



UNIVERSITAT POLITÈCNICA DE CATALUNYA  
BARCELONATECH  
Escola d'Enginyeria de Barcelona Est

END-OF-DEGREE PROJECT

**Degree in Chemical Engineering**

**DEVELOPMENT OF OPTIMIZATION TOOLS FOR THE  
SYSTEMATIC EXPLORATION OF INDUSTRIAL SYMBIOSIS  
OPPORTUNITIES IN THE PROCESS INDUSTRY**



**Report and Annexes**

**Author:** Valeria Giraldo Carvajal  
**Director:** Moisès Graells  
**Call:** June 2017



## Resum

L'avanç de la societat basat en el consum il·limitat de recursos ha derivat en greus problemes mediambientals. Com a resposta, diverses iniciatives han sorgit en els últims anys amb l'objectiu de separar el consum de recursos i el progrés de la humanitat, sent la sostenibilitat un dels seus pilars màxims. En aquest context, els conceptes de ecologia industrial i simbiosi industrial ofereixen alternatives més sostenibles considerant la cooperació de diferents companyies en front de l'explotació de recursos naturals. Mentre que propostes considerant la optimització de xarxes energètiques i d'aigua s'han estudiat àmpliament en la literatura, encara no s'ha aprofundit en el que es refereix a intercanvi de recursos entre diferents indústries, com va esmentar Boix a (Boix et al. 2015). Per tant, existeix la necessitat de desenvolupar procediments sistemàtics que permetin identificar i valorar el potencial d'intercanvi de les diverses alternatives sota estudi. Això permet enfocar els *targets* o blancs que han ser investigats i posteriorment optimitzats.

Amb aquest projecte s'ha pretès desenvolupar models de complexitat creixent que permetin identificar oportunitats de simbiosi considerant l'intercanvi de matèria a la indústria química i de procés. La modelització duta a terme explora el fet que els residus d'un procés puguin emprar-se o transformar-se en matèries primeres amb valor afegit per altres processos, emfatitzant així la reutilització i el reciclatge de materials i disminuint el consum de recursos verges.

Donat un conjunt de corrents de residu que s'han de tractar, un conjunt de matèries primeres demandades per alimentar diferents processos i un conjunt de transformacions materials (reaccions químiques) potencials amb costos associats, l'objectiu és determinar les oportunitats de simbiosi industrial a una xarxa d'indústries de processos químics determinada. Les variables de decisió fan referència a la demanda de matèries primeres que es cobreix mitjançant corrents reutilitzades o reciclades, a la quantitat de residus que entren al sistema per ser tractats i la quantitat d'aquests que es rebutgen, entre d'altres. Els models desenvolupats, que inclouen balanços de matèria i energia i funcions objectiu econòmiques, porten a diferents problemes de Programació Lineal (LP) i de Programació Lineal amb Enters Mixtes (MILP).

Els diferents models s'han implementat en GAMS i provat en un cas d'estudi que recrea una xarxa d'indústries basada en l'etilè, el clor i compostos químics relacionats. Els resultats obtinguts mostren el potencial d'aquesta proposta de *targeting* que permet identificar i analitzar oportunitats prometedores de simbiosi industrial, ajudant en el procés de presa de decisions. En aquest projecte es discuteixen, a més, les limitacions i futurs desenvolupaments a portar a terme per aconseguir un suport sistemàtic per la presa de decisions en a la gestió eficient de xarxes de simbiosi industrial en indústries químiques i de procés.

## Resumen

El avance de la sociedad basado en el consumo ilimitado de recursos ha derivado en graves problemas medioambientales. Como respuesta, diversas iniciativas han surgido en los últimos años con el objetivo de separar el consumo de recursos y el progreso de la humanidad, siendo la sostenibilidad uno de sus pilares máximos. En este contexto, los conceptos de ecología industrial y simbiosis industrial ofrecen alternativas más sostenibles considerando la cooperación de diferentes compañías frente a la explotación de recursos naturales. Mientras que propuestas considerando la optimización de redes energéticas y de agua se han estudiado ampliamente en la literatura, todavía no se ha profundizado en lo que a intercambio de recursos entre diferentes industrias se refiere, como mencionó Boix en (Boix et al. 2015). Por lo tanto, existe la necesidad de desarrollar procedimientos sistemáticos que permitan identificar y valorar el potencial de intercambio de las diversas alternativas bajo estudio. Así, se permiten enfocar los *targets* o blancos que deben ser investigados y posteriormente optimizados.

Con este proyecto se ha pretendido desarrollar modelos de complejidad creciente que permitan identificar oportunidades de simbiosis considerando el intercambio de material en la industria química y de proceso. La modelización llevada a cabo explora el concepto de que los residuos de un proceso puedan usarse o transformarse en materias primas con valor añadido para otros procesos, enfatizando así la reutilización y el reciclaje de materiales y disminuyendo el consumo de recursos vírgenes.

Dado un conjunto de corrientes de residuo que deben ser tratadas, un conjunto de materias primas demandadas para alimentar distintos procesos y un conjunto de transformaciones materiales (reacciones químicas) potenciales con costes asociados, el objetivo es determinar las oportunidades de simbiosis industrial en una red determinada de industrias de procesos químicos. Las variables de decisión hacen referencia a la demanda de materias primas que se cubre mediante corrientes reutilizadas o recicladas, la cantidad de residuos entrando al sistema para ser tratados y la cantidad de estos que se desechan, entre otros. Los modelos desarrollados, que incluyen balances de materia y energía y funciones objetivo económicas, llevan a diferentes problemas de Programación Lineal (LP) y Programación Lineal con Enteros Mixtos (MILP).

Los diferentes modelos se han implementado en GAMS y probado en un caso de estudio que recrea una red industrial basada en el etileno, el cloro y compuestos químicos relacionados. Los resultados obtenidos muestran el potencial de esta propuesta de *targeting* que permite identificar y analizar oportunidades prometedoras de simbiosis industrial, ayudando en el proceso de toma de decisiones. En este proyecto se discuten, además, las limitaciones y futuros desarrollos a llevar a cabo para conseguir un soporte sistemático en la toma de decisiones para la gestión eficiente de redes de simbiosis industrial en industrias químicas y de proceso.

## **Abstract**

Social advance based on unlimited resource consumption has derived in serious environmental problems. As a response, several initiatives to disassociate resources consumption and human progress have arisen over the past few years, being sustainability one of their crucial pillars. In this context, industrial ecology and industrial symbiosis offer more sustainable alternatives to the exploitation of natural resources by considering the co-operation of different companies.

While modelling approaches to optimize energy and water sharing networks have been widely studied in the literature, little attention has been paid to resource sharing between different industries, as outlined by Boix et al. in (Boix et al. 2015). Hence, there is a need of systematic procedures allowing the identification and assessment of potential sharing alternatives. Thus, this permits focusing on the targets to be further investigated and eventually optimized.

This work aims to develop increasing complexity models to identify symbiosis opportunities regarding material sharing in the chemical and process industry. The modelling approach explores the concept that waste from a process may be used as or transformed into added value raw materials for another, emphasizing the reuse and recycling of materials and thus diminishing the consumption of fresh resources.

Given a set of inlet waste streams to be managed or disposed, a set of demanded raw material to feed different processes and a set of potential material transformations (chemical reactions) with related costs, the objective is to determine the targets or symbiosis opportunities within a network of chemical process industries. Decision variables address the amount of raw material demand covered by reused/recycled streams, the amount of waste entering the system to be treated and the amount to be disposed, among others. Models include mass and energy balances and an economic objective function and lead to different Linear Programming (LP) and Mixed Integer Linear Programming (MILP) problems.

The models have been implemented in GAMS and tested on a case study recreating an industrial network based on ethylene, chlorine and related chemicals. Results show the potential of this targeting approach allowing identifying and assessing promising industrial symbiosis opportunities, helping in the decision-making process. The work discusses the limitations and further developments required to address the systematic decision-making support to the efficient management of industrial symbiosis networks in the chemical process industries.

## Acknowledgements

First and foremost, I would like to express my deepest gratitude to my project director, professor Dr. Moisès Graells, for his valuable support and guidance throughout my bachelor studies and specially during the development of this end-of-degree thesis.

I am also very grateful to professor Dr. Antonio Espuña and all the members from the research group CEPIMA (Centre d'Enginyeria de Processos i Medi Ambient), from the Department of Chemical Engineering in the Universitat Politècnica de Catalunya (UPC), for their commitment and help while I was working towards the completion of this thesis. They raised many precious points in our discussion with respect to the topics in my project and I hope that I have managed to address several of them here.

In particular, I would like to express my greatest appreciation to Ana Somoza, a PhD student at CEPIMA, who kindly provided several insights for the development of most of the concepts and approaches in the scope of this project. Her patience and the enthusiasm she always showed for the topic made a strong impression on me and allowed me to fill many of my knowledge gaps. She has been an invaluable source of guidance for both academic and personal growth.

Getting through my project took more than academic support, and in this sense, I would like to thank Ana Somoza, Sergio Medina, Shabnam Morakabatchiankar, Gicela Lupera, Francesca Audino and Canan Dombayci, all of them PhD students at CEPIMA, for their kindness and for making my afternoons working at CEPIMA way more bearable. Lunch times with them could not have been better and I will always carry very positive memories of these moments with all of them.

I would also like to thank all the professors that have guided me through my bachelor studies for bringing light to my knowledge path and allowing me to grow both as a professional and as a person and for being sources of inspiration in the classes they taught.

Furthermore, I would like to extend my deepest thanks to my family and friends because this project would not have been possible without their endless patience, love and helpfulness. They are the driving force behind my life and I would definitely not be at this point in my academic development without their support.



# Contents

<b>RESUM</b>	<b>I</b>
<b>RESUMEN</b>	<b>II</b>
<b>ABSTRACT</b>	<b>III</b>
<b>ACKNOWLEDGEMENTS</b>	<b>IV</b>
<b>1. INTRODUCTION</b>	<b>3</b>
1.1. Objectives	4
<b>2. CONCEPTUAL OVERVIEW</b>	<b>5</b>
2.1. Optimization	5
2.1.1. Concept Definition	5
2.1.2. Classification of Optimization Problems	6
2.1.3. Optimization Applications in Chemical Engineering	8
2.1.4. Optimization methods applied to eco-industrial parks	10
2.1.5. Big M Method	11
2.2. Sustainability and sustainable development	13
2.3. Supply Chain	15
2.3.1. Reverse logistics	16
2.3.2. Closed-loop Supply Chain	18
2.4. Circular Economy	19
2.5. Industrial ecology	22
2.6. Industrial Symbiosis	26
2.7. “Waste-Resource” Initiative	30
<b>3. TOOLS AND SOFTWARE</b>	<b>31</b>
<b>4. METHODOLOGY</b>	<b>36</b>
<b>5. GENERAL PROBLEM STATEMENT</b>	<b>37</b>
<b>6. CASE STUDY</b>	<b>39</b>
<b>7. OPTIMIZATION MODELS</b>	<b>45</b>
7.1. Model 1: Industrial symbiosis LP black-box model considering atomic mass balances	46
7.1.1. Problem Statement	46





7.1.2.	Mathematical formulation .....	48
7.1.3.	Particular Example.....	51
7.1.4.	Results.....	53
7.1.5.	Model limitations .....	56
7.2.	Model 2: Industrial symbiosis LP model considering mass balances.....	57
7.2.1.	Problem Statement .....	57
7.2.2.	Mathematical Formulation .....	58
7.2.3.	Particular Example.....	61
7.2.4.	Results.....	62
7.2.5.	Model limitations .....	64
7.3.	Model 3: Industrial symbiosis MILP model considering mass balances .....	65
7.3.1.	Problem Statement .....	65
7.3.2.	Mathematical Formulation .....	65
7.3.3.	Particular Example.....	68
7.3.4.	Results.....	68
7.3.5.	Model limitations .....	69
7.4.	Model 4: Industrial symbiosis MILP model considering mass and energy balances .....	70
7.4.1.	Problem Statement .....	70
7.4.2.	Mathematical Formulation .....	70
7.4.3.	Particular Example.....	73
7.4.4.	Results.....	75
7.4.5.	Model limitations .....	78
7.5.	Model 5: Industrial symbiosis MILP model considering mass & energy balances, chemical reactions and partial flows .....	79
7.5.1.	Problem Statement .....	79
7.5.2.	Mathematical Formulation .....	81
7.5.3.	Particular Example.....	87
7.5.4.	Results.....	92
<b>8.</b>	<b>COMPARISON AND DISCUSSION</b> .....	<b>98</b>
<b>9.</b>	<b>ECONOMIC ANALYSIS</b> .....	<b>102</b>
<b>10.</b>	<b>ENVIRONMENTAL IMPACT ANALYSIS</b> .....	<b>106</b>

---

<b>11. CONCLUSIONS</b>	<b>108</b>
<b>12. FUTURE WORK</b>	<b>109</b>
<b>13. BIBLIOGRAPHY</b>	<b>110</b>
<b>14. ANNEXES</b>	<b>114</b>
14.1. GAMS codes of each model developed .....	114
14.1.1. Model 1 .....	114
14.1.2. Model 2 .....	120
14.1.3. Model 3 .....	127
14.1.4. Model 4 .....	136
14.1.5. Model 5 .....	149
14.2. Visual Basics for Applications (VBA) code to connect HYSYS with Excel .....	164
14.2.1. Model 4 .....	164
14.2.2. Model 5 .....	172
14.3. Attached Annexes.....	179





## 1. Introduction

Contemporary society is highly industry dependent: our growth and advance as a collective has always been directly proportional to the technological and scientific developments made in each historical period. In addition to this, the use of resources has been intimately related to economic growth and thus, technological advance. This fact has implied a depletion of the world's natural resources that has derived in serious environmental problems that humanity has to cope with every day: air pollution, deforestation or global warming have now become real and the scope of their effects is not completely known yet.

In response to this conflict, society is now starting to give value to initiatives that allow a disassociation between resources consumption and our progress as a collective. In the light of this, sustainable development, circular economy, closed-loop supply chains, industrial ecology and industrial symbiosis are disciplines that have emerged in the context of this environmental crisis, offering solutions and values that are becoming a key for industry, governments and society.

In this context, optimization appears as an opportunity to improve systems or networks and establish a systematic decision making approach that allows finding the best solution that accomplishes a given objective within a series of defined constraints. However, this is not a straightforward task, because it requires a deep understanding of studied network and the context that surrounds it.

