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Design of sustainable chemical processes incorporating the principles of inherent safety

Grado en Ingeniería Química

Trabajo Fin de Grado

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Junio 2017

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ABSTRACT

Nowadays, the incorporation of safety concepts in the design of chemical plants, together the economic criterion, is a priority within the area of process systems engineering. An inherently safer chemical process avoids or reduces the hazards, rather than managing by adding layers of protection with safety devices. In this work, a systematic methodology is proposed for obtaining the optimal operation conditions that simultaneously seek for the minimization of the inherently safer index and the total annualized cost. This approach is applied to the case study of a styrene monomer production plant. The performance of some units of this plant has been rigorously analyzed using process simulators to obtain simplified models suitable for gradient-based optimization. These surrogated models together short-cut models for the remaining units define a nonlinear programing (NLP) model, which has been solved using the state-of-the-art NLP solvers. The results provide the optimal design and its operation conditions which minimize the risks and hazards of a chemical accident, and besides, takes into account the economic criterion.

KEYWORDS

Safety; design of chemical plants; inherently safer design; nonlinear programming (NLP); styrene monomer; Generalized Algebraic Modeling System (GAMS); Aspen-Hysys.

1. INTRODUCTION

Hazard is a situation that can lead to harm people, the environment or property. In all industries, equipment failures and errors by operators and maintenance workers are recognized as major causes in accidents, and much thought has been given to ways of reducing them or minimizing their consequences. A *risk* is the probability that the harm will occur. Traditional plant designs try to reduce the risk by adding protective equipment and following safe methods of working. An inherently safer design of plants pursues to remove or reduce the hazards. The essence of the inherently safer approach to plant design is the avoidance of hazards rather than their control by adding protective equipment. Although we generally think of safety in a comparative sense, one experienced practitioner has made the distinction between *safe* design and *safer* design. He explains that with *safe* design, there are active safeguards to prevent the occurrence of hazardous events and to protect people and plant from the effects. With *safer* design, there are fewer hazards, fewer causes, and fewer people to be exposed to the effects [1].

Some ways by inherent safer plant design can be achieved are summarized below [1]:

1. **Intensification or minimization**. Friendly plants contain low inventories of hazardous materials.
2. **Substitution**. If intensification is not possible, then an alternative is substitution using a safer material in place of a hazardous one.
3. **Attenuation or moderation**. Another alternative to intensification is attenuation by using a hazardous material under the least hazardous conditions.
4. **Limitation of effects** (a form of moderation) by changing designs or reaction conditions rather than by adding protective equipment that may fail or be neglected.

Commonly, safety is examined and incorporated typically as an after-thought to design. Nevertheless, the best strategy seeks to combine inherently safer design with the process design and optimization at the early stages of design [2].

In order to design and develop a safer plant, a process engineer has to focus on: selecting the appropriate flowsheet configuration and determining the optimal operating conditions that minimizes hazard. There are several hazard indices available as tools for chemical process loss prevention and risk management. Although no index methodology can cover all safety parameters, Dow's Fire and Explosion Index (F&EI) is found to be robust. It is the most widely known and used in the chemical industries, as tools to determine relative ranking of fire, explosion, and chemical exposure hazards [2].

The aim of this project is to develop a systematic methodology for obtaining the optimal flowsheet and the operating conditions for a styrene production plant introducing modifications in the initial phases of the process design (i.e., the conceptual design stage), where process engineers have more flexibility and opportunities to improve the design. The driven force of the optimization process not only focuses on an economic criterion, but also uses F&EI as an additional safety objective.

The following four steps were conducted to illustrate the proposal methodology [2]:

1. Dow’s Fire and Explosion Index calculation.
2. Generate F&EI mathematical expressions as a function of operating pressure and the amount of materials (related with energy content) in the process units.
3. Propose a general procedure for integrating the inherent safer objective into the process design and optimization.
4. Validate the proposed framework to a case study whose performance is simultaneously assessed by an economic and inherent safer indicator.

Decision makers in many areas, from industry to engineering and the social sector, face an increasing need to consider multiple, conflicting objectives in their decision processes. In many cases these real world decision problems can be formulated as multicriteria mathematical optimization models. The solution of such models requires appropriate techniques to compute so called efficient, or Pareto optimal frontier [10]. Thus, in this work, a set of viable solutions are presented, not just one. Two objective functions will be considered: the total annualized cost (TAC) and the inherently safer index accounted for by means of the Dow’s F&EI.

To solve this NLP problem, algebraic modeling systems, numerical calculation software and process simulators will be used. Particularly, it has been used the NLP solver CONOPT, within the General Algebraic Modeling System (GAMS). Besides, to form numerical computations and simulations, MATLAB and Aspen Hysys programs have been required respectively.

2. PROBLEM STATEMENT

In this work, the problem of integrating inherent safer design principles into the optimization design of a styrene monomer plant can be stated as follow:

Given the flowsheet in Figure 1, determine the optimal process layout and its operating conditions (pressures, areas, reactor length, and flow rates) that minimize simultaneously the F&EI and total annualized cost (TAC). It is important to note that it is a multi-objective problem.

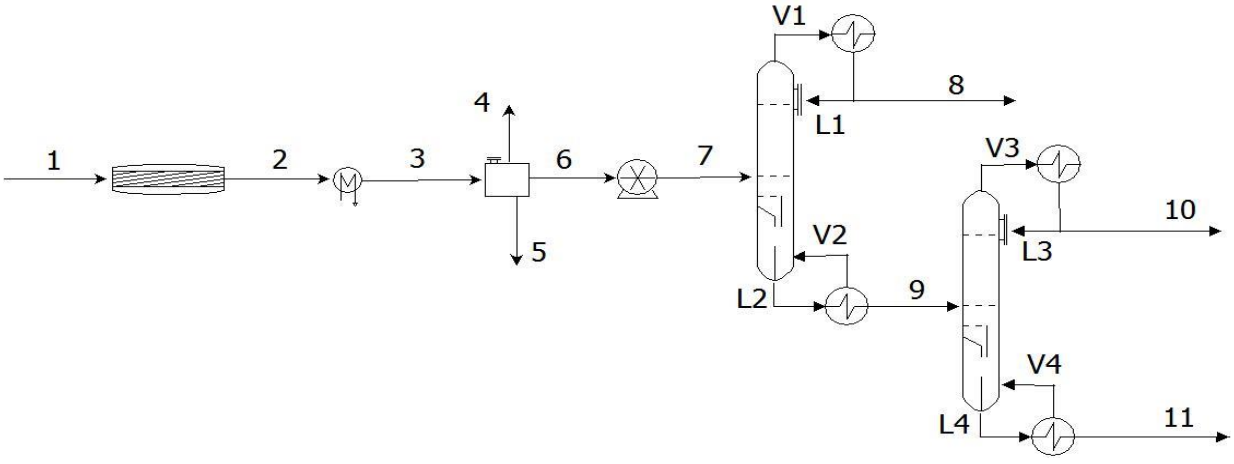


Figure 1. Styrene monomer production flowsheet.

The dehydrogenation of ethylbenzene to styrene (R1) takes place on a promoted iron oxide catalyst in a fixed-bed reactor at high temperature range in the presence of steam. The feed to the reactor (stream 1 in Figure 1) consist only of fresh ethylbenzene mixed with superheated vapor. The reactor produces an effluent stream (containing styrene monomer, ethylbenzene, hydrogen, ethylene, toluene, methane, water, CO and CO_2), which must be separated to purify the product. The reactor effluent goes through a separation sequence in which the gas (hydrogen), byproducts (benzene and toluene), pure products (benzene and toluene), pure product (styrene monomer) and waste water are isolated. First, the effluent from the reactor unit (stream 2) is cooled to 30°C, forming three phases (vapor, organic and aqueous). The condenser styrene together with the main by-products (toluene and benzene) and un-reacted ethylbenzene (stream 3), separates from water and non-condensable gases like H_2 in settling drum (3 phase separator). The crude styrene is then taken to the distillation unit 1 (stream 7), which bottoms stream (stream 9) contains mostly ethylbenzene and styrene monomer, which are sent to the styrene distillation column 2 for the recovery of styrene (stream 11). The distillate of column 2 (stream 10) contains mainly ethylbenzene

.

In order to solve this problem, must be considered the following assumptions:

- The reactor used for the process is a PFR with 1.95 m of diameter, which contains catalyst with the following characteristics:

$$\rho_{cat} = 2350\frac{kg}{m^3}, \qquad D_p = 1\,mm, \qquad \varepsilon = 0.445.$$

  Being, ρ_{cat} catalyst density (kg/m^3), D_p particle diameter (m) and ε bed porosity.

- The six reactions occurring in the styrene reactor are:

$$\underset{\text{E-Benzene}}{C_6H_5CH_2CH_3} \leftrightarrow \underset{\text{Styrene}}{C_6H_5CHCH_2} + H_2 \tag{R1}$$

$$\underset{\text{E-Benzene}}{C_6H_5CH_2CH_3} \rightarrow \underset{\text{Benzene}}{C_6H_6} + \underset{\text{Ethylene}}{C_2H_4} \tag{R2}$$

$$\underset{\text{E-Benzene}}{C_6H_5CH_2CH_3} \rightarrow \underset{\text{Toluene}}{C_6H_5CH_3} + \underset{\text{Methane}}{CH_4} \tag{R3}$$

$$2H_2O + C_2H_4 \rightarrow 2CO + 4H_2 \tag{R4}$$

$$H_2O + CH_4 \rightarrow CO + 3H_2 \tag{R5}$$

$$H_2O + CO \rightarrow CO_2 + H_2 \tag{R6}$$

- The fresh ethylbenzene is mixed with the superheated vapor (mixture ratio 1:2 w% mass flow rate of the vapor is twice the mass flow rate of ethylbenzene) to feed the reactor at the reaction conditions.
- The kinetic laws for the styrene reactions (R1) to (R6) are shown in Table 1.
- The reactor operates under adiabatic conditions. There are competitive reactions that are favored over the desired reaction (R1) when the reactor operates under isothermal conditions. As a result, in isothermal conditions the amount of H_2 increases and the amount of styrene decreases.
- The effluent from the reactor unit is cooled to $30°C$, forming three phases (vapor, organic and aqueous).
- The three phase separator is ideal, each phase is completely separated. The vapor phase is composed of $CO, CO_2, \text{Ethylene}, CH_4$ and H_2. On the other hand, the organic phase consists of Ebenzene, Benzene, Toluene and Styrene and the third stream is the aqueous, only with water.
- The feed which goes to the first column distillation is the organic. In the first column, the light key component (Toluene) must have a molar fraction lower or equal than 0.005 in bottoms, and the heavy key component (Ebenzene) a molar fraction lower or equal to 0.005 in distillate.
- For column 2 the light key component is Styrene monomer and the heavy key component is E-Benzene. The separation required is a molar fraction of heavy key component in bottoms of 0.003 and a molar fraction of light key component of 0.003 in distillate.
- A minimum production rate of 850 kg styrene/h is required.
- Pump and three phase separator are considered as ideal equipments.
- A production rate of 850 kg styrene/h is required at least.
- Pump and three phase separator are considered as ideal equipments.

All the available data can be found in Appendix G (Technical requirements specifications).

Table 1. Kinetic laws for PFR.

Reaction type Hysys	Reaction rate	Constants	Enthalpy
Simple Rate	$r_1 = A_1 \exp\left(-\frac{E_1}{RT}\right)\left(p_{EB} - \frac{p_{ST}p_{H_2}}{K'}\right)$ $\ln(K') = A_1{}'$	$A_1 = 1967 \frac{kmol}{m^3 \cdot atm \cdot s}$ $E_1 = 90792.7 \frac{kJ}{kmol}$ $A_1' = -1.61$	$117 \frac{kJ}{kmol}$
Kinetic	$r_2 = A_2 \exp\left(-\frac{E_2}{RT}\right) p_{EB}$	$A_2 = 7.3 \cdot 10^8 \frac{kmol}{m^3 \cdot atm \cdot s}$ $E_2 = 207944.6 \frac{kJ}{kmol}$	$105.5 \frac{kJ}{kmol}$
Kinetic	$r_3 = A_3 \exp\left(-\frac{E_3}{RT}\right) p_{EB}\, p_{H_2}$	$A_3 = 1748 \frac{kmol}{m^3 \cdot atm^2 \cdot s}$ $E_3 = 91462.1 \frac{kJ}{kmol}$	$-54.68 \frac{kJ}{kmol}$
Kinetic	$r_4 = A_4 \exp\left(-\frac{E_4}{RT}\right) p_{Ethyl}\, p_{H_2O}^2$	$A_4 = 1209 \frac{kmol}{m^3 \cdot atm^3 \cdot s}$ $E_4 = 103972.3 \frac{kJ}{kmol}$	$210.12 \frac{kJ}{kmol}$
Kinetic	$r_5 = A_5 \exp\left(-\frac{E_5}{RT}\right) p_{Met}\, p_{H_2O}$	$A_5 = 69.11 \frac{kmol}{m^3 \cdot atm^2 \cdot s}$ $E_5 = 65688.73 \frac{kJ}{kmol}$	$206.12 \frac{kJ}{kmol}$
Kinetic	$r_6 = A_6 \exp\left(-\frac{E_6}{RT}\right) p_{CO}\, p_{H_2O}$	$A_6 = 7329 \frac{kmol}{m^3 \cdot atm^2 \cdot s}$ $E_6 = 73554.64 \frac{kJ}{kmol}$	$-41.39 \frac{kJ}{kmol}$

3. OPTIMIZATION MODEL REFORMULATION

3.1 SAFETY

3.1.1 Dow's fire and explosion index (F&EI) methodology

In the present work, the F&EI calculation that must be incorporated into the optimization process is based on the work of Jaffee Suardin et al. [2]. To determine F&EI, steps in Figure 2 must be followed. This procedure is taken from Dow's fire and explosion index hazard classification guide [3]. Each of the steps given below is outlined and explained in the following pages.

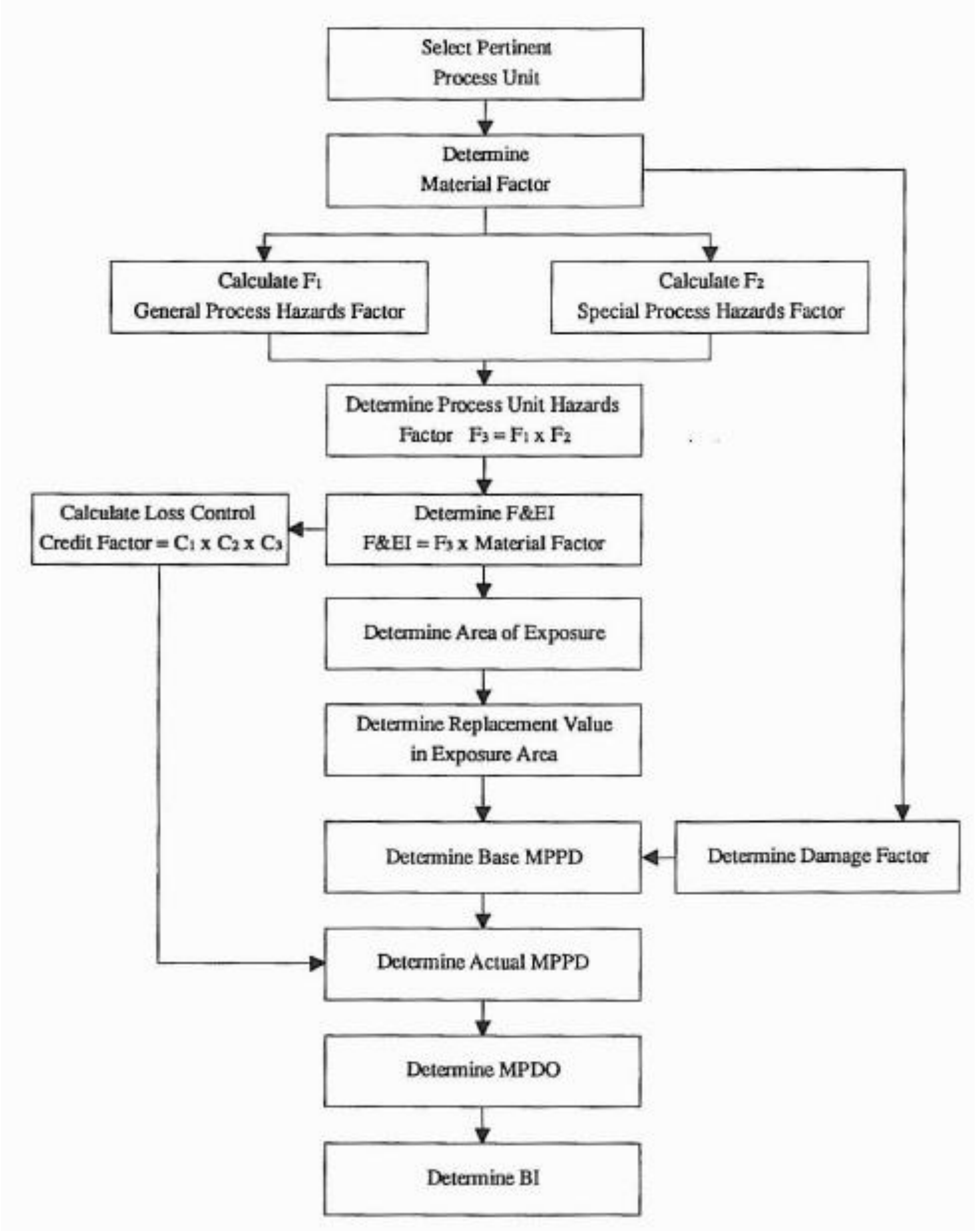


Figure 2. Procedure for calculating Fire & Explosion Index and other risk analysis information.

First, the material factor (MF, the measure of the potential energy released by material under evaluation) is obtained from databases, material safety data sheet (MSDS), or manual calculation (using flammability, NF, and reactivity value, NR). Then, it is determined the sum of penalties that contributes to loss probability and its magnitude (general process hazard factor, F_1) and the sum of factors result in the factor that can increase the probability and historically contributes to major fire and explosion incidents (special process hazards factor, F_2).

General process hazards cover six items, namely, exothermic chemical reactions, endothermic processes, material handling and transfer, enclosed or indoor process units, access and drainage and spill control, although it may not be necessary to apply all of them. Special process hazards cover twelve items: toxic material, sub-atmospheric pressure, operation in or near flammable range, dust explosion, relief pressure, low temperature, quantity of flammable/unstable material, corrosion and erosion, leakage-joints and packing, use of fired equipment, hot oil heat exchange system, and rotating equipment. Each of the items is represented in terms of ‘‘penalties’’ and ‘‘credit factors’’ [2].

The Dow’s fire and explosion index (F&EI) is calculated:

$$\mathrm{F\&EI} = \mathrm{MF} \cdot \mathrm{F_3} \tag{1}$$

where the Process Unit Hazards Factor (F_3) is computed as:

$$F_3 = F_1 \cdot F_2 \tag{2}$$

All penalties in the general process hazard factor (F_1), are constants for our case study, and do not depend on neither the operating conditions, nor equipments size. Therefore, this value is determined by the process itself. However, Special Process Hazards Factor (F_2) includes variables as operating pressure, mole flow rates, equipment volume that could influence in the safety index of the chemical plant. These variables appear in particular in points E (Pressure) and G (Quantity of Flammable/Unstable Material) of F_2. The general equation for calculating F&EI which includes above-mentioned variables is:

$$\mathrm{F\&EI} = \mathrm{MF} \cdot F_1 \cdot F_2 = MF \cdot F_1 \cdot [F_2^{cte} + E_2(P) + G_2(V,n)] \tag{3}$$

Being,

- F_2^{cte} constant penalties in F_2.
- $E_2(P)$ penalty which applies because of operating pressure. Equation (5) shows the expression to calculate this value.
- $G_2(V,n)$ penalty which applies because of the energy liberates in the event of an explosion. This penalty has to be calculated in two ways: considering the total amount of substances inside equipment (considering the equipment volume) and considering a spill during 10 minutes (total mole flow rate). Details of its calculation are shown in equation (10).

3.1.2 Fire & Explosion index analysis

Following the procedure for risk analysis calculations proposed into the literature [3], it analyses step by step each point of F&EI.

Material Factor

To start with, after carrying out a simulation in Hysys of the styrene plant with the values of the expected optimal variables, the qualitative concentration of the components in the flowsheet is shown in Table 2.

Table 2. Qualitative concentration of the components in the flowsheet.

	E-Benzene	Styrene	H_2	Ethylene	Toluene	CO	CO_2	CH_4	H_2O	Benzene
% Molar	high	high	high	low	low	low	low	low	Very high	low

The Material Factor (MF) is the basic starting value in the computation of the F&EI and other risk analysis values. The MF is a measure of the intrinsic rate of potential energy release from fire or explosion produced by combustion or chemical reaction. The Material Factor must adequately reflect the material hazard present in this *unique situation,* and reactive chemical testing data *must* be employed to determine the proper MF [3]. In this particular case, the MF selected is the one corresponding to styrene. Given the low concentration of components (water is not considered to be a fire hazard) styrene and hydrogen are the highest. Between these two components it is selected the one with the highest value of MF, that is to say, styrene (hydrogen has a MF of 21 and styrene has one of 24).

Table 3 shows the MF of styrene and other important information needed in order to analyse the Fire & Explosion Index.

Table 3. Material factors and properties of styrene.

	MF	$H_c\ (BTU/LB)\ \cdot 10^3$	N_H	Flash point (°F)	Boling point (°F)
Styrene	24	17,4	2	88	298

Symbols of Table 3 are defined as:

- MF material factor
- H_c heat of combustion (BTU/LB)
- N_H health factor

1. General Process Hazards

A. Exothermic Chemical Reactions.

The reactivity hazard of the material being evaluated is inherent in the Material Factor, so the reaction selected is hydrogenation with a penalty of 0,30.

B. Endothermic Processes.

In the reactor takes place the thermal decomposition of molecules to smaller ones by use of high temperatures (cracking reactions, which are endothermic), so a penalty of 0,40 is applied to the reactor.

C. Material Handling and Transfer.

This pool contains the potential fire which involves the pertinent Process Unit during the handling, transfer and warehousing of materials. The system, for the case under study, is assumed to be in a steady state. Therefore, there is a penalty of 0 (there is not loading and unloading).

D. Enclosed or Indoor Process Units.

Styrene production is carried out in complex industrial outdoor plants. In the case study it is also considered an outdoor plant, so the penalty applied is 0.

E. Access.

It is supposed the emergency equipment have ready access to the area housing the pertinent Process Unit which is located outdoor. The penalty applied is again 0.

F. Drainage and Spill Control.

The right way of controlling drainage and spill is a diking design that surrounds three sides of an area and directs spills to an impounding basin or non-exposing drainage trench. The plant design plant incorporates this diking and complies with all the criteria, so the penalty is 0.

2. Special Process Hazards.

A. Toxic Material.

For mixtures, the penalty is applied using $0{,}20 \cdot N_H,$ being N_H the highest N_H of all the components. Table 4 shows all the health factors of components. The highest one is 3, so the penalty applied is 0.6.

Table 4. Health factors of components.

	E-Benzene	Styrene	H_2	Ethylene	Toluene	CO	CO_2	CH_4	H_2O	Benzene
N_H	2	2	1	0	2	3	-	1	-	2

B. Sub-Atmospheric Pressure.

This penalty is applied only if the absolute pressure is less than 500 mmHg. In any case, pressure presents such low values, so the penalty is 0.

C. Operation In or Near Flammable Range.

In this section, the penalty applied is 0,80 because of the fact that the reactor operations are always in flammable range (temperatures are very high). Besides, there are very flammable components that are always in range.

D. Dust explosion.

The penalties listed in this section are intended to apply to any Process Unit involving dust handling operations: transferring blending, grinding, bagging. In the case study, there is not dust generation. The penalty applied is 0.

E. Relief Pressure.

Equipments operate at pressure above the atmospheric. To determine the appropriate penalty that depends on the higher operating pressure (one of the equipments), the following equation must be used:

$$Y = 0.16109 + 1.61503\left(\frac{X}{1000}\right) - 1.42879\left(\frac{X}{1000}\right)^2 + 0.5172\left(\frac{X}{1000}\right)^3 \tag{4}$$

Being,

- Y penalty to apply
- X pressure (psig)

To determine the final penalty E_2, the operating pressure penalty and the adjustment factor F are multiplied as it is shown in the below equation:

$$E_2 = F \cdot Y\left(P_{operating}\right) = 1.2\frac{Y\left(P_{operating}\right)}{Y\left(P_{realive}\right)} \cdot Y\left(P_{operating}\right) = 1.2\frac{Y\left(P_{operating}\right)^2}{Y\left(P_{realive}\right)} \tag{5}$$

Note that E_2 appeared in equation (3). This penalty will change its value in function of the operating and relief pressures of each equipment (reactor and distillation columns), so in the mathematical model this equation will appear. The penalty E_2 selected to determine the F&EI will be the highest among the penalties computed for each unit.

F. Low Temperature.

This section makes allowances for the possible brittleness of carbon steel or other metals that may be exposed to temperatures at or below their ductile/brittle transition temperatures. In the range of temperatures where equipments operate, there is no problem, the material is appropriate for the lowest possible operating temperature. So, the penalty applied is 0.

G. Quantity of Flammable/Unstable Material

This section considers the additional exposure to an area as quantities of flammable and unstable material in the process unit are increased. There are three categories in this section, each evaluated by a separate penalty curve: Liquids or Gases in Process, Liquids or Gases in Storage, Combustible Solids in Storage/Dust in Process. Only one penalty must be selected for the entire section, based on the Material Factor (styrene). In this particular case, the penalty called "Liquid or gases in Process" is selected, due to the fact that the two remaining are referred as storage.

The penalty in this section must be calculated with equation (6):

$$logY = 0.17179 + 0.42988(1ogX) - 0.37244(1ogX)^2 + 0.17712(1og\,X)^3 - 0.029984(1ogX)^4 \tag{6}$$

Where,

- Y penalty
- X energy content $(BTU \cdot 10^9)$

To determine energy content X, it is necessary multiply the value of heat of combustion H_c given in Table 3 by the mass of components m_j :

$$X(BTU) = \sum_j H_{C_j}\left(\frac{BTU}{lb}\right) \cdot m_j(lb) \tag{7}$$

Two criteria are to be considered when calculating the total energy content, so two X values will be obtained. The ways must be calculated are: on the one hand, the quantity of energy contained in equipments, taking into account, volume (8). On the other hand, the energy which would be released by the input stream as the result of a leaking during ten minutes (9).

$$E_{volume} = V_{equipment} \cdot \sum_j C_j^{average} \cdot H_{cj} \tag{8}$$

$$E_{stream} = H_{cj} \cdot m_j \cdot t \tag{9}$$

Where,

- E_{volume} energy content in function of equipment volume (BTU)
- E_{stream} energy content in function of a leaking during ten minutes (BTU)
- H_{cj} heat of combustion of component j $\left(\frac{BTU}{lb}\right)$
- $C_j^{average}$ average concentration of component j $\left(\frac{BTU}{m^3}\right)$
- m_j mass flow rate of component j $\left(\frac{lb}{m^3}\right)$
- t leaking time $(10\ minutes)$

The greater value between E_{volume} and E_{stream}, will provide the energy content $X(BTU)$ to calculate F&EI. As a result of equations above, a higher value of $V_{equipment}$ will imply also a higher value of the styrene mass inside the equipment equipment. In other words, the design of equipment determines the energy content, which will cause the G item contribution of the F&EI to increase.

H. Corrosion and Erosion.

Corrosion is the major disadvantage of steels since the iron is oxidized with the sum that facilitates the increase of its volume and that causes superficial cracks that allow the progression of the oxidation until it consumes the piece completely. In the worst case, there is risk that stress-corrosion cracking might develop, so it is applied a penalty of 0.75.

I. Leakage-Joints and Packing.

In equipments do not exert a very high pressure. Materials in equipments are sufficiently prepared to resist the pressure, therefore, there should be no problems. The penalty is 0.

J. Use of Fired Equipment.

In the worst case, if the fired equipment (process side) itself is the Process Unit being evaluated, the distance from the possible leak source becomes zero, the penalty is 1.

I. Hot Oil Heat Exchange System.

The cooler, reboilers and condensers receive a penalty of 0, because of the fact that penalty I is only applied if the hot oil is non-combustible. The utilities type is not hot oil, but cooling water and steam.

K. Rotating Equipment.

Pump is considered as ideal rotating equipment, so a penalty of 0 is applied.

Once all points have been evaluated, the calculation of penalties can be performed. The sum of the base factor and all penalty factors applied in General Process Hazards and Special Process Hazards are summarized in Table 5. Developing equation (3) from equations (5), (8) and (9):

$$F\&EI = 24 \cdot 1.7 \cdot [3.15 + E_2(P) + G_2(V)] =$$

$$= 40.8 \cdot \left[3.15 + 1.2\frac{Y\left(P_{operating}\right)^2}{Y(P_{realive})} + G_2(V)\right] =$$

$$= 128.52 + 40.8\left[1.2\frac{Y\left(P_{operating}\right)^2}{Y(P_{realive})} + G_2(V)\right]$$

Being,

$$X \geq V_{equipment} \cdot \sum_j C_j^{average} \cdot H_{cj}$$
$$X \geq H_{cj} \cdot m_j \cdot t \tag{10}$$

To sum up, F&EI calculation has been implemented into process design and optimization framework. Equation (10) contains key operating variables which guarantee that the design meets certain safety criteria. Pressure, mole flow rates and equipment size are decision variables that will affect the inherently safer index value.

Table 5. Styrene plant F&EI.

Material Factor	24
1. General Process Hazards	
Base Factor	1
A. Exothermic Chemical Reactions	0.3
B. Endothermic Processes	0.4
C. Material Handling and Transfer	0
D. Enclosed or Indoor Process Units	0
E. Access	0
F. Drainage and Spill Control	0
General Process Hazards Factor (F1)	1.7
2. Special Process Hazards	
Base Factor	
A. Toxic Marial(s)	0.6
B. Sub-Atmospheric Pressure (<500 mmHg)	0
C. Operation In or Near Flammable Range	
1. Tank Farms Storage Flammable Liquids	-
2. Process Upset or Purge Failure	-
3. Always in Flammable Range	0.8
D. Dust Explosion	0
E. Pressure	Equation
F. Low Temperature	0
G. Quantity of Flammable/Unstable Material	
1. Liquid or Gases in Process	Equation
2. Liquids or Gases in Storage	-
3. Combustible Solids in Storage, Dust in Process	-
H. Corrosion and Erosion	0.75
I. Leakage-Joints and Packing	0
J. Use of Fired Equipment	1
K. Hot Oil Heat Exchange System	0
L. Rotating Equipment	0
Special Process Hazads Factor (F2)	3.15
Process Unit Hazards Factor (F1xF2)=F3	5.355
Fire and Explosion Index (F3xMF=F&EI)	128.52

3.2 EQUIPMENT DESIGN

The reactor design relies on solving differential equations. These systems of equations in the area of chemical engineering are highly non-linear and hence numerical methods are needed to solve them. Typical numerical schemes are based in Runge-Kutta solvers, which are not appropriate for optimization because for each fixed combination of the decision variables the whole evolution of the dependent variables (concentration, temperature or pressure) with respect the independent variable (time or spatial dimension) must be calculated. Hence, alternative methods, which avoid the need for solving a system of differential equations, must be employed. In the following sections, it is explained how the model equations which describe each equipment have been adapted to a mathematical model suitable for optimization purposes.

3.2.1 Reactor design

The method to be followed for formulating PFR behaviour as algebraic equations derived from Aspen Hysys is described in Figure 3.

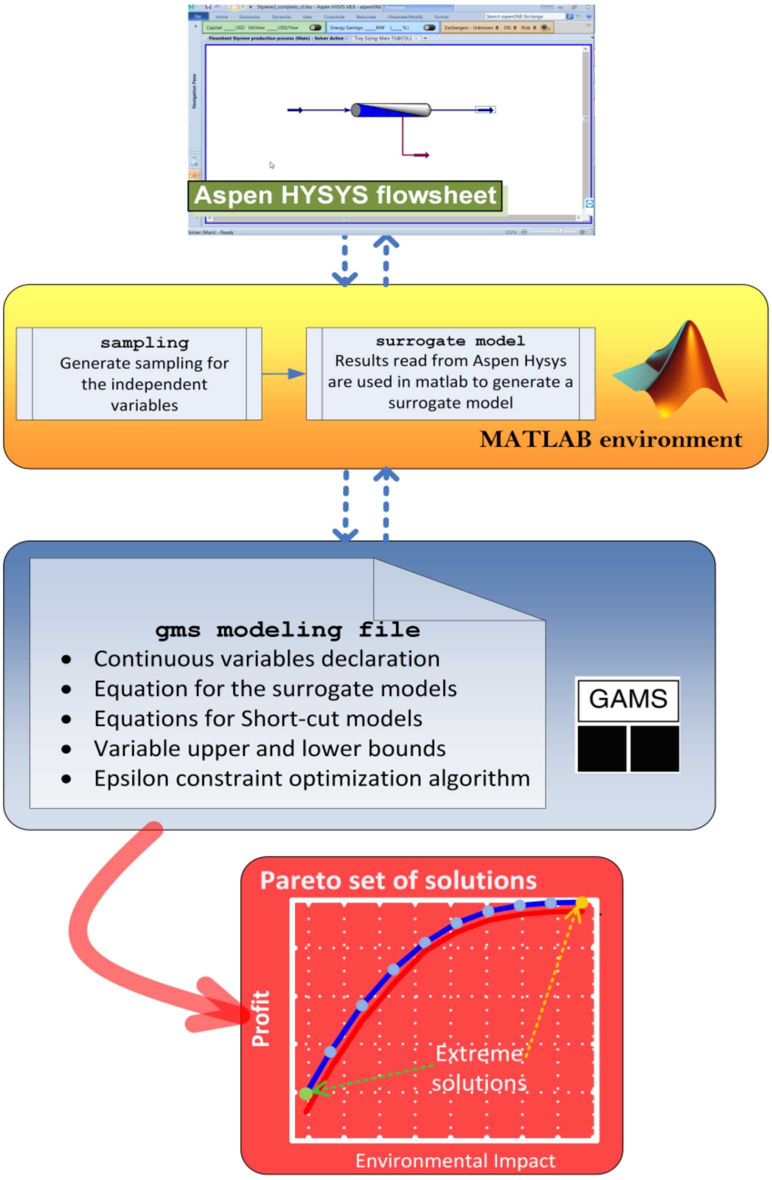


Figure 3. Scheme of the steps to be followed for obtaining the reactor design equations.

