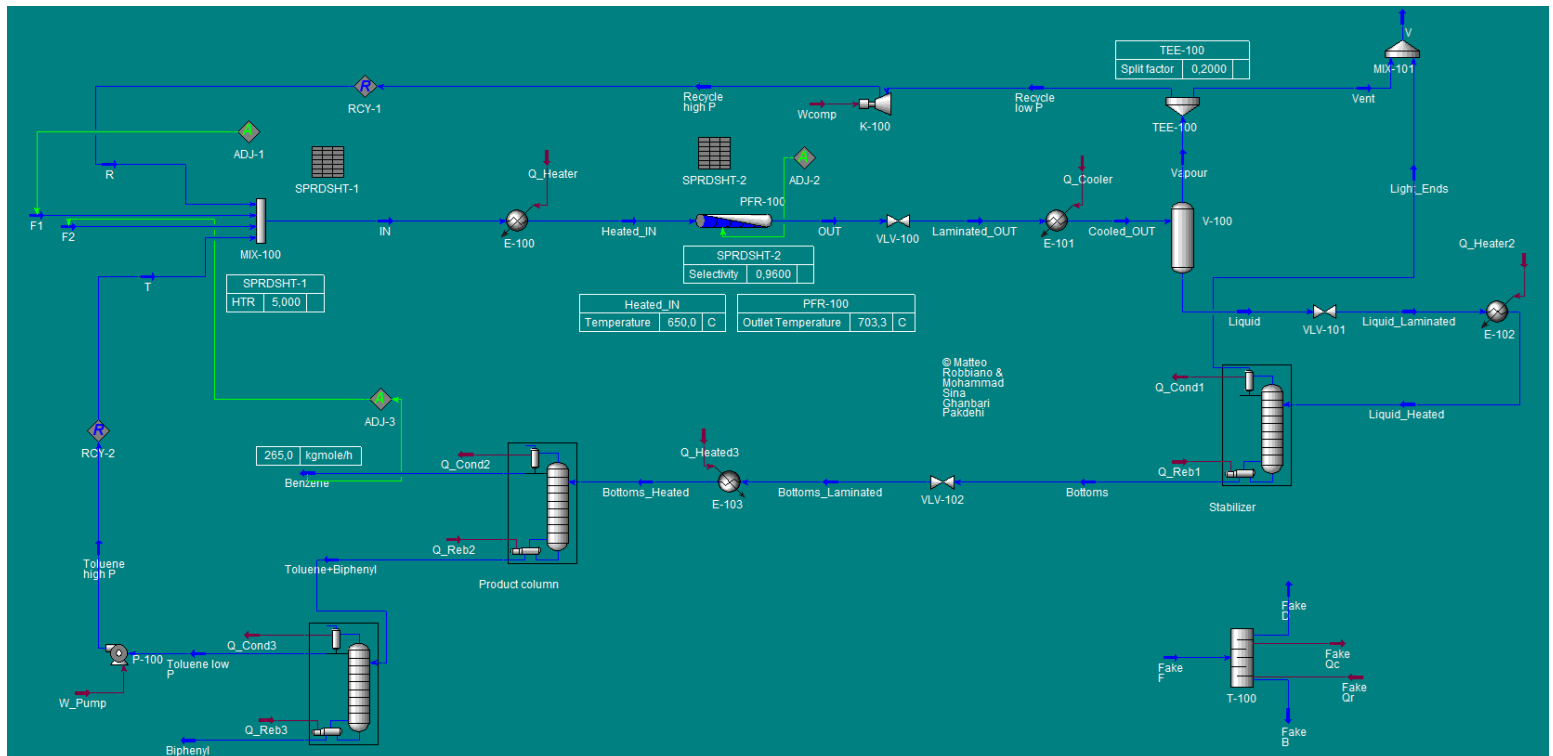


Figure 26- Simulation of the HDA Plant (650°C temperature case).

Following this analysis, it is possible to verify the actual variation of temperature in the reactor:

*Table 12- Variation of temperature in the reactor*

Nominal temperature [°C]	Temperature variation [°C]
600	54.16
650	53.28
700	43.85
750	44.06

It is clear that the hypothesis of the reactor being isothermal is not valid. However, since the temperature variation is not very large (order of magnitude of 50°C), it is still possible to follow this hypothesis without generating great mistakes for this kind of analysis.