In the light of this, this new alternative productive models require a much more complex management, which is studied in the present thesis by developing and optimizing chemical network models, which offer, by means of mathematical programming tools, the exploration of industrial symbiosis opportunities in the process industry.

The present end-of-degree thesis is divided in two main parts: The first of them comprises an overview of the main concepts involved from a theoretical perspective. On the contrary, the second part is experimental and consists of first outlining the methods and framework for the modelling procedure and then developing and analysing different models created by means of mathematical programming tools using different approaches.

In order to introduce this thesis, it is crucial to define its objectives previously, which is done in the lines below.

## 1.1. Objectives

This project is aimed at building optimization tools that allow a systematic exploration of industrial symbiosis opportunities in the process industry. Thus, in the light of this the objectives that have been established for this project are listed below:

- To deeply understand industrial symbiosis concepts and methods from related disciplines.
- To develop chemical-based industrial symbiosis models considering closed-loop supply chain concepts and opportunities for recycling of diverse chemical compounds and the transformation of waste inputs into added-value raw materials.
- To establish different scenarios in a particular case study so that the behaviour of the implemented models can be analysed.
- To set different problems at different stages that allow analysing the connections between the aforementioned models.
- To implement these models using optimization tools and databases in order to demonstrate the potential of a systematic approach to industrial symbiosis.

## 2. Conceptual Overview

### 2.1. Optimization

The existing need in human nature to improve everything that we create is the driving force of optimization. In every person's daily life, optimization problems must be faced constantly. The solution to some of these problems would be answering questions such as "What is the fastest way to get to work today?" or "Which household task should I do first in order to spare the most time?". Thus, we are constantly surrounded of optimization routines without even noticing. However, optimization does not only apply to daily life matters. On the contrary, it is a very important concept in technological environments: In the context of science and engineering, optimization is a key concept that enables the generation of efficient and systematic tools that ease the decision-making process ("Daily Optimization" 2017).

This chapter offers a general description of the implications of optimization problems in the light of chemical engineering, specifically in the context of model development, setting the stage for the development of optimization tools explained in the following sections.

#### 2.1.1. Concept Definition

The optimization concept refers to the whole procedure of searching the optimum or best solution from a set of candidates in a given process or system within established constraints. In order to perform this task, a series of elements are required. These are the following ones (Biegler 2010):

- A model that predicts the behaviour of the system. In mathematical terms, this is equivalent to a set of equations and inequalities, being the latter referred to as constraints. Constraints imply the boundaries of the system, comprising its limits of performance.
- A set of variables which appear in the model and whose values must be found in order to satisfy the constraints. In a big amount of engineering problems, a subspace of these variables could be defined by a set of decision variables which can be equivalent to the degrees of freedom in the studied system.
- An objective function that provides a given scalar measure representing process' performance that has to be minimized or maximized. For instance, this could be the total profit obtained from the system, the process' cost or go beyond economic aspects and refer to environmental impact, for example.

Optimization algorithms in chemical engineering are the key tools for the following disciplines (Biegler 2010):

- Experimental design, parameter estimation, model development and statistical analysis.
- Process synthesis, analysis, design and retrofit.
- Model predictive control and real-time optimization.
- Planning, scheduling and integration of process operations into the supply chain.

As noted before, optimization is a key task in most engineering contexts. Due to this, it is relevant to apply systematic approaches in order to perform this task. These systematic approaches should have a high efficiency and be able to guarantee that the solution found is the best one possible. These approaches lead to a huge amount of methods and algorithms that are under constant research and improvement (Biegler 2010). In this sense, it is relevant to remark that optimization is a very active and fast growing area in terms of research and its implications are enormous on the real world.

### 2.1.2. Classification of Optimization Problems

In the light of what has been explained above, it is relevant to make a distinction between all the different types of optimization problems in the context of chemical engineering. These problems can be classified in terms of the continuity or discretion of their variables as shown below:

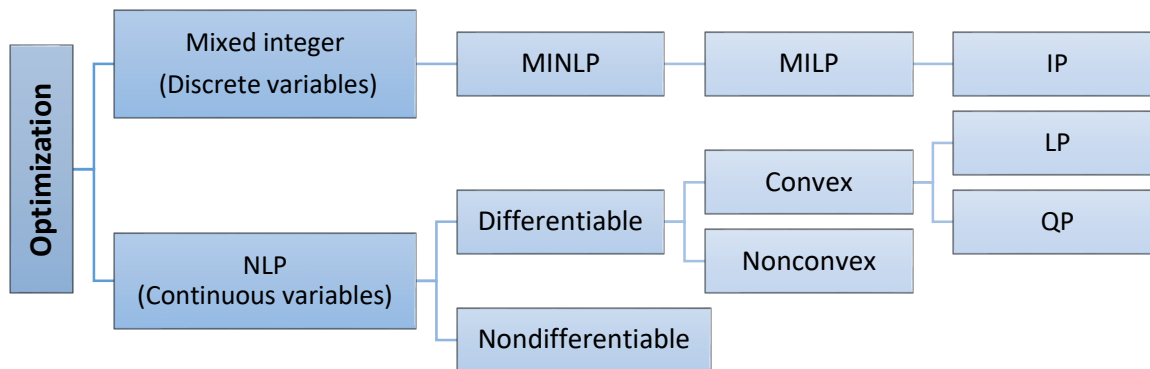


Figure 1. Types of optimization problems. Extracted from (Biegler 2010)

As posed by L.T. Biegler in (Biegler 2010), a general algebraic formulation of discrete or continuous optimization problems could be written as mixed integer optimization problems. From these, the most general is the mixed integer nonlinear program (MINLP) formulated as follows:



$$\begin{aligned}
 & \min_{x,y} f(x,y) \\
 & s. t. \quad h(x,y) = 0, \\
 & \quad \quad g(x,y) \leq 0, \\
 & \quad \quad x \in \mathbb{R}^n, \quad y \in \{0,1\}^t
 \end{aligned} \tag{Eqn. 1}$$

Where:

- $f(x,y)$  is the objective function (for instance cost, or energy consumption)
- $h(x,y) = 0$  are the equations representing the performance of the system (for instance material balances)
- $g(x,y) \leq 0$  are the inequality constraints (for instance process specifications or feasible schedules)
- The real n-vector  $x$  represents the continuous variables
- The t-vector  $y$  represents the discrete variables, restricted to be 0/1 values which would define for example tasks' sequencing or assignment of equipment.

This general problem would be equivalent to a MINLP if and only if any of the functions involved are nonlinear.

In case  $f(x,y)$ ,  $g(x,y)$  and  $h(x,y)$  are linear, then the problem would correspond to a mixed integer linear program (MILP). If for the stated MILP all the variables were integer, the problem would be equivalent to an integer programming (IP) problem.

In the same line, if there were no 0/1 variables, the general problem described at the beginning of this section would be reduced to the following nonlinear program (NLP) problem stated as follows:

$$\begin{aligned}
 & \min_x f(x) \\
 & s. t. \quad h(x) = 0, \\
 & \quad \quad g(x) \leq 0, \\
 & \quad \quad x \in \mathbb{R}^n
 \end{aligned} \tag{Eqn. 2}$$

When having a NLP it is essential to know whether the problem is differentiable or not. Furthermore, a second relevant characteristic is whether the problem is convex or not, in other words, if it has a convex objective function and a convex feasible region. In case it is a convex problem, then any local solution, which means that a better solution in the neighbourhood of this solution cannot be found, it is guaranteed to be a global solution of the problem. On the contrary, non-convex problems could have multiple local solutions.

Apart from all these distinctions, in the given case that the objective and constraint functions from the reduced problem were linear, it would result in a linear program (LP) and that would mean that the problem could be solved in a finite number of steps. Solving methodologies for LPs are well known and widespread.

It must also be pointed out that quadratic programs (QP) are generated when there is a quadratic term added in the objective function of an LP. Thus, they are a slight modification of LPs.

At this point, it is important to note that the models developed in the scope of this project lay between LP and MILP.

### 2.1.3. Optimization Applications in Chemical Engineering

Many chemical engineering applications use optimization as a key tool, especially in terms of system process engineering. Problems in that context often present complex economic and performance interactions, making it difficult to identify the best solution intuitively. Furthermore, from the perspective of the economics of the system, finding the optimum solution could represent great savings or on the other hand, a big price to pay for sticking to not optimal solutions. Thus, optimization represents a key technology that helps the chemical industry to remain competitive and updated (Biegler 2010).

The following table shows how optimization problems are found in all the disciplines composing chemical engineering, comprising all the concepts from model and process development to process operations, control, planning and scheduling:

**Table 1. Mathematical programming in process systems engineering. Extracted from (Biegler 2010)**

	LP	MILP	QP	NLP	MINLP
<b>PROCESS MODEL BUILDING</b>				X	X
<b>PROCESS DESIGN &amp; SYNTHESIS</b>					
<b>Heat Exchangers</b>	X	X		X	X
<b>Mass Exchangers</b>	X	X		X	X
<b>Separations</b>		X		X	X

<b>Reactions</b>	X		X	X
<b>Flowsheeting</b>			X	X
<b>PROCESS OPERATIONS</b>				
<b>Scheduling</b>	X	X		X
<b>Supply Chain</b>	X	X		X
<b>Real-Time Optimization</b>	X		X	X
<b>PROCESS CONTROL</b>				
<b>Model Predictive Control</b>	X		X	
<b>Nonlinear MPC</b>			X	X
<b>Hybrid MPC</b>		X		

The table above is a summary of model types formulated in the context of process systems engineering applications. As it can be seen in the table, design is dominated by NLP and MINLP because of the fact that performance equations need to be handled explicitly. However, simple targeting models also arise LP and MILP problems. On the contrary, operational problems are mostly defined by LPs and MILPs, for planning, scheduling and supply chain problems. Moreover, regarding real-time optimization, non-linear programming presents a huge role. Furthermore, process control relies on LP and NLP models but also on MILPs for hybrid systems (Biegler 2010).

Once this introduction about optimization has been made, it is time to further review optimization methods applied to the modelling of industrial symbiosis networks understood as eco-industrial parks. This is done in the following section.

#### 2.1.4. Optimization methods applied to eco-industrial parks

One of the most important features of industrial symbiosis networks is the geographic proximity there is between the companies taking part in the system. The most extended manifestations of industrial symbioses are eco-industrial parks (Boix et al. 2015). A widespread definition of the concept of “eco-industrial park” is that of “an industrial system of planned materials and energy exchanges that seeks to minimize energy and raw materials use, minimize waste, and build sustainable economic, ecological and social relationships”, as stated in (Harriss Olson 1996). Moreover, another basic point when defining eco-industrial parks is the fact that they have to prove that the total profits achieved by collective working are higher than working as isolated facilities (Boix et al. 2015).

According to Boix in (Boix et al. 2015), there is a lack of data specifically regarding optimization in the industrial symbiosis field. However, the types of cooperation relationships that can be found in literature where different optimization methods have been developed are the following:

- Cooperation through the water network  
This is the most common type of cooperation found in literature. Systems using water in the context of an eco-industrial park, are generally optimized through conceptual graphical designing (pinch technology) and mathematical programming.
- Cooperation via energy  
There is a small amount of publications that deal with energy flow management. In spite of this fact, energy savings in an eco-industrial park can be achieved through mathematical programming or pinch analysis approaches.
- Cooperation through exchanges of materials  
Exchanges of materials in an eco-industrial park can be related to different type of materials, such as by-products, wastes or real-value products. In this sense, in an eco-industrial park, wastes from a company can serve as a feedstock to a different company in the network. Although there are some examples of eco-industrial parks where materials are shared in real life, they are not often taken into account in optimization works. According to Boix et al. in (Boix et al. 2015), future investigation and improvements should face material sharing optimization in eco-industrial parks.

Taking into account the different types of cooperation networks that have just been presented, an eco-industrial park can be optimized from different ways. In this sense, it is relevant to discuss about the different characterizations of the objective functions defined in these networks. The main type of objectives to be achieved are the following:

- Social/managerial objectives
- Economic objectives

- Topological objectives
- Environmental objectives

Thus, there are different criteria taken in literature to define the objective functions in an industrial symbiosis network. Indeed, the characterization of objective functions is a cause for concern in numerous research works nowadays.

The present thesis analyses optimization in the context of environmental matters, specifically in terms of industrial symbiosis. The types of programming taken into account are basically Linear Programs (LP) and Mixed Integer Linear Programs (MILP). In the context of linear programming, there is a method widely used that allows to linearize equations in order to avoid non-linearities, it is explained below.

### 2.1.5. Big M Method

In the context of mathematical programming, the Big M method is a way of solving linear programming problems using an algorithm called the Simplex algorithm. This algorithm is one of the most widely used methods for solving linear maximization problems. The main idea behind this method could be explained in geometric words: it basically moves from a given vertex to an adjacent vertex, while improving the objective function, until it reaches an optimal vertex (Ping-Qi 2014). A brief scheme of the steps to follow Simplex method can be seen below:

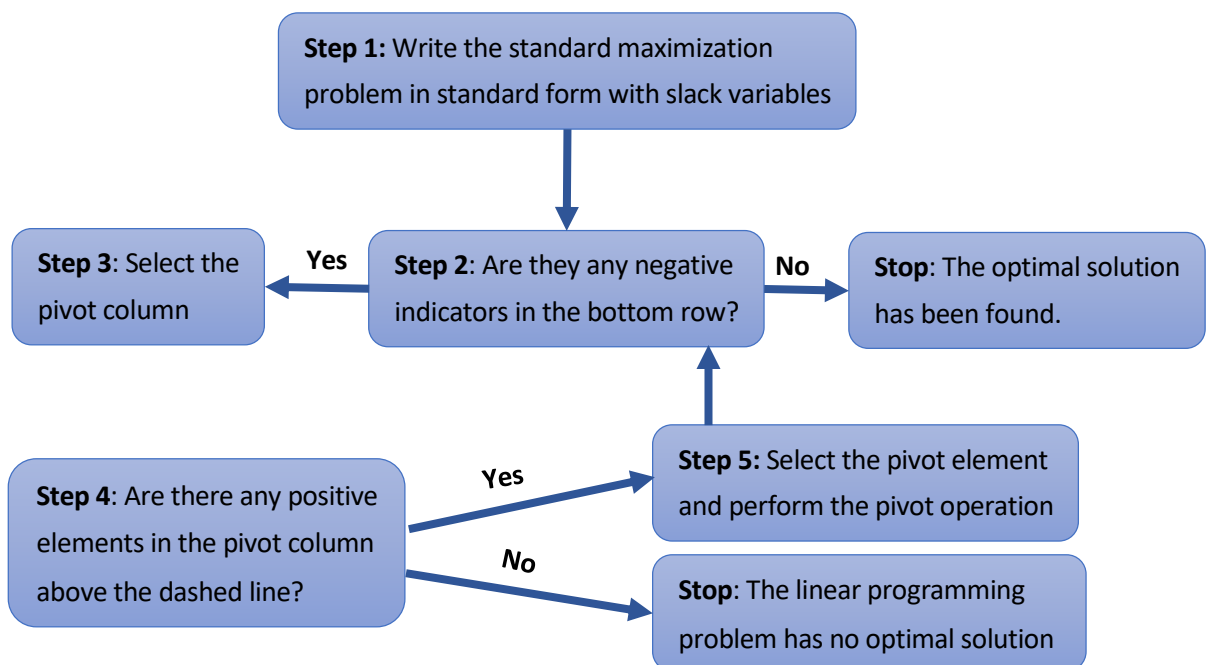


Figure 2. The Simplex method summarized. Extracted from (Dobbyn 2015)

In the case of the Big M method, it extends the power of the simplex method to any problem containing any combination of less than, greater than or equal constraints. This is done by associating these constraints with large negative constants which are not part of any optimal solution. In other words, as stated in (“The Big M Method” 2017) the Big M method is a version of the Simplex algorithm that solves the optimization problem by adding artificial variables to it. Artificial variables are variables with no physical meaning in the original problem. In this sense, they are only added for the purpose of obtaining basic feasible solutions so that the Simplex method can be applied (“The Simplex Method. Maximization and Minimization with Problem Constraints. Introduction to the Big M Method” 2017) .