By writing MATLAB code, it is possible to send and receive information to and from the process simulator (Figure 3). The results obtained will be fitted as algebraic equations. All the equations of the model were directly written in the modeling language GAMS.

3.2.1.1 Design equations

Direct dehydrogenation of ethylbenzene to styrene accounts for 85% of commercial production. The reaction is carried out in industrial fixed bed catalytic reactors, in vapor phase with steam over a catalyst consisting primarily of iron oxide [4].

In order to ensure that the kinetic parameters supplied to Aspen Hysys are correct, a simulation in MATLAB is proposed. To carry out this simulation, molar, energy and momentum balances along reactor must be resolved. For plug flow reactor type, the molar balance for each component j :

$$\frac{dn_j}{dL} = Ar_j \tag{11}$$

where,

- n_j mole flow rate of components j (mol/s)
- L reactor length (m)
- A reactor section, with cylinder surface (m^2)
- r_j reaction rate with respect component j $(mol \cdot m^{-3} \cdot s^{-1})$

The energy balance differential equation is given by:

$$\frac{dT}{dL} = \frac{Ua(T_a - T) - A\sum_{i=1}^{R} r_i \Delta H_i}{\sum_{j=1}^{S} n_j C_{pj}} \tag{12}$$

being,

- T temperature along reactor (K)
- $Ua(T_a - T)$ delivered/lost heat $(J/m \cdot s)$. At the problem, reactor operates in adiabatic conditions.
- C_{pj} heat capacities for component j $\left(\frac{J}{mol \cdot K}\right)$
- r_i reaction rate of reaction i $\left(\frac{mol}{s \cdot m^3}\right)$
- ΔH_i entalphy of reaction i $\left(\frac{J}{mol}\right)$

The Ergun equation issued to compute the pressure profiles along the length of the catalyst bed:

$$\frac{dP}{dL} = -\frac{G}{\rho g_c D_p}\left(\frac{1-\varepsilon}{\varepsilon^3}\right)\left[\frac{150(1-\varepsilon)\mu}{D_p} + 1.75G\right] \tag{13}$$

being,

- P pressure along reactor (Pa)
- G mass flux density ($kg \cdot m^{-2} \cdot s^{-1}$)
- ε porosity
- μ viscosity of the gas passing through the bed ($Pa \cdot s$)
- D_p particle diameter of catalyst
- g_c conversion factor (remember that in the metric system $g_c = 1$).
- ρ gas density ($kg \cdot m^{-3}$)

All balances can be found at reference [5]. The reactor model differential equations given by (11), (12) and (13) introduced into MATLAB must produce similar solutions to Aspen Hysys. The following problem is proposed in order to ensure results are resembled. Input stream conditions into the reactor are presented in Table 6.

Table 6. Input stream conditions.

E-Benzene (kmol/h)	14,250
Styrene (kmol/h)	0,013
Hydrogen (kmol/h)	0,000
Ethylene (kmol/h)	0,000
Toluene (kmol/h)	0,062
CO (kmol/h)	0,000
CO2 (kmol/h)	0,000
Methane (kmol/h)	0,000
H2O (kmol/h)	170,420
Benzene (kmol/h)	0,000
T (°C)	700
P (Pa)	1,60E+05

To simulate the reactor, it is recalled that catalyst density is $2350\ kg/m^3$ with a particle diameter of $1\ mm$ and a bed porosity of 0.445. In addition, a 3 m PFR is fixed for the simulation, with a diameter of 1.95m. In the reactive system reactions presented in Problem Statement (R1), (R2), (R3), (R4), (R5) and (R6) take places. Then, known the problem, calculations are performed. The results obtained are shown below.

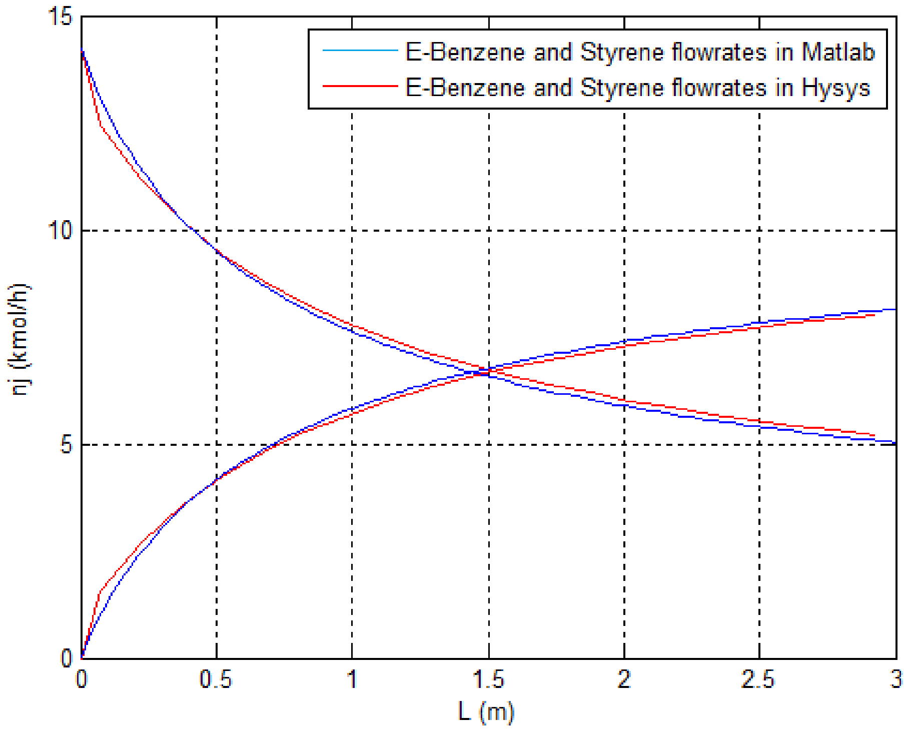


Figure 4. Comparison between Styrene and E-Benzene mole flow rates simulations throughout the reactor in Aspen Hysys and MATLAB.

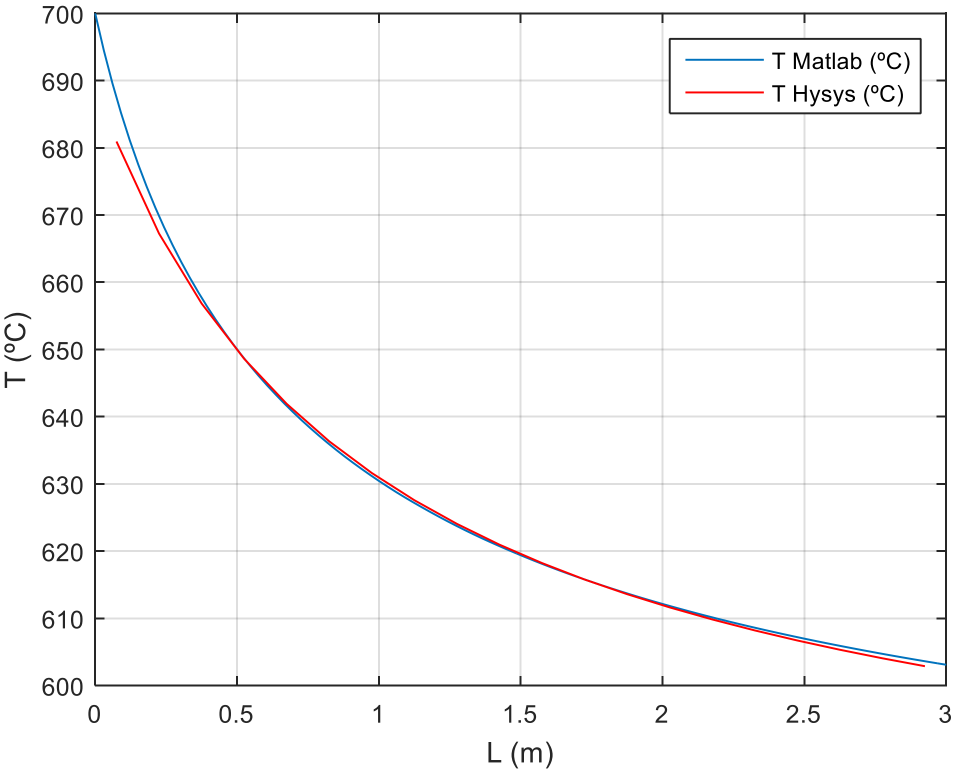


Figure 5. Comparison between temperature simulations throughout the reactor in Hysys and MATLAB.

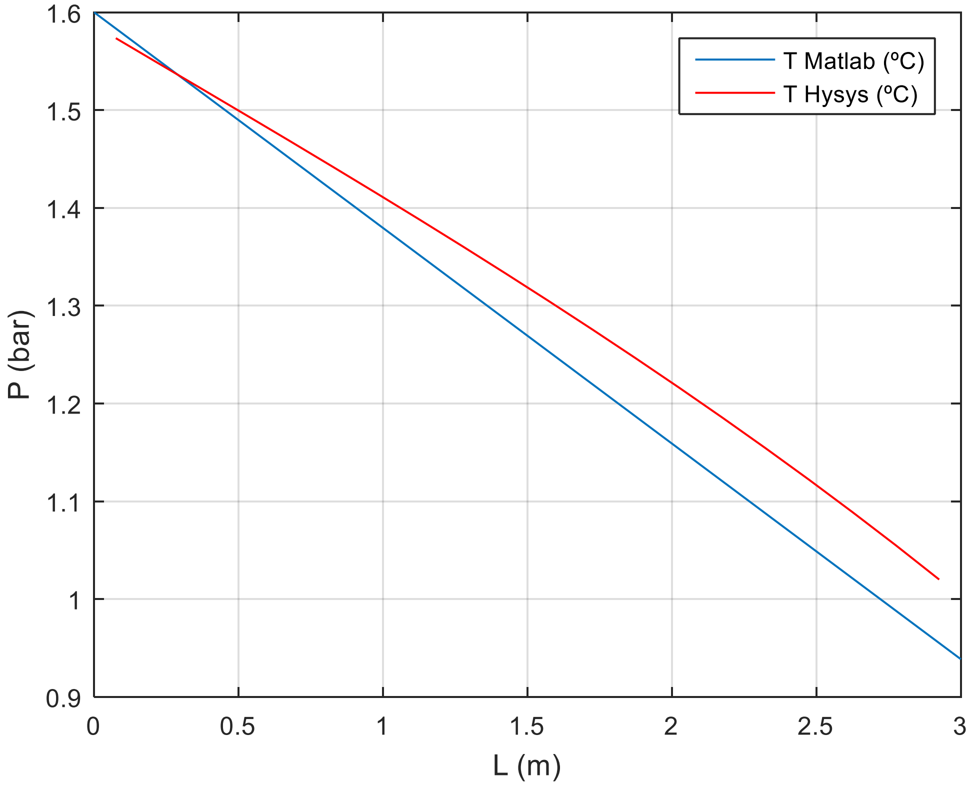


Figure 6. Pressure throughout the reactor in Hysys and MATLAB.

As can be seen in Figures 4, 5 and 6, MATLAB simulations fit the results obtained by Aspen Hysys. Mole flow rates simulations and temperature are practically identical. Pressure drop throughout the reactor in MATLAB slightly deviates from the Aspen Hysys simulation. This intended to demonstrate that kinetic data supplied to Aspen Hysys are correct. Therefore, Aspen Hysys results can be used in order to fit PFR behavior to a surrogate model (or simplified model, which given the input data provides the same output values), without the need to solve a differential system of equations. As mentioned above, an efficient optimization model can only use algebraic equations, so these molar, energy and momentum balances throughout the reactor will be introduced as algebraic equations derived from Aspen Hysys results.

In Appendix B can be found the MATLAB files used to carry out simulations. Output stream is also compared in Table 7, where final results are very similar.

Table 7. Output stream conditions.

	Hysys	MATLAB
E-Benzene (kmol/h)	5.208	5.029
Styrene (kmol/h)	8.018	8.148
Hydrogen (kmol/h)	8.712	8.798
Ethylene (kmol/h)	0,693	0.763
Toluene (kmol/h)	0,320	0.297
CO (kmol/h)	0,007	0.007
CO2 (kmol/h)	0,280	0.263
Methane (kmol/h)	0,153	0.140
H2O (kmol/h)	169,854	169.886
Benzene (kmol/h)	0,781	0.851
T (°C)	594,31	595,34
P (Pa)	1.49E+05	1.50E+05

3.2.1.2 Preliminary study on the reactor

Before continuing, it would be appropriate to make a preliminary study on the reactor, where will be determinated the best range to work. Variables that could affect the final design are: input mole flow rate into reactor, initial temperature, initial pressure and reactor length. Typical operating conditions in commercial reactors are high temperatures with as low pressure as practicable [4]. First, the study is based on these two variables, pressure and temperature. The aim is to determine the system's behavior and fix the input temperature and pressure. Reactor feed and reactor length will be variables to optimize which are studied next. Several simulations in Aspen Hysys are performed in a wide range of temperature and pressure. Figure 7 shows the extent of reaction (R1) in function of pressure and temperature. In this, yellow and blue areas can be distinguished. Yellow area represents the higher values and blue area the lower ones.

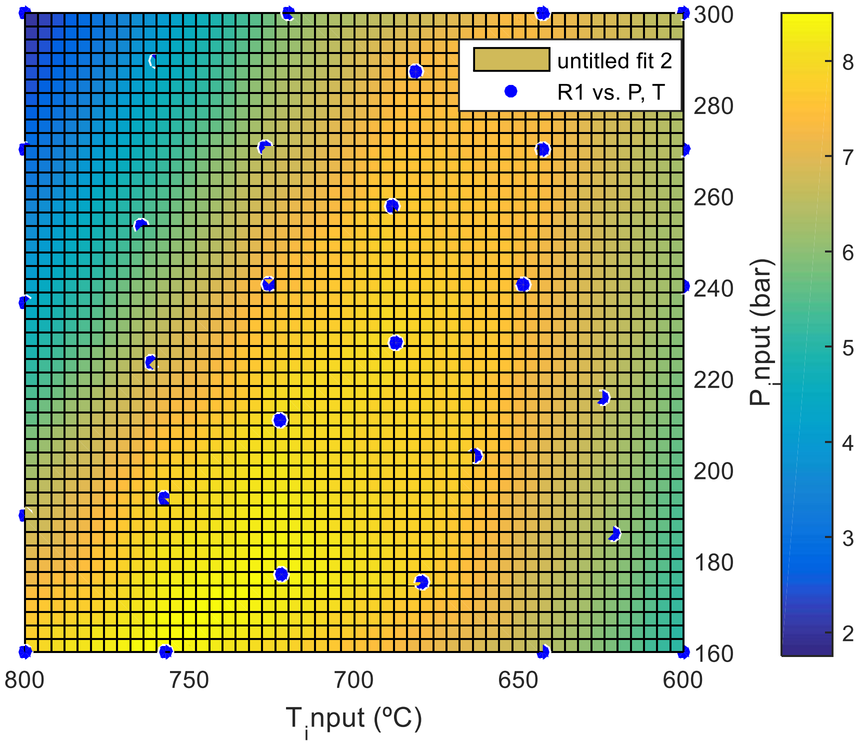


Figure 7. Extent of reaction (R1) (kmol/h) as a function of pressure (kPa) and temperature (°C) in the feed stream to the reactor.

As above mentioned, the reaction (R1) is limited by thermodynamic equilibrium. Figure 7 shows how high temperature and low pressure give raise to the highest values of extent of reaction. Accordingly, an appropriate working range could be $700℃ < T < 760℃$ and $1.6 \text{ bar} < P < 1.8 \text{ bar}$.

The ethylbenzene is co-fed to the reactor with superheated steam. The steam acts as an inert in the reaction and both provides the thermal energy required to preheat the ethylbenzene and dilutes the feed. As the steam to ethylbenzene ratio increases, the equilibrium shifts to the right (Le Chatelier's principle) and the single-pass conversion increases. This is the reason why low pressures are required. On the other hand, as the reaction progresses, the temperature decreases. Styrene formation is highly endothermic, the superheated steam also provides energy to drive the reaction.

Once initial temperature and pressure in the feed stream to the reactor are fixed, this same analysis is carried out varying the reactor length and the input molar flow rate. Figure 8 show the results obtained.

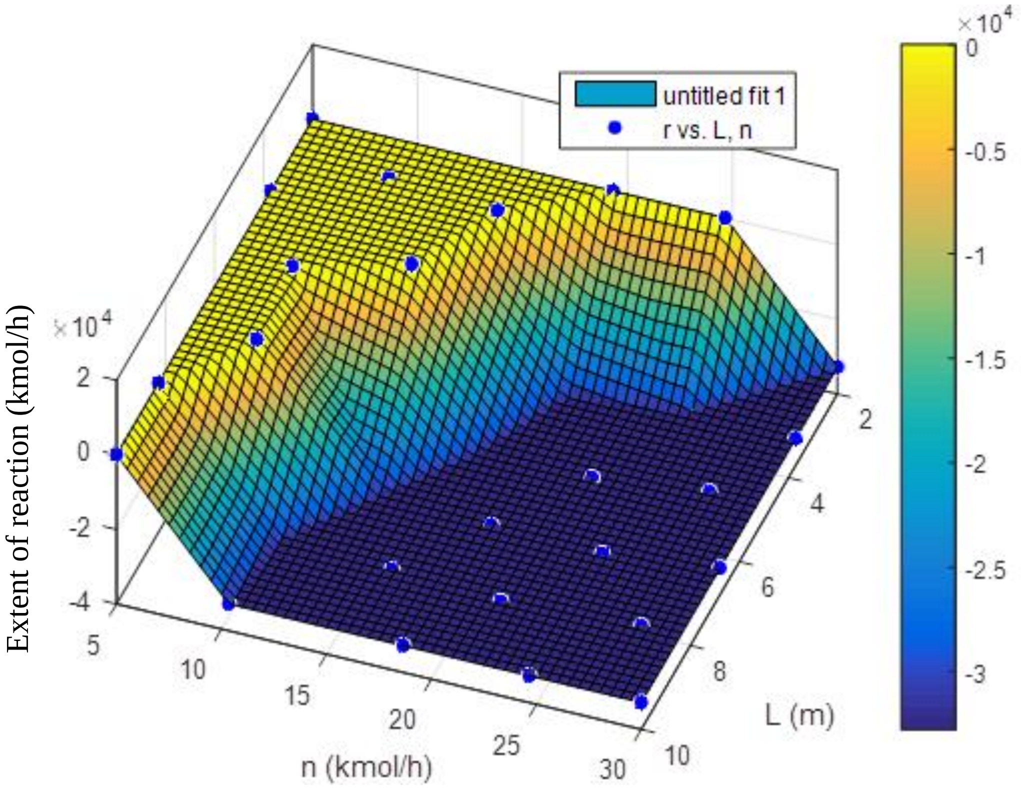


Figure 8. Extent of reaction (R1) (kmol/h) as a function of reactor length (m) and input E-Benzene mole flow rate (kmol/h).

As can be seen in Figure 8, the influence of reactor length and input ethylbenzene mole flow rate to the reactor are two key independent variables, even more than the input temperature and pressure to reactor. In addition, all the combinations between the input molar flow rate and the reactor size are not valid (i.e., blue area of the surface in Figure 8 is not feasible, due to high pressure drop required).

The reactor length and input mole flow rate of ethylbenzene (which is related with the input mole flow rate of water) are the two variables used to fit the extent of reaction with Aspen Hysys simulations as explains in the next section.

3.2.1.3 Fitting reactor equations

Simulations in Aspen Hysys are carried out in order to obtain an equation which relates extent of reaction with ethylbenzene mole flow rate and reactor length. The data obtained from Hysys will be fitted to an equation in MATLAB. The reason why extent of reaction is used, rather than conversion, it is because in a reactive system with more than one equation (as the one studied here) following the progress of a reaction selecting requires the same key component for all the reactions. Finally, extent of reaction fitting equations only depends linearly on the length and ethylbenzene mole flow rate to keep the whole model in the most linear way. This fact, facilitates the optimum process.

All these things considered, simulations are carried out selecting a wide range of independent variables (length and ethylbenzene mole flow rate) in Aspen Hysys. Temperature and pressure are fixed at 700℃ and 1.6 bar after checking that they are good conditions to get a high extent of reaction. If reactor length increases excessively, there is a great pressure drop and as a result initial low pressures cannot be used. On the other hand, higher temperatures will cause that styrene mole flow rate falls, due to the fact that there are other reactions that benefit. In other words, these conditions are good to obtain a great mole flow rate of styrene and will help to establish constraints. Besides, according to previous section they are good conditions to obtain a great extent of reaction. Figure 9 shows extent of reaction obtained in Hysys as a function of reactor length and styrene mole flow rate introduced into reactor.

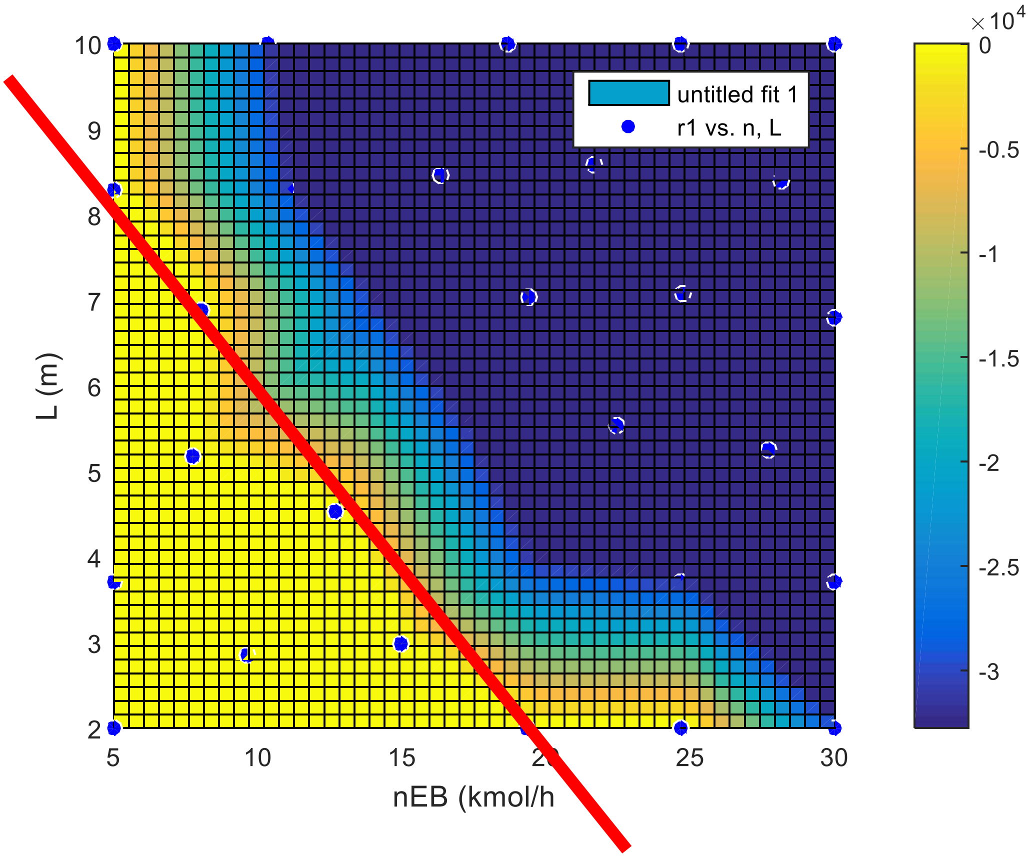


Figure 9. Extent of reaction (R1) (kmol/h) as a function of reactor length (m) and styrene mole flow rate (kmol/h).

In Figure 9, there is a yellow area where reactor can operate and another blue area where it cannot (this takes place when mole flow rates and reactor length are high and cause an excessive pressure drop). All extents of reaction (from R1 to R6) provide same representations as Figure 9. In order to fit the equations to data, blue area is discarded. Later, in the optimization model a constraint given by red line (Figure 9) will be introduced. This forces to seek for the optimum inside the yellow area:

$$L_{reactor} \leq -0.4 \cdot n_{EB}{}^{feed}_{reactor} + 10 \tag{C.1}$$

Data from Hysys can be fitted to planes with equation (14) which depends on parameters show in Table 8. In Appendix C can be found the corresponding planes.

$$\xi_r\left(\frac{kmol}{h}\right) = p00_r + p10_r \cdot L_{reactor}(m) + p01_r \cdot n_{EB}^{Feed}\left(\frac{kmol}{h}\right) \tag{14}$$

where,

- ξ_r extent of reaction r $\left(\frac{kmol}{h}\right)$
- $L_{reactor}$ reactor length (m)
- n_{EB}^{Feed} input molar flow rate into reactor $\left(\frac{kmol}{h}\right)$

Table 8. Parameters for extents of reaction fit.

	$\xi_1\left(\frac{kmol}{h}\right)$	$\xi_2\left(\frac{kmol}{h}\right)$	$\xi_3\left(\frac{kmol}{h}\right)$	$\xi_4\left(\frac{kmol}{h}\right)$	$\xi_5\left(\frac{kmol}{h}\right)$	$\xi_6\left(\frac{kmol}{h}\right)$
p00	2.07	0.104	0.1411	0.06923	0.07666	0.2123
p10	-0.04086	0.007523	0.04501	0.00959	0.045534	0.06483
p01	0.3563	0.04236	-0.002272	-0.001204	-0.006209	-0.008879

Equation (14) is inserted into GAMS in order to ensure fitting has been good. In this way it is possible to check that results coincide in Aspen Hysys, MATLAB and GAMS. Reactor length is supposed to be 2m on this occasion and input stream conditions are shown in Table 6. Table 9 shows the results obtained.

Table 9. Extent of reaction obtains with GAMS, Hysys and MATLAB for each reaction.

	$\xi_1\left(\frac{kmol}{h}\right)$	$\xi_2\left(\frac{kmol}{h}\right)$	$\xi_3\left(\frac{kmol}{h}\right)$	$\xi_4\left(\frac{kmol}{h}\right)$	$\xi_5\left(\frac{kmol}{h}\right)$	$\xi_6\left(\frac{kmol}{h}\right)$
GAMS	7,066	0,723	0,199	0,071	0,079	0,215
Hysys	7,252	0,753	0,209	0,076	0,077	0,221
MATLAB	7,335	0,801	0,187	0,072	0,062	0,198

Results obtain in GAMS, Hysys and MATLAB seem to be very similar, so it concludes that this model can be used in GAMS to optimize reactor conditions and reactor design. In the same way, output reactor temperature and pressure can be fitted to equations that depend on length and initial molar flow rate of ethylbenzene.

$$T_{out}^{reactor}(°C) = 576.5 - 1.148 \cdot L_{reactor}(m) + 2.147 \cdot n_{EB}^{Feed}\left(\frac{kmol}{h}\right) \tag{15}$$

$$P_{out}^{reactor}(bar) = 1.991 - 0.1069 \cdot L_{reactor}(m) - 0.04344 \cdot n_{EB}^{Feed}\left(\frac{kmol}{h}\right) \tag{16}$$

3.2.2 Cooler design

Cooler design basically consists in calculating the cooler area, which in turns, depends on heat transfer. Products that leave the reactor are cooled down to a temperature of 30℃. Besides, in the cooler a pressure drop of 10 kPa is supposed. See figure 10.
Therefore, the heat that must be removed is given by equation (17):

$$\mathrm{Q_{cooler} = m_{product} C_p^{product}\left(T_{out}^{reactor} - T_{out}^{cooler}\right)} \tag{17}$$

It is also worth recalling, output mass flow rate and output reactor temperature are determine by equations (14) and (15). For its part, cooler area is given by:

$$\mathrm{A_{cooler} = \frac{Q_{cooler}}{U\Delta T_{ml}}} \tag{18}$$

where logarithmic mean temperature difference is calculated using Chen's approximation [8].

$$\mathrm{\Delta T_{ml} = [0.5 \cdot (\Delta T_1 \cdot \Delta T_2) \cdot (\Delta T_1 + \Delta T_2)]^{1/3}} \tag{19}$$

being,

- $\mathrm{m_{product}}$ outlet reactor mass flow $\left(\frac{\mathrm{kg}}{\mathrm{h}}\right)$
- $\mathrm{C_p^{product}}$ heat capacity of product $\left(\frac{\mathrm{kJ}}{\mathrm{kg°C}}\right)$
- U overall coefficient of heat transfer $\left(\frac{\mathrm{kJ}}{\mathrm{hm^2°C}}\right)$
- $\mathrm{\Delta T_{ml}}$ logarithmic mean temperature difference
- $\mathrm{\Delta T_1}$ temperature difference between $\mathrm{T_{out}^{reactor}}$ and $\mathrm{T_{out}^{cooling\ water}}$ (°C)
- $\mathrm{\Delta T_2}$ temperature difference between $\mathrm{T_{out}^{cooler}}$ and $\mathrm{T_{in}^{cooling\ water}}$ (°C)

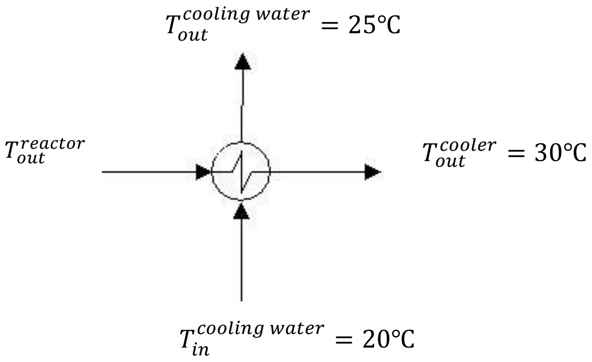


Figure 10. Cooler scheme required for calculations.

It is important to clarify Figure 10 shows a cooler scheme with the temperature data needed to calculate heat exchange and cooler area. It does not reflect a simulation carried out in Aspen Hysys, it is just an informative illustration.

3.2.3 Three phase separator

This equipment is considered as an ideal separator in which the three phases formed previously (organic phase, aqueous phase, and vapor phase) are completely separated. The condensed styrene together with the main product (toluene and benzene) and unreacted ethylbenzene, are the organic phase which separates from water (aqueous phase) and non-condensable gases $(H_2, CO, CO_2, CH_4, C_2H_4)$ which are the vapor phase. Besides, there are no changes in temperature or pressure streams.

3.2.4 Pump

Effluents that arrive to distillation columns are separated into its components with specific condition of temperature and pressure. In other words, temperature and pressure feed to distillation columns is fixed. Between the reactor and the cooler there is a great pressure drop, therefore, a pump which increases pressure before effluent arrives to the first distillation column is needed. In particular, a pressure of 1.026 bar. Therefore, temperature in stream 7 is $30°C$ and mole flow rate is the same as in stream 6. Besides, it is important to mention that pump do not affect neither total cost nor security. Its cost is negligible in front of the columns, and in terms of security, it does not increase F&EI.

3.2.5 Distillation columns design

In order to design distillation columns, the minimum vapor internal mole flow rate criterion has been followed. This criterion is based on the Underwood equations [7]. These Underwood Equations can be used to predict the minimum reflux for multicomponent distillation, so including them, a correct operation with a minimum reflux is ensured.

Distillation column model is developed below. It consists on a set of mole balances along distillation columns as well as Underwood Equations. In the development of equations nomenclature in Figure 11 is used.

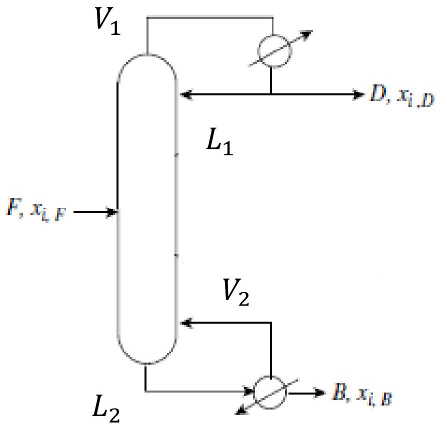


Figure 11. Distillation column nomenclature.