It is also possible to evaluate the number of trays in each column in the plant and the respective diameter if a specific tray spacing is provided, thanks to the “tray sizing” utility available in Aspen HYSYS. The tray spacing (the distance between 2 consecutive trays) investigated is 24 in, 18 in, and 12 in.

*Table 13- Number of trays in the distillation columns*

Temperature	600°C	650°C	700°C	750°C
Stabilizer	3	3	3	3
Product Column	51	52	52	53
Recycle Column	75	74	76	80

Of all the columns in the distillation section, only the stabilizer displayed a minimal diameter for a tray column; therefore, a packed bed column is necessary.

*Table 14- Parameters of the Stabilizer [ft]*

Temperature	600°C	650°C	700°C	750°C
Diameter	3	3	3	3.5
HETP	1.335	1.334	1.333	1.332

Since the stabilizer is a packed column, evaluating different tray spacings is impossible. Moreover, since the HETP (Height Equivalent to a Theoretical Plate) is very close to one of the investigated tray spacings (18 in, or 1.5 ft), this value of tray spacing will be directly used for calculating the total height of the column and its CapEx.

The Product and Recycle Columns are actual tray columns; therefore, it is possible to calculate their diameter at different tray spacing:

Table 15- Diameter of the Product Column [ft]

Tray Spacing [in]	600°C	650°C	700°C	750°C
24	7.5	7.5	8.0	8.0
18	8.0	8.0	8.5	8.5
12	8.5	9.5	9.5	9.5

Table 16- Diameter of the Recycle Column [ft]

Tray Spacing [in]	600°C	650°C	700°C	750°C
24	3.5	4.0	3.5	4.5
18	3.5	4.0	4.0	4.5
12	3.5	4.0	4.5	4.5

Given the number of trays in the column and their distance, it is trivial to determine the total height of each column, thanks to a simple formula:

$$H_{tot} = (N_{trays} - 1) \cdot H_{tray\ spacing} + H_{top-bottom} \quad 7.1$$

$H_{top-bottom}$  is the height of the column's very top and bottom parts, which has been fixed at 5m for all the columns in all the studied cases.

Table 17- Total height of the Stabilizer [ft]

600°C	650°C	700°C	750°C
19.40	19.40	19.40	19.40

Table 18- Total height of the Product Column [ft]

Tray Spacing [in]	600°C	650°C	700°C	750°C
24	116.40	118.40	118.40	120.40
18	91.40	92.90	92.90	94.40
12	66.40	67.40	67.40	68.40

Table 19- Total height of the Recycle Column [ft]

Tray Spacing [in]	600°C	650°C	700°C	750°C
24	164.40	162.40	166.40	174.40
18	127.40	125.90	128.90	134.90
12	90.40	89.40	91.40	95.40

With all this information, it is then possible to calculate the CapEx and the OpEx of the distillation section. While the distillation columns have no OpEx, their heat exchangers do. This is because the heat exchangers need a utility stream to work (steam for the

reboilers and cooling water for the condensers), while the columns do not have such a requirement and can be classified as pressure tanks, just like the reactor. Since it is a very small unit operation compared to the distillation columns, the CapEx of the adiabatic flash will be neglected.

### 7.3 Distillation Columns Costs

In this section, the distillation columns' CapEx will be calculated.

As mentioned, they do not have operational expenditures and can be treated as pressure vessels. Therefore, their costs can be calculated as a sum of two contributions: the costs of a pressure vessel with the exact dimensions of the column and the costs of the trays. For the first one, the same Guthrie's formula used for the reactor (formula 6.1) can be applied:

$$CapEx_{vessel} = \frac{M\&S}{280} \cdot 101.9 \cdot D^{1.066} \cdot H_{tot}^{0.802} \cdot (2.18 + F_p \cdot F_m) \quad 7.2$$

where the result is given in €, while D and H<sub>tot</sub> are the column diameter and total height expressed in ft; since all the columns operate at low pressure, there is no need to account for pressure-resistant materials. Therefore, F<sub>p</sub> is 1 for all the cases. Since the stabilizer deals with a high quantity of Hydrogen, it is necessary to protect the column from corrosion by choosing an appropriate construction material such as stainless steel: in this case, F<sub>m</sub> will be equal to 3.67; the other columns do not have such a problem. Therefore, they can be built out of carbon steel, which has an F<sub>m</sub> value of 1.