When writing a model, sometimes the most straightforward way of writing a constraint is involved with multiplying two or more variables. This product makes the model not to be linear. Most times, it is preferable to have linear programs and thus, there is a need to linearize the model. This can be done with the Big M method.

So, the steps that have to be follow to apply the Big M method are the following (“The Big M Method” 2017):

1. Modify the constraints to that the right hand side (RHS) of each constraint is nonnegative and identify each constraint as a  $\leq$ ,  $\geq$  or  $=$  constraint.
2. Convert each inequality constraint to standard form.
  - If it is a less than constraint, a slack variable  $s_i$  is added.
  - If it is a greater than constraint, an excess variable  $e_i$  is subtracted
3. Add an artificial variable to the constraints identified as  $\geq$  or  $=$  constraints at the end of Step 1. Also add the sign restriction  $a_i \geq 0$ .
4. If the LP is a maximization problem, add for each artificial  $-M \cdot a_i$  to the objective function, where M denotes a very large positive number.
5. If the LP is a minimization problem, add for each artificial  $M \cdot a_i$  to the objective function, where M denotes a very large positive number.
6. Solve the transformed problem by the Simplex algorithm.

If all artificial variables are equal to zero in the optimal solution, the optimal solution to the original problem has been found.

In the following sections several concepts regarding sustainability and contributing disciplines are presented.

## 2.2. Sustainability and sustainable development

Sustainability and sustainable development started being social and scientific movements that aimed to warn of environmental crises and nowadays they have become key values for industry, governments and society. A recurring concern in nowadays society is the effective use of resources. Humanity has an intense written history of resource scarcity warnings and increasing attention to related issues, this is the main reason why the concepts of sustainability and sustainable development emerged.

The concept of sustainability (or sustainable development, more specifically) was first defined in 1987, in the report “Our Common Future” by the Brundtland Commission Report (Brundtland 1987), where it was described as “development that meets the need of the present without compromising the ability of future generations to meet their own needs”. That same document was especially concerned with the existing tension between the aspirations of mankind towards a better life and the limitations imposed by nature. In the course of the time, the concept has been interpreted in order to encompass three dimensions, namely social, economic and environmental. Generally, the components of sustainability are represented as overlapping circles, as it is depicted in the figure below:



Figure 3. The classic factors of sustainability

As represented in the figure above, the three main concepts are economy, society and environment. Thus, sustainability appears in the area where all these three components converge. The overlap of society and environment considers eco-social factors. Then, the overlap of society and economy

considers socio-economic factors and finally, the overlap of economy and environment is eco-economics.

What can be extracted from the Brundtland report is that environmental concerns are relevant, but the basic argument is one of welfare, seen in a perspective of inter-generational equity. In other words, it suggests that we should care for the environment not because of its intrinsic value, but in order to preserve all those resources for our children and the forthcoming generations. Furthermore, it also speaks of two concepts that should be reconciled: development and the environment. This could also be interpreted as need versus resources or as the short versus the long term. Nowadays, however, sustainability is generally seen in terms of the three dimensions that were explained in the Venn diagram above. This fact is contained in the definition of sustainability adopted by the United Nations in its Agenda for Development: "Development is a multidimensional undertaking to achieve a higher quality of life for all people. Economic development, social development and environmental protection are interdependent and mutually reinforcing components of sustainable development" (Kuhlman and Farrington 2010).

Apart from this conception of sustainability in three dimensions. There is another approach that distinguishes between "strong" and "weak" sustainability. Regarding to this second approach, the distinction between "strong" and "weak" sustainability is the following, as stated in Pearce et al. in (Pearce 1992):

- That the next generation should inherit a stock of wealth, comprising man-made assets and environmental assets, no less than the stock inherited by the previous generation.
- That the next generation should inherit a stock of environmental assets no less than the stock inherited by the previous generation.

These two views have thus been called "weak" and "strong" sustainability, respectively. Some resources must fall under the requirements imposed by strong sustainability, while others under the weak one. Which of the two it is will depend on the degree to which they can be substituted by capital. The depletion of fossil fuels, for example, is an issue of weak sustainability, due to the fact that there are other developed sources of energy and we are not obliged to leave our descendants an undiminished stock of petroleum. On the other hand, an extinct species cannot, with the current technologies, be recovered, and must thus be considered an issue in terms of strong sustainability.

According to Tom Kuhlman and John Farrington in (Kuhlman and Farrington 2010), "strong sustainability can be seen as a series of thresholds that must not be crossed. In impact assessment, any outcome of a proposed intervention must fall within those thresholds. Setting such thresholds is largely a matter of socially and politically determined preferences, but also a matter of resilience". On the



other hand, weak sustainability is presented as the yardstick by which policy outcomes within the thresholds of strong sustainability are judged.

Over time, several initiatives in order to promote sustainability have been developed. The UN, for instance, sponsors periodic follow-up summits, including the Millennium Summit in Johannesburg 2002, and Rio+20 2012 again in Brazil. Apart from these, investigation in terms of process and chemical engineering is promoted nowadays by the EU in the SPIRE (Sustainable Process Industry through Resource and Energy Efficiency) summons included in the H2020 (Horizon 2020) programme.

Once sustainability and sustainable development have been presented, it is time to discuss about other concepts. Coming up next, the supply chain concept.

### 2.3. Supply Chain

The term of supply chain refers to a system of independent organizations or participating companies that are inter-connected in a particular way with the objective to deliver products or services from suppliers to consumers. The activities derived from supply chain involve the transformation of natural resources, raw materials and different components into a finished product that is delivered to a given end customer. From another perspective, a supply chain could be defined as a complex and dynamic supply and demand network, where all each of the involved organization adds value to a stream of transformed inputs until they are converted into a given set of end products demanded by the end consumers (Lu 2011).

In an intuitive manner, one can imagine a supply chain as something similar to a “chain” in which the links represent the participating companies which are connected in the adding value process. This is depicted in the figure below:

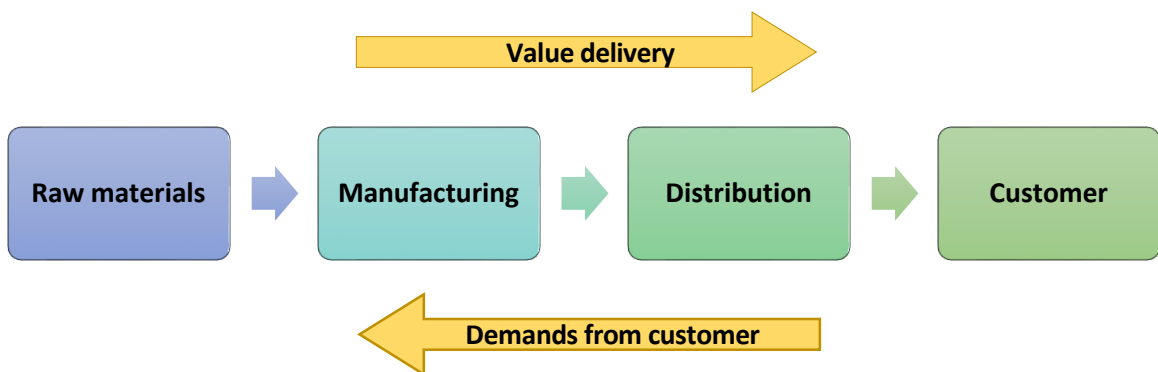


Figure 4. The basic supply chain model – Forward logistics

However, it is obvious that real world supply chains are much more complex than what is shown in the figure above. More than a “chain”, they represent a network when there are multiple suppliers and multiple customers for all the companies participating in the chain (Lu 2011).

Many concepts emerged in the light of supply chain, some of which are relevant for the topic of the present project. These are explained in the lines below.

### 2.3.1. Reverse logistics

According to the Council of Supply Chain Management Professionals (CSCMP) logistics management arises in the context of supply chain management, being it the part in charge of planning, implementing and controlling the efficient, effective forward and reverse flow and storage of goods, services and related information between the point of origin and the point of consumption in order to meet customers' requirements. In spite of the fact that this definition contains both forward and reverse flows, in general when the term “logistics” is used, it refers to a forward flow (from raw materials to end user), while for reverse flows the term “reverse logistics” is used instead, meaning that the flow moves from end user to recovery or to a new user (Rezaei 2015) (de Brito and Dekker 2003).

Thus, reverse logistics is a relatively new research area that concentrates on all the streams where there exists a value of interest that can be recovered so that the outcome of the system is able to enter a new or not necessarily new supply chain. In this context, reverse logistics can be seen as a part of sustainable development, as it can be conceived as “the implementation at the company level by making sure that society uses and re-uses both efficiently and effectively all the value which has been put into the products” (de Brito and Dekker 2003). Subsequently, this discipline emerged as a means to face the most relevant environmental issues in logistics, which are consumption of nonrenewable natural resources, air emissions and both hazardous and non-hazardous waste disposal, among others (de Brito and Dekker 2003).

The following figure depicts the implications of a reverse logistics network:

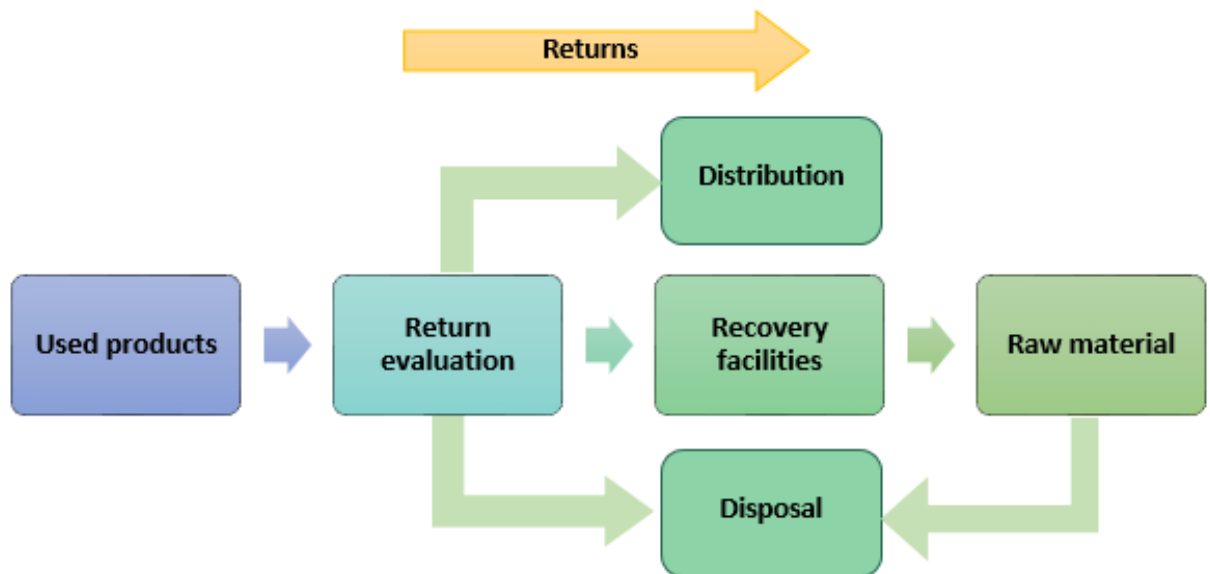


Figure 5. Reverse logistics basic network

It must be noted that reverse logistics are different from waste management because the latter refers to the process of collection and waste processing, understanding waste as a set of products for which there is no potential new use. Moreover, reverse logistics also differs from the concept of green logistics as that considers environmental aspects to all logistic activities and it has specially focused on forward logistics.

In the context of reverse logistics, there are a plenty of alternatives that companies develop with returned products or materials, namely as reutilization, repair, renovation, reprocessing, cannibalization or recycling (Akdoğan and Coşkun 2012).

The border between forward logistics and reverse logistics is not strictly defined because the implications of the definition of the concept “raw material” or about who the “end user” is. Thus, a holistic view on supply chains that combines both forward and reverse logistics and emphasizes the importance of coordinating the forward and reverse streams is included in the closed-loop supply chain concept (de Brito and Dekker 2003). This concept is explained in the following section.

### 2.3.2. Closed-loop Supply Chain

As it has just been stated, closed-loop supply chains represent a holistic view of a supply chain, where the product life cycle does not end when it arrives to the final customer. On the contrary, after the product has arrived to the final customer, it is reintroduced to the chain for its further reuse. In parallel, the amount of non-renewable raw materials required is reduced with time, because of the available amount of recycled material to be used. With this concept, the product life gets longer and thus, represents a more sustainable supply chain.