The component mole balance is given by:

$$\mathrm{F_j} = \mathrm{D_j} + \mathrm{B_j} \quad \forall \text{ component } \mathrm{j} \tag{22}$$

Considering the total mole balance along distillation column:

$$\mathrm{F} = \mathrm{D} + \mathrm{B} \tag{23}$$

The top total mole balance is also considered:

$$V_1 = D + \mathrm{L}_1 \tag{24}$$

The bottom total mole balance:

$$L_2 = V_2 + B \tag{25}$$

The feed total mole balance:

$$F + L_1 + V_2 = V_1 + L_2 \tag{26}$$

Considering the thermal condition of the feed:

$$V_1 = V_2 \tag{27}$$

Besides, it must be considered the total with component molar flow rate relationship in the feed, distillate and bottom streams:

$$F = \sum_{j}^{components} F_j \tag{28}$$

$$D = \sum_{j}^{components} D_j$$

(29)

$$B = \sum_{j}^{components} B_j$$

(30)

There are number of components (NC) minus one real positive values of θ (Underwood's root) that satisfy Underwood Equations (31)-(33), and each one of the θ values lies between the volatiles of the components. For each separation task, the set of Underwood Equations can be written:

$$\sum_{j}^{components} \frac{\alpha_{ij} F_i}{\alpha_{ij} - \theta_r} = V_1 - V_2$$

(31)

$$\sum_{j}^{components} \frac{\alpha_{ij} D_i}{\alpha_{ij} - \theta_r} = V_1$$

(32)

$$\sum_{j}^{components} \frac{\alpha_{ij} B_i}{\alpha_{ij} - \theta_r} = -V_2$$

(33)

Finally, component mole flow rate must be forced at the bottom and distillate according to the given recovery:

$$D_j = F_j \quad \forall\, j < LK$$

(34)

$$D_j = F_j \cdot r_j \quad \forall\, j = LK$$

(35)

$$B_j = F_j \quad \forall\, j > HK$$

(36)

$$B_j = F_j \cdot r_j \quad \forall\, j = HK$$

(37)

where,

- V_1 vapor mole flow rate in the enriching section $\left(\frac{kmol}{h}\right)$
- V_2 vapor mole flow rate in the exhausting section $\left(\frac{kmol}{h}\right)$
- L_1 liquid mole flow rate in the enriching section $\left(\frac{kmol}{h}\right)$
- L_2 liquid mole flow rate in the exhausting section $\left(\frac{kmol}{h}\right)$

- F total mole flow rate in the feed stream $\left(\frac{kmol}{h}\right)$
- D total mole flow rate in the distillate stream $\left(\frac{kmol}{h}\right)$
- B total mole flow rate in the bottom stream $\left(\frac{kmol}{h}\right)$
- F_i mole flow rate for component i in the feed stream $\left(\frac{kmol}{h}\right)$
- D_i mole flow rate for component i in the distillate stream $\left(\frac{kmol}{h}\right)$
- B_i mole flow rate for component i in the bottom stream $\left(\frac{kmol}{h}\right)$
- θ_r Underwood root r for a given separation task
- r_j output to feed stream mole flow rate ratio for component j

Furthermore, the minimum number of stages using the Fenske Equation, the total number of stages using Molokanov Equation, the feed stage using Kirkbride Equation, the column diameter calculated from minimum vapor internal flow rate, heat flow and condenser in the column are needed to design a distillation column. Therefore, these calculations are carried out according to literature correlations [7].

Minimum number of stages is given by Fenske Equation:

$$N_{min} = \frac{\log\left(\frac{r_{LK,D}}{1 - r_{LK,D}} \cdot \frac{r_{HK,B}}{1 - r_{HK,B}}\right)}{\log(\alpha_{LH})} \tag{38}$$

being,

- $Nmin$ minimum number of theoretical stages
- α_{LH} relative volatility between light component and heavy component
- $r_{LK,D}$ recovery of Component *i* in the distillate
- $r_{HK,B}$ recovery of Component *i* in the bottoms

The total number of stages can be calculated with Molokanov Equation:

$$\frac{NP - N_{min}}{NP + 1} = 1 - \exp\left[\frac{1 + 54.4X}{11 + 117.2X} \cdot \frac{X - 1}{X^{0.5}}\right]$$

$$X = \frac{R - R_{min}}{R + 1} \tag{39}$$

where

- X, Y correlating parameters

- NP actual number of theoretical stages
- $Nmin$ minimum number of theoretical stages
- R actual reflux ratio
- $Rmin$ minimum reflux ratio

Besides, feed stage is determined by Kirkbride Equation:

$$\frac{NR}{NS} = \left[\frac{z_{HK}}{z_{LK}} \cdot \frac{x_{LK,B}^2}{x_{HK,D}^2} \cdot \frac{B}{D}\right]^{0.206} \tag{40}$$

with

- NS number of stages below the feed
- NR number of stages above the feed
- z_{HK} concentration of the heavy key in the feed
- z_{LK} concentration of the light key in the feed
- $x_{LK,B}$ concentration of the light key in the bottom
- $x_{HK,D}$ concentration of the heavey key in the top

Moreover, the annualized total cost is calculated from the estimated minimum vapor internal flow rate (the capital cost and the operation depend mainly on this parameter) which in turn determinates column diameter. This column diameter is estimated using Fair method [7]. In order to calculate the settling velocity, K_T parameter must be specified. For distillation using tray columns, K_T is correlated in terms of a liquid–vapor flow parameter F_{LV}, defined by:

$$F_{LV} = \left(\frac{M_L L}{M_V V}\right)\left(\frac{\rho_V}{\rho_L}\right)^{0.5} \tag{41}$$

where

- F_{LV} liquid–vapor flow parameter (–)
- L liquid molar flow rate (kmol· s^{-1})
- V vapor molar flow rate (kmol· s^{-1})
- M_L liquid molar mass (kg·$kmol^{-1}$)
- M_V vapor molar mass (kg·$kmol^{-1}$)
- ρ_V vapor density (kg·m^{-3})
- ρ_L liquid density (kg·m^{-3})

Fair also defines a capacity factor as:

$$CP = u_f \left(\frac{\theta_0}{\theta}\right)^{0.2} \left(\frac{\rho_V}{\rho_L - \rho_V}\right)^{\frac{1}{2}} \tag{42}$$

being,

- CP capacity parameter ($m \cdot s^{-1}$)
- u_f flood velocity ($m \cdot s^{-1}$)
- θ surface tension ($mN \cdot m^{-1}$)

The surface tension can be estimated if it is not known. However, in many cases the answers are insensitive to the value of surface tension (the equation is normalized to $\theta_0 = 20\ mN\ /\ m$).

For the calculation of f, Fair proposes the following correlation:

$$C = \frac{C_o}{1 + C_1 \cdot fC_2} \tag{43}$$

Considering tray columns with spacing of 24 in or 0.6096 m:

$$C_o = 439;\ C_1 = 2.25;\ C_2 = 1.2$$

It is important to say that equation (44) is valid assuming:

- Liquid density is much higher than gas density.
- $\frac{L}{V}\left(\frac{Mv}{ML}\right)^{1.5} << \sqrt{\frac{\rho_L}{\rho_V}}$ so $C \approx C_o$
- $\theta/\theta_0 \approx 1$

Then,

$$F_F = \mathrm{C_o} \cdot \left(\frac{\mathrm{A_n}}{\mathrm{A}}\right) \cdot \sqrt{\rho_L}$$

where

- F_F F-factor
- $\mathrm{A_n}$ column net area $\left(\frac{A_n}{A} \approx 0.8\right)$

Finally column area is calculated considering a flooding factor of 0.7:

$$A = \frac{M_V}{(\rho_L \cdot \rho_V)^{0.5}} \cdot \frac{1}{0.7} \cdot \frac{1}{C_o} \cdot \frac{A}{A_n} \cdot V_{real} \tag{44}$$

In this way, if all the data are known the above equation is linear. Note that an average liquid density and an average vapor density can be used at an average temperature (errors are mitigated by the flood percentage). Besides, the steam flow calculated with Underwood is the minimum value, the real value which is introduced in equation (45) is:

$$V_{real} = V + L_1 \cdot (a - 1) \tag{45}$$

3.3 ECONOMIC EVALUATION

As the optimization of a process is usually based on economic considerations, it is essential the economic method of analysis used and the selected economic parameters to find the optimal solution.

In this case, the economic evaluation will be based on the calculation of the annualized total capital expenditure (CAPEX) and the annualized operation expense (OPEX) of the different equipments. The sum of this two costs results in total annualized cost (TAC). This work has followed the purchased equipment cost presented by Richard Turton [6]. In order to estimate these costs, equipments have been separated into several paragraphs. It is important to mention that the three phase separator as well as pump are assumed to be a negligible costs.

3.3.1 Total capital expenditure (CAPEX)

3.3.1.1 Reactor CAPEX

First, the equipment type has to be selected. Reaction system takes place in a horizontal packing process vessel. According to literature, reactor total capital cost can be estimated as follows:

$$Vessel_{CBM}^{update} = Vessel_{CBM} \cdot UpdateFactor \quad (\$)$$

(46)

The purchased costs were obtained in 2003 , but the cost given here has been normalized to 2001. For new equipment, it is to be multiplied by a specific factor:

$$UpdateFactor = \frac{CEPIC_{Current}}{CEPIC_{2001}}$$

$CEPIC_{Current}$ is referred to annual Index (576.1) and $CEPIC_{2001}$ to base annual Index (397). Futhermore, bare module cost is calculated as:

$$Vessel_{CBM} = Vessel_{Cp0} \cdot FBM_{vessel} \quad (\$)$$

(47)

Where purchased cost for base conditions is determined by vessel volume:

$$Vessel_{Cp0} = 10^{K_1 + K_2 \cdot \log_{10} V_{vessel} + K_3 [\log_{10} V_{vessel}]^2}$$

(48)

And bare model factor:

$$FBM_{vessel} = B_1 + B_2 \cdot F_M \cdot F_P$$

(49)

Constant for bare module factor (B_1, B_2) and constants for the purchased cost of the equipment at ambient operating pressure and using carbon steel construction (K_1, K_2, K_3) are shown in Table 10.

Pressure factor for process vessels is given by:

$$F_P = \frac{\frac{(P+1)D}{2[850 - 0.6 \cdot (P+1)]} + 0.00315}{0.0063} \qquad t_{vessel} > 0.0063m$$

(50)

But, if $F_P < 1$, then $t_{vessel} < 0.0063\,m$ and $F_P = 1$.

- P operating pressure in vessel (bar)
- D vessel diameter (m)

Finally, the material construction is carbon Steel, so $F_M = 1$.

In addition, catalyst used in the reactor must be considered as a reactor CAPEX, due to the fact that the useful lives of dehydrogenation catalysts vary from one to four years, and in most cases 18-24 months, depending on the nature of the catalyst [4]. Dehydrogenation catalysts usually contain $40 - 90\%$ Fe_2O_3. According to literature [9], iron(III) oxide price from chemical supply houses is 10$/kg. Taking into account the catalyst characteristics mentioned in the problem statement:

$\rho_{cat} = 2350\frac{kg}{m^3}$, $\varepsilon = 0.445$

being,

- ρ_{cat} catalyst density
- ε bed porosity

$$CatalystCost(\$) = CatalystPrice\left(\frac{\$}{kg}\right) \cdot V_{reactor}(m^3) \cdot \rho_{cat}\left(\frac{kg}{m^3}\right) \cdot (1 - \varepsilon)$$

(51)

3.3.1.2 Cooler CAPEX

In the same way, cooler total capital cost is estimated as was made in the reactor. The cooler is supposed to be fixed tube heat exchanger.

$$Cooler_{CBM}^{Update} = Cooler_{CBM} \cdot UpdateFactor \quad (\$)$$

(52)

$$Cooler_{CBM} = Cooler_{Cp0} \cdot FBM_{cooler} \quad (\$)$$

(53)

In this case, purchased cost of the equipment at ambient operating pressure is based on cooler area:

$$Cooler_{Cp0} = 10^{K_1 + K_2 \cdot \log_{10} A_{cooler} + K_3 [\log_{10} A_{cooler}]^2}$$

(54)

$$FBM_{cooler} = B_1 + B_2 \cdot F_M \cdot F_P$$

(55)

Constants are included in Table 10. Since cooler is a fixed tube sheet heat exchanger, constructed out of carbon steel: $F_P = 1.3$ and $F_M = 1$.

3.3.1.3 Distillation columns CAPEX

A conventional distillation column consists of: tower, trays, reboiler and condenser. All these parts of column must be estimated as proposed below:

$$C_{CAT}^{distillation\ column} = Colum_{CBM}^{update} + Tray_{CBM}^{update} + Condenser_{CBM}^{update} + Reboiler_{CBM}^{update} \ (\$)$$

(56)

$Condenser_{CBM}^{update}$ and $Reboiler_{CBM}^{update}$ are just fixed tube heat exchanger and their purchased calculations is identical to cooler calculation.

$$Condenser_{CBM}^{update} = Condenser_{CBM} \cdot UpdateFactor \ (\$)$$

(57)

$$Condenser_{CBM} = Condenser_{Cp0} \cdot FBM_{Condenser} \ (\$)$$

(58)

$$Condenser_{Cp0} = 10^{K_1 + K_2 \cdot \log_{10} A_{condenser} + K_3 [\log_{10} A_{condenser}]^2}$$

(59)

$$FBM_{Condenser} = B_1 + B_2 \cdot F_M \cdot F_P$$

(60)

$$Reboiler_{CBM}^{update} = Reboiler_{CBM} \cdot UpdateFactor \ (\$)$$

(61)

$$Reboiler_{CBM} = Reboiler_{Cp0} \cdot FBM_{Reboiler} \ (\$)$$

(62)

$$Condenser_{Cp0} = 10^{K_1 + K_2 \cdot \log_{10} A_{reboiler} + K_3 [\log_{10} A_{reboiler}]^2} \tag{63}$$

$$FBM_{Reboiler} = B_1 + B_2 \cdot F_M \cdot F_P \tag{64}$$

Both are fixed tube heat exchangers, constructed out of carbon steel, so $F_P = 1.3$ and $F_M = 1$. Constants are presented in Table 10.

Moreover, column tower purchased is calculated through the following equations:

$$Tower_{CBM}^{update} = Tower_{CBM} \cdot UpdateFactor \quad (\$) \tag{65}$$

$$Tower_{CBM} = Tower_{Cp0} \cdot FBM_{Tower} \quad (\$) \tag{66}$$

$$Tower_{Cp0} = 10^{K_1 + K_2 \cdot \log_{10} V_{Tower} + K_3 [\log_{10} V_{tower}]^2} \tag{67}$$

$$FBM_{Tower} = B_1 + B_2 \cdot F_M \cdot F_P \tag{68}$$

Keep in mind those constants for the purchased cost of the equipment at ambient operating pressure uses volume in this case. Identification number for stainless steel vertical vessel give a $F_P = 1$ and $F_M = 1$. And finally, sieve trays purchased are calculated as follows:

$$Tray_{CBM}^{update} = Tray_{CBM} \cdot NT \cdot UpdateFactor \quad (\$) \tag{69}$$

NT is the number of trays which depends on the desired separation.

$$Tray_{CBM} = Tray_{Cp0} \cdot FBM_{tray} \cdot F_q \quad (\$) \tag{70}$$

F_q is the tray factor which is calculated:

$F_q = 10^{0.47771 + 0.0816 \cdot \log_{10}(NT) - 0.3473 \cdot \log_{10}(NT)^2}$ if $NT < 20$

$F_q = 1$ if $NT > 20$

(71)

The purchased cost of the equipment at ambient operating pressure is calculated in function of column area:

$$Tray_{Cp0} = 10^{K_1 + K_2 \cdot \log_{10} A_{column} + K_3 [\log_{10} A_{column}]^2} \tag{72}$$

As column consist of sieve trays $FBM_{tray} = 1$.

Table 10. Constant for bare module factor and constants for the purchased cost of the equipment at ambient operating pressure.

		K_1	K_2	K_3	B_1	B_2	F_M	F_P
	Vessel	3.5565	0.3776	0.0905	1.49	1.52	1.0	Equation
	Cooler	4.3247	-0.3030	0.1634	1.63	1.66	1.0	1.3
Distillation Columns	Tower	3.4974	0.4485	0.1074	2.25	1.82	1.0	1.0
	Trays ($Fq = eq.$)	2.9949	0.4465	0.3961	1.00	1.00	1.0	1.0
	Condenser	4.3247	-0.3030	0.1634	1.63	1.66	1.0	1.3
	Reboiler	4.3247	-0.3030	0.1634	1.63	1.66	1.0	1.3

3.3.2 Operation expenditure (OPEX)

An operating expense results from the ongoing costs the chemical plant pays to run its basic business, which consist of producing styrene. OPEX is divided into cooling water and steam needed in heat exchanger.

$$OPEX = coolingWaterCost + SteamCost \quad \left(\frac{\$}{year}\right) \tag{73}$$

$$coolingWaterCost = Qcond \cdot WATER \cdot YEAR \quad \left(\frac{\$}{year}\right) \tag{74}$$

$$SteamCost = Qreb \cdot STEAM \cdot YEAR \quad \left(\frac{\$}{year}\right) \tag{75}$$

According with literature [6], utility that would likely be provided in a comprehensive chemical plant complex is show in Table 11. Besides, it is considered 8000 h/year (operating hours per year).

Table 11. Utility costs.

Steam ($\$/GJ$)	Cooling Water
0.0506	0.0013

3.3.3 Annualized total capital expenditure (TAC)

Finally, the sum of OPEX ($/year) and CAPEX($) gives TAC. To obtain same unit in both cost, CAPEX is multiplied by an annualization factor.

$$TAC\left(\frac{M\$}{year}\right) = (OPEX + CAPEX \cdot F) \cdot 10^{-6} \tag{76}$$

According to Robin Smith [7]:

$$F = \frac{i \cdot (1+i)^n}{(1+i)^n - 1}\ (yr^{-1}) \tag{77}$$

where,

- i Interest rate
- n Equipment life time

These two annualization parameter are fixed to 0.1 and 8 year, respectively.

3.4 MULTI-OBJECTIVE SOLUTION ALGORITHM

Then, the optimal solution to the problem proposed is explained. Using the procedure in Appendix A, all the required equations are written in the modeling language GAMS. In this work, two objective functions will be considered: the total annualized cost (TAC) and the inherently safer index accounted for by means of the Dow's F&EI. For the calculation of the Pareto frontier, the epsilon-constraint method is used [10], which entails solving a set of instances of the following single-objective problem (S.1) for each value of the auxiliary parameter ε_p that corresponds to each Pareto point p:

$$\begin{aligned} &\min_{x,y} \; TAC \\ &s.t. \; \text{constraints} \\ &\qquad F\,\&\,EI \le \varepsilon_p \\ &\qquad \underline{\varepsilon} \le \varepsilon_p \le \overline{\varepsilon} \end{aligned} \tag{S.1}$$

where the lower ($\underline{\varepsilon}$) and upper ($\overline{\varepsilon}$) limits, within which the epsilon parameter must fall, are obtained from the optimization of each objective separately (problems (S.2) and (S.3)):
:

$$\begin{aligned} &(\tilde{x}, \tilde{y}) = \arg\min_{x,y} \{\text{TAC}\} \\ &s.t. \; \text{constraints} \end{aligned} \tag{S.2}$$

which defines $\overline{\varepsilon} := F\,\&\,EI(\tilde{x}, \tilde{y})$ and:

$$\begin{aligned} &\underline{F\,\&\,EI} = \min_{x,y} \{F\,\&\,EI\} \\ &s.t. \quad \text{constraints} \end{aligned} \tag{S.3}$$

which defines $\underline{\varepsilon} := \underline{F\,\&\,EI}$.

4. RESULTS

In theory, the most economical a plant is, the greater influences on the risk there should be. On the contrary, the safest plants present the highest TAC. This shall be verified by minimizing the two objective functions as has been explained in section 3.4 and plotting a Pareto curve, whose extreme points represent the designs with this minimum risk and annualized plant cost.

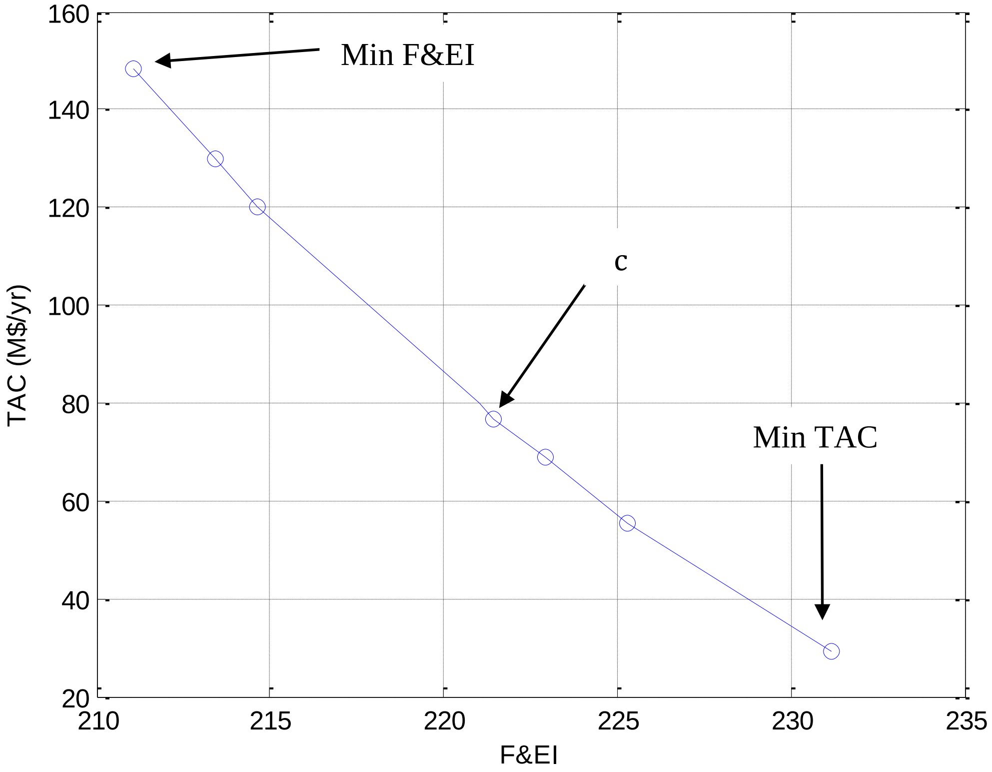


Figure 12. Styrene plant TAC in function of F&EI.

As can be seen in Figure 12, the extreme right point represents the most economical styrene plant design and the extreme left point the inherent safest plant. The points above Pareto frontier are feasible and the points below are unfeasible, so the best operation range is in points represented by Pareto frontier, because it is the best possible combination of cost and inherent safety, fixed only one of these two variables. This plot gives a lot of information, thus, if the optimization with constraint is performed, the result will be as acceptable as the designer considers until adjust the final styrene plant design variables. In other words, F&EI is incorporated as a cutting point between inherently safer and non-inherently safer based on F&EI target value and not a variable. So, F&EI constraints can be added to the mathematical model with which maximum F&EI value is imposed. Decision-maker could select whatever point of Pareto frontier, considering how much costs and styrene plant design vary in function of inherent safety. In appendix D can be found the final styrene production GAMS code used in order to plot Pareto frontier.

From the inherent safest point to the most economical point there is a change of 411.2% in cost and 9.51 % in F&EI (the latter data would be presented below). Then, the three point shown in Figure 12 are studied, with the objective of obtain more information.

4.1 THE INHERENTLY SAFEST DESIGN SOLUTION

As it has been mentioned before, in order to obtaining the safest design plant, the objective function must be minimizing F&EI. This safest design presents the results shown in Table 11.

Table 11. Summary results for the minimum F&EI extreme solution.

Inherent Safety		Economic	
Constant Part	128.520	OPEX (M$/yr)	146.820
E contribution	7.507	CAPEX (M$/yr)	1.713
G contribution	75.031		-
F&EI	**211.073**	**TAC (M$/yr)**	**148.530**

As can be seen, the minimum F&EI possible to obtain in our mathematical optimization model is 211.073, resulting from: 128.520 which are constant contributions due to the material and the equipment used, 7.507 due to pressure relief in equipments and 75.031 due to inflammable material. Penalty E involves a small contribution since equipments pressures are not excessive high. For its part, a 35.55% of the total F&EI is as a result of penalty G. This last one is a very important part, that supposes a high contribution and it may even causes a higher values of F&EI if F&EI optimization would not have been implemented. The optimization ensures this two F&EI contributions are the lowest possible. On the other hand, TAC amounts to a very high price. OPEX is the highest cost, which is almost two orders of magnitude higher than CAPEX.

Results can be broken down for easier understanding of optimization. In Table 12 is shown a more detail breakdown of costs, in Table 13 a F&EI breakdown and in Table 14 the equipment design obtained.

Table 12. Breakdown of cost obtained for the inherent safest styrene plant.

Services ($/yr)		Equipment CBM Update ($/yr)	
Cooling water in Cooler	3.22E+04	Condenser 1	5.46E+05
Cooling water in Condenser 1	3.50E+06	Reboiler 1	5.03E+05
Cooling water in Condenser 2	1.91E+06	Tower 1	2.97E+04
Steam in Reboiler 1	6.36E+07	Tray 1	1.67E+04
Steam in Reboiler 2	7.75E+07	**Distillation column 1**	**1.09E+06**
OPEX	**1.47E+08**	Condenser 2	1.61E+05
		Reboiler 2	3.53E+05
		Tower 2	4.71E+04
		Tray 2	1.77E+04
		Distillation column 2	**5.79E+05**
		Cooler	**1.78E+04**
		Vessel	6.99E+03
		Catalyst cost	1.46E+04
		Reactor	**2.16E+04**
		CAPEX	**1.71E+06**

As can be seen in Table 12, OPEX contributes the most to the overall cost. In detail, the required steam in reboiler 2 is the higher cost, it involves even a higher value than the total CAPEX. It is also important to mention, distillation columns are the more expensive equipments (especially distillation column 1), in both OPEX and CAPEX. On the contrary, cooler is the cheapest equipment CAPEX (although its OPEX cost relatively small compared with steam cost). Finally, reactor is the third higher CAPEX cost, below distillation columns.

Table 13. Breakdown of F&EI obtained for the inherent safest styrene plant.

Pressure Operation (bar)	1.254
Pressure relief (bar)	1.505
Y operation	0.190
Y relief	0.195
Penalty E	0.184
E Contribution	**7.507**
TotalBTU (BTU)	1.88E+09
Penalty G	1.839
G Contribution	**75.031**
Constant part	**128.520**
F&EI	**211.073**

From Table 13 can be extracted basic information about the styrene plant. The pressure used in equipment is relatively low, therefore the penalty associated is very small and basically does not contribute to F&EI. On the contrary, the quantity of flammable material has an important power. Attending to equation (10), these penalties can cause a great increase since they are multiplied by a great factor (small changes contribute greatly to inherent safety). Besides, distillation columns are the most dangerous equipments, they hold a considerable quantity of inflammable material. For this reason, a safety inherent design reduces as much as possible equipment size. Table 14, collects this information that can be compared with equipment size for the most economic plant in next section.

Table 14. Summary of equipment design obtained after minimizing F&EI.

Reactor		Cooler		Column1		Column 2	
$L\ (m)$	2.000	$A\ (m^2)$	31.875	$D\ (m)$	1.554	$D\ (m)$	1.417
$V\ (m^3)$	5.973		-	NP	24	NP	55
	-		-	L (m)	18.007	$L\ (m)$	38.128
	-		-	V (m3)	33.711	$V\ (m^3)$	60.105

As shown Table 14, equipments are quite small. Reactor length concurs with the lower bound imposed, cooler area is not excessive high, as well as columns diameters, which presents a normal values. These equipment sizes help to reduce hazard in the event of an explosion, the smaller equipments are, the inherently safer a plant would be. Finally, in Figure 13 is shown the optimal material streams conditions which ensure an inherent plant design.

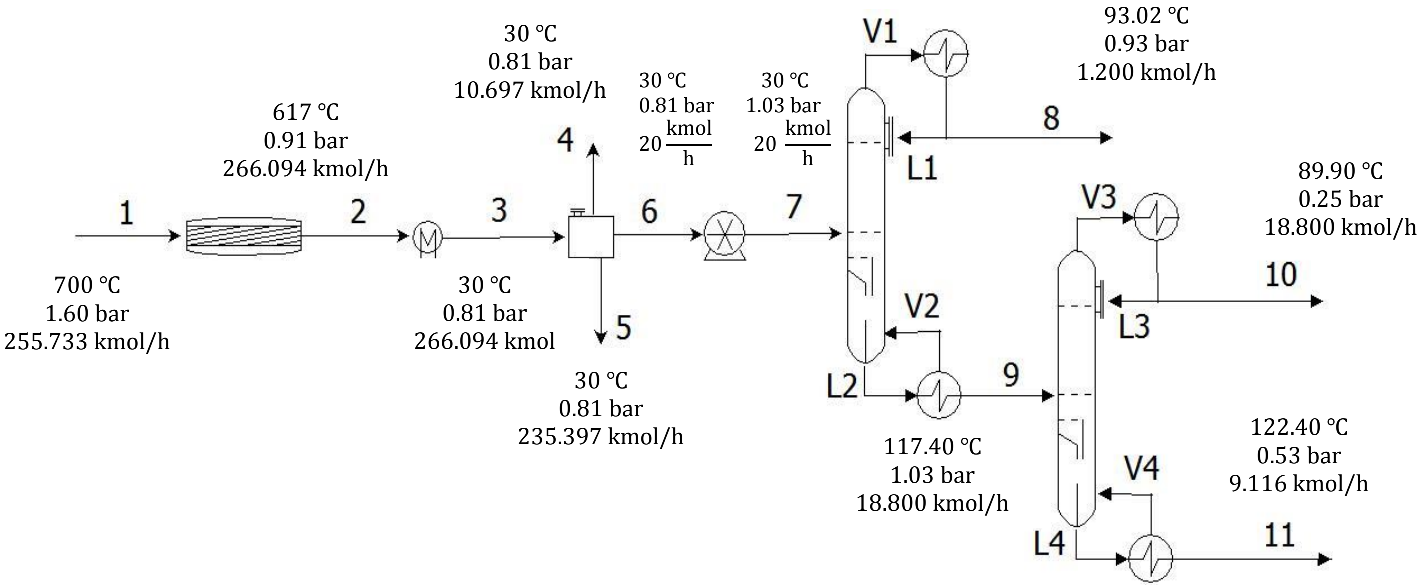


Figure 13. Summary of streams conditions obtained after minimizing F&EI.

In Figure 13 can be observed that there is a big change between mole flow rates of stream 3, 4, 5 and 6. According to flowsheet presented in Figure 1, these streams correspond to input three phase separator and outputs streams. It is clear the most part of mole flow rates is water input to reactor, which is separated in stream 5, and it is a significant amount of 235.397 kmol/h. Water together with ethylbenzene are the two reagents introduced into reactor. Initial ethylbenzene and water mole flow rates are respectly 20.000 kmol/h and 235.733 kmol/h. This means, water acts as an inert in the reaction and both provides the thermal energy required to preheat the ethylbenzene and dilutes the feed. As the steam to ethylbenzene ratio increases, the equilibrium shifts to the right of reaction (R1) (Le Chatelier's principle) and the single pass conversion increases. All the streams data can be found in Appendix E.

4.2 THE MOST ECONOMICAL SOLUTION

In this case, the objective function to optimize is the TAC. As it has been analysed the solution obtained for the inherent safest styrene plant design, it is proceed then. In Table 16, it can be seen how TAC decreases in a significant extent, as well as F&EI increases. As above mentioned, the most economical plants are usually the most dangerous too.

Table 16. Summary results obtained considering the minimum TAC.

Inherent Safety		Economic	
Constant Part	128.520	OPEX (M$/yr)	28.113
E contribution	7.507	CAPEX (M$/yr)	0.941
G contribution	95.105	-	
F&EI	**231.156**	**TAC (M$/yr)**	29.055

There is a very high decrease of TAC, as it was advanced above. In detail, there is a difference of 411.20%, which implies significant saving in the TAC (see Tables 11 and 16). For its part, F&EI is increased at a rate of 9.51%. It is important to note that the contribution due to inflammable materials has increased in 20.074 units, that is to say, is strongly increased and the styrene production plant is far from been an inherent safety design, since the criterion is purely economic. More details of TAC and F&EI can be found below, in Tables 16 and 17 respectly.

Table 16. Breakdown of cost obtained in the most economic styrene plant.

Services ($/yr)		Equipment CBM Update ($/yr)	
Cooling water in Cooler	2.78E+04	Condenser 1	1.37E+05
Cooling water in Condenser 1	7.55E+05	Reboiler 1	1.11E+05
Cooling water in Condenser 2	3.81E+05	Tower 1	1.26E+05
Steam in Reboiler 1	1.15E+07	Tray 1	9.23E+04
Steam in Reboiler 2	1.54E+07	**Distillation column 1**	**4.66E+05**
OPEX	**2.81E+07**	Condenser 2	5.19E+04
		Reboiler 2	9.02E+04
		Tower 2	1.97E+05
		Tray 2	8.78E+04
		Distillation column 2	**4.27E+05**
		Cooler	**1.75E+04**
		Vessel	8.23E+03
		Catalyst cost	2.19E+04
		Reactor	**3.01E+04**
		CAPEX	**9.41E+05**

Figure 16 shows how OPEX and CAPEX have both decreased with respect to the most inherently safety design, however there are some costs which have been increased (towers and trays of distillation columns) due to the fact that their dimensions have increased too (columns diameters are higher and reactor length is larger than before). Since reactor length has been increased, the outlet temperature of the reactor is lower and the cooler does not need to cold products so much than before, so a cooler with a lower area is needed. Moreover, OPEX implies the most important cost, especially steam cost such as it occurred before.