The second contribution to the columns CapEx can be calculated by another Guthrie's formula designed for the distillation trays:

$$CapEx_{trays} = \frac{M\&S}{280} \cdot 4.7 \cdot D^{1.55} \cdot H_{tot} \cdot (F_s + F_t + F_m) \quad 7.3$$

where the result is given in €; the parameter F<sub>s</sub> takes into account the tray spacing itself (1.0 for 24 in, 1.4 for 18 in, and 2.2 for 12 in), F<sub>t</sub> takes into account the tray type used in the column (“sieve,” with F<sub>t</sub> equal to 0.0 for all the cases). F<sub>m</sub> takes into account the construction material: as usual, the stabilizer has to be made of stainless steel, which has a value of F<sub>m</sub> equal to 1.7; for the other columns, the trays can be built out of carbon steel. Therefore, the factor F<sub>m</sub> is equal to 0.0.

The CapEx of the various distillation columns in the plant are schematized in the tables below.

Table 20- Total CapEx of the Stabilizer [M€]

	600°C	650°C	700°C	750°C
Vessel	0.0815	0.0815	0.0815	0.0960
Trays	0.0061	0.0061	0.0061	0.0077
Total	0.0876	0.0876	0.0876	0.1038

*Table 21- CapEx related to the Product Column “vessel” [M€]*

Tray spacing [in]	600°C	650°C	700°C	750°C
24	0.4949	0.5018	0.5375	0.5446
18	0.4367	0.4423	0.4720	0.4781
12	0.3606	0.4109	0.4109	0.4157

*Table 22- CapEx related to the Product Column trays [M€]*

Tray spacing [in]	600°C	650°C	700°C	750°C
24	0.0488	0.0497	0.0549	0.0558
18	0.0593	0.0603	0.0662	0.0673
12	0.0744	0.0897	0.0897	0.0911

*Table 23- Total CapEx of the Product Column [M€]*

Tray spacing [in]	600°C	650°C	700°C	750°C
24	0.5438	0.5514	0.5924	0.6006
18	0.4961	0.5028	0.5383	0.5454
12	0.4350	0.5006	0.5006	0.5068

*Table 24- CapEx related to the Recycle Column “vessel” [M€]*

Tray spacing [in]	600°C	650°C	700°C	750°C
24	0.2897	0.3308	0.2925	0.3971
18	0.2361	0.2697	0.2748	0.3232
12	0.1793	0.2049	0.2365	0.2448

*Table 25- CapEx related to the Recycle Column trays [M€]*

Tray spacing [in]	600°C	650°C	700°C	750°C
24	0.0212	0.0257	0.0214	0.0331
18	0.0230	0.0279	0.0286	0.0359
12	0.0256	0.0311	0.0382	0.0399

*Table 26- Total CapEx of the Recycle Column [M€]*

Tray spacing [in]	600°C	650°C	700°C	750°C
24	0.3109	0.3565	0.3140	0.4302
18	0.2591	0.2976	0.3034	0.3591
12	0.2049	0.2361	0.2747	0.2847

Generally, the closer two consecutive trays are, the larger their diameter will be. In addition, the column will be shorter. Furthermore, the diameter of the columns barely

increases by decreasing the tray spacing, while the total height decreases much more. Since the “vessel” CapEx is almost linearly dependent on both the diameter and the height, this can explain why the cost of the columns “vessel” decreases with the tray spacing.

On the other hand, the trays’ CapEx is more than linearly dependent on the diameter and still linearly dependent on the height. Therefore, an increase in the diameter will be more influential on the trays’ cost with respect to a decrease in the total height.

Since the vessels’ costs are generally one order of magnitude higher than the trays’ costs, they will be more influential on the total costs of the columns. Therefore, despite the trays costing more, choosing the smallest tray spacing will result in cheaper distillation columns.

## 7.4 Heat Exchangers Costs

This section will evaluate the costs related to the heat exchanger directly linked to the distillation columns. The other heat exchangers in the plant should be studied in their own Economic Potential (EP5), which will not be done in the case of this plant.