Before explaining the concept in a deeper way, it must be outlined that close-loop supply chain is the network that results from considering forward and reverse supply chains simultaneously. The following figure depicts a closed-loop supply network:

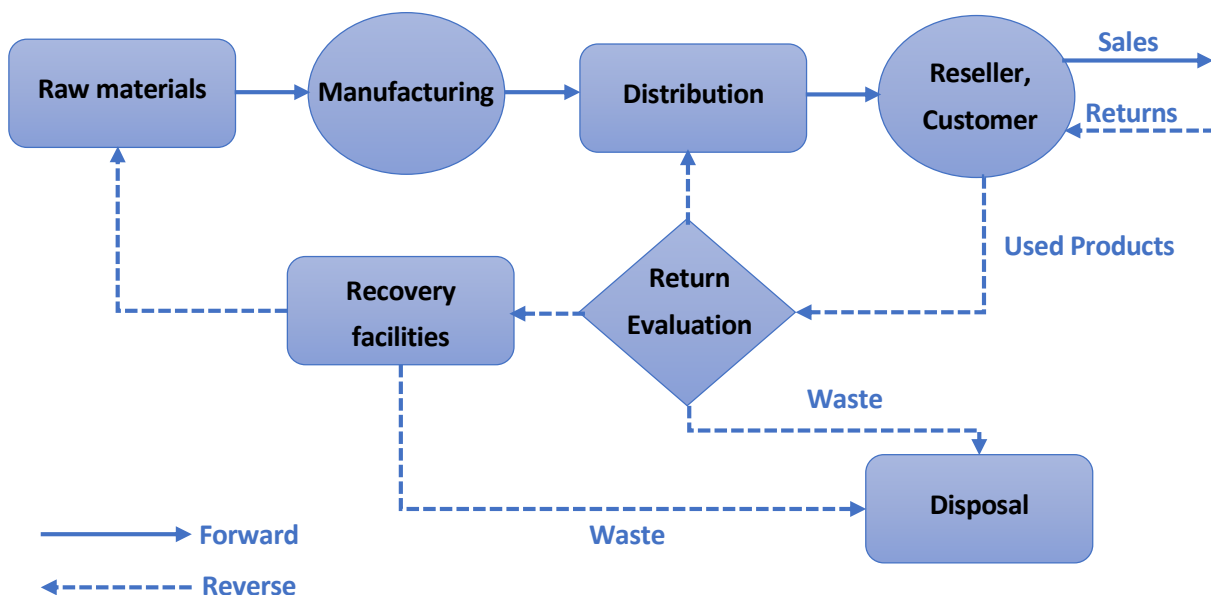


Figure 6. A Generic Form of Closed-loop Supply Chain. Extracted from (Govindan, Soleimani, and Kannan 2015)

As shown in the picture, the classical (forward) and reverse supply chains are represented by solid lines and dashes respectively. There is a stage called “Return Evaluation” where possible decisions on return products are made, to decide whether a used product should be send to a recovery facility, directly to the distribution process or to disposal.

There is a more recent definition of closed-loop supply chain, stated by Guide and Van Wassenhove (2009) . Based on this definition, closed-loop supply chain management is “the design, control and operation of a system to maximize value creation over the entire life cycle of a product with dynamic

recovery of value from different types and volumes of returns over time”. What is important about this definition is the explicit economical or business perspective beyond other factors such as social and legal responsibilities, for example (Govindan, Soleimani, and Kannan 2015).

Once these relevant topics in supply chain management have been introduced, further discussion on other concepts is now made.

## **2.4. Circular Economy**

From an economics perspective, environment is a public good, resulting this in the thorny issue of the adequate allocation of costs and profits. In this sense, the profit of generating growth and the pollution associated to it is mainly private whereas the social or environmental cost is shared. This results in a big amount of pollution. This same public good problem is shared with renewable resources that are openly accessible. For example, the benefits obtained by harvesting a given amount of fishes is private, while the cost of the overexploitation derived from this is shared by a whole community or even by the entire population. With respect to renewable resources, the problem regarding sustainability is linked to the misuse of the resource and not whether or not it can be renewed. In general terms, the public good issue justifies public interventions through regulations, taxes, emissions permits, etc. and both environmental protection and sustainable development are generally predicated on the intervention by a public authority.

In addition to this, there is a fundamental question posed by environmental scientists and professionals as to whether our development has already been excessive. Many professionals suggest that humanity has already had overshoot or will soon overshoot the carrying capacity of our planet. Seen from this perspective, sustainable development is perceived by some people as a paradox, because the term “development” is associated with continuous growth from the point of view of industry, economy, agriculture and consumption. Thus, eternal growth cannot be sustainable. On the contrary, the only sustainable development that is possible is when the carrying capacity of a given environment is at steady state or equilibrium. If carrying capacity has already been exceeded, sustainability demands a contraction in the consumption of environmental resources.

As suggested by Sauvé et al. in (Sauvé, Bernard, and Sloan 2016), given that “environmental sciences” are defined as the set of aspects dealing with environmental issues in the broadest context of disciplines and applications, and “sustainable development” as a conceptual framework where the welfare of present and future generations is taken into account and where the effects of humanity’s current growth efforts have to deal with an environmental constraint, the question then becomes

whether certain sustainable development approaches are more sustainable than others. This is where circular economy emerged.

Thus, “Circular economy” refers to a model of production and consumption that completely differs from the “linear economy” model that has dominated society along the years. To understand circular economy, it is first necessary to define what linear economy is. This latter concept is based on a simple, linear process: first extract, then produce, afterwards consume and finally trash, paying little or no attention to the pollution generated at each step. Moreover, the linear economy model is characterized by the big importance it gives to economic objectives, with little or no regard for ecological and social concerns. However, the planet has finite boundaries, and even in this linear economy model of production and consumption, the wastes that are generated through extraction of raw materials and production of the goods and the consumption of the final products come around to haunt society as pollution due to the fact that they will eventually end up either in a landfill or dispersed in ways that pollute the environment.

On the contrary, circular economy aims to decouple prosperity from resource consumption. For example, it aims to find solutions for being able to consume goods and services and yet not depend on the extraction of virgin materials, ensuring at the same time closed loops that will prevent the eventual disposal of consumed goods in landfills.

The following figure aims to contrast the concepts of linear and circular economy. If economy is put in a global context, it takes place in a loop where the planet plays a key role in providing resources and absorbing waste and pollution. This model holds as long as the carrying capacity of the planet is not overshoot. The left model, depicting linear economy, ignores the environmental impacts arising from resource consumption and waste disposal, and results in extracting too many virgin resources, pollution and waste. Because linear economy ignores much of the loop, it is usually represented as a line, with a beginning (extraction) and an end (disposal), and the potential returns to Earth are lost through pollution. In contrast, circular economy, which is shown in the right part of the figure, takes into account the impact of resource consumption and waste on the environment. This generates closed loops where resources follow circular movements within a system of production and consumption. Thus, the objective of circular economy is to optimize the use of virgin natural resources and reduce pollution and waste at each step.

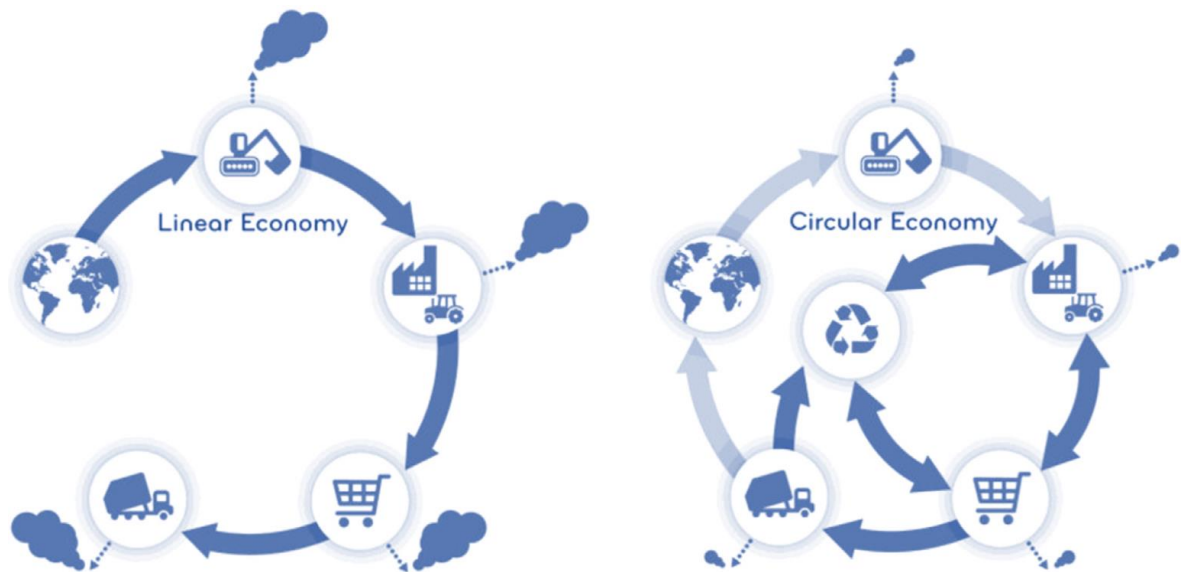


Figure 7. Comparison between linear and circular economy. Extracted from (Sauvé, Bernard, and Sloan 2016)

However, the concept of “circular economy” is not new. It has its origins in a wide variety of disciplines related to, for instance, product life and the substitution of services for products (Stahel 1997), cradle-to-cradle approaches, where waste becomes a value-producing resource (McDonough et al. 2003) and industrial ecology (Graedel and Allenby 1995). What is new is the importance that the concept is gaining amongst business professionals (Ellen MacArthur Foundation 2014), policy advocates (Preston 2012) and teachers (Webster and Johnson 2010). Moreover, the concept is being adopted by governments in both Europe (Bonciu 2014) and Asia (Geng and Doberstein 2008).

This increased attention to the “circular economy” concept may be partially due to its capacity to provide a solid basis for reconciling the issue of how to promote productivity while considering the external parts of the production process, the consumption of products and the end-of-life impacts. In this sense, circular economy promotes the production of goods via closed-loop material flows and could provide the economic incentives to ensure that products that have already been consumed get reintegrated into the manufacturing process. In circular economy, the consumption of virgin raw resources is reduced to optimize the use of by-products, wastes or recycling of discarded products and reduce the pollution generated at each step. In these loops, combination of integrated processes or industrial activities act synergistically to feed and be fed by one another. Thus, the by-products from one industry serve as resources for the next and energy consumption is shared for optimal use (Sauvé, Bernard, and Sloan 2016).

Circular economy promotes the resiliency of resources and it aims to replace the traditional linear economy model of fast and cheap production and cheap disposal with the production of long lasting goods that can be repaired, or easily dismantled and recycled. In this sense, circular economy production models aim to emulate processes similar to those that happen in natural environments,

where little is wasted and most is recovered by different species. Cooperation and competition among species occur in nature, maintaining thus the efficiency of natural ecosystems and providing flexibility and adaptability to the system. If this metaphor was applied to economic systems, it would help improve healthy competition and maximum efficiency for using the available resources (Sauvé, Bernard, and Sloan 2016).

## 2.5. Industrial ecology

This section describes the field of industrial ecology, identifying its key topics, characteristic approaches and tools. The objective of this description is to provide an overview of the endeavours that comprise the topic and the relation between them.

The concept “industrial ecology” conveys some of the content of the field itself. Industrial ecology relates to industry in the fact that it focuses on manufacturing processes and product design. From this perspective, firms are seen as agents for environmental improvement due to the fact that they possess the technological expertise needed to successfully design products and processes with an environmental concern. In this sense, industry is relevant because it is an important source of environmental damage. Furthermore, it represents the portion of society that produces most goods and services (Lifset and Graedel 2002).

On the other hand, “industrial ecology” is ecological in at least two senses. As stated in (Frosch and Gallopoulos 1989) who did much to start this field, industrial ecology looks to non-human “natural” ecosystems as models for industrial activity. A plenty of biological ecosystems are particularly effective at recycling resources and due to this, they are posed as an example for efficient cycling of materials and energy in industry. Secondly, industrial ecology places human technological activity in the context of the bigger ecosystems that support it, examining the sources of resources that are used in society and the means that might act to absorb or process wastes. This latter sense of “ecological” links industrial ecology to questions of carrying capacity and ecological resilience, putting into question whether, how and to what degree technological society is endangering the ecosystems that provide a critical service to humanity (Lifset and Graedel 2002).

In this line, the development of industrial ecology is an attempt to provide a new framework for understanding the impacts of industrial systems on the environment. Thus, it is useful to identify and then implement strategies to reduce the environmental impacts of products and processes associated with industrial systems, having as an ultimate objective sustainable development.



Although there is not an only definition of the “industrial ecology” concept, it could be said that industrial ecology refers to the study of the physical, chemical and biological interactions and interrelationships both within and between industrial and ecological systems. Moreover, some researchers believe that industrial ecology involves the identification and implementation of strategies for industrial systems to emulate sustainable and ecological ecosystems.

Apart from this, it should be noted that most definitions of the concept comprise similar attributes with different emphases. These attributes are the following (Garner 1995):

- A systems view of the interactions between industrial and ecological systems
- The study of material and energy flows and transformations
- A multidisciplinary approach
- An orientation towards the future
- A change from linear (open) processes to cyclical (closed) processes, so the waste from one industry is used as an input for another
- An effort to reduce the environmental impacts of industrial systems
- An emphasis on integrating the industrial activity into ecological systems
- The idea of making industrial systems emulate more efficient and sustainable natural systems
- The identification and comparison of industrial and natural systems hierarchies, which indicate areas of potential study and action

This description of industrial symbiosis can even be made more specific by defining the core elements in the field. These are the following:

- The biological analogy  
This analogy has been applied basically at the level of facilities, districts and regions, using notions borrowed from ecosystem ecology regarding material and energy flow, especially regarding to the cycling of materials, nutrients and energy in ecosystems as a potential model for relationships between facilities and firms (Lifset and Graedel 2002).
- The use of systems perspectives  
Industrial ecology emphasizes the critical need for a systems perspective in the context of environmental analysis and decision making. This would allow to avoid narrow or partial analyses that can overlook relevant variables or even lead to unintended consequences. This systems perspective is manifested in several forms, namely (Lifset and Graedel 2002):
  - Use of life-cycle perspective
  - Use of materials and energy flow analysis
  - Use of systems modelling
  - Sympathy for multidisciplinary and interdisciplinary research and analysis.