Table 17. Breakdown of F&EI obtained in the most economic styrene plant.

Pressure Operation (bar)	1.262
Pressure relief (bar)	1.514
Y operation	0.190
Y relief	0.196
Penalty E	0.184
E Contribution	**7.507**
TotalBTU (BTU)	9.00E+09
Penalty G	2.331
G Contribution	**95.105**
Constant part	**128.520**
F&EI	**231.156**

As can be seen in Table 187, the penalty due to pressure has not increased, even though pressure has increased slightly. The penalty due to the inflammable material, however, has been increased considerably This is because pressure operation in equipments remains low. This is not the case for the amount of material inside equipments. Equipments size is higher, so the energy in the event of an explosion will be much higher. These variables cause a great increase in F&EI (there is a difference of 20.083 units between the inherently safest and the most economical design). Now penalty due to inflammable material implies the 41.14% of the total F&EI, that is to say, F&EI increasingly depends on this variable. Penalty due to pressure relief is not a primary importance, pressure still remains in low values.

Table 18. Summary of equipment design obtained after minimizing TAC.

Reactor		Cooler		Column1		Column 2	
$L\ (m)$	2.997	A (m2)	27.797	$D\ (m)$	3.639	$D\ (m)$	3.174
$V\ (m^3)$	8.949		-	NP	24	NP	55
	-		-	$L\ (m)$	17.300	$L\ (m)$	36.393
	-		-	$V\ (m^3)$	179.963	$V\ (m^3)$	287.873

As it can be checked in Table 18, reactor and distillation columns have increased their volumes. This explains why F&EI has increased in so many quantity. They retain a greater amount of flammable materials, so the total amount of energy in the event of explosion increases a lot. Distillation columns are especially increased in a great amount as compared with previous case. This is partly explained by column diameter, which causes a significant increase in columns volume.

Finally, in Figure 14 streams conditions obtained are shown.

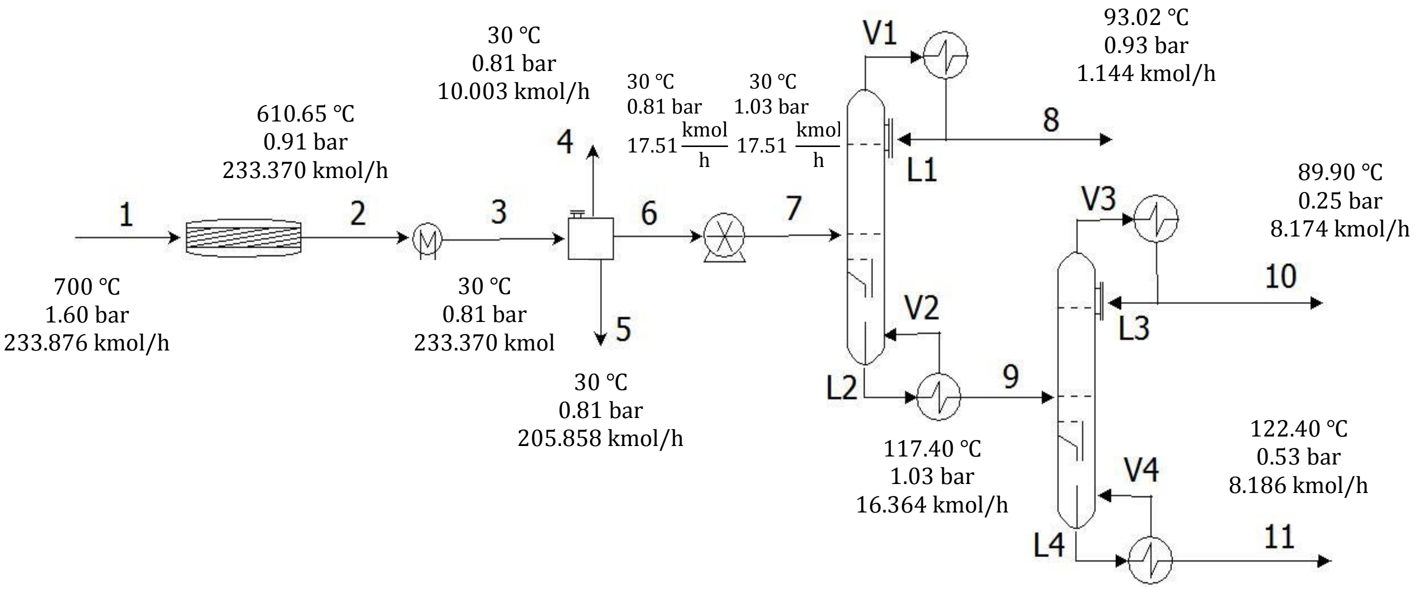


Figure 14. Summary of streams conditions obtained after minimizing TAC.

As can be seen in Figure 14, the total mole flow rates, temperatures and pressures are quite similar to results obtained for the inherent safest plant. The initial ethylbenzene mole flow rate is a bit lower, however, reactor length is higher, so the extent of reaction 1 (R1) will be increased, with the final result that a quantity of 850 kg styrene/h, as it is required, but feeding the reactor an amount of 17.509 kmol/h of ethylbenzene. All these data are presented in Appendix E.

4.3 STUDY ON POINT C

After the inherently safest and the most economical styrene plant have been analysed, the following important idea should be emphasized: it is possible design a chemical plant following economical criteria, but also imposing a maximum of hazard. Comparing the results in section 4.1 and 4.2, a chemical plant could be design in this intermediate range. This is what is proposed next, studying the results obtained imposing a maximum of hazard. What follow are the results obtained in point "*c*" of Figure 12.

Table 19. Summary results for point "*c*".

Inherent Safety		Economic	
Constant Part	128.520	OPEX (M$/yr)	75.660
E contribution	7.548	CAPEX (M$/yr)	1.114
G contribution	85.354		-
F&EI	**221.415**	**TAC (M$/yr)**	**76.774**

Table 19 presents the exact data from point "*c*", showed in Figure 12. It can be observed how TAC and F&EI occupy an intermediate position between the most inherent safety plant and the most economical. If a decision-maker makes the final design decision of the styrene production plant considering that TAC value cannot be higher than 76.774 M$/yr, the inherent safest plants possible would present a F&EI equal to 221.415.

Table 20. Breakdown of cost obtained in point "*c*".

Services ($/yr)		Equipment CBM Update ($/yr)	
Cooling water in Cooler	2.81E+04	Condenser 1	3.16E+05
Cooling water in Condenser 1	1.96E+06	Reboiler 1	2.61E+05
Cooling water in Condenser 2	1.01E+06	Tower 1	5.13E+04
Steam in Reboiler 1	3.16E+07	Tray 1	3.37E+04
Steam in Reboiler 2	4.10E+07	**Distillation column 1**	**6.62E+05**
OPEX	**7.57E+07**	Condenser 2	9.69E+04
		Reboiler 2	1.99E+05
		Tower 2	8.00E+04
		Tray 2	3.32E+04
		Distillation column 2	**4.09E+05**
		Cooler	**1.75E+04**
		Vessel	7.56E+03
		Catalyst cost	1.79E+04
		Reactor	**2.55E+04**
		CAPEX	**1.11E+06**

Table 20 shows how the tendency continues as occurred with the inherent safest and the most economical design (OPEX is higher than CAPEX). The most important cost is the steam required for reboilers in distillation columns and after the cooling water needed in condensers. Distillation columns CAPEX is the most costly of all equipments, after the cooler and finally the reactor.

Table 21. Breakdown of F&EI obtained in point "*c*".

Pressure Operation (bar)	1.287
Pressure relief (bar)	1.544
Y operation	0.191
Y relief	0.196
Penalty E	0.185
E Contribution	**7.548**
TotalBTU (BTU)	3.44E+09
Penalty G	2.092
G Contribution	**85.354**
Constant part	128.520
F&EI	**221.415**

Concerning safety, Table 21 shows the different contributions of F&EI. There are no great differences in penalty E, because pressure is not very high in the styrene plant presented.

However, penalty G easily varies from one to another case. This translates into a different equipment size and mole flow rate conditions.

Table 22. Summary of equipment design obtained in point "c".

Reactor		Cooler		Column1		Column 2	
$L\ (m)$	2.456	A (m2)	28.047	$D\ (m)$	2.195	$D\ (m)$	1.946
$V\ (m^3)$	7.334		-	NP	24	NP	55
	-		-	$L\ (m)$	17.538	$L\ (m)$	36.976
	-		-	$V\ (m^3)$	66.394	$V\ (m^3)$	110.03

From Table 22, one can conclude that intermediate values between the inherent safest design and the most economical design give as a result intermediate values between extreme right point and extreme left point from Figure 12, since equipment design is in an intermediate range between these two extreme points. The highest values of equipment size are obtained in the TAC optimization and the lowest values in the F&EI optimization (without imposing F&EI or TAC constraints).

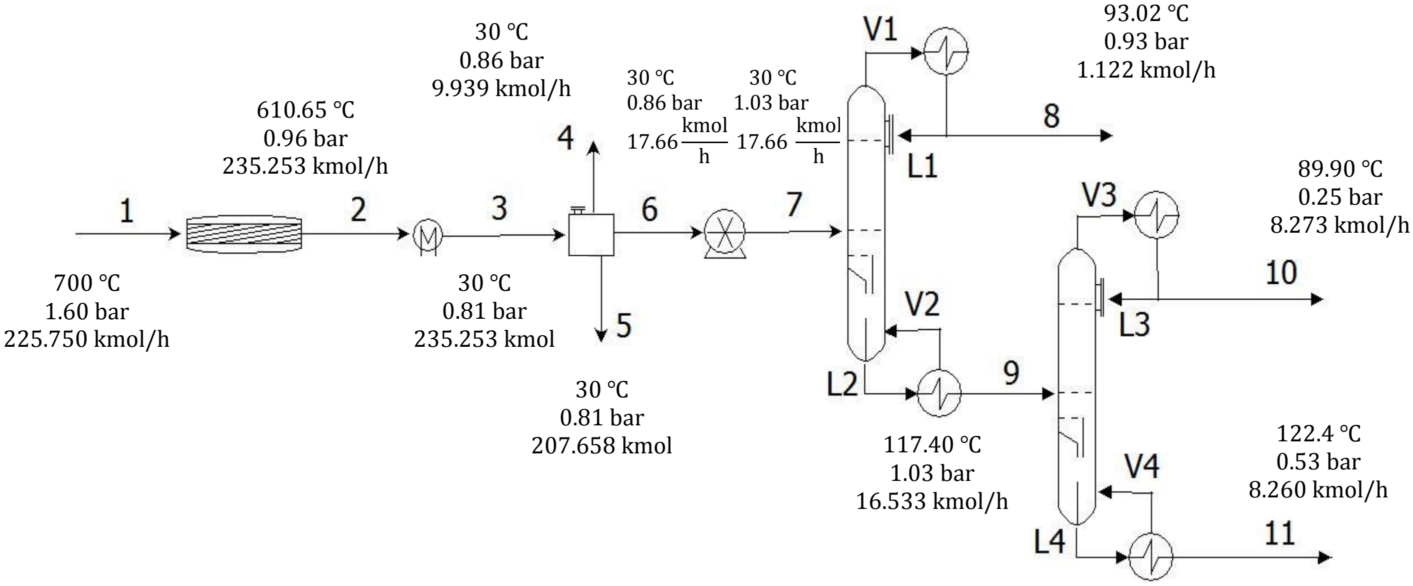
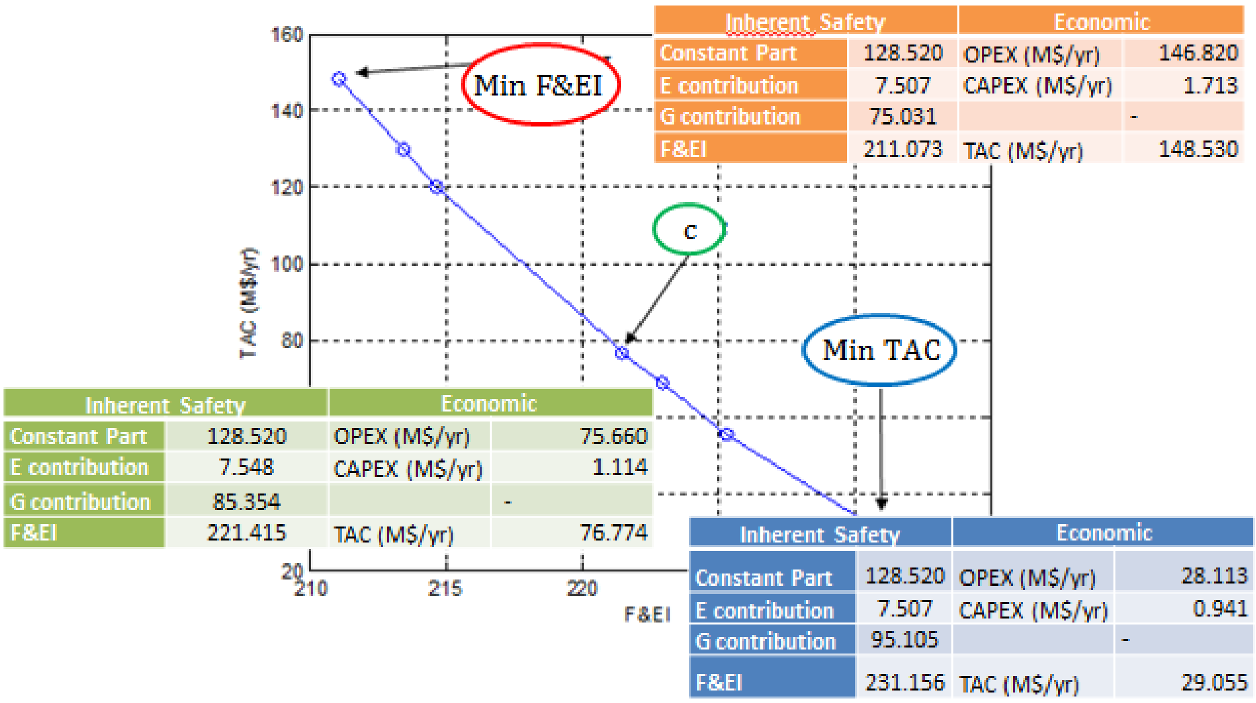


Figure 15. Summary of streams conditions obtained in point "c".

Finally, in Figure 15 are shown the optimal stream conditions obtained in point "c". Input reactor total mole flow rate is quite similar to that achieved in section 4.2. This time, the final styrene mass flow rate is 857.67 kg/h. Temperature in stream 2 is lower than in section 4.2, because reactor length is shortest, but higher than in section 4.1 since is longer. There are not great differences because reactor length does not change in a great amount, besides temperature tends to stabilize over a certain length (see Figure 5). More information about flow rates can be found in Appendix E, where all components flow rates are presented for a better analysis.

Results obtained can be summarised as Figure 16 shows.



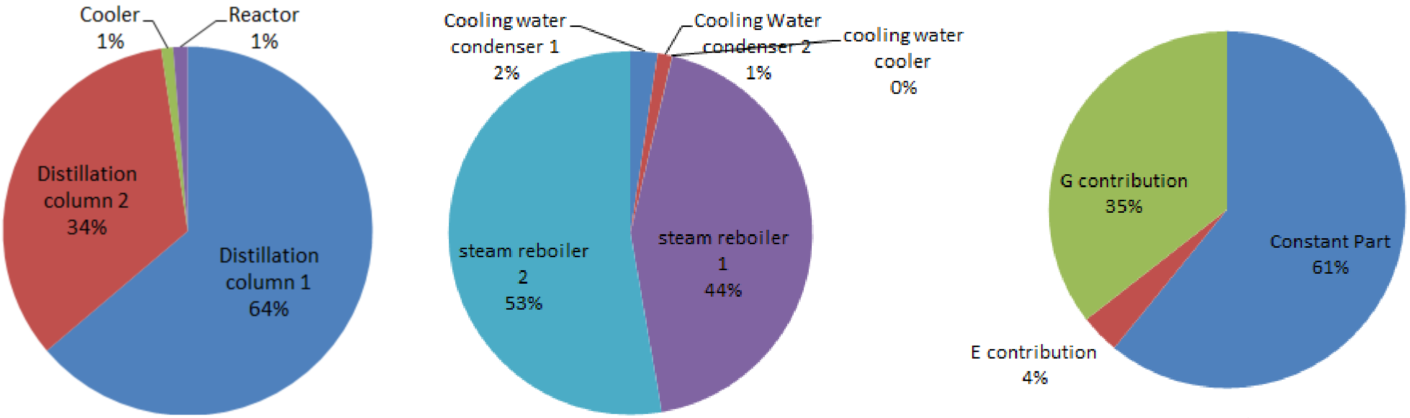
Inherent Safety		Economic	
Constant Part	128.520	OPEX (M$/yr)	146.820
E contribution	7.507	CAPEX (M$/yr)	1.713
G contribution	75.031		-
F&EI	211.073	TAC (M$/yr)	148.530

Inherent Safety		Economic	
Constant Part	128.520	OPEX (M$/yr)	75.660
E contribution	7.548	CAPEX (M$/yr)	1.114
G contribution	85.354		-
F&EI	221.415	TAC (M$/yr)	76.774

Inherent Safety		Economic	
Constant Part	128.520	OPEX (M$/yr)	28.113
E contribution	7.507	CAPEX (M$/yr)	0.941
G contribution	95.105		-
F&EI	231.156	TAC (M$/yr)	29.055

Figure 16. Summary of main results.

TAC varies from 148.530 M$/yr to 29.055 M$/yr. At these points F&EI are 211.073 and 231.156 respectively. Intermediate points (i.e. point "c") present intermediate values of TAC and F&EI. TAC and F&EI are 76.774 M$/yr and 221.415 in point "c". In all cases studied, OPEX is the main cost and G contribution (quantity of flammable material) has a considerable influence in the total F&EI. On the other hand, in Figure 17 can be seen how equipment OPEX, CAPEX and F&EI are distributed.



a) b) c)

Figure 17. Summary of the inherentlysafest design: a) CAPEX, b) OPEX, c) F&EI.

The distillation columns are the principal cost within CAPEX. They represent the 98% of the total CAPEX. Besides, these equipments explain the high values of OPEX required and the G contribution.

5. CONCLUSIONS

After solving the problem and perform the study, the following conclusions can be enumerated:

- This work offers new methology to incorporate inherent safety into chemical plants. The importance of this method is that can be employed during primitive stage of a process design. Therefore, it is considered at the same time, the economic and the inherent safety to drive the design of the plant. Hazards reduction during the design phase is a challenging task and it is sometimes difficult to measure precisely. Using this method, can be achieved a decrease in hazards in a process design, which not only improves process safety, but also protects the environment from potential impacts of the process.
- In this work a Pareto set of solutions are presented, not just only one. The points above Pareto frontier (Figure 12) are feasible and the points below are unfeasible, so the optimal styrene plant (the best combination of inherent safety and the lowest cost) are defined by the Pareto frontier. Decision maker will decide the final design of the styrene production plant, taking into consideration its own preferences respect the economic and inherent safety criteria.
- The case study on the styrene production plant proves how process variables can affect F&EI and TAC. In the case study, the most economic plant is not the inherent safest according to F&EI methodology. This implies great equipments, with higher pressure drops and quantity of flammable material internally. On the contrary, the inherently safest styrene plant presents lower pressures and much smaller equipments. The system under study is a styrene production plant where pressure penalty are practically negligible. However, penalties due to inflammable material are very important. So much that, optimize the styrene plant considering only the economic criteria would bring a 41.14 % contribution due to inflammable materials of the total F&EI. This means that energy released by explosion equipments is much more likely.
- With the mathematical model proposed, an economic analysis has been carried out. It has been noted that distillation columns implies the highest cost in the styrene plant, both CAPEX and OPEX. The main reason why TAC presents high values is due to OPEX, and especially steam of reboiler needed in distillation columns. The applied optimization approach achieves the best design (equipment parameters and operation conditions) of a styrene production plant. That is to say, it is not just a styrene production plant feasible design, hence its importance.
- It is also important to clarify which this styrene production plant is only a first step until the final design. The ethylbenzene separated in distillation column 2 (see Figure 1) would be recycled, and these same applies to all the products (included toluene and benzene) which could be sold.
- As proven, the conceptual design process stage could implement this way to measure safety, and optimize the mathematical model considering a F&EI index as an additional objective to the economic one.

NOMENCLATURE

- **Sets**

$COLUMN\ =\ \{c|c$ is a distillation column$\}$
$COMP\ =\ \{j|j$ is a component$\}$
$EQUIPMENT\ =\ \{e|e$ is one of the main equipment$\}$
$ORGANIC\ =\ \{i|i$ is a organic component$\}$
$PURCHASED\ =\ \{p|p$ is one of the purchased CAPEX$\}$
$REACTION\ =\ \{w|w$ is a reaction$\}$
$ROOT\ =\ \{r|r$ is an Underwood root$\}$
$SECTION\ =\ \{s|s$ is a section of the distillation column$\}$
$STREAM\ =\ \{m|m$ is a stream$\}$

- **Variables**

a	Number of times over minimum reflux
$AreaCond_c$	Condenser area (m^2)
$AreaReb_c$	Reboiler area (m^2)
$Area_e$	Equipment area (m^2)
$Bi_{c,i}$	Mole flow rate for component i in the bottom $(kmol/h)$
B_c	Total molar flow rate in the bottom stream $(kmol/h)$
$CAPEX$	Total capital expenditure $(\$/yr)$
$catalystCost$	Catalyst cost $(\$/yr)$
$concentrationComponent_{j,e}$	Concentration of component j in equipment e (lb/m^3)
$coolingWaterCondenser1$	Cooling water cost of condenser 1 operation $(\$/yr)$
$coolingWaterCondenser2$	Cooling water cost of condenser 2 $(\$/yr)$
$coolingWaterCooler$	Cooling water cost of cooler operation $(\$/yr)$
E_2	Penalty due to pressure relief
$EquipmentCBM_p$	Bare module cost of each equipment ($)
$EquipmentCBMUpdate_p$	Bare module cost update of each equipment ($)
$EquipmentCp0_p$	Purchased cost for base conditions
$density3$	Density of stream 3 (kg/m^3)
$density9$	Density of stream 9 (kg/m^3)
$Di_{c,i}$	Molar flow rate for component i in the distillate $(kmol/h)$
D_c	Total molar flow rate in the distillate stream
$Diameter_c$	Total molar flow rate in the feed stream $(kmol/h)$r
$F\&EI$	Fire and explosion index
F_c	Total molar flow rate in the feed stream $(kmol/h)$
$Fi_{c,i}$	Molar flow rate for component i in the feed $(kmol/h)$
G_2	Penalty due to inflammable material
$H_{c,s}$	Height of column section s (m)
L_c	Length of equipment e (m)
$L1_c$	Liquid molar flow rate in the enriching section $(kmol/h)$
$L2_c$	Liquid molar flow rate in the exhausting section $(kmol/h)$
$massFlowComponent_{j,m}$	Mass flow rate of components in each stream (kg/h)
$massFlowEquipment_{j,e}$	Average mass flow rate in equipments (kg/h)
$massFraction_{j,e}$	Mass fraction of each component j in equipment e
$molarFlowComponent_{j,m}$	Molar flow rate of each component j in each stream i $(kmol/h)$

NP_c	Number of real stages
$Qreb_c$	Heat provided by reboiler(kJ/h)
$Qcond_c$	Heat dissipated by condenser(kJ/h)
$\mathrm{Q_{cooler}}$	Heat dissipated by cooler (kJ/h)
$Rmin$	Minimum reflux
$OPEX$	Total annualized operation expense $(\$/yr)$
$penaltyYoperation$	Penalty due to operation pressure in equipments
$penaltyYrelief$	Penalty due to relief pressure in equipments
P_m	Pressure of stream m (Pa)
$pressureOperationEquipment$	Operation pressure in equipments (bar)
$steamReboiler1$	Steam cost of reboiler 1 $(\$/yr)$
$steamReboiler2$	Steam cost of reboiler 2 $(\$/yr)$
TAC	Total annualized cost $(M\$/yr)$
T_m	Temperature of stream m (℃)
$totalBTUinProcess$	Total energy released in the event of an explosion (BTU)
$totalMolarFlow_m$	Total energy released in the event of an explosion (BTU)
ΔT_{ml}	Logarithmic mean temperature difference in cooler (℃)
ΔT_{cond1}	Condenser inlet difference temperature in column 1 (℃)
ΔT_{cond2}	Condenser outlet difference temperature in column 2 (℃)
ΔT_{reb1}	Reboiler inlet difference temperature in column 1 (℃)
ΔT_{reb2}	Reboiler outlet difference temperature in column 1 (℃)
$\mathrm{V1_c}$	Vapor molar flow rate in the enriching section $(kmol/h)$
$\mathrm{V2_c}$	Vapor molar flow rate in the exhausting section $(kmol/h)$
$Volume_e$	Equipment volume (m^3)
$volumetricFlow_e$	Average volumetric flow in each equipment (m^3/h)
$volumetricFlowComponent_m$	Volumetric flow in each stream m (m^3/h)
X_c	Parameter needed to calculate the real number of stages
ξ_r	Extent of reaction r $(kmol/h)$
$\theta_{c,r}$	Underwood root for a given separation task

- **Parameters**

$B1_p$	First factor needed for the calculation of bare module factor
$B2_p$	Second factor needed for the calculation of bare module factor
$B3_p$	Third factor needed for the calculation of bare module factor
$catalystPrice$	Catalyst Price $(\$/yr)$
$catalystDensity$	Catalyst Price (kg/m^3)
Cp_j	Heat capacity of component j $(kJ \cdot kg^{-1} \cdot ℃^{-1})$
Fm_p	Material factor needed for the calculation of bare module cost
Fp_p	Pressure factor needed for the calculation of bare module cost
Hc_j	Heat of combustion of component j (BTU/lb)
$\Delta Hvap_i$	Enthalpy of vaporization of components i $(kJ/kmol)$
MW_j	Molecular weight of component j $(kg/kmol)$
$M1$	Average molecular weight of column 1 (kg/m^3)
$M2$	Average molecular weight of column 2 (kg/m^3)
$p00_w$	First parameter needed to calculate extent of reaction
$p10_w$	Second parameter needed to calculate extent of reaction
$p01_w$	Third parameter needed to calculate extent of reaction

$Recovery_{c,i}$	Mole flow rate ratio distillate for component i in column c
$Recovery\_LK_c$	Mole flow rate ratio for light key component in column c
$RecoveryBottoms\_HK_c$	Mole flow rate ratio bottoms for heavy key in column c
$TraySpacing$	Trays separation (m)
$UpdateFactor_p$	Update factor applied to bare module cost
$Ucond_c$	Overall coefficient of heat transfer $(kJ \cdot s^{-1} \cdot m^{-2} \cdot ℃^{-1})$
$Ureb_c$	Overall coefficient of heat transfer $(kJ \cdot h^{-1} \cdot m^{-2} \cdot ℃^{-1})$
$\rho 1$	Average density of column 1 (kg/m^3)
$\rho 2$	Average density of column 2 (kg/m^3)

- **Tables**

$alpha_{c,i}$	Relative volatility for component i in column c
$stoichiometric_{w,j}$	Stoichiometric coefficients of components j in reactions w

APPENDIXES

Appendix A. Final styrene production plant model

The mathematical model in order to optimize styrene production plant is present below. It is divided in various parts for a good understanding of the equations.

A.1 FIRE & EXPLOSION INDEX ANALYSIS

$$FireExplosion\ Index = 128.52 + 40.8 \cdot (E_2 + G_2) \tag{A.1}$$

- **Penalty calculations due to relief pressure**

$$E_2 = 1.2 \cdot \frac{penaltyYoperation^2}{penaltyYrelief}$$

$$penaltyYoperation = 0.02254 \cdot pressureOperationEquipment + 0.1615$$

$$penaltyYrelief = 0.02254 \cdot (1.2 \cdot pressureOperationEquipment) + 0.1615$$

(A.2)

- **Top value of pressure which determines penalty E.**

$$\begin{aligned} pressureOperationEquipment &\geq \frac{P_1 + P_2}{2} \\ pressureOperationEquipment &\geq \frac{P_2 + P_3}{2} \\ pressureOperationEquipment &\geq P_7 \\ pressureOperationEquipment &\geq P_8 \\ pressureOperationEquipment &\geq P_9 \end{aligned}$$

(A.3)

- **Penalty calculations due to quantity of Flammable/Unstable Material**

$$G_2 = \frac{2.509 \cdot (TotalBTU \cdot 10^{-9}) + 0.01545}{TotalBTU \cdot 10^{-9} + 0.6932}$$

$$TotalBTU \geq V_{reactor} \cdot \sum_j C_{j,reactor} \cdot Hc_j$$

$$TotalBTU \geq spillDuration \cdot \sum_j Hc_j \cdot massFlowComponent_{j,1} \cdot 2.20462$$

(A.4)

- **Top value of energy in the event of an explosion which determines the quantity of Flammable/Unstable Material**

$$
\begin{aligned}
&TotalBTU \geq V_{reactor} \cdot \sum_{j} C_{j,reactor} \cdot Hc_j \\
&TotalBTU \geq spillDuration \cdot \sum_{j} Hc_j \cdot massFlowComponent_{j,1} \cdot 2.20462 \\
&\\
&TotalBTU \geq V_{cooler} \cdot \sum_{j} C_{j,cooler} \cdot Hc_j \\
&TotalBTU \geq spillDuration \cdot \sum_{j} Hc_j \cdot massFlowComponent_{j,2} \cdot 2.20462 \\
&\\
&TotalBTU \geq V_{column1} \cdot \sum_{j} C_{j,column1} \cdot Hc_j \\
&TotalBTU \geq spillDuration \cdot \sum_{j} Hc_j \cdot massFlowComponent_{j,7} \cdot 2.20462 \\
&\\
&TotalBTU \geq V_{column2} \cdot \sum_{j} C_{j,column2} \cdot Hc_j \\
&TotalBTU \geq spillDuration \cdot \sum_{j} Hc_j \cdot massFlowComponent_{j,9} \cdot 2.20462
\end{aligned}
\tag{A.5}
$$

- **Upper and lower bounds**

$$
\begin{aligned}
&0 < pressureOperationEquipment < 3 \\
&1 \cdot 10^9 < TotalBTU < 9 \cdot 10^9
\end{aligned}
\tag{A.6}
$$

A.2 EQUIPMENT DESIGN

- **Reactor molar, energy and momentum balances.**

$$
\begin{aligned}
&molarFlowComponents_{j,2} = molarFlowComponents_{j,1} + \sum_{r} \alpha_{rj} \xi_r \qquad \forall j \\
&\xi_r = p00_r + p10_r \cdot L_{reactor} + p01_r \cdot molarFlowComponents_{EBenzene,1} \quad \forall r \\
&T_1(^{\circ}\mathrm{C}) = 700 \\
&P_1(bar) = 1.6 \\
&T_2(^{\circ}\mathrm{C}) = 576.5 - 1.148 \cdot L_{reactor}(m) + 2.147 \cdot n_{EB}^{Feed}\left(\frac{kmol}{h}\right)
\end{aligned}
$$

$$P_2(bar) = 1.991 - 0.1069 \cdot L_{reactor}(m) - 0.04344 \cdot n_{EB}^{Feed}\left(\frac{kmol}{h}\right)$$

(A.7)

- **Cooler molar, energy and momentum balances.**

$$molarFlowComponents_{j,3} = molarFlowComponents_{j,2} \quad \forall j$$

$$T_3(°C) = 30$$

$$P_3(bar) = P_2 - 0.1$$

(A.8)

- **Three phase separator molar, energy and momentum balances.**

$$molarFlowComponents_{j,4} = molarFlowComponents_{j,3} \cdot Factor4_j \quad \forall j$$
$$molarFlowComponents_{j,5} = molarFlowComponents_{j,3} \cdot Factor5_j \quad \forall j$$
$$molarFlowComponents_{j,6} = molarFlowComponents_{j,3} \cdot Factor6_j \quad \forall j$$

$$T_4(°C) = T_3 \quad ; \quad P_4(bar) = P_3$$
$$T_5(°C) = T_3 \quad ; \quad P_5(bar) = P_3$$
$$T_6(°C) = T_3 \quad ; \quad P_6(bar) = P_3$$

(A.9)

- **Pump molar, energy and momentum balances.**

$$molarFlowComponents_{j,7} = molarFlowComponents_{j,6}$$
$$T_7(°C) = T_6$$
$$P_7(bar) = 1.026$$

(A.10)