The heat exchangers’ CapEx depends on the heat transfer area and the chosen construction material. A Guthrie’s formula for heat exchangers can be used:

$$CapEx_{heat\ exchanger} = \frac{M\&S}{280} \cdot 101.3 \cdot A^{0.65} \cdot [0.29 + F_m \cdot (F_d + F_p)] \quad 7.4$$

the result is given in €, and A is the heat transfer area expressed in ft<sup>2</sup>. F<sub>p</sub> is a parameter that considers the pressure at which the heat exchanger operates: since all the heat exchangers operate at low pressure, this parameter is 0.0 for all the cases. F<sub>d</sub> considers the type of heat exchanger involved: all the condensers are a “fixed tubes” type with an F<sub>d</sub> value of 0.8, while all the reboilers are a “kettle” type with an F<sub>d</sub> value of 1.35. F<sub>m</sub> is a parameter that considers the heat exchanger's construction material. The only heat exchanger that requires special materials is the condenser of the Stabilizer because of the high amount of Hydrogen being processed on the tube side. Therefore, the construction material for the tube side will be stainless steel, while the shell side will be made of carbon steel. The F<sub>m</sub> value of this combination of materials is 2.81. All the other heat exchangers can be built entirely with carbon steel, which has an F<sub>m</sub> value of 1.0.

In the case of the condensers, the heat transfer area can be calculated by a simple formula:

$$A = \frac{\dot{Q}_c}{U \cdot \Delta T_{ml}} \quad 7.5$$

where  $\dot{Q}_c$  is the heat exchanged (“duty”) by the condenser and is available as a number from the Aspen HYSYS simulation; U is the heat transfer coefficient, which has been assumed to be 580 W/m<sup>2</sup>K;  $\Delta T_{ml}$  is the logarithmic mean temperature, which is defined as:

$$\Delta T_{ml} = \frac{(T_{process,IN} - T_{w,OUT}) - (T_{process,OUT} - T_{w,IN})}{\ln\left(\frac{T_{process,IN} - T_{w,OUT}}{T_{process,OUT} - T_{w,IN}}\right)} \quad 7.6$$

$T_{process\ IN/OUT}$  are the temperatures of the fluid being processed by the condenser and are available from the Aspen HYSYS simulation, while  $T_w$  is the cooling water temperature. The cooling water can be assumed to enter the condenser at 30°C and exiting at 50°C, except for the condenser of the stabilizer where the cooling water exits at 38°C. It is worth mentioning that the condensers of the Product and Recycle Columns can be considered as isothermal on the process side, while the condenser of the Stabilizer is characterized by a variation of process-side temperature of more than 50°C.

The resulting data is summarized in the tables below:

*Table 27- Duty of the condensers of the various distillation columns in the plant [kW]*

	600°C	650°C	700°C	750°C
Stabilizer	123.72	123.42	145.54	144.04
Product Column	5830.01	5823.72	5956.73	6080.93
Recycle Column	837.58	1080.49	1242.01	1503.67

*Table 28- Heat exchange area of the condensers of the various distillation columns in the plant [ft<sup>2</sup>]*

	600°C	650°C	700°C	750°C
Stabilizer	84.55	83.71	98.27	96.52
Product Column	2791.15	2786.68	2848.82	2907.45
Recycle Column	225.55	290.54	333.48	403.15

Since the condenser of the Product Column is the largest one, this piece of equipment will be the major contributor to the total CapEx of the condensers of the distillation section.

*Table 29- CapEx of the various condensers in the distillation section [M€]*

	600°C	650°C	700°C	750°C
Stabilizer	0.0323	0.0321	0.0356	0.0352
Product Column	0.2136	0.2134	0.2164	0.2193
Recycle Column	0.0416	0.0491	0.0537	0.0607
TOTAL	0.2875	0.2945	0.3057	0.3153

In the case of the reboilers, the heat transfer area can be calculated by the same formula:

$$A = \frac{\dot{Q}_r}{U \cdot \Delta T_{ml}} \quad 7.7$$

but in this case, a fixed value of 11250  $\frac{BTU}{h \cdot ft^2}$  has been used for the quantity  $U \cdot \Delta T_{ml}$  while  $\dot{Q}_r$  is available from the Aspen HYSYS simulation.



The resulting data is summarized in the tables below:

*Table 30- Duty of the reboilers of the various distillation columns in the plant [kW]*

	600°C	650°C	700°C	750°C
Stabilizer	736.08	819.27	882.86	976.40
Product Column	4989.19	5836.98	6042.35	6198.85
Recycle Column	901.12	1138.26	1296.29	1553.07

*Table 31- Heat exchange area of the reboilers of the various distillation columns in the plant [ft<sup>2</sup>]*

	600°C	650°C	700°C	750°C
Stabilizer	223.40	248.65	267.95	296.34
Product Column	1514.24	1771.55	1833.88	1881.38
Recycle Column	273.49	345.47	393.43	471.36

Again, since the reboiler of the Product Column is the largest one, this piece of equipment will be the major contributor to the total CapEx of the reboilers of the distillation section.