- The role of technological change  
Technological change is an outstanding path for pursuing the achievement of environmental goals as well as a very relevant object of study (Lifset and Graedel 2002).
- The role of companies  
Business plays an important role in industrial ecology because of two main reasons. First, because business is directly related to technological innovation and to the potential for environmental improvement (Lifset and Graedel 2002).
- Dematerialization and eco-efficiency  
In order to achieve more complex ecosystems, it requires to diminish resource consumption and environmental releases. This translates into a cluster of related concepts, which are dematerialization, materials intensity of use, decarbonisation and eco-efficiency, among others (Lifset and Graedel 2002).
- Forward-looking research and practice  
Much of the research in the field of industrial ecology is intentionally prospective. It puts into question how things might be done in a different way to avoid the generation of environmental problems in the first place, avoiding irreversible harms and damages (Lifset and Graedel 2002).

Finally, it is important to note some options in which these topics and frameworks could be integrated to turn into a larger whole. There are two main ways studied, which are now explained.

The first one is to conceive industrial ecology as operating at a variety of levels, namely at the firm or unit process level, at the inter-firm, district or sector level and finally at the regional, national or global level. This is depicted in the image below:

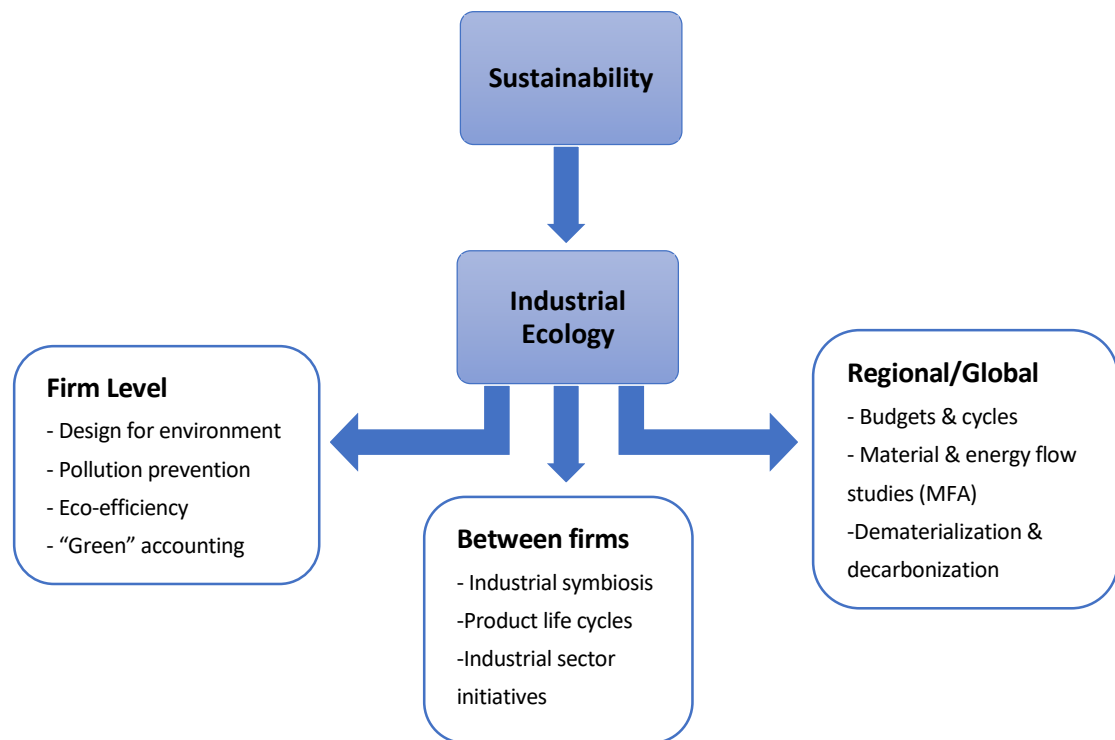


Figure 8. The elements of industrial ecology viewed as operating at different levels. Extracted from (Lifset and Graedel 2002)

The second way to tie elements together is to see them as a reflexion of the conceptual or theoretical aspects of industrial ecology on the one and on the other as more focused, application-oriented tools and activities. This is depicted in the image below and it must be stated that many of the conceptual and interdisciplinary aspects of industrial ecology as comprised in the left side of the figure whereas the more practical and applied aspects appear on the right hand side of the figure.

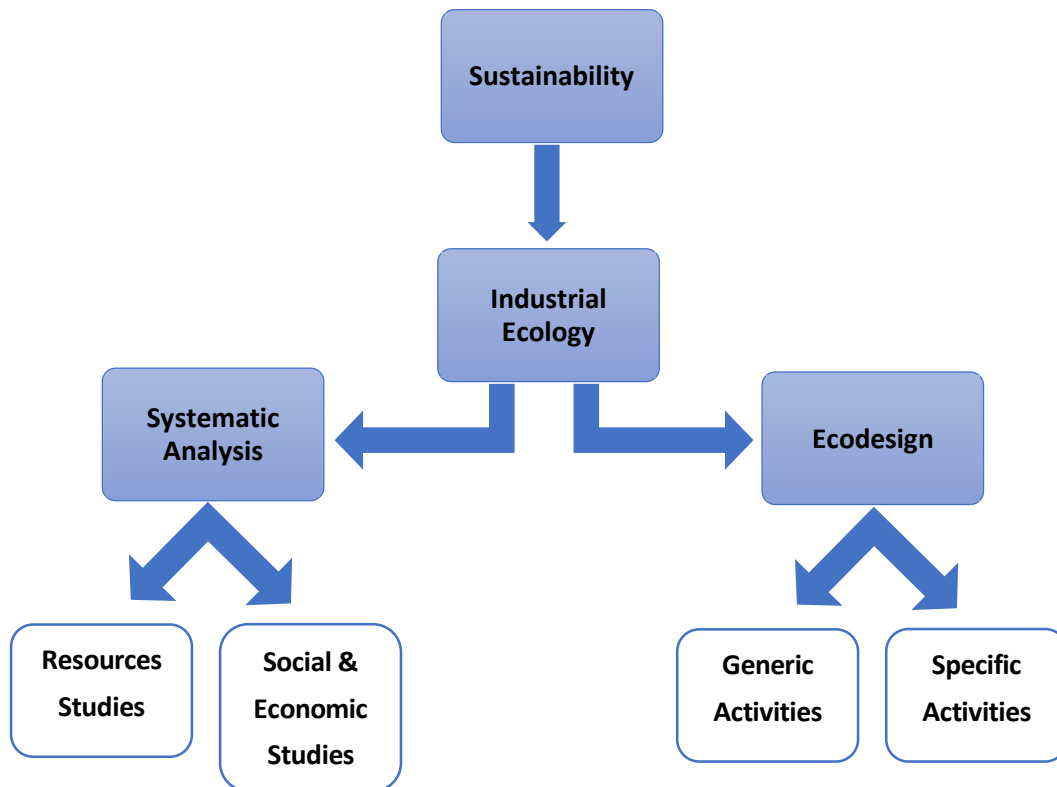


Figure 9. Industrial ecology conceptualized in terms of its system-oriented and application oriented elements. Extracted from (Lifset and Graedel 2002).

Environmental problems are systemic and for this reason they require a systematic approach so that the links between industrial practices or human activities with environmental or ecological processes can be more easily identified. This holistic view of environmental problems included in the concept of industrial ecology makes them easier to recognize and solve.

## 2.6. Industrial Symbiosis

With the rising of human civilizations, societies started to extract and use resources from nature in order to subsist and develop as a collective. These resources seemed to be unlimited at first and gave humanity the opportunity to generate unlimited waste. At that time, resources were not a matter of concern because the amount of population on Earth was insignificant in comparison to the amount of resources available. However, this unlimited resource consumption generated unlimited waste which later became a great concern. From there, different strategies have been taken to back the waste into production systems. This thinking gave birth to an idea where different entities or companies

collaborate together to enhance sustainable use of resources. This concept is generally termed as industrial ecology, which has just been explained. On contraposition, previously common thought was that industries go opposite to the environment. This new conception helped to establish a connection between industries and environment to attain sustainability as the resources are limited (Rahman, Islam, and Islam 2016).

Industrial symbiosis emerged as a part of industrial ecology and it consists of engaging traditionally separate entities in a collective approach to competitive advantage involving physical exchange of materials, energy, water and by-products. The key concepts to industrial symbiosis are collaboration and the synergistic possibilities offered by geographic proximity (Chertow 2000)

According to Frosch & Gallopoulos (1989), an industrial ecosystem is a system where the consumption of materials and energy is optimized, waste generation is minimized and the effluents of one process serve as raw materials for another process (Frosch and Gallopoulos 1989). It works as an analogous of biological ecosystems. In that same article by Frosch & Gallopoulos, "Strategies for Manufacturing" (Frosch and Gallopoulos 1989) it is suggested that an ideal industrial ecosystem may never be achieved in practice, but both manufactures and consumers must change their habits to approach it more closely if the industrialized world is to maintain its living standard and the developing countries are to raise theirs to a similar level without affecting to the environment in an adverse manner (Rahman, Islam, and Islam 2016). Furthermore, it was also denoted that the consumption of energy and materials is optimized and the effluent of one process serve as raw material for a different process (Frosch and Gallopoulos 1989). In the light of this, industrial symbiosis creates a sense what we should do and industrial symbiosis shows us a prospect of what we can do in the future (Rahman, Islam, and Islam 2016).

Symbiosis came from the Greek word "syn", which means together, and "biosis" which means living. Therefore, symbiosis literally means short term or long term relationship between two individuals. The concept builds on the notion of biological relationships in nature, in which at least two otherwise unrelated species exchange materials, energy, or information in a mutually beneficial manner (Chertow 2000). Comparatively, the industrial symbiosis concept is used to describe geographically proximate inter-firm relationships involving the exchange of residual materials, water and energy.

IS thus engages different organizations in a network to foster eco-innovation and long-term cultural change. According to Rahman et al. (Rahman, Islam, and Islam 2016) "creating and sharing knowledge through the network leads to mutually profitable transactions for novel sourcing of required inputs, value-added destinations for non-product outputs, and improved business and technical processes."

According to Chertow and Lombardi (2005), "the environmental benefits of industrial symbiosis are quantified by measuring the changes in consumption of natural resources, and in emissions to air

water, through increased recycling of materials and energy”. Even though this way of accounting for the benefits of IS (industrial symbiosis) might not take into account secondary effects, for instance efficient use of buildings, personnel, etc., it is still a reasonable way of simplifying the system and focusing on the effects of IS (Wolf and Karlsson 2008).

In this context, eco-industrial parks are conceived as particular realizations of the industrial symbiosis concept. The first approach in this field appeared in 1989 when some interrelated firms started to share their resources in Kalundborg, Denmark. This set a milestone in the field of industrial ecology and justified the theory of Frosch & Gallopoulos as it was the first fully realized model of industrial symbiosis (Rahman, Islam, and Islam 2016). The primary partners in Kalundborg, an oil refinery, a power station, a gypsum board facility, a pharmaceutical plant and the same city of Kalundborg, started to share ground water, surface water and waste water, steam and electricity and also a wide range of residues that became feedstock in other processes. The very initial industrial symbiosis scheme of Kalundborg is depicted in the figure below:

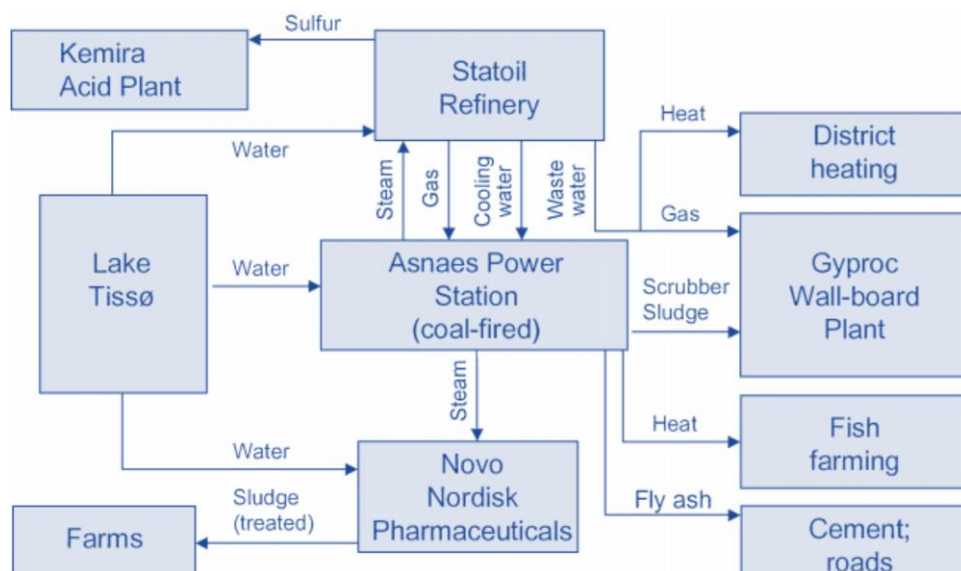


Figure 10. Industrial symbiosis at Kalundborg. Extracted from (Chertow 2000)

Cooperation of such nature has significantly increased both environmental and economic efficiency and it has also created less tangible benefits for all the industries involved, regarding shared personnel, equipment and information sharing (Chertow 2000).

After the emergence of Kalundborg, several industrial synergies have been discovered and initiated in at least 27 countries. Moreover, more than 300 European and non-European eco-industrial parks have already shown greater prospects. These industrial clusters will very likely form a symbiotic network if they are provided with three main privileges (Rahman, Islam, and Islam 2016):

- By product reuse
- Utility or infrastructure sharing
- Joint provision of services

Furthermore, another important component is policy instruments, which can have a two-sided effect. On the one hand, sometimes it helps in symbiosis formation. On the other hand, it can impose several restrictions on industrial owners hindering potential projects and making them unsuccessful.

Thus, approaches, opportunities and barriers and policy instruments are three important attributes of industrial symbiosis networks.

In this context, literature review gives us two different processes for arising industrial symbiosis networks. The first, is a self-organization process and the second is third party planning or engineered process. Spontaneous processes happen through the “happenstance of people meeting and liking one another”, while goal-directed processes occur when “parties interact to achieve, plan, coordinate, or decide on their individual and collective activities”. From these two approaches of industrial symbiosis, it is clear that the different parts or entities have some key roles to accomplish in order to achieve certain goals. In this sense, government together with its institutions can play lead roles by adopting some programs that would be for instance reducing taxes or providing incentives for companies who adopt symbiosis in their processes and production systems. Furthermore, research organizations can help the organizations that adopt industrial symbiosis by providing tools, design approaches, information on resources to make the best decisions possible (Rahman, Islam, and Islam 2016).