- **Distillation columns molar, energy and momentum balances.**

$$\text{molarFlowComponent}_{j,7} = \text{molarFlowComponent}_{j,8} + \text{molarFlowComponent}_{j,9} \quad \forall\ j$$
$$\text{molarFlowComponent}_{j,9} = \text{molarFlowComponent}_{j,10} + \text{molarFlowComponent}_{j,11} \quad \forall\ j$$

$$F_7 = D_8 + B_9 \quad ; \quad D_8 = \text{molarFlowComponent}_{j,8}$$
$$B_9 = D_{10} + B_{11} \quad ; \quad F_7 = \text{molarFlowComponent}_{j,7}$$

$$V_1 = D_8 + L_1 \quad ; \quad B_9 = \text{molarFlowComponent}_{j,9}$$
$$V_3 = D_{10} + L_3 \quad ; \quad B_{11} = \text{molarFlowComponent}_{j,11}$$

$$L_2 = V_2 + B_9$$
$$L_4 = V_4 + B_{11}$$

$$F_7 + L_1 + V_2 = V_1 + L_2$$
$$B_9 + L_3 + V_4 = V_3 + L_4$$

$$V_1 = V_2$$
$$V_3 = V_4$$

$$F_7 = \sum_{j}^{components} \mathrm{molarFlowComponent_{j,7}}$$
$$D_8 = \sum_{j}^{components} \mathrm{molarFlowComponent_{j,8}}$$
$$D_{10} = \sum_{j}^{components} \mathrm{molarFlowComponent_{j,10}}$$
$$B_9 = \sum_{j}^{components} \mathrm{molarFlowComponent_{j,9}}$$
$$B_{11} = \sum_{j}^{components} \mathrm{molarFlowComponent_{j,11}}$$

$$T_8 = 78.3 \quad ; \quad P_8 = 0.932$$

$$T_9 = 117.4 \quad ; \quad P_9 = 1.026$$

$$T_{10} = 89.9 \quad ; \quad P_{10} = 0.2464$$

$$T_{11} = 122.1 \quad ; \quad P_{11} = 0.5264$$

(A.11)

- **Underwood equations**

$$\sum_{j}^{components} \frac{\alpha_{ij} \cdot \mathrm{molarFlowComponent_{j,7}}}{\alpha_{HK,j} - \theta_{c1,1}} = V_1 - V_2$$
$$\sum_{j}^{components} \frac{\alpha_{ij} \cdot \mathrm{molarFlowComponent_{j,9}}}{\alpha_{HK,j} - \theta_{c2,1}} = V_3 - V_4$$

$$\sum_{\mathrm{j}}^{\mathrm{components}} \frac{\mathrm{\alpha_{ij} \cdot molarFlowComponent_{j,8}}}{\mathrm{\alpha_{HK,j} - \theta_{c1,2}}} = \mathrm{V_1}$$

$$\sum_{j}^{components} \frac{\alpha_{ij} \cdot \mathrm{molarFlowComponent_{j,10}}}{\alpha_{HK,j} - \theta_{c2,2}} = V_3$$

$$\sum_{j}^{components} \frac{\alpha_{ij} \cdot \mathrm{molarFlowComponent}_{\mathrm{j,9}}}{\alpha_{HK,j} - \theta_{c1,3}} = -V_2$$
$$\sum_{j}^{components} \frac{\alpha_{ij} \cdot \mathrm{molarFlowComponent}_{\mathrm{j,11}}}{\alpha_{HK,j} - \theta_{c2,3}} = -V_4$$

$$\mathrm{molarFlowComponent}_{\mathrm{j,7}} = \mathrm{molarFlowComponent}_{\mathrm{j,8}} \quad \forall\, \mathrm{j} < \mathrm{LK}$$
$$\mathrm{molarFlowComponent}_{\mathrm{j,9}} = \mathrm{molarFlowComponent}_{\mathrm{j,10}} \quad \forall\, \mathrm{j} < \mathrm{LK}$$

$$\mathrm{molarFlowComponent}_{\mathrm{j,8}} = \mathrm{molarFlowComponent}_{\mathrm{j,7}} \cdot r_{c1,j} \quad \forall\, j = LK$$
$$\mathrm{molarFlowComponent}_{\mathrm{j,10}} = \mathrm{molarFlowComponent}_{\mathrm{j,9}} \cdot r_{c2,j} \quad \forall\, j = LK$$

$$\mathrm{molarFlowComponent}_{\mathrm{j,9}} = \mathrm{molarFlowComponent}_{\mathrm{j,7}} \quad \forall\, j > HK$$
$$\mathrm{molarFlowComponent}_{\mathrm{j,11}} = \mathrm{molarFlowComponent}_{\mathrm{j,9}} \quad \forall\, j > HK$$

$$\mathrm{molarFlowComponent}_{\mathrm{j,9}} = \mathrm{molarFlowComponent}_{\mathrm{j,7}} \cdot r_{c1,j} \quad \forall\, j = HK$$
$$\mathrm{molarFlowComponent}_{\mathrm{j,11}} = \mathrm{molarFlowComponent}_{\mathrm{j,9}} \cdot r_{c2,j} \quad \forall\, j = HK$$

(A.12)

- **Constraints**

$$molarFlowComponents_{H_2O,1} = 11.786 \cdot molarFlowComponents_{EB,1}$$
$$molarFlowComponents_{EBenzene,1} \geq 25 \cdot L_{reactor} - 70$$

(A.13)

- **Upper and lower bounds**

$$2 < molarFlowComponents_{EB,1} < 30$$

$$\theta_{c,r} > \alpha_{C,i} \quad \forall i = r$$
$$\theta_{c,r} < \alpha_{C,i} \quad \forall i = r + 1$$

(A.14)

- **Equipment size**

$$\left.\begin{array}{l} V_{reactor} = A_{reactor} \cdot L_{reactor} \\ A_{reactor} = \frac{\pi D_{reactor}^2}{4} \\ D_{reactor} = 1.95 \\ 2 < L_{reactor} < 10 \end{array}\right\} \text{Reactor size}$$

(A.15)

$$\left.\begin{array}{l} A_{cooler} = \dfrac{Q_{cooler}}{U \cdot \Delta T_{ml}} \\[2ex] \mathrm{massFlowComponent_{j,i}} = \mathrm{molarFlowComponent_{j,i}} \cdot MW_j \quad \forall j \\[2ex] \mathrm{Q_{cooler}} = \mathrm{massFlowComponent_{j,2}} \cdot \mathrm{C_p^{product}}(\mathrm{T_2} - \mathrm{T_3}) \\[2ex] \Delta \mathrm{T_1} = \mathrm{T_2} - \mathrm{T_{out}^{cooling\ water}} \\ \Delta \mathrm{T_2} = T_3 - \mathrm{T_{in}^{cooling\ water}} \\[2ex] \Delta T_{ml}[0.5 \cdot (\Delta \mathrm{T_1} \cdot \Delta \mathrm{T_2}) \cdot (\Delta \mathrm{T_1} + \Delta \mathrm{T_2})]^{1/3} \\[2ex] L_{cooler} = \dfrac{A_{cooler}}{2\pi R_{cooler}} \\[2ex] \mathrm{T_{in}^{cooling\ water}} = 20 \\ \mathrm{T_{out}^{cooling\ water}} = 25 \\[2ex] U = 2880 \\ 10 < A_{cooler} < 10000 \end{array}\right\} \text{Cooler size}$$

(A.16)

$$\left.\begin{array}{l} N_{min_c} = \dfrac{\log\left(\dfrac{r_{LK,D,c}}{1 - r_{LK,D,c}} \cdot \dfrac{r_{HK,B,c}}{1 - r_{HK,B,c}}\right)}{\log(\alpha_{LH,c})} \quad \forall c \\[3ex] \frac{NP_c - N_{min_c}}{NP_c + 1} = 1 - \exp\left[\frac{1 + 54.4X_c}{11 + 117.2X_c} \cdot \frac{X_c - 1}{X_c^{0.5}}\right] \quad \forall c \\[3ex] X = \dfrac{R_c - R_{\mathrm{min},c}}{R_c + 1} \qquad \forall c \end{array}\right\} \text{Distillation columns size}$$

$$\left.\begin{array}{l}
\frac{NR_c}{NS_c} = \left[\frac{z_{HK}}{z_{LK}} \cdot \frac{x_{LK,B}^2}{x_{HK,D}^2} \cdot \frac{B}{D}\right]^{0.206} \quad \forall c \\[2ex]
R_{\min} = \frac{L_{1_c}}{D_c} \quad \forall c \\[2ex]
NP_c = NS_{c,s1} + NS_{c,s2} \quad \forall c \\[2ex]
H_c = TraySpacing \cdot (NP_c - 1) + 3 \quad \forall c \\[2ex]
A_{c,s1} = \frac{M_V}{(\rho_L \cdot \rho_V)^{0.5}} \cdot \frac{1}{0.7} \cdot \frac{1}{C_o} \cdot \frac{A}{A_n} \cdot \left[V + [L_1 \cdot (a-1)]\right] \quad \forall c \\
A_{c,s2} = \frac{M_V}{(\rho_L \cdot \rho_V)^{0.5}} \cdot \frac{1}{0.7} \cdot \frac{1}{C_o} \cdot \frac{A}{A_n} \cdot \left[V + [L_1 \cdot (a-1)]\right] \quad \forall c \\[2ex]
\mathrm{D}_{c,s1} = \sqrt{4 \cdot \frac{A_{c,s1}}{\pi}} \quad \forall c \\[2ex]
\mathrm{D}_{c,s2} = \sqrt{4 \cdot \frac{A_{c,s2}}{\pi}} \quad \forall c \\[2ex]
V_c = A_c \cdot H_c \quad \forall c \\[2ex]
0.1642 < A_c < 12, \quad 1.2 < R_{min} < 80
\end{array}\right\} \text{Distillation columns size}$$

(A.17)

- **Concentrations of components in equipment**

$$ConcentrationComponent_{j,e} = \frac{MassFlowEquipment_{j,e}}{Qv_e}$$

$$\begin{array}{l}
MassFlowEquipment_{j,reactor} = (massReactor) \cdot MW_j \cdot 2.20462 \\
MassFlowComponent_{j,cooler} = MassFlowComponent_{j,2} \cdot 2.20462 \\
MassFlowComponent_{j,column1} = MassFlowComponent_{j,7} \cdot 2.20462 \\
MassFlowComponent_{j,column2} = MassFlowComponent_{j,9} \cdot 2.20462
\end{array}$$

(A.18)

$$\left. Qv_{reactor} = \frac{\left(\sum_j molarFlowComponent_{j,1}\right) \cdot R_{gas} \cdot T_1}{P_1} \right\} \text{Volumetric flow in the reactor}$$

(A.19)

$$Q_{v,cooler} = \frac{\left(\sum_j molarFlowComponent_{j,2}\right) \cdot R_{gas} \cdot T_2}{P_2}$$

Volumetric flow in the cooler

(A.20)

$$Qv_{column1} = \frac{\sum_j molarFlowComponent_{j,7} \cdot MW_7}{\rho_7}$$

$$Qv_{column2} = \frac{\sum_j molarFlowComponent_{j,9} \cdot MW_9}{\rho_9}$$

Volumetric flow in the distillation columns

(A.21)

A.3 ECONOMIC EVALUATION

$$\mathrm{TAC} = (\mathrm{OPEX} + \mathrm{CAPEX}) \cdot 10^{-6}$$

(A.22)

- **CAPEX**

$$\mathrm{CAPEX} = \left(\sum_p EquipmentCBMUpdate_p \quad + catalystCost \right) \cdot \mathrm{AnnualizationFactor}$$

$$EquipmentCBMUpdate_p = EquipmentCBM_p \cdot UpdateFactor_p \quad \forall p$$

$$EquipmentCBM_p = EquipmentCp0_p \cdot EquipmentFBI_p \quad \forall p$$

$$EquipmentFBI_p = B_{1_p} + B_{2_p} \cdot Fm_p \cdot Fp_p \quad \forall p$$

(A.23)

$$\left.\begin{array}{l}
EquipmentCp0_{vessel} = 1529 \cdot L_{reactor} + 5477 \\
EquipmentCp0_{cooler} = 50.56 \cdot \mathrm{A}_{\mathrm{cooler}} + 2.401 \cdot 10^{4} \\
EquipmentCp0_{tower1} = 604.3 \cdot V_{Column1} + 5740 \\
EquipmentCp0_{tower2} = 604.3 \cdot V_{Column2} + 5740 \\
EquipmentCp0_{tray1} = 488.1 \cdot A_{Column1} + 580.8 \\
EquipmentCp0_{tray2} = 488.1 \cdot A_{Column2} + 580.8 \\
EquipmentCp0_{condenser1} = 50.56 \cdot \mathrm{A}_{\mathrm{condenser1}} + 2.401 \cdot 10^{4} \\
EquipmentCp0_{condenser2} = 50.56 \cdot \mathrm{A}_{\mathrm{condenser2}} + 2.401 \cdot 10^{4} \\
EquipmentCp0_{reboiler1} = 50.56 \cdot \mathrm{A}_{\mathrm{reboiler\ 1}} + 2.401 \cdot 10^{4} \\
EquipmentCp0_{reboiler2} = 50.56 \cdot \mathrm{A}_{\mathrm{reboiler\ 2}} + 2.401 \cdot 10^{4} \\
\\
0.3848 < A_{column\ 1} < 4.9087 \\
0.3848 < A_{column\ 2} < 4.9087 \\
10 < A_{reboiler1} < 10000 \\
10 < A_{reboiler2} < 10000 \\
10 < A_{condenser1} < 10000 \\
10 < A_{reboiler2} < 10000 \\
30 < V_{column\ 1} < 400 \\
30 < V_{column\ 2} < 400
\end{array}\right\} \text{Purchase cost for base conditions}$$

(A.24)

$$CatalystCost = CatalystPrice \cdot V_{reactor} \cdot \rho_{cat} \cdot (1 - \varepsilon)$$

(A.25)

- **OPEX**

$$\begin{array}{l}
\mathrm{OPEX} = \mathrm{coolingWaterCondenser1} + \mathrm{coolingWaterCondenser2} + \\
\qquad\qquad \mathrm{steamReboiler1} + \mathrm{steamReboiler2} + \mathrm{coolingWaterCooler}
\end{array}$$

$$\begin{array}{l}
\mathrm{coolingWaterCooler} = \mathrm{Water} \cdot \mathrm{Q}_{\mathrm{cooler}} \cdot YEAR/3600 \\
\mathrm{coolingWaterCondenser1} = \mathrm{Water} \cdot \mathrm{Q}_{\mathrm{condenser1}} \cdot YEAR/3600 \\
\mathrm{coolingWaterCondenser2} = \mathrm{Water} \cdot \mathrm{Q}_{\mathrm{condenser1}} \cdot YEAR/3600 \\
\mathrm{steamReboiler1} = \mathrm{Steam} \cdot \mathrm{Q}_{\mathrm{reboiler1}} \cdot YEAR/3600 \\
\mathrm{steamReboiler2} = \mathrm{Steam} \cdot \mathrm{Q}_{\mathrm{reboiler2}} \cdot YEAR/3600
\end{array}$$

(A.26)

- **Condenser and reboiler areas**

$$\mathrm{Q_{condenser_c}} = \frac{\sum_j Di_{c,i} \cdot \lambda_\mathrm{i}}{D_c(V1_c + aL1_c)} \quad \forall c$$

$$\mathrm{Q_{reboiler_c}} = \frac{\sum_j Bi_{c,i} \cdot \lambda_\mathrm{j}}{B_c(V2_c + aL1_c)} \quad \forall c$$

$$A_{condenser1} = \frac{Q_{condenser1}}{U_{cooler} \cdot \Delta T_{cond1}} \quad ; \quad \Delta T_{cond1} = 43.1$$

$$A_{condenser2} = \frac{Q_{condenser2}}{U_{cooler} \cdot \Delta T_{cond2}} \quad ; \quad \Delta T_{cond2} = 35.3$$

$$A_{reboiler1} = \frac{Q_{reboiler1}}{U_{reboiler} \cdot \Delta T_{reb1}} \quad ; \quad \Delta T_{reb1} = 42.6$$

$$A_{reboiler2} = \frac{Q_{reboiler2}}{U_{reboiler} \cdot \Delta T_{reb2}} \quad ; \quad \Delta T_{reb2} = 37.9$$

(A.27)

- **Minimum production required**

$$massFlowComponent_{Sty,11} \geq 850$$

(A.28)

Appendix B. MATLAB verification

In this Appendix, it is presented MATLAB files used in order to verify Hysys simulations are corrected.

- **Main file**

```
clear all;clc;close all;

global vis A  R E ko Href alfa dQdL Tref Cpj
global MW dp Por d0  dcat


%% PROBLEM DATA
M=184.7 * 10^3 / 3600 ;  % [mol/s] total input molar flow rate feed


%  E-benz  Styrene   H2  Ethylene  Toluene   CO    CO2     CH4
MW=[106    104.15    2    25.05    92.14    28.01  44.01  16.04

%H2O     Benz
 18      78.11   ]; % [g/mol] molecular weight


ni=[14.25   1.34e-2   0     0      6.19e-2     0     0       0

170.42   0.0002] * 1000/3600 ; % [mol/s] input molar flow rate to reactor



alfa=[  -1   1   1   0   0   0   0   0   0   0   ;   %1
        -1   0   0   1   0   0   0   0   0   1   ;   %2
        -1   0  -1   0   1   0   0   1   0   0   ;   %3
         0   0   4  -1   0   2   0   0  -2   0   ;   %4
         0   0   3   0   0   1   0  -1  -1   0   ;   %5
         0   0   1   0   0  -1   1   0  -1   0  ] ;  %6

%stoichometric coefficients of reactions



Cpj=[301.795803874600  277.188875848083   30.2388208892725
91.9827389727751 250.975686103559 32.7070798588799 52.7026167287852
69.0339845402977 40.3392353348438 202.636986558307];

% [J/mol] molar heat capacity


%>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>
Pen=1.6*10^5 ; % [Pa] input pressure to reactor

Ten=700+273  ; % [K]  input temperature to reactor
%<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<
```

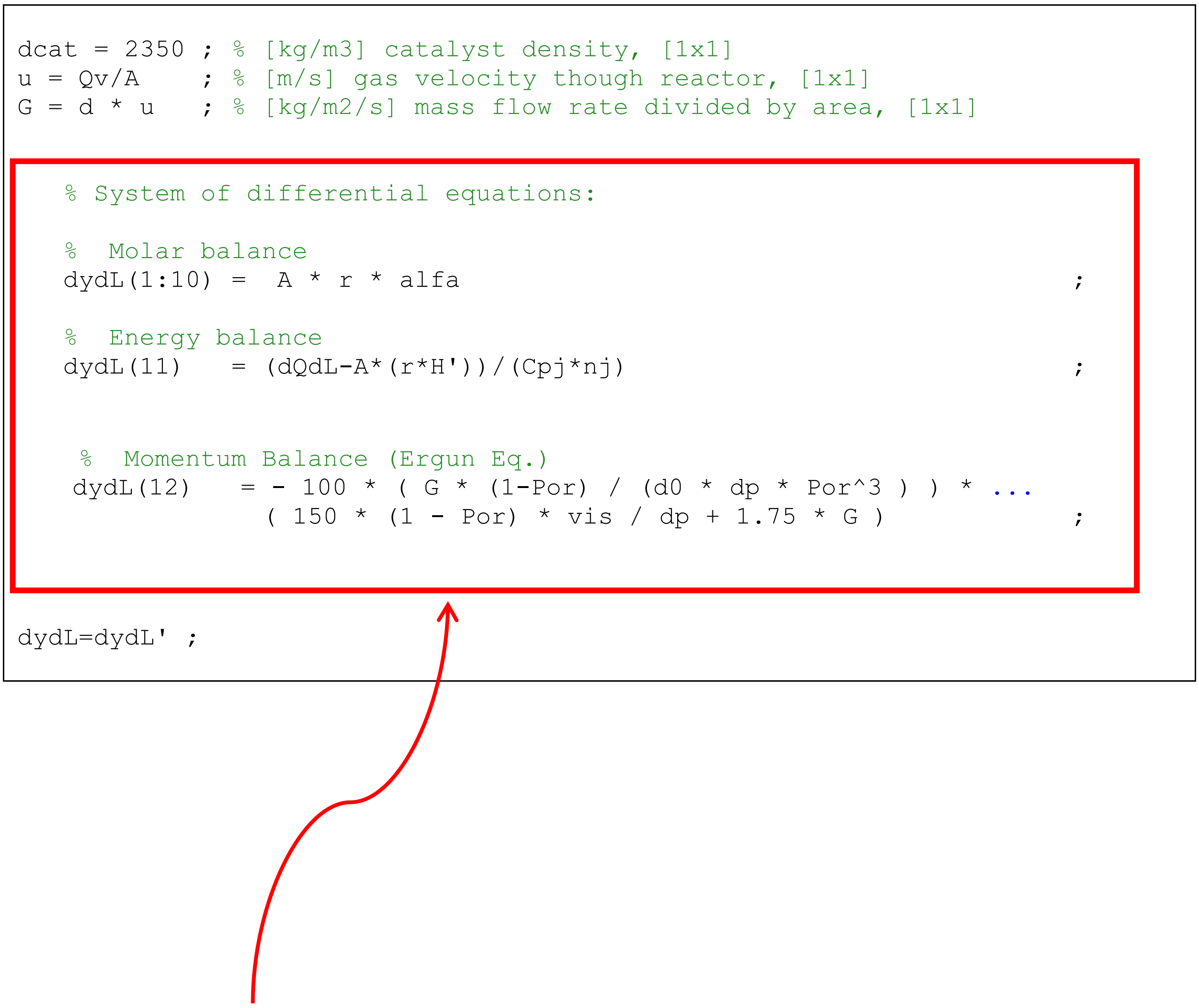
```
Href= [117.6   105.5   -54.68  210.11819921875  206.124 -41.386] * 10^3;

% [J/mol] enthalpy of reaction

E = [90792.7  207944.6  91462.1   103972.3  65688.73   73554.64];

 % [J/mol] activation energy



ko=   [1967 * 10^3 / 101325         7.3e8 * 10^3 / 101325
       1748 * 10^3 / (101325^2)     1209 * 10^3 / (101325^3)
       69.11 * 10^3 /(101325^2)    7329 * 10^3 / (101325^2)];

% [mol/m3/Pa/s] pre-exponential factor


Radio=1.95/2 ; % [m] reactor radius
D=1.95       ; % [m] reactor diameter

dQdL=0  ;  % adiabatic process implies

Tref=298       ; % [K] reference temperature
R=8.314        ; % [J/mol/K] ideal gases constant
A = pi*Radio^2 ; % [m2] reactor area
a=0.5;
vis=2.86*10^-5 ; % [Pa·s] viscosity
dp= 1*10^-3    ; % [m] particle diameter
Por= 0.445     ; % porosity
PMi=MW.*xi     ; % [g/mol] average molecular weight, [1x1]
dcat=2350      ; % [kg/m3] catalys density

Qv0=sum(ni)*R*Ten/Pen ; % [m3/s]
d0 = sum(ni.*xi)/Qv0  ; % [kg/m3]
u0 = Qv0/A            ; % [m/s]



%% PROBLEM SOLUTION
L = linspace(0,3,100); % [m] independient variable fixed
CI=[ni Ten Pen]      ; % [mol/s, K, Pa] initial conditions
lengthspan = L * Por ; % [m] length where there is reaction

[Lcat Y]=ode23s(@fStyrene, lengthspan, CI) ;

njout=Y(:,1:10);        % [mol/s] molar flow rates along reactor
T=Y(:,11);              % [K]     temperature along reactor
P=Y(:,12);              % [Pa]    pressure alog reactor
njout=njout*3600/1000 ; % [kmol/h]

%FIG. MOLAR FLOW RATES OF ALL COMPONENTS AND STYRENE
figure(1)
subplot(1,2,1)
plot(L,njout)
```

```
xlabel('L (m)')
ylabel('nj (kmol/h)')
legend('Ebenz','Styrene','H_2','Ethylene','Toluene','CO','CO2','CH4','H2O',
'Benz')
grid on
subplot(1,2,2)
plot(L,njout(:,2))
xlabel('L (m)')
ylabel('n styrene (kmol/h)')
grid on

%FIG. TEMPERATURE
T=T-273; %°C
figure(2)
plot(L,T)
xlabel('L (m)')
ylabel('T (°C)')
grid on

%FIG. PRESSURE
figure(3)
plot(L,P/10^5)
xlabel('L (m)')
ylabel('P (bar)')
grid on

% FIG.  E-BENCENE CONVERSION
conv = (ni(1)-njout(:,1)*1000/3600)/ni(1) ; % E-Benzene conversion
figure(4)
plot(L,conv)
xlabel('L (m)')
ylabel('conv E-Benzene')
grid on

% FIG. CONCENTRACION
for i=1:100
    Qv_1(i) = sum(njout(i,:))*R*T(i)./P(i) ;

% [m3/h] volumetric flow along reactor

    C_1(i,:) = njout(i,:)/Qv_1(i) ;

% [kmol/m3] concentration of component along the reactor

end

figure(5)
plot(L,C_1)
xlabel('L (m)')
ylabel('C (mol/m3')
grid on
legend('E-benz','Styrene','H_2','Ethylene','Toluene','CO','CO2','CH4',
       'H2O'   ,'Benz')

% Extents of reactions calculations
extentReaction(1) =   njout(end,2) - njout(1,2)             ; % [kmol/h]
```

```
extentReaction(2) =  njout(end,10) - njout(1,10)            ; % [kmol/h]

extentReaction(3) =   njout(end,5) - njout(1,5)             ; % [kmol/h]

extentReaction(4) = - ( ( njout(end,4) - njout(1,4)   )  - ...
                           extentReaction(2)    )           ; % [kmol/h]

extentReaction(5) = - ( ( njout(end,8) - njout(1,8)   )  - ...
                           extentReaction(3)    )           ; % [kmol/h]

extentReaction(6) = ( njout(end,7) - njout(1,7)   )         ; % [kmol/h]
```

- **Function file**

```
function dydL=etano(L,y);
nj=y(1:10); % [mol/s] molar flow rates of each component
T=y(11);    % [K] temperature
P=y(12);    % [Pa] pressure

global vis A  R E ko Href alfa dQdL Tref Cpj
global MW dp Por d0  dcat


Xj=nj/sum(nj)     ; % molar   fraction of each component, [1x10]
Pj=Xj*P           ; % [Pa]    partial pressure of each  component, [1x10]
PM=MW*Xj          ; % [g/mol] average molecular weight
Qv=sum(nj)*R*T/P  ; % [m3/s]  volumetric flow

d=(P/R/T)*PM / 10^3;  % [kg/m3] density of the gas mixture, [1x1]

H=Href +Cpj*alfa'*(T-Tref);
% [J/mol] enthalpy of reaction to the temperature, [1x6]

k=ko.*exp(-E/(R*T))       ; % [mol/m3/s] constant rate, [1x6]
K = exp(-1.6) * 101325    ; % [Pa] equilibrium constant of the 1st reaction,
                              % [1x1]


%  Reactions kinetics
%  E-benz  Styrene   H2  Ethylene  Toluene   CO    CO2     CH4    H2O
Benz
r(1)=k(1)*  ( Pj(1)  - Pj(2)*Pj(3)/K)  ;
r(2)=k(2)*Pj(1)                        ;
r(3)=k(3)*Pj(1)*Pj(3)                  ;
r(4)=k(4)*Pj(4)*Pj(9)^2                ;
r(5)=k(5)*Pj(8)*Pj(9)                  ;
r(6)=k(6)*Pj(6)*Pj(9)                  ;
```



```
dcat = 2350 ; % [kg/m3] catalyst density, [1x1]
u = Qv/A    ; % [m/s] gas velocity though reactor, [1x1]
G = d * u   ; % [kg/m2/s] mass flow rate divided by area, [1x1]

   % System of differential equations:

   %  Molar balance
   dydL(1:10)  =  A * r * alfa                                       ;

   %  Energy balance
   dydL(11)    = (dQdL-A*(r*H'))/(Cpj*nj)                            ;


    %  Momentum Balance (Ergun Eq.)
    dydL(12)    = - 100 * ( G * (1-Por) / (d0 * dp * Por^3 ) ) * ...
                 ( 150 * (1 - Por) * vis / dp + 1.75 * G )           ;

dydL=dydL' ;
```

System of differential equations (molar, energy and momentum balances along reactor) presented in section 3.2.1.1

Appendix C. Correlations

Optimization involved problems when working with nonlinear functions. Looking for global optimum becomes an complicated task. In other words, there is no algorithm with any guarantees regarding solution. At this point, it is useful to proceed with the problem linearizing these nonlinear function about the operating point that cause problems. In this appendix, correlations and a representation of these fits are presented.

C.1 Safety

a) Pressure penalty E for flammable & combustible liquids.

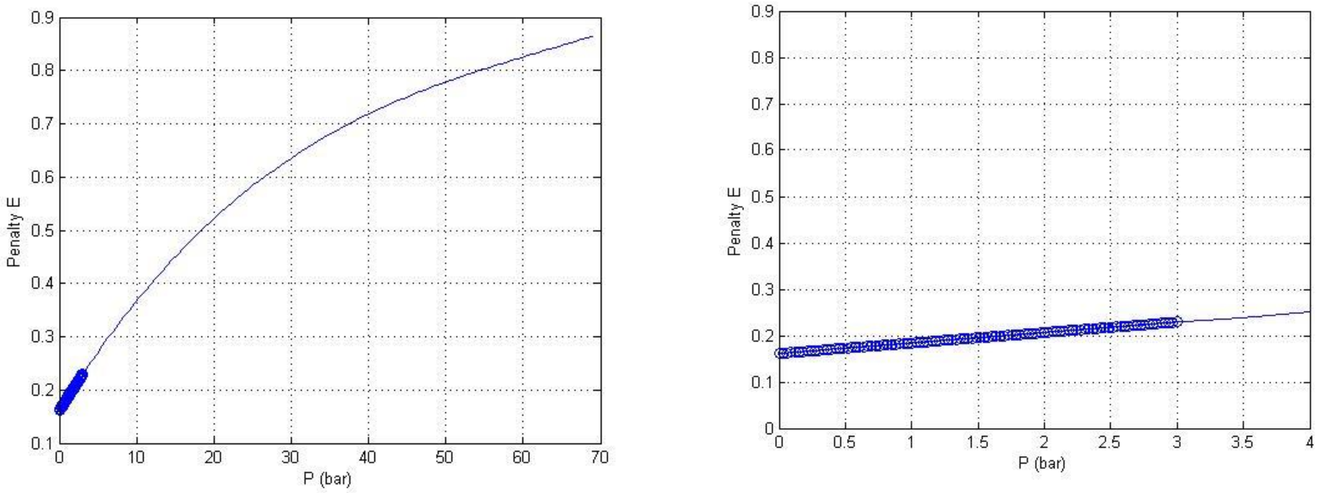


Figure C.1. F&EI pressure penalty E for flammable & combustible liquids calculated from [3].

The operating pressure range does not go beyond 3 bar, so the penalty can be replaced by the linear expression:

$$Y = 0.02254 \cdot P(bar) + 0.1615 \qquad\qquad 0 < P < 3\ bar$$

a) Quantity of Flammable/Unstable Material (liquids or gases in process).