*Table 32- CapEx of the various reboilers in the distillation section [M€]*

	600°C	650°C	700°C	750°C
Stabilizer	0.0487	0.0522	0.0549	0.0586
Product Column	0.1691	0.1872	0.1915	0.1947
Recycle Column	0.0556	0.0647	0.0704	0.0792
TOTAL	0.2734	0.3042	0.3167	0.3324

The utility flow rates must be calculated first to evaluate the heat exchangers OpEx.

Regarding the condensers, the cooling water flowrate can be determined by solving an enthalpic balance on the shell side of the condensers:

$$W_{cw} = \frac{\dot{Q}_c}{c_{H_2O} \cdot (T_{OUT} - T_{IN})} \quad 7.8$$

where  $c_{H_2O}$  is the specific heat of water, and its value is 4186 J/kg·K.

*Table 33- Utility flowrates of the various condensers in the distillation section [galus/s]*

	600°C	650°C	700°C	750°C
Stabilizer	0.3904	0.3895	0.4592	0.4545
Product Column	18.3961	18.3763	18.7960	19.1879
Recycle Column	2.6429	3.4094	3.9191	4.7447

Finally, the OpEx of the condensers can be calculated simply by multiplying the cooling water flow rate by the price of cooling water and the operational time. The formula below

gives the result in €/y, but the results are shown in M€/y for better comparison concerning the various CapEx results.

$$OpEx_{condenser} = W_{cw} \cdot \frac{0.06\text{€}}{1000\text{gal}_{US}} \cdot 3600 \frac{s}{h} \cdot 8000 \frac{h}{y} \quad 7.9$$

Table 34- OpEx of the various condensers in the distillation section [M€/y]

	600°C	650°C	700°C	750°C
Stabilizer	0.0007	0.0007	0.0008	0.0008
Product Column	0.0318	0.0318	0.0325	0.0332
Recycle Column	0.0046	0.0059	0.0068	0.0082
TOTAL	0.0370	0.0383	0.0400	0.0421

Regarding the reboilers, the utility stream is made of steam, available at medium (30 bar) and high pressure (70 bar). The steam flowrates can be calculated by solving an enthalpic balance on the tube side of the reboilers:

$$W_{steam} = \frac{\dot{Q}_r}{\Delta H_{ev,steam}} \quad 7.10$$

Thanks to Antoine’s Equation, it is possible to calculate the condensation temperature of the available steam:

Table 35- Condensation temperature of the available steam

Pressure	30 bar	70 bar
T <sub>cond</sub> [°C]	233.87	285.71

The temperatures of the shell side of the reboilers are available from the Aspen HYSYS simulation:

Table 36- The highest temperature in the shell-side of all the reboilers in the distillation section [°C]

	600°C	650°C	700°C	750°C
Stabilizer	134.61	136.01	136.84	138.14
Product Column	111.56	111.24	111.09	110.90
Recycle Column	211.62	203.22	198.39	191.38

It is clear that both the available utilities are hot enough to guarantee the passage of heat from the steam to the process fluid. However, since the enthalpy of vaporization decreases with pressure, high-pressure steam will be needed in larger quantities to deliver the required energy. Furthermore, since high-pressure steam is generally more expensive than medium-pressure steam, it is more economically convenient to use it in all the distillation section reboilers.

The vaporization enthalpy is evaluated using the steam tables available in Aspen HYSYS. It is possible to calculate the required flow rate of medium-pressure steam using the enthalpy of vaporization of pure steam at 30 bar.

*Table 37- Utility flowrates of the various reboilers in the distillation section [lb/s]*

	600°C	650°C	700°C	750°C
Stabilizer	0.9043	1.0066	1.0847	1.1996
Product Column	6.1297	7.1713	7.4236	7.6159
Recycle Column	1.1071	1.3985	1.5926	1.9081

Finally, the OpEx of the reboilers can be calculated simply by multiplying the steam flow rate by the price of steam and the operational time. The formula below gives the result in €/y, but the results are shown in M€/y for better comparison with respect to the various CapEx results.

$$OpEx_{reboiler} = W_{steam} \cdot \frac{1.65\text{€}}{1000\text{lb}} \cdot 3600 \frac{\text{s}}{\text{h}} \cdot 8000 \frac{\text{h}}{\text{y}} \quad 7.11$$

*Table 38- OpEx of the various reboilers in the distillation section [M€/y]*

	600°C	650°C	700°C	750°C
Stabilizer	0.0430	0.0478	0.0515	0.0570
Product Column	0.2913	0.3408	0.3528	0.3619
Recycle Column	0.0526	0.0665	0.0757	0.0907
TOTAL	0.3869	0.4551	0.4800	0.5096

Finally, the total separation section costs can be calculated by adding all the CapEx and OpEx of reboilers, condensers, and distillation columns and considering the depreciation time of 5 years for the CapEx. The distillation column's chosen CapEx is the lowest for each temperature.