It must be especially outlined that bilateral resource sharing can be of great importance as it would increase performance of the industries were both of the parties are in a win-win situation and all the related environmental aspects are also ensured. For this, before waste disposal, usable items should be separated from non-usable. Again, the non-usable items for one production system might be required by others. This whole procedure would lead to a diminishment of the waste volume to a smaller one and industries would be benefited as well (Rahman, Islam, and Islam 2016).

## 2.7. “Waste-Resource” Initiative

In the context of the topics that have been explained in this chapter, there is a governmental initiative in Spain called “Waste-Resource” that aims to help enterprises in their waste management with the ultimate objective of turning the waste materials of a company into profitable compounds for another. It is a virtual and free data base from companies around Spain that can contact each other in order to negotiate waste and byproducts management or the trading of industrial raw materials. This idea allows companies to reduce costs in terms of searching for materials and it helps diminishing the consumption of virgin raw materials. In this sense, any company willing to buy and sell by-products, wastes and secondary raw materials can sign in to become a user of the virtual platform. Thus, any user can publish and search as many offers or requests as desired. Summarizing, “Waste-Resource” is a secure and efficient way to negotiate with other users and transform waste into added-value resources. The image below shows a screenshot of the platform:

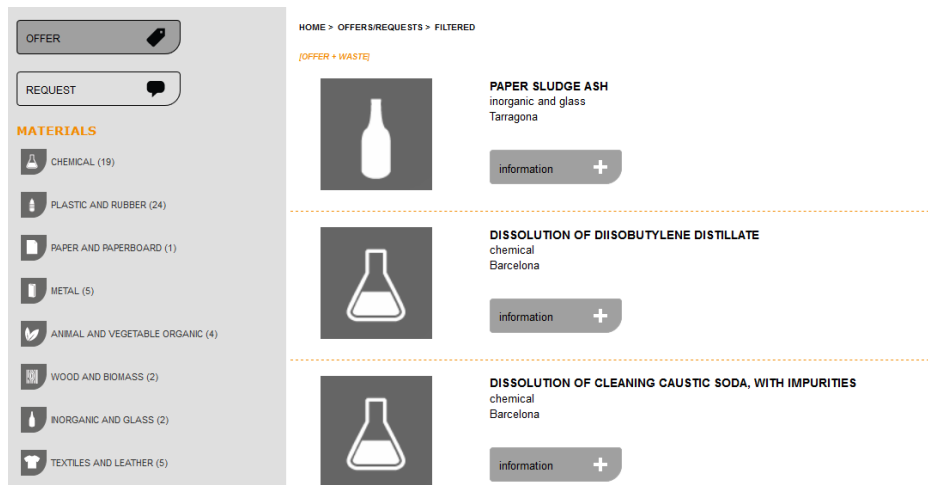


Figure 11. Screenshot of the "Waste-Resource" platform. Extracted from (“Residuo-Recurso” 2017)



### 3. Tools and Software

The present section aims to describe the tools and software that have been used during the development of this project. In this sense, the main software involved are Microsoft Excel, HYSYS and the General Algebraic Modelling System (GAMS).

On the one hand, MS Excel is a spreadsheet developed by Microsoft which features several tools involving calculation, graphing tools, pivot tables and a macro programming language called Visual Basic for Applications. The initial release of the program was in 1987, 30 years ago (“History of Excel - Excel Chronology” 2015). From then, Microsoft has pushed the tool with regular new releases, approximately one every two years. In the context of chemical engineering, MS Excel is a widely used tool that allows the user to perform from simple arithmetic operations to complex problems involving iterations or optimization. Moreover, this tool can be helpful to build simulators of chemical engineering process units such as reactors, distillation columns, splitters and so on. The following picture shows a screenshot of MS Excel 2016 default screen. In this sense, one of the features that makes Excel attractive is its interface, which allows the user to perform whatever operation or procedure required in a very intuitive way.

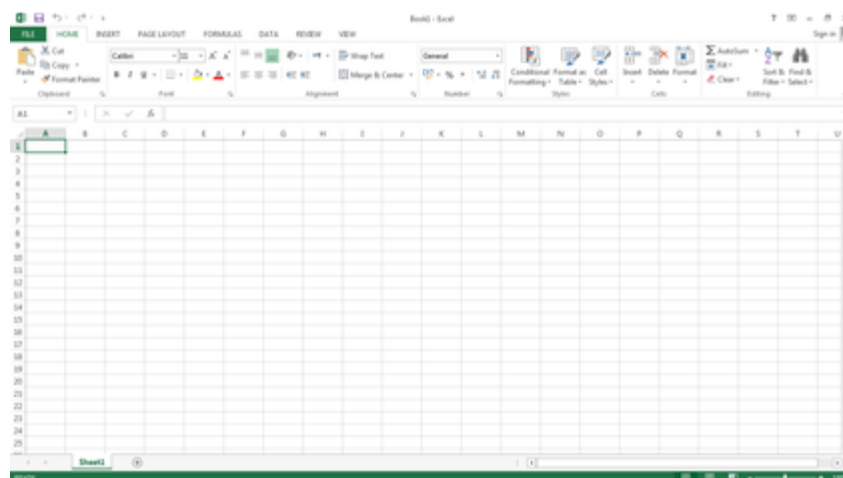


Figure 12. MS Excel 2016 default screen

On the other hand, Aspen HYSYS is a process modelling environment for conceptual design and operations improvements in the context of chemical processes. Nowadays, it is the market-leading process simulator as it potentially provides great economic profits throughout the process engineering lifecycle (“HYSYS and UniSim” 2017). Moreover, it contains tools that allow the user to estimate physicochemical properties, mass and energy balances, liquid-vapour equilibrium and the simulation of several equipment in chemical engineering. Something that should especially be pointed out is the fact that HYSYS database contains the information of more than 15000 solid, liquid and gaseous

components and pure substances. The following figure shows a screenshot of the HYSYS software interface:

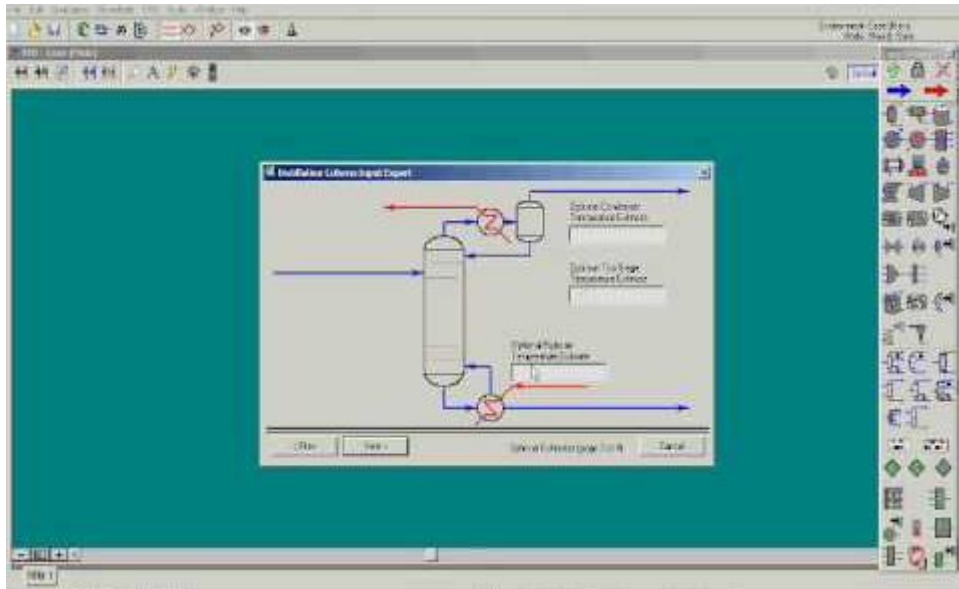


Figure 13. HYSYS software interface

Furthermore, the General Algebraic Modelling System (GAMS) is a high level modelling system for mathematical optimization. In this sense, GAMS is designed for modelling and solving several types of optimization problems, namely linear, nonlinear and mixed-integer. GAMS was first released as a commercial product in 1987 and it represented the first algebraic modelling language (AML) (“GAMS - Cutting Edge Modeling” 2017). Even though it was initially designed for applications related to economics and management science, it now has a wide community of users from diverse disciplines in engineering and science. In this sense, the main features of this software are, among others, the possibility of building large-scale modelling applications, formulating optimization problems in a notation similar to their algebraic notation with a powerful but relatively easy language. Moreover, one of the main design principles of GAMS is that it presents an open architecture and independent layers: model, solver, data, platform and user interface, allowing the user freedom to handle the software. In contraposition to the long list of pros it offers, the main disadvantage it presents is the lack of user-friendliness in terms of reading or representing the obtained results. The following picture shows a screenshot of the user interface:

```
display i, j, k, Cj, Ck, Cw, Mj, Mk, Q, D, H, CD;

*Context
Variables
    Fin(j)    Reagent's molar flow [mol per h]
    Fout(k)   Product's molar flow [mol per h]
    MFin(j)   Reagent's mass flow [kg per h]
    MFout(k)  Product's mass flow [kg per h]
    W(i)      Leftover atoms
    B         Benefits
    z(k)      Binary variable representing if suppliers' demand has been covered;

Positive variables    Fin, Fout, W;
Binary variables     z;

Equations
    Eqn1(i)
    Eqn2(j)
    Eqn3(k)
    Eqn4(k)
    Eqn5(k)
    Benefits
    Constz2(j);

*Equations
Eqn1(i) .. sum(j, Fin(j)*Mj(j,i)) =E= sum(k, Fout(k)*Mk(k,i))+W(i) ;
Eqn2(j) .. MFin(j) =E= Fin(j)*MWj(j) ;
Eqn3(k) .. MFout(k) =E= Fout(k)*MWk(k) ;
Eqn4(k) .. D(k)*z(k) =L= Fout(k) ;
Eqn5(k) .. Fout(k) =L= D(k)*z(k) ;
```

Figure 14. GAMS user interface

Thus, taking into account the user-friendliness limitations that GAMS presents, the procedure that has been followed consists of connecting GAMS with Excel in order to make the user experience more intuitive. Moreover, the HYSYS tool is used in order to obtain several parameters regarding thermodynamic data from the compounds involved in the explored system. In this sense, it is relevant to outline that to connect HYSYS with Excel, the Microsoft Visual Basic for Applications (VBA) programming software has been used. Moreover, regarding the obtaining of parameters from HYSYS, it should be stated that any external thermodynamic database could be used, in this case, HYSYS has been chosen because of its easiness to work with.

Thus, the steps that have been followed in order to accomplish it, is summarized in the following figure:

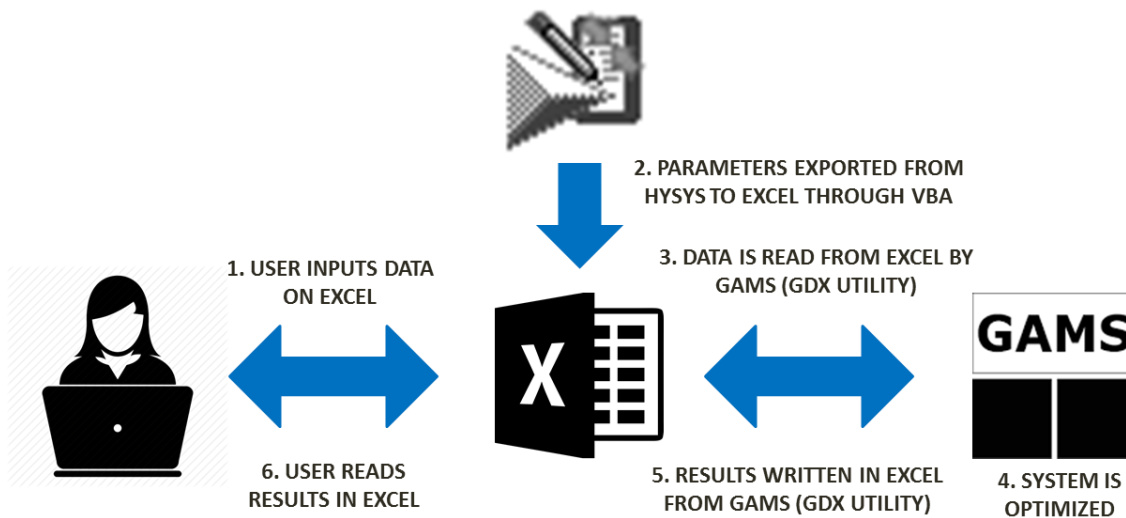


Figure 15. Tools & software procedure description

Thus, as depicted in the image above, the procedure is the following:

1. On the first place, the user introduces the necessary data in Excel
2. Secondly, the thermodynamic parameters at a given temperature and pressure are obtained from the HYSYS database and exported to Excel through VBA.
3. Then, the data is read from Excel by GAMS, by means of the GDx utility, which is later explained.
4. Afterwards, with all the necessary data now in GAMS, the system is optimized with the chosen Solver.
5. Then, the results are exported from GAMS to Excel.
6. Finally, the user is allowed to read the results obtained in a friendly way using Excel.

In the light of the points explained above, Microsoft Visual Basic for Applications (VBA) is a programming language used to program Windows applications and allows users and programmers to broaden the functionality of every Microsoft Office program. Generally, VBA code runs only within a host application, not as a standalone program. As stated before, in this case it is used to import data from HYSYS to Excel (“Getting Started with VBA in Office 2010” 2016).

Furthermore, it is essential to present the GDx utility. GAMS communicates with Excel via GDx (GAMS Data Exchange) files. These files store the values of one or more symbols from GAMS such as sets, parameters, variables and equations. These files can be used to prepare data for a model in GAMS, to present results of a model in GAMS, to store results of the same model changing parameters, etcetera. These GDx files are binary files portable between different platforms. These files are written using the

byte ordering original to the hardware platform they are generated on, but they can be read on a platform which uses a different byte ordering. Thus, in order to write data from GAMS to Excel, the user creates a GDX file and then the Excel file is generated from this GDX file following this procedure: GAMS → GDX → Excel. The opposite procedure works in a similar way: Excel → GDX → GAMS (“Data Exchange with Excel” 2017).