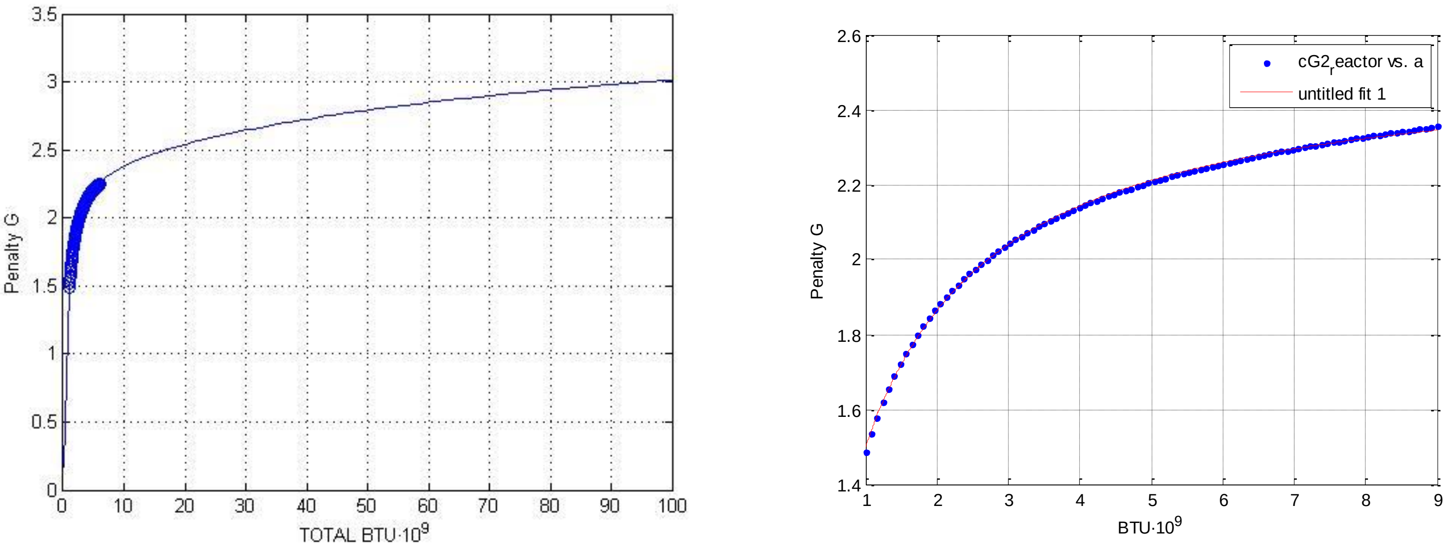


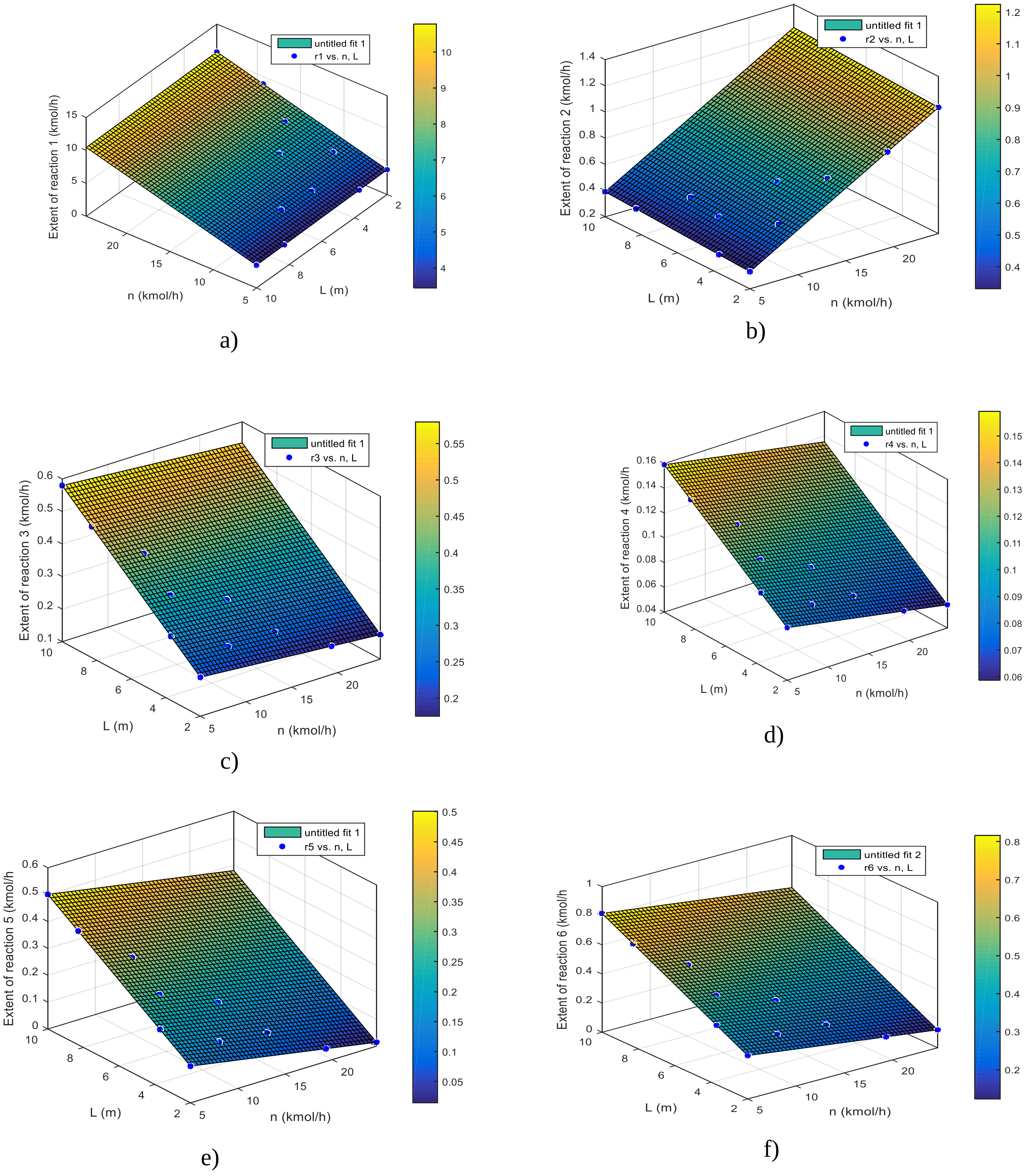
Figure C.2. Quantity of flammable/unstable material penalti G calculated from F&EI [3].

Such as it occurs with pressure, penalty G_2 can be replaced by the equation below in the range indicated:

$$G_2 = \frac{2.509x + 0.01545}{x + 0.6932} \quad 1 < X < 9 \quad BTU \cdot 10^9$$

C.2 Equipment design

a) Extent of reaction



a) b) c) d) e) f)

Figure C.3. Extent of reaction of reactions (kmol/h) fit in function of input E-Benzene molar flow rate (kmol/h) and reactor length(m): a) Extent of reaction 1, b) Extent of reaction 2, c) Extent of reaction 3, d) Extent of reaction 4, e) Extent of reaction 5 and f) Extent of reaction 6.

$$\xi_r\left(\frac{kmol}{h}\right) = p00_r + p10_r \cdot L_{reactor}(m) + p01_r \cdot n_{EB}^{Feed}\left(\frac{kmol}{h}\right)$$

Parameters for extents of reaction fit to equations are shown above, in Table 8.

b) Output reactor temperature

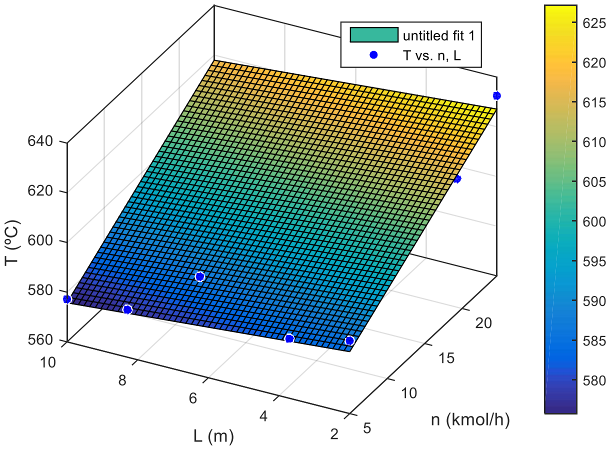


Figure C.4. Output reactor temperature(℃) fit in function of input E-Benzene molar flow rate (kmol/h) and reactor length(m).

$$T_{out}^{reactor}(°C) = 576.5 - 1.148 \cdot L_{reactor}(m) + 2.147 \cdot n_{EB}^{Feed}\left(\frac{kmol}{h}\right)$$

c) Output reactor pressure

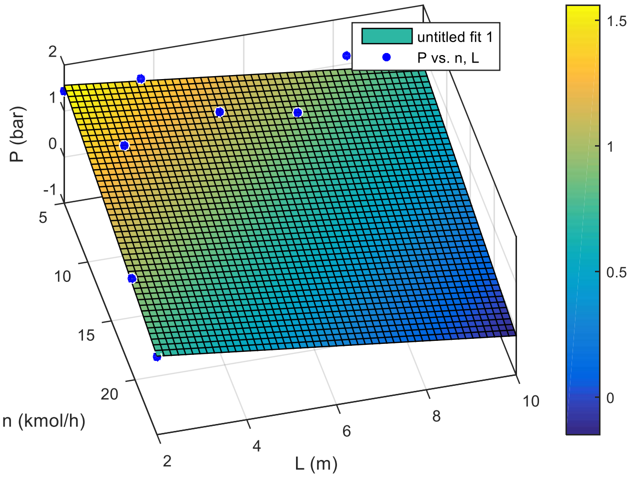


Figure C.5. Output reactor pressure (bar) fit in function of input E-Benzene molar flow rate (kmol/h) and reactor length(m).

$$P_{out}^{reactor}(bar) = 1.991 - 0.1069 \cdot L_{reactor}(m) - 0.04344 \cdot n_{EB}^{Feed}\left(\frac{kmol}{h}\right)$$

C.3 Economic evaluation

a) Purchased cost of fixed tube heat exchanger.

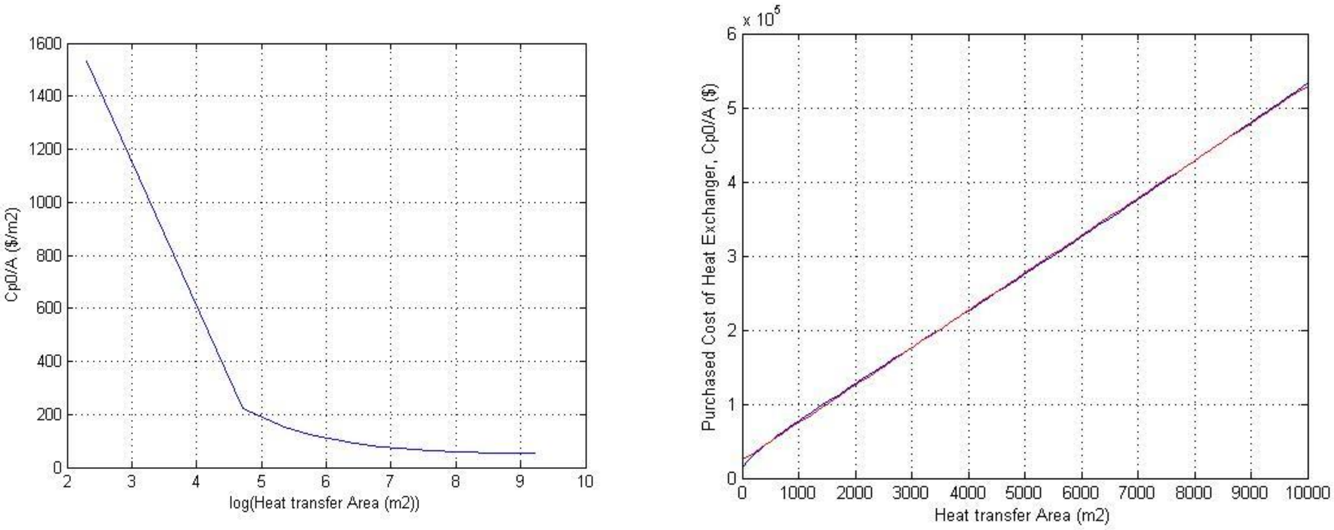


Figure C 6. Heat exchanger cost per unit of heat transfer area (←) and purchased (→), calculated using the correlations presented by Turton et al [6].

The purchased cost of fixed tube heat exchanger can be calculated:

$$Heat\ Exchanger^{fit}_{Cp0}(\$) = 50.56 \cdot \mathrm{A}(\mathrm{m}^2) + \ 2.401 \cdot 10^4 \quad \forall \quad 60 < A < 10000\, m^2$$

$$Heat\ Exchanger^{fit}_{Cp0}(\$) = 94.04 \cdot A(m^2) + 1.433 \cdot 10^4 \quad \forall \quad 10 < A < 60 m^2$$

b) Purchased Cost of Tray

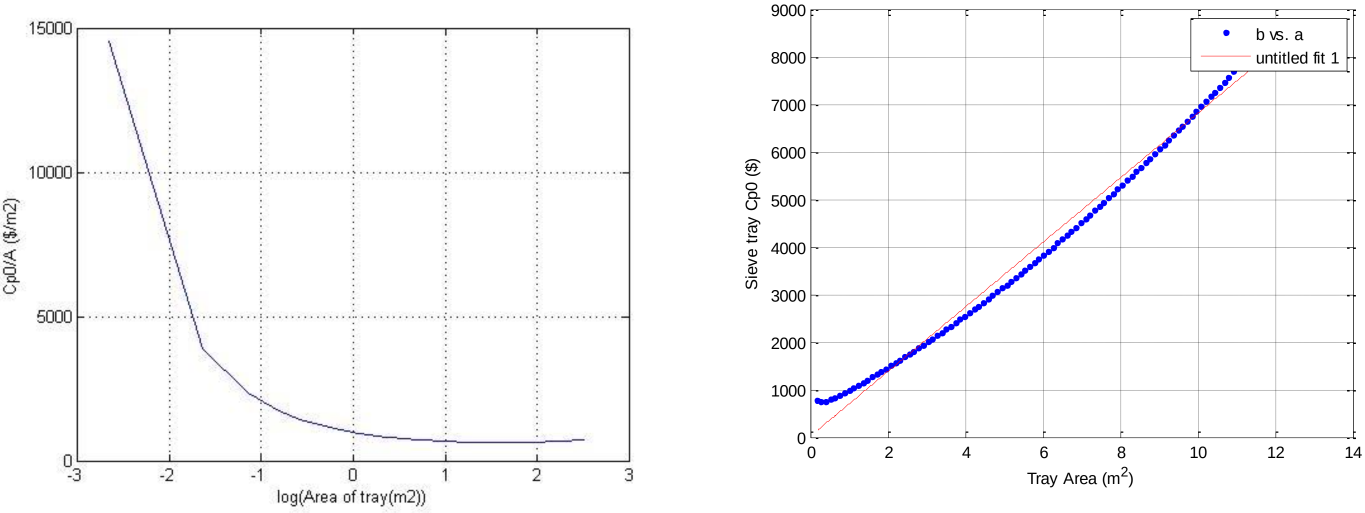


Figure C.7. Sieve tray cost per unit of tray area (←) and purchased (→), calculated using the correlations presented by Turton et al [6].

Between $0.1641 < A_{column} < 12\ m^2$, purchased cost for trays can be calculated:

$$Tray_{Cp0}^{linearised}(\$) = 678.9 \cdot A_{Column}(m^2) + 11.66$$

d) Purchased Cost of Tower

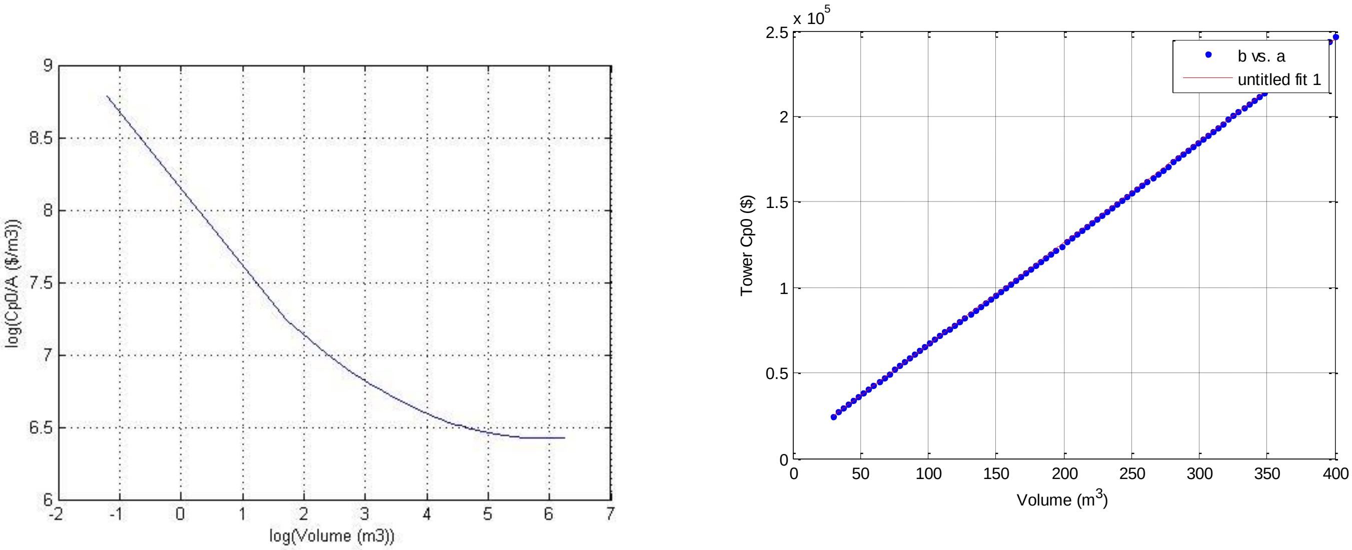


Figure C.8. Tower cost per unit of volumen (←) and purchased (→), calculated using the correlations presented by Turton et al [6].

Beetwen $30 < V_{column} < 400\ m^3$, purchased cost for tower can be calculated:

$$Column_{Cp0}^{linearised}(\$) = 595.7\ \cdot V_{Column}(m^3) + 6762$$

d) Purchased Cost of Vessel

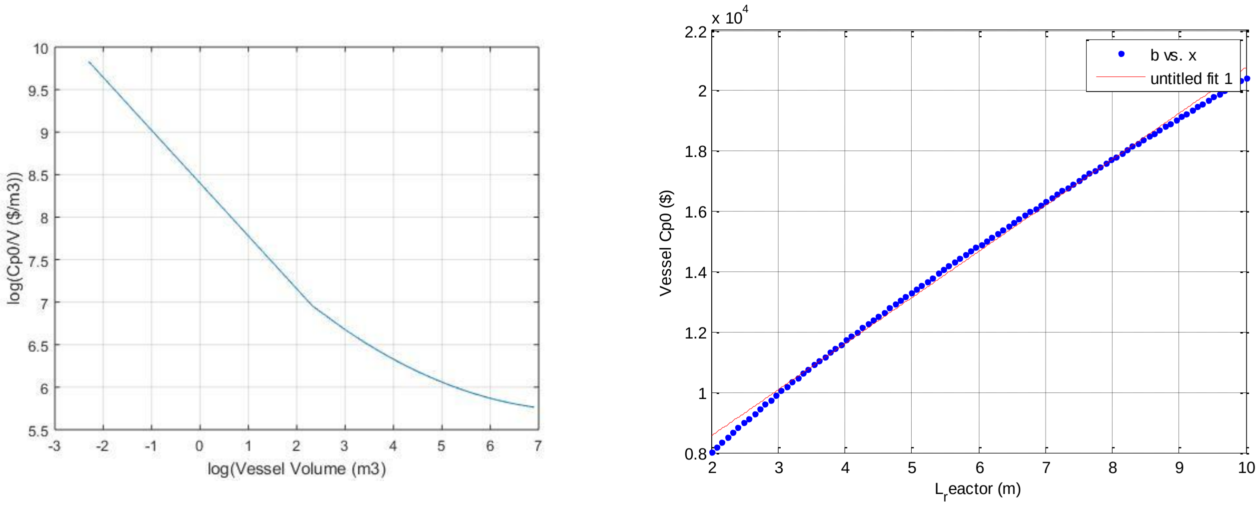


Figure C.9. Vessel cost per unit of volumen (←) and purchased calculated in function of reactor length (→), calculated using the correlations presented by Turton et al [6].

Beetwen $2 < L_{reactor} < 10\ m$, purchased cost for vessel can be calculated:

$$Vessel_{Cp0}^{linearised}(\$) = 1529\ \cdot L_{reactor}(m) + 5477$$

Appendix D. GAMS final styrene production plant model

```
*Option for the display statement to print 8 decimals
option decimals=8;

SETS
I i is organic components /Benz, Tol, EBenz, Sty /
m streams    /1*11/
j components /EB, Sty, H2, Ethy, Tol, CO, CO2, CH4, H2O, Benz /
w reactions  /R1, R2, R3, R4, R5, R6 /
e equiment   /Reactor, Cooler, Column1, Column2/
p purchased CAPEX /Vessel, Cooler, Tower1, Tower2, Tray1, Tray2, Condenser1,
              Condenser2, Reboiler1, Reboiler2 /
R r is Underwood root  /r1*r3/
C c is a column (separation task) /Tol_EBenz, EBenz_Sty/
s secciones de columna /s1, s2/

active_root(c,r) active Underwood root
 alias (i,t);

* Set the active root
 active_root('Tol_EBenz','r2') = YES;
 active_root('EBenz_Sty','r3') = YES;

PARAMETERS
 RECOVERY(c,i)  mole flow rate ratio between distillate to feed stream for component
i in column c
 RECOVERY_LK(c) mole flow rate ratio distillate to feed stream for light key
component in column c
* RECOVERY_BOTTOMS(c,i)  mole flow rate ratio bottoms to feed stream for component i
in column c
 RECOVERY_BOTTOMS_HK(c) mole flow rate ratio bottoms to feed stream for heavy key
component in column c

 LK(c) position for the light key component in column c
 HK(c) position for the heavy key component in column c ;

* Column 1
 LK('Tol_EBenz') = 2;
 HK('Tol_EBenz') = 3;

* Column 2
 LK('EBenz_Sty') = 3;
 HK('EBenz_Sty') = 4;

PARAMETERS
p00(w)  /R1 2.07,     R2  0.104,    R3  0.1411,    R4  0.06923 ,    R5  0.07666 ,
R6  0.2123     /
p10(w)  /R1 -0.04086, R2  0.007523, R3  0.04501,   R4  0.00959 ,    R5  0.045534 ,
R6  0.06483    /
p01(w)  /R1 0.3563,   R2  0.04236,  R3  -0.002272, R4  -0.001204  , R5  -0.006209 ,
R6   -0.008879 /


       factor_3_phase_separator_factor_4(j)    factor which multiply molar balance in
       efluent 4
               /EB 0, Sty 0, H2 1, Ethy  1, Tol  0, CO  1, CO2  1, CH4   1, H2O  0,
       Benz 0/
       factor_3_phase_separator_factor_5(j)    factor which multiply molar balance in
       efluent 5
               /EB 0, Sty 0, H2 0, Ethy  0, Tol  0, CO  0, CO2  0, CH4   0, H2O  1,
       Benz 0/
```

```
       factor_3_phase_separator_factor_6(j)     factor which multiply molar balance in
       efluent 6/EB 1, Sty 1, H2 0, Ethy  0, Tol  1, CO  0, CO2  0, CH4   0, H2O  0,
       Benz 1/
       factor_column1_distillate(j)             factor which multiply molar balance in
       efluent 8 /EB 0.005, Sty 0, H2 0, Ethy  0, Tol  0.995, CO  0, CO2  0, CH4   0,
       H2O  0, Benz 1/
       factor_column1_bottom(j)                 factor which multiply molar balance in
       efluent 9 /EB 0.995, Sty 1, H2 0, Ethy  0, Tol  0.005, CO  0, CO2  0, CH4   0,
       H2O  0, Benz 0/
       factor_column2_distillate(j)             factor which multiply molar balance in
       efluent 10 /EB 0, Sty 0, H2 0, Ethy  0, Tol  0.001, CO  0, CO2  0, CH4   0,
       H2O  0, Benz 0.999/
       factor_column2_bottom(j)                  factor which multiply molar balance
       in efluent 11 /EB 1, Sty 0, H2 0, Ethy  0, Tol  0.999, CO  0, CO2  0, CH4   0,
       H2O  0, Benz 0.001/
       factor_column3_distillate(j)              factor which multiply molar balance
       in efluent 10 /EB 0.997, Sty 0.003, H2 0, Ethy  0, Tol  1, CO  0, CO2  0, CH4
       0, H2O  0, Benz 0/;
factor_column3_bottom(j)                    factor which multiply molar balance in
efluent 11 /EB 0.997, Sty 0.003, H2 0, Ethy  0, Tol  1, CO  0, CO2  0, CH4   0, H2O
0, Benz 0/;

TABLE  alpha(c,i) relative volatility for component i in column c
              Benz          Tol           EBenz          Sty
Tol_EBenz    7.2557262     2.4049244     1.55383517       1
EBenz_Sty    5.3263        2.66089       1.28397          1 ;

TABLE  stoichiometric(w,j)
       EB      Sty      H2   Ethy        Tol      CO     CO2      CH4     H2O      Benz
R1     -1        1       1     0           0       0       0        0       0         0
R2     -1        0       0     1           0       0       0        0       0         1
R3     -1        0      -1     0           1       0       0        1       0         0
R4      0        0       4    -1           0       2       0        0      -2         0
R5      0        0       3     0           0       1       0       -1      -1         0
R6      0        0       1     0           0      -1       1        0      -1         0   ;

* Column 1
 RECOVERY_LK('Tol_EBenz') = 0.995  ;
 RECOVERY_BOTTOMS_HK('Tol_EBenz') = 0.995 ;

* Column 2
 RECOVERY_LK('EBenz_Sty') = 0.997  ;
 RECOVERY_BOTTOMS_HK('EBenz_Sty') = 0.997 ;

    RECOVERY(c,i)$(ord(i) < LK(c) ) = 1;
    RECOVERY(c,i)$(ord(i) = LK(c) ) = RECOVERY_LK(c);
    RECOVERY(c,i)$(ord(i) = HK(c) ) = 1 - RECOVERY_BOTTOMS_HK(c);
    RECOVERY(c,i)$(ord(i) > HK(c) ) = 0;

 display recovery;

POSITIVE VARIABLES
temperature(m)          temperature of each efluent (i)  [°C]
molarFlowComponent(j,m) mole flow rate of each component j in streams m [kmol·h^-1]
pressure(m)             pressure of each efluent(i)      [bar]
reactionExtent(w)       extent of reaction r             [kmol·h^-1]
Length(e)               length of equipments e           [m]

* Columns
 V1(c)    vapor mole flow rate in the enriching section
 V2(c)    vapor mole flow rate in the exhausting section
 L1(c)    liquid mole flow rate in the enriching section
 L2(c)    liquid mole flow rate in the exhausting section
```

```
 F(c)     total mole flow rate in the feed stream
 D(c)     total mole flow rate in the distillate stream
 B(c)     total mole flow rate in the bottom stream
 Fi(c,i) mole flow rate for component i in the feed stream [kmol·h^{-1}]
 Di(c,i) mole flow rate for component i in the distillate stream
 Bi(c,i) mole flow rate for component i in the bottom stream
 root_UW(c,r) Underwood root for a given separation task   ;

VARIABLES
 objfunValue ;

EQUATIONS
* SPECIFIC MOLAR BALANCES IN DISTILLATION COLUMNS
FEED_COLUMN1_EBENZENE
FEED_COLUMN1_STYRENE
FEED_COLUMN1_TOLUENE
FEED_COLUMN1_BENZENE
* COLUMNS_ BALANCES
COMPONENT_MOLE_BALANCE
TOTAL_MOLE_BALANCE
TOP_TOTAL_MOLE_BALANCE
BOTTOM_TOTAL_MOLE_BALANCE
FEED_TOTAL_MOLE_BALANCE
THERMAL_CONDITION_OF_THE_FEED
TOTAL_COMPONENT_RELATION_FEED
TOTAL_COMPONENT_RELATION_DISTILLATE
TOTAL_COMPONENT_RELATION_BOTTOM
UNDERWOOD_1
UNDERWOOD_2
UNDERWOOD_3
COMPONENT_RECOVERY_IN_DISTILLATE
FEED_COLUMN2
TOTAL_FEED_COLUMN2
* MOLAR, ENERGY AND MOMENTUM BALANCES IN EQUIPMENT
INITIAL_TEMPERATURE
INITIAL_PRESSURE
MOLAR_BALANCE_REACTOR
EXTENT_OF_REACTIONS
ENERGY_BALANCE_REACTOR
MOMENTUM_BALANCE_REACTOR
MOLAR_BALANCE_COOLER
ENERGY_BALANCE_COOLER
MOMENTUM_BALANCE_COOLER
MOLAR_BALANCE_THREE_PHASE_SEPARATOR_4
MOLAR_BALANCE_THREE_PHASE_SEPARATOR_5
MOLAR_BALANCE_THREE_PHASE_SEPARATOR_6
ENERGY_BALANCE_THREE_PHASE_SEPARATOR_4
ENERGY_BALANCE_THREE_PHASE_SEPARATOR_5
ENERGY_BALANCE_THREE_PHASE_SEPARATOR_6
MOMENTUM_BALANCE_THREE_PHASE_SEPARATOR_4
MOMENTUM_BALANCE_THREE_PHASE_SEPARATOR_5
MOMENTUM_BALANCE_THREE_PHASE_SEPARATOR_6
MOLAR_BALANCE_PUMP
ENERGY_BALANCE_PUMP
MOMENTUM_BALANCE_PUMP
MOLAR_BALANCE_COLUMN1_DISTILLATE
ENERGY_BALANCE_COLUMN1_DISTILLATE
MOMENTUM_BALANCE_COLUMN1_DISTILLATE
MOLAR_BALANCE_COLUMN1_BOTTOM
ENERGY_BALANCE_COLUMN1_BOTTOM
MOMENTUM_BALANCE_COLUMN1_BOTTOM
MOLAR_BALANCE_COLUMN3_DISTILLATE
ENERGY_BALANCE_COLUMN3_DISTILLATE
```

```
MOMENTUM_BALANCE_COLUMN3_DISTILLATE
MOLAR_BALANCE_COLUMN3_BOTTOM
ENERGY_BALANCE_COLUMN3_BOTTOM
MOMENTUM_BALANCE_COLUMN3_BOTTOM
OBJECTIVE_FUNCTION
INPUT_WATER_REACTOR
MOLAR_LENGTH_CONTRAINT;

* SPECIFIC MOLAR BALANCES IN DISTILLATION COLUMNS
FEED_COLUMN1_EBENZENE..
Fi('Tol_EBenz','EBenz') =E= molarFlowComponent('EB','7') ;

FEED_COLUMN1_STYRENE..
Fi('Tol_EBenz','Sty')   =E= molarFlowComponent('Sty','7') ;

FEED_COLUMN1_TOLUENE..
Fi('Tol_EBenz','Tol')   =E= molarFlowComponent('Tol','7') ;

FEED_COLUMN1_BENZENE..
Fi('Tol_EBenz','Benz')  =E= molarFlowComponent('Benz','7') ;

* COLUMNS
COMPONENT_MOLE_BALANCE(c,i)..
    Fi(c,i) =E= Di(c,i) + Bi(c,i) ;

TOTAL_MOLE_BALANCE(c)..
    F(c) =E= D(c) + B(c) ;

TOP_TOTAL_MOLE_BALANCE(c)..
    V1(c) =E= D(c) + L1(c) ;

BOTTOM_TOTAL_MOLE_BALANCE(c)..
    L2(c) =E= V2(c) + B(c) ;

FEED_TOTAL_MOLE_BALANCE(c)..
    F(c) + L1(c) + V2(c) =E= V1(c) + L2(c) ;

THERMAL_CONDITION_OF_THE_FEED(c)..
    V1(c) =E= V2(c) ;

TOTAL_COMPONENT_RELATION_FEED(c)..
    F(c) =E= sum(i, Fi(c,i)) ;

TOTAL_COMPONENT_RELATION_DISTILLATE(c)..
    D(c) =E= sum(i, Di(c,i)) ;

TOTAL_COMPONENT_RELATION_BOTTOM(c)..
    B(c) =E= sum(i, Bi(c,i)) ;

UNDERWOOD_1(active_root(c,r))..
    sum(i, alpha(c,i) * Fi(c,i) / (alpha(c,i) - root_UW(c,r)) ) =E= V1(c) - V2(c) ;

UNDERWOOD_2(active_root(c,r))..
    sum(i, alpha(c,i) * Di(c,i) /(alpha(c,i) - root_UW(c,r)) ) =L= V1(c) ;

UNDERWOOD_3(active_root(c,r))..
    sum(i, alpha(c,i) * Bi(c,i) / (alpha(c,i) - root_UW(c,r))) =G= -V2(c) ;

* Force component mole flow rate at the at bottoma and distillate according to the
given recovery
COMPONENT_RECOVERY_IN_DISTILLATE(c,i)$(ord(i) <= LK(c) OR ord(i) >= HK(c) )..
    Di(c,i) =E= RECOVERY(c,i)*Fi(c,i) ;
```

```
FEED_COLUMN2(i)..
    Fi('EBenz_Sty',i) =E= Bi('Tol_EBenz',i) ;

TOTAL_FEED_COLUMN2..
    F('EBenz_Sty') =E= B('Tol_EBenz') ;

* MOLAR, ENERGY AND MOMENTUM BALANCES IN EQUIPMENT
* REACTOR  BALANCES
INITIAL_TEMPERATURE..
temperature('1') =E= 700 ;
INITIAL_PRESSURE..
pressure('1') =E= 1.6 ;

MOLAR_BALANCE_REACTOR(j)..
molarFlowComponent(j,'2') =E= molarFlowComponent(j,'1') + sum(w, stoichiometric(w,j)
* reactionExtent(w) ) ;

EXTENT_OF_REACTIONS(w)..
reactionExtent(w) =E= p00(w) + p10(w) * Length('reactor') +  p01(w) *
molarFlowComponent('EB','1') ;

ENERGY_BALANCE_REACTOR..
temperature('2') =E= 576.5 - 1.148 * Length('reactor') + 2.147 *
molarFlowComponent('EB','1') ;

MOMENTUM_BALANCE_REACTOR..
pressure('2') =E= 1.991 - 0.1069 * Length('reactor') - 0.04344 *
molarFlowComponent('EB','1') ;

*COOLER BALANCES
MOLAR_BALANCE_COOLER(j)..
molarFlowComponent(j,'2') =E= molarFlowComponent(j,'3') ;

ENERGY_BALANCE_COOLER..
temperature('3') =E= 30 ;

MOMENTUM_BALANCE_COOLER..
pressure('3') =E= pressure('2')-0.1 ;

*THREE PHASE SEPARATOR BALANCES
MOLAR_BALANCE_THREE_PHASE_SEPARATOR_4(j)..
molarFlowComponent(j,'4') =E= molarFlowComponent(j,'3') *
factor_3_phase_separator_factor_4(j) ;

MOLAR_BALANCE_THREE_PHASE_SEPARATOR_5(j)..
molarFlowComponent(j,'5') =E= molarFlowComponent(j,'3') *
factor_3_phase_separator_factor_5(j) ;

MOLAR_BALANCE_THREE_PHASE_SEPARATOR_6(j)..
molarFlowComponent(j,'6') =E= molarFlowComponent(j,'3') *
factor_3_phase_separator_factor_6(j) ;

ENERGY_BALANCE_THREE_PHASE_SEPARATOR_4..
temperature('4') =E= temperature('3') ;

ENERGY_BALANCE_THREE_PHASE_SEPARATOR_5..
temperature('5') =E= temperature('3') ;

ENERGY_BALANCE_THREE_PHASE_SEPARATOR_6..
temperature('6') =E= temperature('3') ;

MOMENTUM_BALANCE_THREE_PHASE_SEPARATOR_4..
pressure('4') =E= pressure('3') ;
```

```
MOMENTUM_BALANCE_THREE_PHASE_SEPARATOR_5..
pressure('5') =E= pressure('3') ;


MOMENTUM_BALANCE_THREE_PHASE_SEPARATOR_6..
pressure('6') =E= pressure('3') ;

*PUMP BALANCES
MOLAR_BALANCE_PUMP(j)..
molarFlowComponent(j,'7') =E= molarFlowComponent(j,'6') ;

ENERGY_BALANCE_PUMP..
temperature('7') =E= 30 ;

MOMENTUM_BALANCE_PUMP..
pressure('7') =E= 1.026 ;

* COLUMN 1 BALANCES
MOLAR_BALANCE_COLUMN1_DISTILLATE(j)..
molarFlowComponent(j,'8') =E= molarFlowComponent(j,'7') *
factor_column1_distillate(j) ;

ENERGY_BALANCE_COLUMN1_DISTILLATE..
temperature('8') =E= 93.02 ;

MOMENTUM_BALANCE_COLUMN1_DISTILLATE..
pressure('8') =E= 0.932 ;

MOLAR_BALANCE_COLUMN1_BOTTOM(j)..
molarFlowComponent(j,'9') =E= molarFlowComponent(j,'7') * factor_column1_bottom(j) ;

ENERGY_BALANCE_COLUMN1_BOTTOM..
temperature('9') =E= 117.4 ;

MOMENTUM_BALANCE_COLUMN1_BOTTOM..
pressure('9') =E= 1.026 ;


* COLUMN 2 BALANCES
MOLAR_BALANCE_COLUMN3_DISTILLATE(j)..
molarFlowComponent(j,'10') =E= molarFlowComponent(j,'9') *
factor_column3_distillate(j) ;

ENERGY_BALANCE_COLUMN3_DISTILLATE..
temperature('10') =E= 89.9 ;

MOMENTUM_BALANCE_COLUMN3_DISTILLATE..
pressure('10') =E= 0.2464 ;

MOLAR_BALANCE_COLUMN3_BOTTOM(j)..
molarFlowComponent(j,'11') =E= molarFlowComponent(j,'9') * factor_column3_bottom(j)
;

ENERGY_BALANCE_COLUMN3_BOTTOM..
temperature('11') =E= 122.4 ;

MOMENTUM_BALANCE_COLUMN3_BOTTOM..
pressure('11') =E= 0.5264 ;

OBJECTIVE_FUNCTION..
         objfunValue =E= V1('Tol_EBenz') ;
```

```
INPUT_WATER_REACTOR..
molarFlowComponent('H2O','1') =E= (106.17 * 2 / 18.01528 ) *
molarFlowComponent('EB','1') ;

MOLAR_LENGTH_CONTRAINT..
 Length('Reactor') =L= -0.4 * molarFlowComponent('EB','1') + 10   ;

model oneColum / all / ;

loop( (c,r,i)$(ord(i) = ord(r)),
             root_UW.up(c,r) = alpha(c,i)  - 0.01;
      );

loop( (c,r,i)$(ord(i) = ord(r)+1 ),
             root_UW.lo(c,r) = alpha(c,i)  + 0.01;
   );

molarFlowComponent.fx('Sty','1')= 0;
molarFlowComponent.fx('H2','1')= 0 ;
molarFlowComponent.fx('Ethy','1')= 0 ;
molarFlowComponent.fx('Tol','1')=0;
molarFlowComponent.fx('CO','1')=0;
molarFlowComponent.fx('CO2','1')=0;
molarFlowComponent.fx('CH4','1')=0;
molarFlowComponent.fx('Benz','1')=0;

molarFlowComponent.up('EB','1')=30  ;
molarFlowComponent.lo('EB','1')=5   ;
Length.lo('reactor') = 2  ;
Length.up('reactor') = 10 ;

display root_UW.up,root_UW.lo;
root_UW.l(c,r) = (root_UW.lo(c,r) + root_UW.up(c,r))/2;

solve oneColum using NLP min objfunValue  ;

display Fi.l, Di.l, Bi.l ;

PARAMETER
Nmin(c)   minimum number of stages
SepPisos  trays separation  [m] ;
Nmin(c) = sum((i,t)$(ord(i) = LK(c) and ord(t) = HK(c)),
          log(  RECOVERY_LK(c)         / ( 1-RECOVERY_LK(c) )
              * RECOVERY_BOTTOMS_HK(c) / ( 1-RECOVERY_BOTTOMS_HK(c) ) )
              / log( alpha(c,i) / alpha(c,t) )
               );

SepPisos = 0.6096;

display Nmin;
POSITIVE VARIABLES
         a    number of times above minimun reflux (ej 1.2 times at least)
         Rmin    Minimum reflux
         NP(c)    Number of real stages
         X(c)     parameter
         H(c,s)   height of the column
         NS(c,s)   Pisos en cada seccion;
         a.lo = 1.01;
         NP.lo(c) = Nmin(c) + 0.0001;
         X.lo(c) = 0.00000001;

EQUATIONS
         pisos01, Pisos02, pisos03, pisos04, pisos05, pisos06, pisos07;
```