*Table 39- Total costs of the separation section [M€/y]*

	600°C	650°C	700°C	750°C
Total costs	0.6816	0.7780	0.8171	0.8603

The costs tend to increase because the flow rates are higher at higher temperatures, and the amount of Benzene in the mixtures is also higher. Therefore, the separation requires larger unit operations. Consequently, at higher temperatures, the impact of the separation costs on the economic potential will be higher: the economic potential decreases more at higher temperatures.

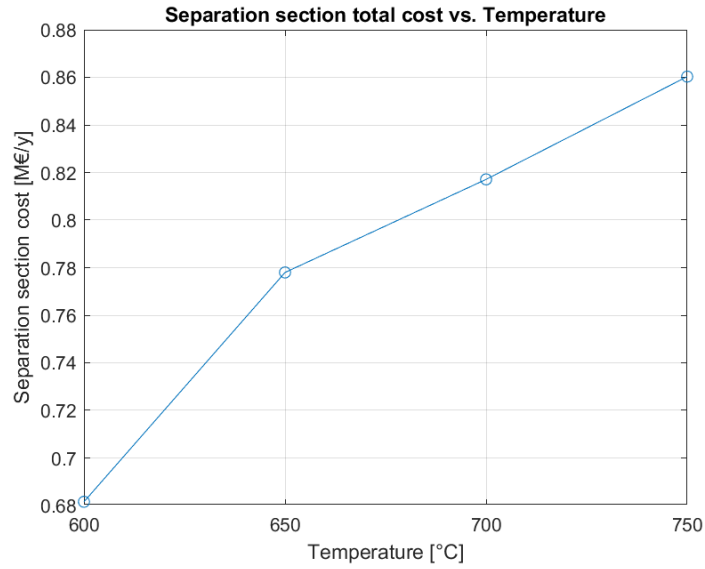


Figure 27- Separation section total costs at different temperatures

Finally, the EP4 can be calculated by subtracting the separation costs from the EP3.

$$EP4 = EP3 - \sum \left( \frac{CapEx}{5y} + OpEx \right)_{separation\ section} \quad 7.12$$

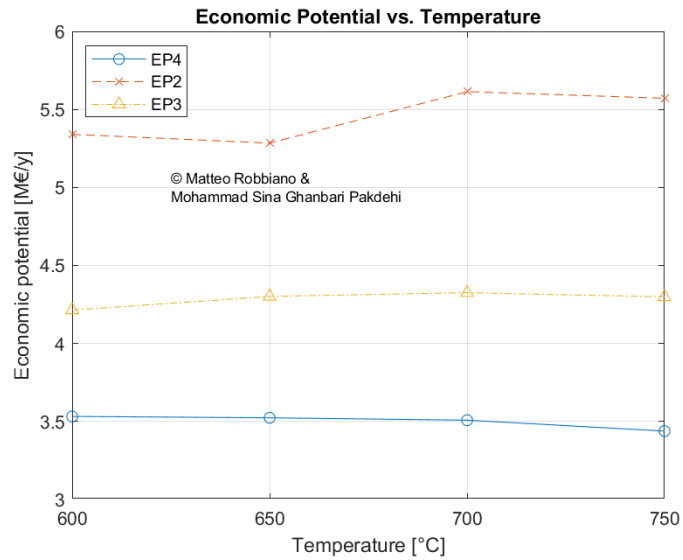


Figure 28- Various economic potentials at different temperatures

## **8. Conclusion**

An economic potential evaluation of an HDA plant has been carried out through various hypotheses and calculations. Based on the displayed data, the conclusion is that, from an economic point of view, the best temperature at which to conduct the process is the lowest one, which is 600°C. Several techniques are available in order to obtain more accurate data: evaluating the EP5, which considers the costs related to heating (furnaces, heat exchangers, ...), or using the data from the Aspen HYSYS simulation to calculate the lower level economic potentials such as the EP2 or EP3.