## 4. Methodology

At this point, it is crucial to define the working methodology that has been followed in order to achieve the set objectives. Thus, this section presents the methodology that has been followed during the development of this end of degree thesis.

It consists of the development of increasing complexity models that allow the identification of industrial symbiosis opportunities regarding material sharing in the chemical and process industry. So, this allows a systematic procedure to identify and assess the potential sharing alternatives, finding the targets or symbiosis opportunities that should be further investigated and eventually optimized.

In other words, it could be said that new considerations are taken into account at each model. This goes in line with the software learning procedure in the sense that with the development of each model, there are new features of GAMS, Excel and HYSYS that are learnt and can be implemented and included in the next model. Thus, there is an increasing difficulty at each step.

Furthermore, it should be stated that given a complex and a simple model, setting some values of the complex model to zero would result in obtaining the simple model. Apart from this, the simple model would be considered a simplification of the complex model, which would allow to establish bounds in the studied system.

This targeting approach allows to see promising industrial symbiosis opportunities, helping in the decision-making process. The following diagram depicts the modelling methodology that has just been explained:

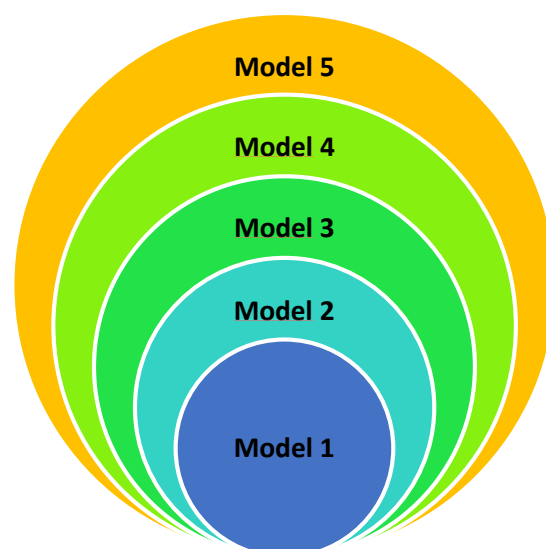


Figure 16. Modelling methodology

## 5. General Problem Statement

Research regarding industrial symbiosis (IS) networks has become increasingly popular during the last years due to the fact that IS offers a sustainable alternative for obtaining useful products without the usage of virgin materials by means of increasing materials' reuse and recycle.

As stated before, the objective of this thesis is to develop different quantitative modelling approaches related to IS and industrial ecology focusing in the optimization of these systems. For each of the developed models, different scenarios are established in order to solve a given problem.

The general problem statement consists of obtaining a given set of raw materials with a known characterization from the transformation of some waste compounds coming from diverse processes, being these the inputs of the system. Thus, given a set of inlet waste streams to be managed or disposed, a set of demanded raw material to feed different processes and a set of potential material transformations (chemical reactions) with related costs, the objective is to determine the targets or symbiosis opportunities within a network of chemical process industries. Decision variables address the amount of raw material demand covered by reused/recycled streams, the amount of waste entering the system to be treated and the amount to be disposed, among others. The models that have been developed include mass and energy balances and an economic objective function and lead to different Linear Programming (LP) and Mixed Integer Linear Programming (MILP) problems.

In this sense, the aforementioned raw materials, which are the system's obtained products, are demanded compounds to be introduced in further processes. In other words, this allows a conversion of leftover compounds into useful raw materials, being this last point the key objective of the industrial symbiosis' concept. The following figure shows a general scheme of what has just been explained:

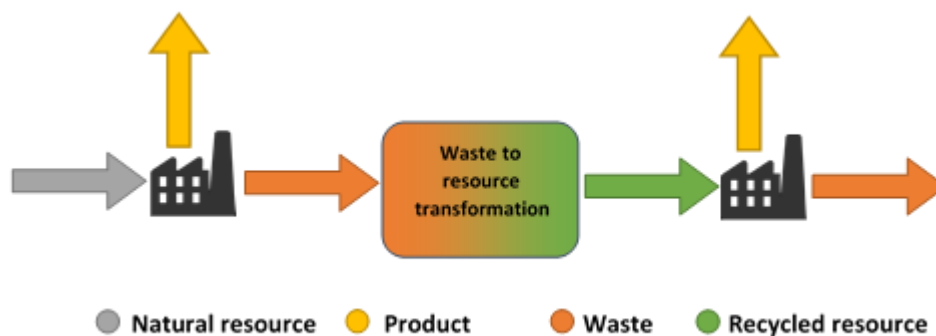


Figure 17. General problem scheme

As depicted in Figure 17, the most extended conception for a given industry in order to obtain a product of interest comes from the usage of natural resources or virgin materials that are transformed into the valuable product, generating some waste materials in the process. Generally, the life cycle of these waste materials is considered to be over. Thus, they are treated for their further disposal. In contraposition to this conception, the idea behind industrial symbiosis consists in being aware of the potential that these waste compounds present: with a series of transformations, which are studied and analysed in the developed models framed in this thesis, these leftover compounds could be transformed into useful raw materials that would input new processes. This fact would allow a minimization of the amount of natural resources consumed, which would imply at the same time a decrease of the environmental impact related to the studied process.

Moreover, in order to convince companies to change their production paradigm, the solutions implemented should be economically profitable. Due to this, all the objective functions that have been considered in this project are economic.

At this point, it is important to outline that all the models developed have been implemented in GAMS and solved using CPLEX/DICOPT through GAMS (General Algebraic Modelling System).

Coming up next, there is an exhaustive explanation of each of the models developed in the context of this general problem, specially emphasizing the procedure followed to advance from one model to the next one.



## 6. Case Study

This section presents and justifies the case study that has been selected to test the each of the developed models.

The selected case study recreates an industrial network based on ethylene, chlorine and related chemicals. In it, there is a set of waste streams each of which is coming from a given company or process in an industrial park. Thus, the symbiosis network proposed could be represented as a cluster of facilities that are designed to allow the exchange, conversion, mixture, treatment or even separation of streams containing C-H-O-Cl compounds. In this sense, it is relevant to outline that the focus of the industrial symbiosis proposed emanates from the atomic level. It is also worth noting that the elements that form the studied compounds (C, H, O and Cl) offer many opportunities for synergism as they are primary building blocks for many industrial compounds that could be exchanged and integrated in the system.

In this sense, the compounds that have been considered have a known chemical composition and are presented in the table below in an alphabetical order:

Table 2. Compounds considered in the case study

Name	Formula	Description
Acetic acid	CH <sub>3</sub> COOH	It is an important chemical reagent used primarily in the production of cellulose acetate for photographic film, polyvinyl acetate for wood glue and synthetic fibres and fabrics.
Benzene	C <sub>6</sub> H <sub>6</sub>	Benzene is used mainly as an intermediate to make other chemicals, such as ethylbenzene, cumene or cyclohexane. More than half of the entire benzene production is processed into ethylbenzene. Smaller amounts of benzene are used to make some types of gasoline additives, rubbers, lubricants, dyes, detergents and pesticides.
Chlorine	Cl <sub>2</sub>	Chlorine has a huge variety of uses: as a disinfectant or in organic chemistry as an oxidising agent. However, about 20% of chlorine produced worldwide is used to make PVC, a type of plastic widely used.

<b>Chloroethene (VCM)</b>	$C_2H_3Cl$	Vinyl chloride is a chemical intermediate, not a final product. As it is hazardous to human health, there are not end products that use vinyl chloride in its monomer form. However, vinyl chloride is polymerized and converted into PVC.
<b>Ethanol</b>	$CH_3CH_2OH$	It is the principal alcohol found in alcoholic beverages. Moreover, it is used medically as an antiseptic and as a medicinal solvent. It is also an important precursor for other organic compounds and a solvent. However, the largest single use of ethanol is as an engine fuel and fuel additive.
<b>Ethylbenzene</b>	$C_6H_5C_2H_5$	It is important in the petrochemical industry as an intermediate in the production styrene, a precursor of polystyrene, a common plastic. It is also used to make other chemicals, in fuel and as a solvent.
<b>Ethylene</b>	$C_2H_4$	It is widely used in the chemical industry, and its worldwide production exceeds that of any other organic compound. It is mainly used to obtain polyethylene, a widely used plastic. However, it is useful to produce several compounds such as ethylene oxide, ethylene dichloride or ethylbenzene.
<b>Ethylene Dichloride (EDC)</b>	$C_2H_4Cl_2$	The most common use of EDC is the production of vinyl chloride, which is used to make PVC. It is also used as an intermediate for other organic chemical compounds and as a solvent.
<b>Ethylene oxide / Epoxyethane</b>	$CH_2OCH_2$	It is one of the most important raw materials used in large-scale chemical production. Most of it is used for the synthesis of ethylene glycols, which are used as antifreeze or in the production of polyester and polyethylene terephthalate (PET).
<b>Hydrochloric acid</b>	$HCl$	It is used in many industrial processes such as pickling of steel, production of organic compounds (vinyl chloride or dichloroethane, for example), production of inorganic

		compounds, pH control and neutralization or regeneration of ion exchangers.
<b>Oxygen</b>	O <sub>2</sub>	Industrially, it is mostly used in the smelting of iron ore into steel. Furthermore, reacted with ethylene, forms ethylene oxide, a precursor of ethylene glycol, which is a basis to manufacture a host of products. Apart from this, it is used in medical applications, metal cutting and welding, as an oxidizer and in water treatment, among others.
<b>Tetrachloroethylene (PERC)</b>	C <sub>2</sub> Cl <sub>4</sub>	It is an excellent solvent for organic materials and widely used in dry cleaning. It is also used to degrease metals in the automotive and other metalworking industries.
<b>Trichloroethylene</b>	C <sub>2</sub> HCl <sub>3</sub>	It is used as a solvent and in the manufacture of fluorocarbon refrigerants.
<b>Vinyl acetate</b>	CH <sub>3</sub> CO <sub>2</sub> CHCH <sub>2</sub>	It is the precursor of polyvinyl acetate, an important polymer in industry.
<b>Water</b>	H <sub>2</sub> O	Manufacturing and other industries use water during the production process for either creating products or for cooling equipment. Industrial water is used for fabricating, processing, washing, diluting, cooling or transporting a product. It is used in smelting facilities, petroleum refineries, in the production of several chemicals, food and paper products.

Once the list of compounds considered in the chemical network posed in this case study has been defined, it is important to present the set of potential main chemical reactions to transform from one waste compound or reagent into a given raw material or reaction product required. However, it must be noted that these reactions are not considered in all the models that have been developed.

These reactions are presented in the next lines and it is relevant to remark that a colour scheme has been followed in order to clarify whether a given compound is contained in the waste inlet streams, is demanded as a raw material or could be considered a reaction byproduct that can be reintroduced

again in the network to be processed or be disposed. So, first the following table shows a summary of the colour scheme further used when describing the reactions:

**Table 3. Color scheme to distinguish between compounds**

<b>Inlet waste</b>	●
<b>Outlet raw materials</b>	●
<b>System by-product</b>	●

The first reaction that has been considered is the synthesis of ethylene dichloride - EDC ( $C_2H_4Cl_2$ ) from ethylene ( $C_2H_4$ ) and chlorine ( $Cl_2$ ). This is made by the direct chlorination of ethylene in liquid phase. This reaction can be carried out at either low (20-70°C) or high temperatures (100-150°C), having the low temperature process the advantage of low by-product formation:



Moreover, the synthesis of tetrachloroethylene – PERC ( $C_2Cl_4$ ) has also been taken into account. When ethylenedichloride – EDC is heated up to 400°C with chlorine, PERC is synthesized. This reaction is catalysed by potassium chloride and aluminium chloride or by activated carbon.



Another reaction that has been considered is the oxychlorination of ethylene to obtain EDC. In this sense, oxychlorination is a process to generate C-Cl bonds. This reaction uses hydrogen chloride combined with oxygen, instead of using chlorine as in the direct chlorination of ethylene. The industrial attractive of this reaction comes from the fact that hydrogen chloride is cheaper than chlorine.



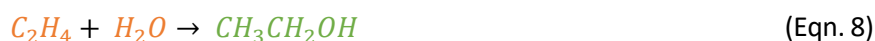
Furthermore, the synthesis of vinyl chloride monomer – VCM ( $C_2H_3Cl$ ) has also been considered. It generates from the high temperature thermal cracking of EDC and forms hydrochloric acid as a by-product.



The next reaction considered is the synthesis of trichloroethylene ( $C_2HCl_3$ ), which is obtained when heating EDC up to 400°C at atmospheric pressure with an additional chlorine input. Hydrogen chloride is obtained as a byproduct, as can be seen below:



Moreover, the hydration of ethylene, which takes place under acidic conditions allows the formation of ethanol, as shown below:



Then, the synthesis of epoxyethane or ethylene oxide ( $CH_2OCH_2$ ) can be obtained when ethylene is partially oxidized when mixed with air or oxygen passing over a silver catalyst at high temperature (520-550 K) and high pressure (15 atm). The selectivity being achieved nowadays is around 90% and the reaction is shown below:



It must be noted that a competing reaction for the synthesis of epoxyethane is the total oxidation of oxygen. However, competing or secondary reactions do not lie in the scope of this thesis.

Moreover, when ethylene reacts with acetic acid and oxygen with the presence of a palladium catalyst, vinyl acetate ( $CH_3CO_2CHCH_2$ ) is obtained, with water as a byproduct. It must be stated that the main side reaction of the combustion of the organic precursors of the reaction but this has not been taken into account.



The last one of the reactions that has been considered is the synthesis of ethylbenzene ( $C_6H_5C_2H_5$ ) from ethylene and benzene. In order to happen, benzene vapour and ethane are mixed and passed over an acid catalyst, at around 650 K and 20 atm pressure. This reaction can be seen below:



Therefore, once a general overview of the case study considered in this project, each of the models developed is exhaustively defined and analysed. This is performed in the section coming up next.