Initial mole flow rate of water and ethylbenzene imposed in problem statemen and constraint (C.1) studied in section 3.2.1.3.

Upper and lower bound on reactor variables studied in section 3.2.1.2

```
pisos01(c)..  (NP(c) - Nmin(c))/(NP(c) + 1) =E=
               1 - exp(
                        ( 1+ 54.4*X(c))/(11+117.2*X(c)) * (X(c)-1)/sqrt(X(c))) ;

pisos02(c).. X(c) =E= Rmin(c)*(a-1)/(a*Rmin(c)+1) ;

pisos03(c)..  Rmin(c)*D(c) =E= L1(c);

pisos04(c)..     NS(c,'s1') * (sum(i$(ord(i) = HK(c)), Fi(c,i))  )=E=
NS(c,'s2')*(sum(i$(ord(i) = LK(c)), Fi(c,i)) * D(c)/(B(c)+ 1e-6))**0.206;

pisos05(c)..     NP(c) =E= NS(c,'s1') + NS(c,'s2');

pisos06(c)..  H(c,'s1') =E= SepPisos*(NS(c,'s1') - 1) + 1.5;
pisos07(c)..  H(c,'s2') =E= SepPisos*(NS(c,'s2')) + 1.5;

SCALAR
         rol "densidad media del liquido kg/m3" /895.222011789494 /
         rov " average vapor density kg/m3" /38/
         rol2 "average liquid density kg/m3" /811.003743700133/
         rov2 " average vapor density kg/m3 " /35/
         Mv  average molecular weight (feed) /102.056346288162 /


POSITIVE VARIABLE  AreaColumn(c,s);

EQUATIONS
         ec01, ec02 ;
ec01(c)..       AreaColumn(c,'s1') =E= Mv/(rol*rov)**0.5* 1/0.7 * 1/439 * 1/0.8 *
(V1(c) + L1(c)*(a-1));
ec02(c)..       AreaColumn(c,'s2') =E= Mv/(rol*rov)**0.5* 1/0.7 * 1/439 * 1/0.8 *
(V2(c) + L1(c)*(a-1));

PARAMETERS
DHvap(i)  "kJ/kmol"
 / Benz    30970.600197494
   Tol     333358.5514600167
   EBenz   35754.7740996288
   Sty     37228.6166554207
 /;

POSITIVE VARIABLES
         Qreb(c)     kW
         Qcond(c)    kW ;

EQUATIONS
         heat01, heat02;
heat01(c)..
    Qcond(c)  * D(c)*(V1(c)+ L1(c)*(a-1))/3600 =E= sum(i, Di(c,i)*DHvap(i)) ;

heat02(c)..
    Qreb(c)  * B(c)*(V2(c)+ L1(c)*(a-1))/3600  =E= sum(i, Bi(c,i)*DHvap(i)) ;

*Area_column_s1
AreaColumn.lo('Tol_EBenz','s1')= 0.1642 ;
AreaColumn.lo('EBenz_Sty','s1')= 0.1642 ;
AreaColumn.up('Tol_EBenz','s1')= 12;
AreaColumn.up('EBenz_Sty','s1')= 12;

*Area_column_s2
AreaColumn.lo('Tol_EBenz','s2')= 0.1641 ;
AreaColumn.lo('EBenz_Sty','s2')= 0.1641 ;
```

```
AreaColumn.up('Tol_EBenz','s2')= 12 ;
AreaColumn.up('EBenz_Sty','s2')= 12 ;

PARAMETERS
         DTMLCond(c)   °C   /Tol_EBenz 42.055 , EBenz_Sty 87.9052 /
         DTMLReb(c)    °C   /Tol_EBenz 21.5   , EBenz_Sty  37.9/

SCALAR
         Ureb     "kW/m2/K"  /0.8/
         Ucond    "kW/m2/K"  /0.8/ ;
POSITIVE VARIABLES
      AreaCond(c)
      AreaReb(c) ;

EQUATIONS
         Cambcal01, Cambcal02;
Cambcal01(c)..    Qreb(c)  =E= Ureb*AreaReb(c)*DTMLReb(c);
Cambcal02(c)..    QCond(c) =E= Ucond*AreaCond(c)*DTMLCond(c);


* SAFETY
PARAMETER
deltaCombustionComponent(j)   heat of combustion of components j [BTU·lb^-1]
/EB 17.6e3, Sty 17.4e3, H2  51.6e3, Ethy 20.8e3,Tol 17.4e3,
CO 4.3e3,CO2 0, CH4 21.5e3, H2O 0, Benz 17.3e3 /


molecularWeight(j)     molecular weight of components j [kg·kmol^-1]
/EB  106 ,Sty    104.15, H2   2 ,Ethy   25.05 , Tol   92.14,
CO  28.01,CO2  44.01,CH4  16.04, H2O  18 , Benz   78.11/
heatCapacity(j)        heat capacity of components j   [kJ·kg^-1·°C^-1]
/EB 2.248,Sty   2.172,H2    14.51, Ethy  2.386, Tol    2.161,
CO 1.097, CO2 0.7766, CH4 3.216, H2O  3.3137 ,Benz  2.083/

DensityOrganicComponent(I) density of organic components in columns [kg·m3^-1]
/Benz   876, Tol    867, Ebenz  866, Sty    909 / ;

POSITIVE VARIABLES
Area(e)                  area of equipment e    [m2]
Volume(e)                volume of equipment e  [m3]
column1Diameter          diameter of column 1   [m]
column2Diameter          diameter of column 2   [m]
column3Diameter          diameter of column 3   [m]
coolerQ                  heat dissipated by cooler [kJ·h^-1]
coolerdeltaTml           Logarithmic mean temperature difference in cooler [°C]
massFlowComponent(j,m) mass flowrate of each component j in each efluent i [kg·h^-1]

FireExplosionIndex        fire & explosion index
penaltyE2                 penalty due to relief pressure
pentalyG2                 penalty due to quantity of flammable or unstable material
penaltyYoperation              penalty due to operating pressure in equipments [bar]
penaltyYrelief                 penalty due to realive pressure in equipments   [bar]
pressureOperationEquipment     pressure operation  in equipments  [bar]
totalBTUinProcess              Total BTU in process  [BTU]
concentrationComponent(j,e)    concentration component j in equipment e (lb·m3^-1)
averageMassFlowComponent(j,e) average molar flow rate of each component j in each
equipment e [lb·h^-1]
averageMolarFlowComponent(j,e)  average molar flow rate of each component j in each
equipment e [kmol·h^-1]
averageReactionExtent(w)        average extent of reaction r [kmol·h^-1]
density(e)                      density in each equipmente e [kg·m3^-1]
averagePressure(e)              average pressure of each equipment [Pa]
averageMolecularWeight(e)      average molecular weight in each equipment [g·mol^-1]
```

```
averageTemperature(e)           average temperature in each equipment [K]
massFraction(j,e)               mass fraction of each component j in the equipment e
volumetricFlow(e)             average voluntric flow of each equipment e [m3·h^-1]
MassFlow                        total mass flow
volumetricFlowComponent(m)      volumetric flow rate os each stream i [m3·h^-1]
totalMolarFlow(m)               total molar flow rate of each stream i [kmol·h^-1]
volumetricFlowVapor             vapor volumetric flow rate    [m^3·h^-1]
volumetricFlowOrganic           organic volumetric flow rate [m^3·h^-1]
volumetricFlowWater             water volumetric flow rate    [m^3·h^-1]
massFractionOrganic3(I)
density3
density9
massFractionOrganic9(i) ;

SCALARS
reactorDiameter          reactor diameter [m]  /1.95/
CoolerSection            cooler  section  [m2] /0.1963/
coolerU         overall coeficient of heat transfer [kJ·h^-1·°C^-1]  /2880/
heaterU        overall coeficient of heat transfer (reboiler) [kJ·h^-1·°C^-1]
/2880/
coolerTubes               number of tubes in the cooler  /15/
trayspacingColumn         spacing between trays in columns [m]  /0.6096/
Rgases                    constant of ideal gases   [J·mol^-1·K^-1]  /8.31/
spillDuration             duration of spill [h]  /0.1666667/
inc_T_cond1       logarithmic mean temperature difference in condenser 1 /43.1069 /
inc_T_cond2       logarithmic mean temperature difference in condenser 2 / 35.3143 /
inc_T_cond3       logarithmic mean temperature difference in condenser 3 / 54.7479 /
inc_T_reb1        logarithmic mean temperature difference in reboiler  1 / 42.6    /
inc_T_reb2         logarithmic mean temperature difference in reboiler  2 / 52.2   /
inc_T_reb3         logarithmic mean temperature difference in reboiler  3 / 37.9   /
YEAR               hours in a year each equipment work [hr·yr^-1]    /8000/
WATER           water cost (utility)  [$·kW^-1·h^-1]              / 0.0013 /
STEAM           steam cost (utility)  [$·kW^-1·h^-1]              / 0.0506 /
annualizationFactor    annualization factor                       /0.1874   /
Rgas            ideal gases constant    [kJ·kmol^-1·K^-1]         /8.31    /

EQUATIONS
*SAFETY
DOWS_FIRE_EXPLOSION_INDEX
PENALTY_E2
PENALTY_Y_OPERATION_E2
PENALTY_Y_RELIEF_E2
PRESSURE_OPERATION_EQUIPMENT_E2_REACTOR
PRESSURE_OPERATION_EQUIPMENT_E2_COOLER
PRESSURE_OPERATION_EQUIPMENT_E2_COLUMN_1
PRESSURE_OPERATION_EQUIPMENT_E2_COLUMN_2
PENALTY_G2
TOTAL_BTU_IN_PROCESS_REACTOR_VOLUME
TOTAL_BTU_IN_PROCESS_COOLER_VOLUME
TOTAL_BTU_IN_PROCESS_COLUMN1_VOLUME
TOTAL_BTU_IN_PROCESS_COLUMN2_VOLUME
TOTAL_BTU_IN_PROCESS_REACTOR_SPILL
TOTAL_BTU_IN_PROCESS_COOLER_SPILL
TOTAL_BTU_IN_PROCESS_COLUMN1_SPILL
TOTAL_BTU_IN_PROCESS_COLUMN2_SPILL
MASS_FLOW_COMPONENT;

*SAFETY
DOWS_FIRE_EXPLOSION_INDEX..
FireExplosionIndex =E=  128.52 + 40.8 * (penaltyE2 + pentalyG2) ;

PENALTY_E2..
penaltyE2 * penaltyYrelief =E= 1.2 * POWER(penaltyYoperation,2) ;
```

```
PENALTY_Y_OPERATION_E2..
penaltyYoperation =E= 0.02254 * pressureOperationEquipment + 0.1615 ;

PENALTY_Y_RELIEF_E2..
penaltyYrelief =E= 0.02254 * (pressureOperationEquipment * 1.2) + 0.1615 ;

PRESSURE_OPERATION_EQUIPMENT_E2_REACTOR..
pressureOperationEquipment =G= ( pressure('1') + pressure('2') ) / 2 ;

PRESSURE_OPERATION_EQUIPMENT_E2_COOLER..
pressureOperationEquipment =G= ( pressure('2') + pressure('3') ) / 2 ;

PRESSURE_OPERATION_EQUIPMENT_E2_COLUMN_1..
pressureOperationEquipment =G= pressure('7') ;

PRESSURE_OPERATION_EQUIPMENT_E2_COLUMN_2..
pressureOperationEquipment =G= pressure('9') ;

PENALTY_G2..
pentalyG2 * (totalBTUinProcess *1e-9 + 0.6932) =E=  (2.509 * totalBTUinProcess*1e-9
+ 0.01545) ;

TOTAL_BTU_IN_PROCESS_REACTOR_VOLUME..
totalBTUinProcess =G= Volume('Reactor') * sum(j, concentrationComponent(j,'Reactor')
*  deltaCombustionComponent(j) ) ;


TOTAL_BTU_IN_PROCESS_COOLER_VOLUME..
totalBTUinProcess =G= Volume('Cooler') * sum(j, concentrationComponent(j,'Cooler') *
deltaCombustionComponent(j) ) ;

TOTAL_BTU_IN_PROCESS_COLUMN1_VOLUME..
totalBTUinProcess =G= Volume('Column1') * sum(j, concentrationComponent(j,'Column1')
* deltaCombustionComponent(j) ) ;

TOTAL_BTU_IN_PROCESS_COLUMN2_VOLUME..
totalBTUinProcess =G= Volume('Column2') * sum(j, concentrationComponent(j,'Column2')
* deltaCombustionComponent(j) ) ;

TOTAL_BTU_IN_PROCESS_REACTOR_SPILL..
totalBTUinProcess =G=   sum(j, deltaCombustionComponent(j) *
massFlowComponent(j,'1') * 2.20462 ) * spillDuration ;

TOTAL_BTU_IN_PROCESS_COOLER_SPILL..
totalBTUinProcess =G=   sum(j, deltaCombustionComponent(j) *
massFlowComponent(j,'2') * 2.20462 ) * spillDuration ;

TOTAL_BTU_IN_PROCESS_COLUMN1_SPILL..
totalBTUinProcess =G=   sum(j, deltaCombustionComponent(j) *
massFlowComponent(j,'7') * 2.20462 ) * spillDuration ;

TOTAL_BTU_IN_PROCESS_COLUMN2_SPILL..
totalBTUinProcess =G=   sum(j, deltaCombustionComponent(j) *
massFlowComponent(j,'9') * 2.20462 ) * spillDuration ;


* CONCENTRATION OF COMPONENT J IN EQUIPMENT
EQUATIONS
CONCENTRATION_COMPONENT_EQUIPMENT
MASS_FLOW_COMPONENT_REACTOR
MASS_FLOW_COMPONENT_COOLER
MASS_FRACTION_ORGANIC_EBENZ_STREAM3
```

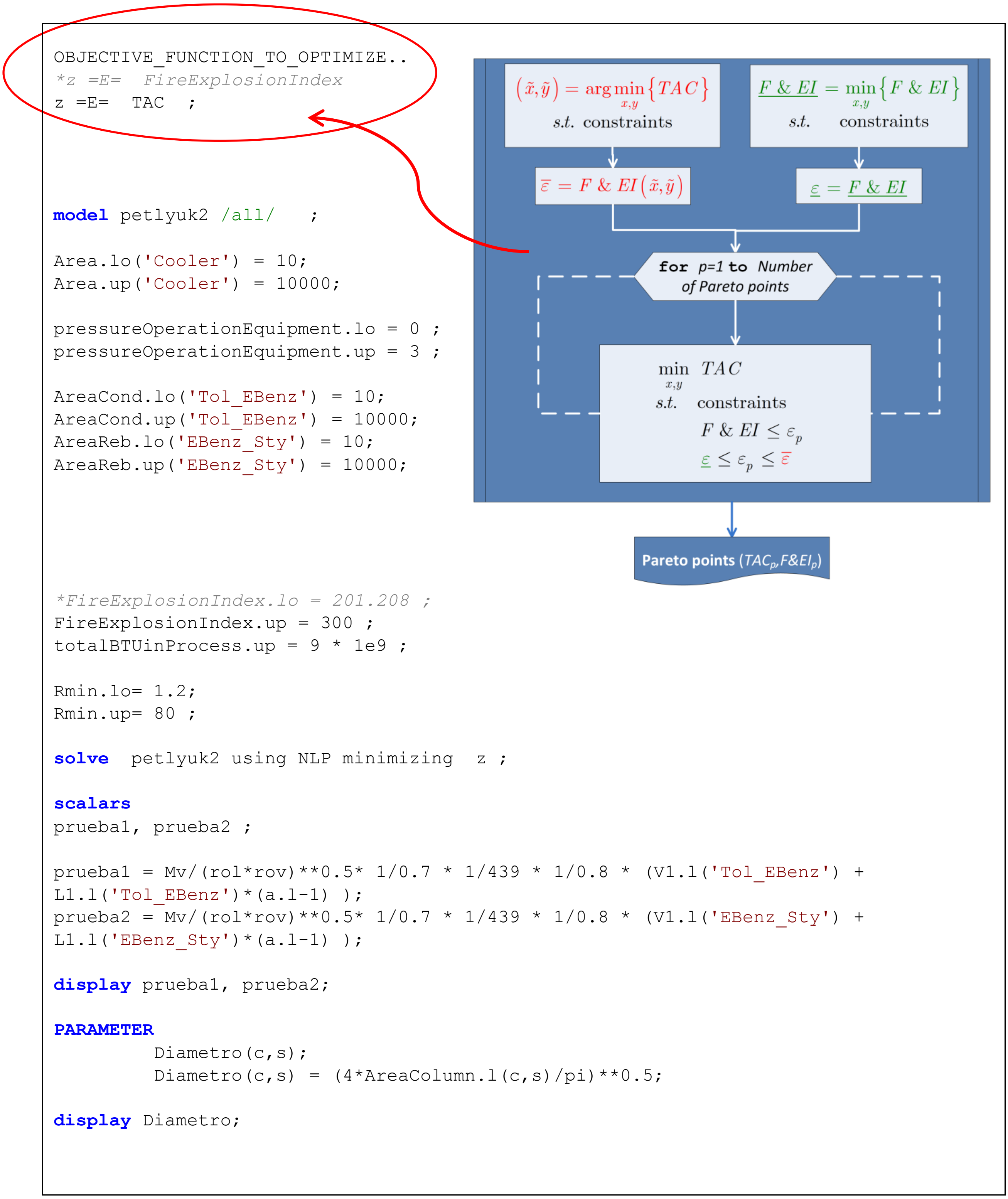
```
MASS_FRACTION_ORGANIC_STY_STREAM3
MASS_FRACTION_ORGANIC_TOL_STREAM3
MASS_FRACTION_ORGANIC_BENZ_STREAM3
DENSITY_STREAM_3
MASS_FLOW_COMPONENT_COLUMN1
MASS_FLOW_COMPONENT_COLUMN2
VOLUMETRIC_FLOW_REACTOR
TOTAL_MOLAR_FLOW
VOLUMETRIC_FLOW_COOLER
VOLUMETRIC_FLOW_COLUMN1
VOLUMETRIC_FLOW_COLUMN2 ;

CONCENTRATION_COMPONENT_EQUIPMENT(j,e)..
concentrationComponent(j,e) * volumetricFlow(e)=E= averageMassFlowComponent(j,e) ;

MASS_FLOW_COMPONENT_REACTOR(j)..
averageMassFlowComponent(j,'Reactor') =E= massFlowComponent(j,'1') * 2.20462 ;

MASS_FLOW_COMPONENT_COOLER(j)..
averageMassFlowComponent(j,'Cooler') =E= massFlowComponent(j,'2') * 2.20462 ;

MASS_FLOW_COMPONENT_COLUMN1(j)..
averageMassFlowComponent(j,'Column1') =E= massFlowComponent(j,'7') * 2.20462 ;

MASS_FLOW_COMPONENT_COLUMN2(j)..
averageMassFlowComponent(j,'Column2') =E= massFlowComponent(j,'9') * 2.20462 ;



* VOLUMETRIC FLOW
VOLUMETRIC_FLOW_REACTOR..
volumetricFlow('Reactor') * pressure('1') * 1e5 =E=  totalMolarFlow('1')* Rgas *
(temperature('1') + 273 ) * 1e3  ;

TOTAL_MOLAR_FLOW(m)..
totalMolarFlow(m) =E= sum(j, molarFlowComponent(j,m) ) ;

VOLUMETRIC_FLOW_COOLER..
volumetricFlow('Cooler') * pressure('2')*1e5 =E= totalMolarFlow('2') * Rgas * ( 273
+ temperature('2') )  * 1e3 ;


MASS_FRACTION_ORGANIC_EBENZ_STREAM3..
massFractionOrganic3('Ebenz') * ( massFlowComponent('EB','3') +
massFlowComponent('Sty','3')  + massFlowComponent('Tol','3') +
massFlowComponent('Benz','3') ) =E= massFlowComponent('EB','3') ;

MASS_FRACTION_ORGANIC_STY_STREAM3..
massFractionOrganic3('Sty') * ( massFlowComponent('EB','3') +
massFlowComponent('Sty','3')  + massFlowComponent('Tol','3') +
massFlowComponent('Benz','3') ) =E= massFlowComponent('STY','3') ;

MASS_FRACTION_ORGANIC_TOL_STREAM3..
massFractionOrganic3('Tol') * ( massFlowComponent('EB','3') +
massFlowComponent('Sty','3')  + massFlowComponent('Tol','3') +
massFlowComponent('Benz','3') ) =E= massFlowComponent('Tol','3') ;

MASS_FRACTION_ORGANIC_BENZ_STREAM3..
massFractionOrganic3('Benz') * ( massFlowComponent('EB','3') +
massFlowComponent('Sty','3')  + massFlowComponent('Tol','3') +
massFlowComponent('Benz','3') ) =E= massFlowComponent('Benz','3') ;

DENSITY_STREAM_3..
```

```
density3   =E=  sum (i,   DensityOrganicComponent(i) * massFractionOrganic3(i) ) ;

PARAMETER
M1 “average molecular weigh column 1 kg/kmol”   / 880.672886 /
d1 “average density column 1 kg/m3”             / 103.22577  /
M2 “average molecular weigh column 2 kg/kmol”   / 802.878038 /
d2 “average density column 2 kg/m3”             / 104.110256 / ;

VOLUMETRIC_FLOW_COLUMN1..
volumetricFlow('Column1') =E= sum(j,molarFlowComponent(j, '7')) * M1 / d1  ;
VOLUMETRIC_FLOW_COLUMN2..
volumetricFlow('Column2') =E= sum(j,molarFlowComponent(j, '9')) * M2 / d2  ;

POSITIVE VARIABLE
AT1    Cooler inlet difference temperature  [°C]
AT2    Cooler outlet difference temperature [°C]

SCALAR
coolerDiameter cooler diameter [m];
coolerDiameter= 0.05 * 20    ;

EQUATIONS
* EQUIPMENT SIZE
REACTOR_VOLUME
REACTOR_AREA
COOLER_VOLUME
COOLER_AREA
COOLER_Q
MASS_FLOW_COMPONENT
COOLER_DELTA_TML
COOLER_DELTA_TML_IN
COOLER_DELTA_TML_OUT
COOLER_LENGTH
COLUMN1_VOLUME
COLUMN1_AREA
COLUMN2_VOLUME
COLUMN2_AREA
COLUMN1_LENGTH
COLUMN2_LENGTH ;

REACTOR_VOLUME..
Volume('Reactor') =E= Area('Reactor') * Length('Reactor');

REACTOR_AREA..
Area('Reactor') =E= pi * POWER(reactorDiameter,2)/4 ;

COOLER_VOLUME..
Volume('Cooler') =E= pi * POWER( coolerDiameter, 2 ) * Length('Cooler') ;

COOLER_AREA..
Area('Cooler') * (coolerU * coolerdeltaTml)  =E= coolerQ ;

COOLER_Q..
coolerQ =E=  sum(j, massFlowComponent(j,'2') * heatCapacity(j) ) * (
temperature('2') - temperature('3') ) ;

MASS_FLOW_COMPONENT(j,m)..
massFlowComponent(j,m) =E= molarFlowComponent(j,m) *  molecularWeight(j) ;

COOLER_DELTA_TML_IN..
 AT1 =E= temperature('2') - 25 ;

COOLER_DELTA_TML_OUT..
```

```
 AT2 =E= temperature('3') - 20 ;

COOLER_DELTA_TML..
coolerdeltaTml =E= ( 0.5 * AT1 * AT2 * ( AT1 + AT2 ) ) ** (1/3) ;

COOLER_LENGTH..
Length('Cooler') * pi * coolerDiameter  =E= Area('Cooler') ;

COLUMN1_VOLUME..
Volume('Column1') =E= Area('Column1') * Length('Column1') ;

COLUMN1_AREA..
Area('Column1') =E= AreaColumn('Tol_EBenz','s1') ;

COLUMN1_LENGTH..
Length('Column1') =E= H('Tol_EBenz','s1') +  H('Tol_EBenz','s2') ;

COLUMN2_VOLUME..
Volume('Column2') =E= Area('Column2') * Length('Column2') ;

COLUMN2_AREA..
Area('Column2') =E= AreaColumn('EBenz_Sty','s1') ;

COLUMN2_LENGTH..
Length('Column2') =E= H('EBenz_Sty','s1') +  H('EBenz_Sty','s2') ;

* ECONOMICS
SCALARS
CatalystPrice  Catalyst price [$·yr^-1]        /10/
catalystDensity catalyst density [kg·m^-3]     /2350/  ;

PARAMETERS
UpdateFactor(p)  update factor applied to bare module cost
/Vessel  1.4511, Cooler  1.4511, Tower1 1.4511, Tower2 1.4511, Tray1  34.8264,
Tray2  43.5330, Condenser1  1.4511, Condenser2  1.4511, Reboiler1  1.4511,
Reboiler2  1.4511/

B1(p)  bare module factor FBM = B1 + B2 * Fm * Fp
/Vessel  1.49, Cooler  1.63, Tower1      2.25, Tower2      2.25, Tray1   1,
Tray2        1, Condenser1  1.63, Condenser2  1.63, Reboiler1  1.63, Reboiler2
1.63/

B2(p)  bare module factor FBM = B1 + B2 * Fm * Fp
/Vessel  1.52, Cooler  1.66, Tower1      1.82, Tower2      1.82, Tray1  1, Tray2
1,
Condenser1  1.66, Condenser2  1.66, Reboiler1  1.66, Reboiler2  1.66/

Fm(p)  bare module factor FBM = B1 + B2 * Fm * Fp
/Vessel  1, Cooler  1, Tower1     1, Tower2     1, Tray1  1, Tray2        1,
Condenser1  1, Condenser2  1, Reboiler1  1, Reboiler2  1/

Fp(p)  bare module factor FBM = B1 + B2 * Fm * Fp
/Vessel  1, Cooler  1.3, Tower1      1, Tower2      1, Tray1  1, Tray2        1,
Condenser1  1.3, Condenser2  1.3, Reboiler1  1.3, Reboiler2  1.3 / ;

POSITIVE VARIABLES
TAC                           total annualised cost [MM$·year^-1]
CAPEX                         total capital expediture [$]
OPEX                          total annualised operation expense [$·year^-1]
EquipmentCBMUpdate(p)         bare module cost Update of each part of equipment [$]
EquipmentCBM(p)               bare module cost of each part of equipment [$]
EquipmentCp0(p)               purchased cost for base conditions
EquipmentFBMI(p)              bare module factor
```

```
coolingWaterCondenser1        cooling water cost condenser 1 [$·yr^-1]
coolingWaterCondenser2        cooling water cost condenser 2 [$·yr^-1]
steamReboiler1                steam cost reboiler  1 [$·yr^-1]
steamReboiler2                steam cost reboiler  2 [$·yr^-1]
coolingWaterCooler            cooling water cost cooler      [$·yr^-1]
catalystCost                  Catalyst cost [$·year]
Qcondenser1                   duty exchange in condenser 1 [kJ·h^-1]
Qcondenser2                   duty exchange in condenser 2 [kJ·h^-2]
Qcondenser3                   duty exchange in condenser 3 [kJ·h^-1]
Qreboiler1                    duty exchange in reboiler  1 [kJ·h^-1]
Qreboiler2                    duty exchange in reboiler  2 [kJ·h^-1]
Qreboiler3                    duty exchange in reboiler  3 [kJ·h^-1] ;

VARIABLE
z        Objective function to optimize;

EQUATIONS
TOTAL_ANNUALISED_COST
TOTAL_CAPITAL_EXPEDITURE
TOTAL_ANNUALISED_OPERATION_EXPENSE
EQUIPMENT_CBM_UPDATE
EQUIPMENT_CBM
EQUIPMENT_BARE_MODULE_FACTOR
PURCHASED_COST_FOR_BASE_CONDITIONS_VESSEL
PURCHASED_COST_FOR_BASE_CONDITIONS_COOLER
PURCHASED_COST_FOR_BASE_CONDITIONS_TOWER1
PURCHASED_COST_FOR_BASE_CONDITIONS_TOWER2
PURCHASED_COST_FOR_BASE_CONDITIONS_TRAY1
PURCHASED_COST_FOR_BASE_CONDITIONS_TRAY2
PURCHASED_COST_FOR_BASE_CONDITIONS_CONDENSER1
PURCHASED_COST_FOR_BASE_CONDITIONS_CONDENSER2
PURCHASED_COST_FOR_BASE_CONDITIONS_REBOILER1
PURCHASED_COST_FOR_BASE_CONDITIONS_REBOILER2
DUTY_CONDENSER_1
DUTY_CONDENSER_2
DUTY_REBOILER_1
DUTY_REBOILER_2
COOLING_WATER_CONDENSER1
COOLING_WATER_CONDENSER2
STEAM_REBOILER1
STEAM_REBOILER2
COOLING_WATER_COOLER
CATALYST_COST_CAPEX
OBJECTIVE_FUNCTION_TO_OPTIMIZE ;

TOTAL_ANNUALISED_COST..
TAC =E= (OPEX + CAPEX) * annualizationFactor ) * 1e-6 ;

TOTAL_CAPITAL_EXPEDITURE..
CAPEX =E= sum(p, EquipmentCBMUpdate(p) ) + catalystCost ;

TOTAL_ANNUALISED_OPERATION_EXPENSE..
OPEX =E=  coolingWaterCondenser1 + coolingWaterCondenser2  + steamReboiler1 +
          steamReboiler2  + coolingWaterCooler  ;

EQUIPMENT_CBM_UPDATE(p)..
EquipmentCBMUpdate(p) =E= EquipmentCBM(p) * UpdateFactor(p) ;

EQUIPMENT_CBM(p)..
EquipmentCBM(p) =E= EquipmentCp0(p) * EquipmentFBMI(p) ;


EQUIPMENT_BARE_MODULE_FACTOR(p)..
```

```
EquipmentFBMI(p) =E=  B1(p) + B2(p) * Fm(p) * Fp(p) ;

PURCHASED_COST_FOR_BASE_CONDITIONS_VESSEL..
EquipmentCp0('Vessel') =E=   1529 * length('Reactor') + 5477 ;

PURCHASED_COST_FOR_BASE_CONDITIONS_COOLER..
EquipmentCp0('Cooler') =E=  94.04 * Area('Cooler') + 1.433e4 ;

PURCHASED_COST_FOR_BASE_CONDITIONS_TOWER1..
EquipmentCp0('Tower1') =E= 595.7 * Volume('Column1') + 6762 ;

PURCHASED_COST_FOR_BASE_CONDITIONS_TOWER2..
EquipmentCp0('Tower2') =E= 595.7 * Volume('Column2') + 6762 ;

PURCHASED_COST_FOR_BASE_CONDITIONS_TRAY1..
EquipmentCp0('Tray1') =E= 678.9 * Area('Column1') + 11.66 ;

PURCHASED_COST_FOR_BASE_CONDITIONS_TRAY2..
EquipmentCp0('Tray2') =E= 678.9 * Area('Column2') + 11.66 ;

PURCHASED_COST_FOR_BASE_CONDITIONS_CONDENSER1..
EquipmentCp0('Condenser1') =E= 50.56 * AreaCond('Tol_EBenz') + 2.401e4 ;

PURCHASED_COST_FOR_BASE_CONDITIONS_CONDENSER2..
EquipmentCp0('Condenser2') =E= 50.56 * AreaCond('EBenz_Sty') + 2.401e4 ;

PURCHASED_COST_FOR_BASE_CONDITIONS_REBOILER1..
EquipmentCp0('Reboiler1') =E=  50.56 * AreaReb('Tol_EBenz') + 2.401e4 ;

PURCHASED_COST_FOR_BASE_CONDITIONS_REBOILER2..
EquipmentCp0('Reboiler2') =E=  50.56 * AreaReb('EBenz_Sty') + 2.401e4 ;

DUTY_CONDENSER_1..
Qcondenser1 =E= Qcond('Tol_EBenz') * 3600 ;

DUTY_CONDENSER_2..
Qcondenser2 =E=  Qcond('EBenz_Sty') * 3600 ;

DUTY_REBOILER_1..
Qreboiler1  =E= Qreb('Tol_EBenz') * 3600 ;

DUTY_REBOILER_2..
Qreboiler2 =E= Qreb('EBenz_Sty') * 3600 ;

COOLING_WATER_CONDENSER1..
coolingWaterCondenser1 =E= WATER * Qcondenser1 * YEAR / 3600 ;

COOLING_WATER_CONDENSER2..
coolingWaterCondenser2 =E= WATER * Qcondenser2 * YEAR / 3600 ;

STEAM_REBOILER1..
steamReboiler1 =E= STEAM * Qreboiler1 * YEAR / 3600 ;

STEAM_REBOILER2..
steamReboiler2 =E= STEAM * Qreboiler2 * YEAR / 3600 ;

COOLING_WATER_COOLER..
coolingWaterCooler =E= WATER * coolerQ * YEAR / 3600 ;

CATALYST_COST_CAPEX..
catalystCost =E= catalystPrice * Volume('Reactor') * catalystDensity * (1 - 0.445) ;
```



```
OBJECTIVE_FUNCTION_TO_OPTIMIZE..
*z =E=  FireExplosionIndex
z =E=  TAC  ;



model petlyuk2 /all/   ;

Area.lo('Cooler') = 10;
Area.up('Cooler') = 10000;

pressureOperationEquipment.lo = 0 ;
pressureOperationEquipment.up = 3 ;

AreaCond.lo('Tol_EBenz') = 10;
AreaCond.up('Tol_EBenz') = 10000;
AreaReb.lo('EBenz_Sty') = 10;
AreaReb.up('EBenz_Sty') = 10000;




*FireExplosionIndex.lo = 201.208 ;
FireExplosionIndex.up = 300 ;
totalBTUinProcess.up = 9 * 1e9 ;

Rmin.lo= 1.2;
Rmin.up= 80 ;

solve  petlyuk2 using NLP minimizing  z ;

scalars
prueba1, prueba2 ;

prueba1 = Mv/(rol*rov)**0.5* 1/0.7 * 1/439 * 1/0.8 * (V1.l('Tol_EBenz') +
L1.l('Tol_EBenz')*(a.l-1) );
prueba2 = Mv/(rol*rov)**0.5* 1/0.7 * 1/439 * 1/0.8 * (V1.l('EBenz_Sty') +
L1.l('EBenz_Sty')*(a.l-1) );

display prueba1, prueba2;

PARAMETER
         Diametro(c,s);
         Diametro(c,s) = (4*AreaColumn.l(c,s)/pi)**0.5;

display Diametro;
```

Appendix E. Results obtained from case studies in section 4

In this appendix are shown the inherent safest, the most economic and point "*c*" styrene production plant results obtained in the optimizations. Tables only includes the results which were not presented in section 4.

a) The inherent safest styrene plant results.

Table E.1. Mass flow rates of components in each stream for the inherent safest styrene plant..

	Organic Components (kg/h)				Vapor Components (kg/h)					Aqueous Component (kg/h)
Stream	Ebenzene	Styrene	Toluene	Benzene	H_2	CO	CO_2	CH_4	Ethylene	Water
1	2120.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	4243.198
2	1031.782	949.252	17.109	75.473	18.962	0.219	7.234	2.280	22.593	4237.139
3	1031.782	949.252	17.109	75.473	18.962	0.219	7.234	2.280	22.593	4237.139
4	0.000	0.000	0.000	0.000	18.962	0.219	7.234	2.280	22.593	0.000
5	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	4237.139
6	1031.782	949.252	17.109	75.473	0.000	0.000	0.000	0.000	0.000	0.000
7	1031.782	949.252	17.109	75.473	0.000	0.000	0.000	0.000	0.000	0.000
8	5.159	0.000	17.023	75.473	0.000	0.000	0.000	0.000	0.000	0.000
9	1026.623	949.252	0.086	0.000	0.000	0.000	0.000	0.000	0.000	0.000
10	1023.543	2.848	0.086	0.000	0.000	0.000	0.000	0.000	0.000	0.000
11	3.080	946.405	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000

Table E.2. Mole flow rates of components in each stream for the inherent safest plant.

	Organic Components (kmol/h)				Vapor Components (kmol/h)					Aqueous Component (kmol/h)
Stream	Ebenzene	Styrene	Toluene	Benzene	H_2	CO	CO_2	CH_4	Ethylene	Water
1	20.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	235.733
2	9.734	9.114	0.186	0.966	9.481	0.008	0.164	0.142	0.902	235.397
3	9.734	9.114	0.186	0.966	9.481	0.008	0.164	0.142	0.902	235.397
4	0.000	0.000	0.000	0.000	9.481	0.008	0.164	0.142	0.902	0.000
5	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	235.397
6	9.734	9.114	0.186	0.966	0.000	0.000	0.000	0.000	0.000	0.000
7	9.734	9.114	0.186	0.966	0.000	0.000	0.000	0.000	0.000	0.000
8	0.049	0.000	0.185	0.966	0.000	0.000	0.000	0.000	0.000	0.000
9	9.685	9.114	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000
10	9.656	0.027	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000
11	0.029	9.087	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000

Table E.3. Distillation columns results for the inherent safest plant.

	Column 1	Column 2
F (kmol/h)	20.000	18.800
V1=V2 (kmol/h)	97.173	89.495
L1 (kmol/h)	95.973	79.811
L2 (kmol/h)	115.973	98.611
D (kmol/h)	1.200	9.684
B (kmol/h)	18.800	9.116
NS_{s1}	1.014	24.604
NS_{s2}	8.831	49.794
θ_c	2.386	1.101
X	0.883	0.872
$\mathrm{A_{condenser}}\ (\mathrm{m}^2)$	10000.000	9180.680
$\mathrm{A_{reboiler}}\ (\mathrm{m}^2)$	2615.740	6310.462

Table E.4. Extents of reaction.

Extent of reaction (kmol/h)	
ξ_1	9.114
ξ_2	0.966
ξ_3	0.186
ξ_4	0.064
ξ_5	0.044
ξ_6	0.164

Table E.5. Heat Exchange.

Q (kJ/h)	
Condenser 1	1.21E+06
Condenser 2	6.62E+05
Reboiler 1	5.68E+05
Reboiler 2	6.89E+05
Cooler	1.11E+07

Table E.6. Concentration of components in equipments.

	Organic Components (lb/m^3)				Vapor Components (lb/m^3)					Aqueous.Component (lb/m^3)
Equipm.	Ebenzene	Styrene	Toluene	Benzene	H_2	CO	CO_2	CH_4	Ethylene	Water
Reactor	0.362	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.724
Cooler	0.105	0.097	0.002	0.008	0.002	2.23E-05	7.36E-04	2.32E-04	0.002	0.431
Column1	970.327	892.713	16.090	70.978	0.000	0.000	0.000	0.000	0.000	0.000
Column2	928.400	858.432	0.077	0.000	0.000	0.000	0.000	0.000	0.000	0.000

Table E.7. Volumetric flow in equipments.

$Qv\ (m3/h)$	
Reactor	12923.526
Cooler	21668.008
Column1	2.344
Column2	2.438

b) The most economical styrene plant results.

Table E.8. Mass flow rates of components in each stream for the most economical styrene plant..

	Organic Components (kg/h)				Vapor Components (kg/h)					Aqueous Component (kg/h)
Stream	Ebenzene	Styrene	Toluene	Benzene	H2	CO	CO2	CH4	Ethylene	Water
1	1855.908	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	3714.616
2	871.140	852.558	21.763	67.816	17.643	0.198	11.051	2.114	19.823	3705.449
3	871.140	852.558	21.763	67.816	17.643	0.198	11.051	2.114	19.823	3705.449
4	0.000	0.000	0.000	0.000	17.643	0.198	11.051	2.114	19.823	0.000
5	0.000	0.000	0.000	9.000	0.000	0.000	0.000	0.000	0.000	3705.449
6	871.140	852.558	21.763	67.816	0.000	0.000	0.000	0.000	0.000	0.000
7	871.140	852.558	21.763	67.816	0.000	0.000	0.000	0.000	0.000	0.000
8	4.356	0.000	21.654	67.816	0.000	0.000	0.000	0.000	0.000	0.000
9	866.784	852.558	0.109	0.000	0.000	0.000	0.000	0.000	0.000	0.000
10	864.184	2.558	0.109	0.000	0.000	0.000	0.000	0.000	0.000	0.000
11	2.600	850.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000

Table E.9. Mole flow rates of components in each stream for the most economical plant.

	Organic Components (kmol/h)				Vapor Components (kmol/h)					Aqueous Component (kmol/h)
Stream	Ebenzene	Styrene	Toluene	Benzene	H2	CO	CO2	CH4	Ethylene	Water
1	17.509	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	206.368
2	8.218	8.186	0.236	0.868	8.822	0.007	0.251	0.132	0.791	205.858
3	8.218	8.186	0.236	0.868	8.822	0.007	0.251	0.132	0.791	205.858
4	0.000	0.000	0.000	0.000	8.822	0.007	0.251	0.132	0.791	0.000
5	0.000	0.000	0.000	0.115	0.000	0.000	0.000	0.000	0.000	205.858
6	8.218	8.186	0.236	0.868	0.000	0.000	0.000	0.000	0.000	0.000
7	8.218	8.186	0.236	0.868	0.000	0.000	0.000	0.000	0.000	0.000
8	0.041	0.000	0.235	0.868	0.000	0.000	0.000	0.000	0.000	0.000
9	8.177	8.186	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000
10	8.153	0.025	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000
11	0.025	8.161	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000

Table E.10. Distillation columns results for the most economical plant.

	Column 1	Column 2
F (kmol/h)	17.509	16.364
V1=V2 (kmol/h)	109.054	85.832
L1 (kmol/h)	91.545	69.468
L2 (kmol/h)	109.054	85.832
D (kmol/h)	1.144	8.178
B (kmol/h)	16.364	8.186
NS_{s1}	1.631	15.670
NS_{s2}	6.279	30.115
θ_c	2.377	1.105
X	0.980	0.978
$A_{condenser}$ (m^2)	2158.882	521.505
$A_{reboiler}$ (m^2)	1653.606	1257.621

Table E.11. Extents of reaction.

Extent of reaction (kmol/h)	
ξ_1	8.186
ξ_2	0.868
ξ_3	0.236
ξ_4	0.077
ξ_5	0.104
ξ_6	0.251

Table E.12. Heat Exchange.

Q (kJ/h)	
Condenser 1	2.61E+05
Condenser 2	1.32E+05
Reboiler 1	1.02E+05
Reboiler 2	1.37E+05
Cooler	9.64E+06

Table E.13. Concentration of components in equipments.

	Organic Components (lb/m^3)				Vapor Components (lb/m^3)					Aqueous.Component (lb/m^3)
Equipm.	Ebenzene	Styrene	Toluene	Benzene	H_2	CO	CO_2	CH_4	Ethylene	Water
Reactor	0.362	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.720
Cooler	0.102	0.100	0.003	0.008	0.002	2.32E-05	0.001	2.48E-04	0.002	0.434
Column1	935.831	915.869	23.379	72.851	0.000	0.000	0.000	0.000	0.000	0.000
Column2	900.543	885.763	0.113	0.000	0.000	0.000	0.000	0.000	0.000	0.000

Table E.14. Volumetric flow in equipments.

Qv ($m3/h$)	
Reactor	11313.623
Cooler	18829.543
Column1	2.052
Column2	2.122

c) Styrene plant results at point c.

Table E.15. Mass flow rates of components in each stream for point "*c*".

	Organic Components (kg/h)				Vapor Components (kg/h)					Aqueous Component (kg/h)
Stream	Ebenzene	Styrene	Toluene	Benzene	H2	CO	CO2	CH4	Ethylene	Water
1	1871.441	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	3745.704
2	881.185	860.296	19.490	67.983	17.572	0.201	9.451	2.128	20.010	3737.844
3	881.185	860.296	19.490	67.983	17.572	0.201	9.451	2.128	20.010	3737.844
4	0.000	0.000	0.000	0.000	17.572	0.201	9.451	2.128	20.010	0.000
5	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	3737.844
6	881.185	860.296	19.490	67.983	0.000	0.000	0.000	0.000	0.000	0.000
7	881.185	860.296	19.490	67.983	0.000	0.000	0.000	0.000	0.000	0.000
8	4.406	0.000	19.393	67.983	0.000	0.000	0.000	0.000	0.000	0.000
9	876.779	860.296	0.097	0.000	0.000	0.000	0.000	0.000	0.000	0.000
10	874.148	2.581	0.097	0.000	0.000	0.000	0.000	0.000	0.000	0.000
11	2.630	857.715	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000

Table E.16. Mole flow rates of components in each stream for point "*c*".

	Organic Components (kmol/h)				Vapor Components (kmol/h)					Aqueous Component (kmol/h)
Stream	Ebenzene	Styrene	Toluene	Benzene	H2	CO	CO2	CH4	Ethylene	Water
1	17.655	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	208.095
2	8.313	8.260	0.212	0.870	8.786	0.007	0.215	0.133	0.799	207.658
3	8.313	8.260	0.212	0.870	8.786	0.007	0.215	0.133	0.799	207.658
4	0.000	0.000	0.000	0.000	8.786	0.007	0.215	0.133	0.799	0.000
5	0.000	0.000	0.000	0.000	0.000	0.007	0.000	0.000	0.000	207.658
6	8.313	8.260	0.212	0.870	0.000	0.000	0.000	0.000	0.000	0.000
7	8.313	8.260	0.212	0.870	0.000	0.000	0.000	0.000	0.000	0.000
8	0.042	0.000	0.210	0.870	0.000	0.000	0.000	0.000	0.000	0.000
9	8.272	8.260	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000
10	8.247	0.025	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000
11	0.025	8.235	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000

Table E.17. Distillation columns results for point "c".

	Column 1	Column 2
F (kmol/h)	17.655	16.533
V1=V2 (kmol/h)	90.913	78.456
L1 (kmol/h)	89.790	70.184
L2 (kmol/h)	107.445	86.716
D (kmol/h)	1.122	8.273
B (kmol/h)	16.533	8.260
NS_{s1}	1.188	8.944
NS_{s2}	23.661	47.791
θ_c	2.380	1.105
X	0.946	0.941
$A_{condenser}$ (m^2)	5588.825	1386.060
$A_{reboiler}$ (m^2)	4543.230	3342.974

Table E.18. Extents of reaction.

Extent of reaction (kmol/h)	
ξ_1	8.260
ξ_2	0.870
ξ_3	0.212
ξ_4	0.072
ξ_5	0.079
ξ_6	0.215

Table E.19. Heat Exchange.

Q (kJ/h)	
Condenser 1	6.77E+05
Condenser 2	3.51E+05
Reboiler 1	2.81E+05
Reboiler 2	3.65E+05
Cooler	9.73E+06

Table E.20. Concentration of components in equipments.

	Organic Components (lb/m^3)				Vapor Components (lb/m^3)					Aqueous.Component (lb/m^3)
Equipm.	Ebenzene	Styrene	Toluene	Benzene	H_2	CO	CO_2	CH_4	Ethylene	Water
Reactor	0.362	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.724
Cooler	0.108	0.105	0.002	0.008	0.002	0.000	0.001	2.70E-04	0.002	0.458
Column1	938.765	916.512	20.764	72.425	0.000	0.000	0.000	0.000	0.000	0.000
Column2	901.645	884.695	0.100	0.000	0.000	0.000	0.000	0.000	0.000	0.000

Table E.21. Volumetric flow in equipments.

$Qv\ (m3/h)$	
Reactor	11408.307
Cooler	17985.067
Column1	2.069
Column2	2.144

Appendix F. Budget

This document breaks down the overall project budget.

Table F.1. Reactor budget.

	The Inherent safest	The most economic	Point "c"
Vessel ($/yr)	6.99E+03	8.23E+03	7.56E+03
Catalyst cost ($/yr)	1.46E+04	2.19E+04	1.79E+04
Reactor ($/yr)	**2.16E+04**	**3.01E+04**	**2.55E+04**

Table F.2. Cooler budget.

	The Inherent safest	The most economic	Point "c"
Cooler ($/yr)	**1.78E+04**	**1.75E+04**	**1.75E+04**

Table F.3. Distillation columns budget

	The Inherent safest	The most economic	Point "c"
Condenser 1 ($/yr)	5.46E+05	1.37E+05	3.16E+05
Reboiler 1 ($/yr)	5.03E+05	1.11E+05	2.61E+05
Tower 1 ($/yr)	2.97E+04	1.26E+05	5.13E+04
Tray 1 ($/yr)	1.67E+04	9.23E+04	3.37E+04
Distillation column 1 ($/yr)	**1.09E+06**	**4.66E+05**	**6.62E+05**
Condenser 2 ($/yr)	1.61E+05	5.19E+04	9.69E+04
Reboiler 2 ($/yr)	3.53E+05	9.02E+04	1.99E+05
Tower 2 ($/yr)	4.71E+04	1.97E+05	8.00E+04
Tray 2 ($/yr)	1.77E+04	8.78E+04	3.32E+04
Distillation column 2 ($/yr)	**5.79E+05**	**4.27E+05**	**4.09E+05**

Table F.4. Servicies budget.

	The Inherent safest	The most economic	Point "c"
Cooling water cooler ($/yr)	3.22E+04	2.78E+04	2.81E+04
Cooling water condenser 1 ($/yr)	3.50E+06	7.55E+05	1.96E+06
Cooling water condenser 2 ($/yr)	1.91E+06	3.81E+05	1.01E+06
Steam in Reboiler 1 ($/yr)	6.36E+07	1.15E+07	3.16E+07
Steam in reboiler 2 ($/yr)	7.75E+07	1.54E+07	4.10E+07
OPEX ($/yr)	**1.47E+08**	**2.81E+07**	**7.57E+07**

Table F.5. Total TAC budget.

	The Inherent safest	The most economic	Point "c"
OPEX (M$/yr)	146.82	28.113	75.66
CAPEX (M$/yr)	1.713	0.941	1.114
TAC (M$/yr)	**148.530**	**29.055**	**76.774**

Appendix G. Technical requirements specifications

Technical requirements specifications shows all the characteristics of the equipment, its operation and installation required initially to solve problem statement.

- Fresh ethylbenzene is mixed with superheat vapor (mixture ratio 1:2 w%). That is to say, mass flow rate of vapor is twicethe mass flow rate of ethylbenzene.
- The reactor used for the process is a PFR with 1.95 m of diameter, which contains catalyst with the following characteristics:

$$\rho_{cat} = 2350\frac{kg}{m^3}, \qquad D_p = 1\,mm, \qquad \varepsilon = 0.445.$$

- The six reactions occurring in the styrene reactor are:

$$\underset{\text{E-Benzene}}{C_6H_5CH_2CH_3} \leftrightarrow \underset{\text{Styrene}}{C_6H_5CHCH_2} + H_2 \tag{R1}$$

$$\underset{\text{E-Benzene}}{C_6H_5CH_2CH_3} \rightarrow \underset{\text{Benzene}}{C_6H_6} + \underset{\text{Ethylene}}{C_2H_4} \tag{R2}$$

$$\underset{\text{E-Benzene}}{C_6H_5CH_2CH_3} \rightarrow \underset{\text{Toluene}}{C_6H_5CH_3} + \underset{\text{Methane}}{CH_4} \tag{R3}$$

$$2H_2O + C_2H_4 \rightarrow 2CO + 4H_2 \tag{R4}$$

$$H_2O + CH_4 \rightarrow CO + 3H_2 \tag{R5}$$

$$H_2O + CO \rightarrow CO_2 + H_2 \tag{R6}$$

- The kinetic laws for the styrene reactions (1) to (6) are shown in Table G.5.
- The reactor operates under adiabatic conditions, because there are competitive reactions that are favored over the desired reaction (R1). As a result, in isothermal conditions the amount of H_2 increases and the amount of styrene decreases.
- The effluent from the reactor unit is cooled to 30°C, forming three phases (vapor, organic and aqueous).
- The three phase separator is ideal, each phase is completely separated. The vapor phase is composed of $\mathrm{CO}, \mathrm{CO_2}, \mathrm{Ethylene}, \mathrm{CH_4}$ and $\mathrm{H_2}$. On the other hand, the organic phase consists of EBenzene, Benzene, Toluene and Styrene and the third stream is the aqueous, only with water.
- The feed which goes to the first column distillation is the organic. In the first column, the light key component (Toluene) must have a molar fraction lower or equal than 0.005 in bottoms, and the heavy key component (Ebenzene) a molar fraction lower or equal to 0.005 in distillate.
- For column 2 the light key component is Styrene monomer and the heavy key component is E-Benzene. The separation required is a molar fraction of heavy key component in bottoms of 0.003 and a molar fraction of light key component of 0.003 in distillate.
- A minimum production rate of 850 kg styrene/h is required (stream 11).

- Pump and three phase separator are considered as ideal equipments.
- A production rate of 850 kg styrene/h is required at least.
- Pump and three phase separator are considered as ideal equipments.
- Relative volatilities of components are show in Table G.1:

Table G.1. Relative volatility in column 1 and 2.

	Benzene	Toluene	Ebenzene	Styrene
Column 1	7.256	2.405	1.554	1.000
Column 2	5.326	2.661	1.234	1.000

- Trays spacing is 0.6096 m.
- Liquid density in column 1 is considered $895\ kg/m^3$ and in column 2, $811\ kg/m^3$.
- Vapor density in column 1 is considered $38\ kg/m^3$ and in column 2, $35\ kg/m^3$.
- The entalphy of vaporization of components is shown in Table G.2:

Table G.2. Enthalpy of vaporization of component.

	Benzene	Toluene	Ebenzene	Styrene
$\Delta H_{vap}\ (kJ/kmol)$	30970.600	333358.551	35754.774	37228.617

- Overall coefficient of heat transfer is for all equipments (cooler, condensers and reboilers) $0.8\ kW \cdot m^{-2} \cdot K^{-1}$.
- Logarithmic mean temperature difference in condenser 1 is 42.0℃ and in condenser 2 is 87.9℃. On the other hand, in reboiler 1 logarithmic mean temperature difference is 87.5℃. and in reboiler 2, 37.9℃.
- Entalphy of combustion used for computing F&EI, the heat capacity of each component and its molecular weight is shown in Table F.3

Table G.3. Enthalpy of combustions of component.

	E-Benzene	Styrene	H2	Ethylene	Toluene	CO	CO2	CH4	H2O	Benzene
$C_p\ (BTU/lb)$	2.248	2.172	14.510	2.386	2.161	1.097	0.777	3.216	3.314	2.083
$H_c \cdot 10^{-3}\ (kJ/kmol)$	17.6	17.4	51.6	20.8	17.4	4.3	0	21.5	0	17.3
$MW\ (kg/kmol)$	106.00	104.15	2.00	25.05	92.14	28.01	44.01	16.04	18.00	78.11

- The constant for ideal gases is $8.31\ \frac{kJ}{kmolK}$.
- Catalyst cost is 10$/yr and services cost are presented in Table F.4.

Table G.4. Services cost.

Steam ($\$/GJ$)	Cooling Water
0.0506	0.0013

Table G.5. Kinetic laws for reactions.

Reaction type Hysys	**Reaction rate**	**Constants**	**Entalphy**
Simple Rate	$r_1 = A_1 \exp\left(-\frac{E_1}{RT}\right)\left(p_{EB} - \frac{p_{ST}p_{H_2}}{K'}\right)$ $\ln(K') = A_1{}'$	$A_1 = 1967 \frac{kmol}{m^3 \cdot atm \cdot s}$ $E_1 = 90792.7 \frac{kJ}{kmol}$ $A_1' = -1.61$	$117 \frac{kJ}{kmol}$
Kinetic	$r_2 = A_2 \exp\left(-\frac{E_2}{RT}\right) p_{EB}$	$A_2 = 7.3 \cdot 10^8 \frac{kmol}{m^3 \cdot atm \cdot s}$ $E_2 = 207944.6 \frac{kJ}{kmol}$	$105.5 \frac{kJ}{kmol}$
Kinetic	$r_3 = A_3 \exp\left(-\frac{E_3}{RT}\right) p_{EB}\, p_{H_2}$	$A_3 = 1748 \frac{kmol}{m^3 \cdot atm^2 \cdot s}$ $E_3 = 91462.1 \frac{kJ}{kmol}$	$-54.68 \frac{kJ}{kmol}$
Kinetic	$r_4 = A_4 \exp\left(-\frac{E_4}{RT}\right) p_{Ethyl}\, p_{H_2O}^2$	$A_4 = 1209 \frac{kmol}{m^3 \cdot atm^3 \cdot s}$ $E_4 = 103972.3 \frac{kJ}{kmol}$	$210.12 \frac{kJ}{kmol}$
Kinetic	$r_5 = A_5 \exp\left(-\frac{E_5}{RT}\right) p_{Met}\, p_{H_2O}$	$A_5 = 69.11 \frac{kmol}{m^3 \cdot atm^2 \cdot s}$ $E_5 = 65688.73 \frac{kJ}{kmol}$	$206.12 \frac{kJ}{kmol}$
Kinetic	$r_6 = A_6 \exp\left(-\frac{E_6}{RT}\right) p_{CO}\, p_{H_2O}$	$A_6 = 7329 \frac{kmol}{m^3 \cdot atm^2 \cdot s}$ $E_6 = 73554.64 \frac{kJ}{kmol}$	$-41.39 \frac{kJ}{kmol}$

- Animalization factor is 0.1873.
- Density and molecular weight in stream 7 are $880.67\ kg/m^3$ and $103.23\ kg/kmol$ and in stream 9 are 802.87 kg/m^3 and 104.11 kg/m^3.
- Constant required for the calculations of bare module factor and for purchased cost of equipment at ambient operating pressure are shown in Table G.6.

Table G.6. Constant for bare module factor and constants for the purchased cost of the equipment at ambient operating pressure.

		K_1	K_2	K_3	B_1	B_2	F_M	F_P
	Vessel	3.5565	0.3776	0.0905	1.49	1.52	1.0	Equation
	Cooler	4.3247	-0.3030	0.1634	1.63	1.66	1.0	1.3
Distillation Columns	Tower	3.4974	0.4485	0.1074	2.25	1.82	1.0	1.0
	Trays ($Fq = eq.$)	2.9949	0.4465	0.3961	1.00	1.00	1.0	1.0
	Condenser	4.3247	-0.3030	0.1634	1.63	1.66	1.0	1.3
	Reboiler	4.3247	-0.3030	0.1634	1.63	1.66	1.0	1.3

- Update factor of equipment is shown in Table G.7.

Table G.7. Update factor of equipment.

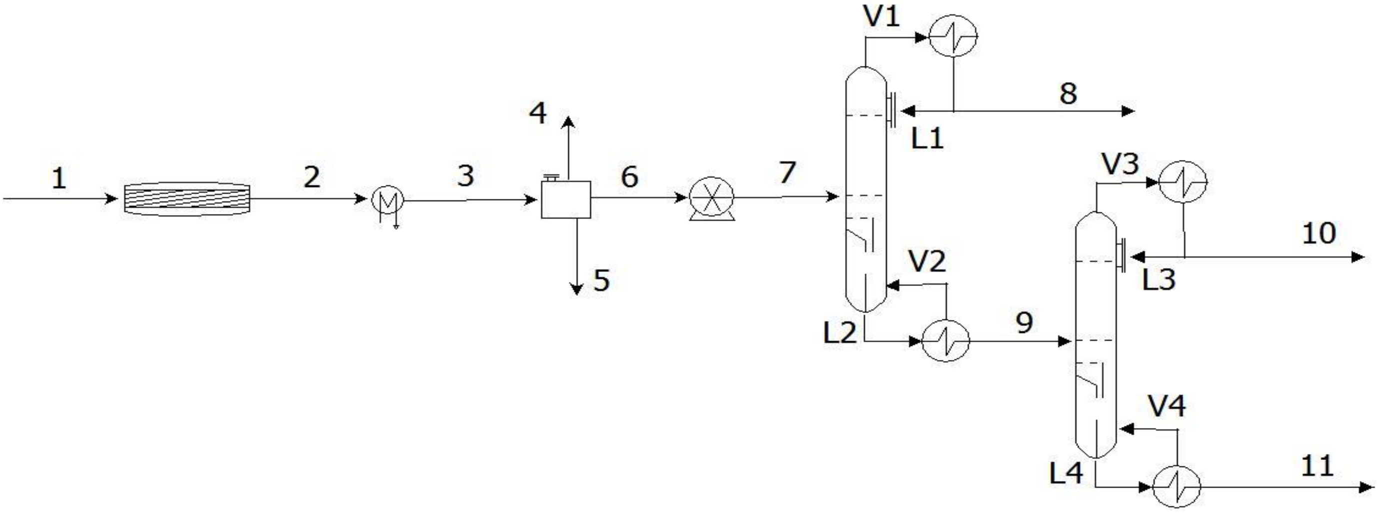
		$Update\ Factor$
	Vessel	1.4511
	Cooler	1.4511
Distillation Columns	Tower1	1.4511
	Trays 1	34.826
	Condenser 1	1.4511
	Reboiler 1	1.4511
	Tower2	1.4511
	Trays 2	43.533
	Condenser 2	1.4511
	Reboiler 2	1.4511

- Parameters required calculating extent of reactions is presented in Table G.8.

Table G.8. Parameters for extents of reaction fit.

	$\xi_1 \left(\frac{kmol}{h}\right)$	$\xi_2 \left(\frac{kmol}{h}\right)$	$\xi_3 \left(\frac{kmol}{h}\right)$	$\xi_4 \left(\frac{kmol}{h}\right)$	$\xi_5 \left(\frac{kmol}{h}\right)$	$\xi_6 \left(\frac{kmol}{h}\right)$
p00	2.07	0.104	0.1411	0.06923	0.07666	0.2123
p10	-0.04086	0.007523	0.04501	0.00959	0.045534	0.06483
p01	0.3563	0.04236	-0.002272	-0.001204	-0.006209	-0.008879

Appendix F. Process Flow Diagram



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