## 7. Optimization Models

This section introduces each of the models that have been developed in the context of this project. It is worth noting that the methodology followed has consisted of a multilevel procedure, where new features are added to each model at each time. In the light of this, there are five increasing difficulty models that have been developed. The following table shows a summary of the main features of each one of these models:

Table 4. Summary of the features of each developed model

Model / Features	Model 1	Model 2	Model 3	Model 4	Model 5
Program	LP	LP	MILP	MILP	MILP
Unbounded atoms	x				
Mass balances	x	x	x	x	x
Energy balances				x	x
Pure compound streams	x	x	x	x	
Compound mixture streams					x
Big Ms			x	x	x
Chemical reactions					x
External supply					x

Therefore, in table 4 it can be seen that the programs developed vary between Linear Programs (LP) and Mixed-Integer Linear Programs (MILP). Moreover, mass balances are considered in every model developed but energy balances are introduced only from model number 4. It can also be seen that the streams are defined at first as pure compound streams and in the end as mixtures of different compounds. With respect to chemical reactions, they are not introduced until the last of the models developed. Furthermore, it should also be stated that the possibility of an external supply is also added in the last model. In general terms, table 4 depicts how as each model advances, new considerations are taken into account, thus depicting that the models are multilevel.

So, once a general overview of the developed models has been shown, the particular explanation of each of them is made.

## 7.1. Model 1: Industrial symbiosis LP black-box model considering atomic mass balances

### 7.1.1. Problem Statement

The model represents a system having diverse waste streams from external sources. There is a demand of various raw materials that could be produced from these waste inputs. Inputs and outputs have a related economic cost, and their supply and demand is limited. Thus, the model seeks the maximization of the conversion of this input waste, conceived as a resource, into added-value raw materials while satisfying mass balances. It is important to point out the fact that only mass balances are considered at this time.

In this approach, material flows are characterized as pure chemical compounds with a defined chemical formula. Such limitation is similar to that used in commercial process simulators, for example Aspen HYSYS, where there is a component list to be defined by the user before entering the simulation environment. This component list contains compounds with a known molecular composition, as depicted in the figure below:

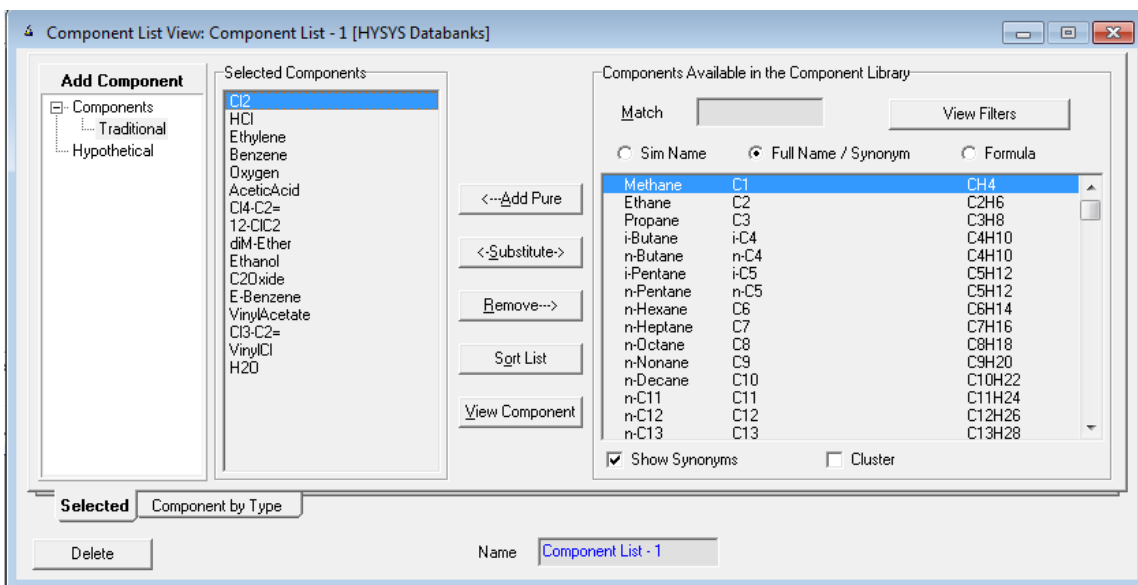


Figure 18. Component List in Aspen HYSYS

This first optimization problem is a linear program (LP). The objective is that of finding the waste inlet's flow that maximizes the profit of the system subject to a finite capacity and demand. Additionally, this allows the determination of the obtained raw material flow and a final waste flow. In this first model,



this waste is characterized as the amount of left over atoms, being this the amount of atoms that have not been able to recombine and turn into one of the required raw materials whose demand has to be covered.

In this context, Figure 19 shows a scheme of the stated problem. As it is depicted in the figure, first, the items in an orange box are the different available waste supplies (Waste A, B and so on) that will be converted into the demanded raw materials, which are outlined in green (Raw material X, Y and Z, for example). In other words, the atoms composing the waste supply are the building blocks that conform these raw materials. Furthermore, there is a leftover stream representing all those leftover atoms that could not be turned into one of the demanded raw materials and are disposed.

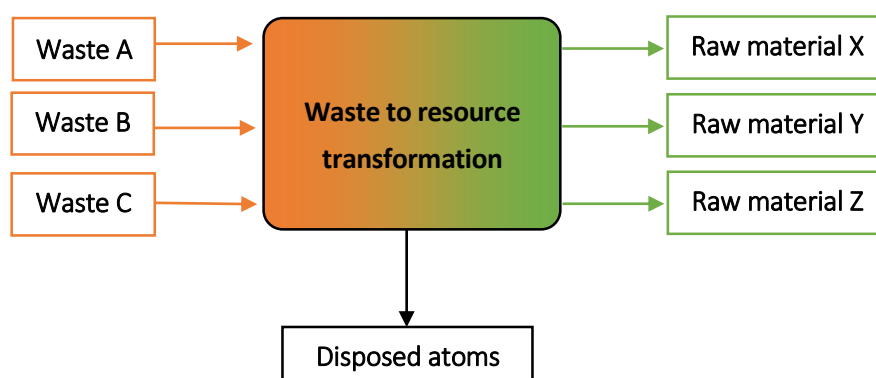


Figure 19. Problem scheme example in Model 1

At this point, it is relevant to outline the assumptions that have been considered for this first model. They are now explained:

- The system works in continuous mode.
- Any chemical reaction is considered. Thus, any transformation from one compound to another is possible as long as it meets the atomic balance.
- The presence of any catalyzers that would allow or facilitate the conversion of one compound into another has not been considered.
- No equipment considerations have been taken into account.
- In order to convert one or more compounds into a different one, a mere balance of the atoms present in them has been done.
- It has been assumed that the waste stream is defined by all the amount of leftover atoms that are not turned into raw materials.
- All the compounds involved in the model are pure and have a known chemical formula.

Then, in order to define this problem completely the data that has to be given is listed below:

- Chemical composition of each compound involved, both waste inlets and raw materials required.
- Molar weight of each compound or atom involved.
- Associated cost or selling price for both waste inlets and desired raw materials.
- Associated cost for the atoms or compounds that are not turned into raw materials.
- Flow capacity allowed for each of the input waste compounds.
- Required demand for each of the output raw materials.

Therefore, the variables that have to be computed starting with the data that has just been previously defined are the following ones:

- Total economic profit obtained from the system.
- Amount of raw materials obtained.
- Amount of waste that has to be introduced in the system.
- Amount of leftovers, which are the atoms coming from the waste inputs that could not be converted into raw materials.

In the following subsections, the model is defined in a more exhaustive way.

### 7.1.2. Mathematical formulation

The mathematical formulation regarding to this first black box model is described in this section, this includes an explanation of the sets, parameters, variables, equations and objective function that define the studied model.

#### 7.1.2.1. Sets

The sets involved in the model are shown below:

- Atoms ( $i$ )
- Waste input compounds ( $j$ )
- Raw materials output streams ( $k$ )

#### 7.1.2.2. Parameters

The parameters that are defined in the present model are these:

- Cost of each of the involved waste input compounds ( $C_j$ )
- Selling price of each of the demanded raw materials or output compounds ( $C_k$ )
- Cost of the leftovers ( $C_i$ ), understood as the amount of atoms that could not be recombined.
- Chemical composition of each of the involved waste input compounds ( $M_{j,i}^{in}$ )
- Chemical composition of each of the output raw materials ( $M_{k,i}^{out}$ )

- Molecular weight of the involved waste input compounds ( $MW_j$ )
- Molecular weight of the output raw materials ( $MW_k$ )
- Capacity of each of the involved waste input compounds ( $Q_j$ )
- Demand of each of the output raw materials ( $D_k$ )
- Annual working hours ( $H$ )

### 7.1.2.3. Variables

The variables that are included in the model are defined below:

- Molar flow from the waste supply that enters the system to be processed ( $F_j^{in}$ )
- Molar flow from the processed raw materials that exit the system to satisfy the demand of raw materials. ( $F_k^{out}$ )
- Mass flow from the waste supply that enters the system to be processed ( $MF_j^{in}$ )
- Mass flow from the processed raw materials that exit the system to satisfy the demand of raw materials. ( $MF_k^{out}$ )
- Amount of leftover atoms ( $W_i$ )
- Profit obtained ( $B$ )

At this point, it should be outlined that all those variables referring to flows, whether they are mass or molar ones, are positive variables.

### 7.1.2.4. Equations

At this point, it is crucial to define the equations behind the model. These equations consist of mass balances with respect to the atoms that enter and exit in the inlets and the outlets of the system. The first of these is shown below:

$$\sum_j F_j^{in} \cdot M_{j,i}^{in} = \sum_k F_k^{out} \cdot M_{k,i}^{out} + W_i \quad \forall i \quad (\text{Eqn. 12})$$

Equation 12 represents a decomposition the waste inlets that enter the system into atoms. Then, it equates the fact that all the atoms entering the system must be the same as the addition of the atoms that exit the system both composing raw materials and as leftover atoms. Finally, it implies a conversion of the outlet atoms in outlet raw materials. Briefly, this equation represents a mass balance of the whole system.

Then, the next two equations represent the change of units between molar flow and mass flow with respect to input waste streams and output raw materials:

$$MF_j^{in} = F_j^{in} \cdot MW_j \quad \forall j \quad (\text{Eqn. 13})$$

$$MF_k^{in} = F_k^{in} \cdot MW_k \quad \forall k \quad (\text{Eqn. 14})$$

Then, two constraints have been set in order to define the system completely. They are explained below:

$$F_k^{out} \leq D_k \quad \forall k \quad (\text{Eqn. 15})$$

$$F_j^{in} \leq Q_j \quad \forall j \quad (\text{Eqn. 16})$$

Equation 15 represents the fact that the amount of Raw materials obtained should be less or equal than the demand. On the other hand, equation 16 involves that the amount of Waste inlets used should be less or equal than the system's storage capacity.

#### 7.1.2.5. Objective Function

Finally, the objective function that has to be maximized is defined by the profit obtained from the system, which take into account the cost of the waste inlets and the disposed atoms and the profit derived from the raw materials obtained:

$$B = \sum_k MF_k^{out} \cdot C_k - \sum_j MF_j^{in} \cdot C_j - \sum_i W_i \cdot C_i \quad (\text{Eqn. 17})$$

Once the mathematical formulation defining the model has been presented, a particular example is developed in order to appreciate in a more intuitive way the way this first model behaves.

### 7.1.3. Particular Example

Once the mathematical formulation of this first model has been described, it is time to see how it behaves in a particular example.

The particular example that has been analyzed considers each of the compounds that were presented in the Case Study section. In this sense, it is relevant to outline which compounds were considered as waste inlets and which ones were the raw materials outlets to be obtained. This can be seen in the following lines.

First, the atoms involved are the following:

$$i = \langle C, H, Cl, O \rangle$$

Then, the waste input streams are:

$$j = \langle CH_3COOH, C_6H_6, Cl_2, C_2H_4, C_2H_4Cl_2, HCl, O_2, H_2O \rangle$$

Whilst the raw material streams or compounds considered are:

$$k = \langle C_2H_3Cl, CH_3CH_2OH, C_6H_5C_2H_5, CH_2OCH_2, C_2Cl_4, C_2HCl_3, CH_3CO_2CHCH_2 \rangle$$

In this sense, it is relevant to define the specific values of the parameters that have been considered.

On the first place, the cost of each waste inlet ( $C_j$ ) has been set to zero due to the fact that in general terms waste materials have no related cost as there is no demand for them.

Then, the selling price of the outlet raw materials that are demanded ( $C_k$ ) is shown below and it must be noted that the values have been considered an 80% of the selling price that has been found in literature for each compound, the webpage references with respect to this can be found in the bibliography:

Table 5. Values for parameter  $C_k$  in Model 1 particular example

Raw Material Outlet	Selling price [€/kg]
$C_2H_3Cl$	1,738
$CH_3CH_2OH$	1,077
$C_6H_5C_2H_5$	0,152
$CH_2OCH_2$	0,001
$C_2Cl_4$	0,046
$C_2HCl_3$	0,075
$CH_3CO_2CHC_2$	0,010

Moreover, the cost that has been considered for the atoms that could not be recombined and thus had to be disposed is the following:

Table 6. Values for parameter  $C_i$  in Model 1 particular example

Atom	Cost [€·10 <sup>-5</sup> /mol]
C	6,01
H	5,00
Cl	1,77
O	8,00

These values have been considered as 0,5% of the atomic mass of each element in order to make an estimation.

Furthermore, the following matrices define the chemical composition of the compounds involved.

First, the inlet waste compounds:

$$M_{j,i}^{in} = \begin{pmatrix} 2 & 4 & 0 & 2 \\ 6 & 6 & 0 & 0 \\ 0 & 0 & 2 & 0 \\ 2 & 4 & 0 & 0 \\ 2 & 4 & 2 & 0 \\ 0 & 1 & 1 & 0 \\ 0 & 0 & 0 & 2 \\ 0 & 2 & 0 & 1 \end{pmatrix}$$

Then, the outlet raw materials:

$$M_{k,i}^{out} = \begin{pmatrix} 2 & 3 & 1 & 0 \\ 2 & 6 & 0 & 1 \\ 8 & 10 & 0 & 0 \\ 2 & 4 & 0 & 1 \\ 2 & 0 & 4 & 0 \\ 2 & 1 & 3 & 0 \\ 4 & 6 & 0 & 2 \end{pmatrix}$$

Moreover, the parameter  $H$ , which are the annual working hours of the system, has been set to 4380 h, which comes from assuming that the system works 12 h per day, 365 days per year.

Finally, for this particular example the demand of each raw material ( $D_k$ ) and the capacity of each waste inlet stream ( $Q_j$ ) has been set to 100 mol/h.

The following subsection presents and discusses the results that have been obtained for this particular example.

#### 7.1.4. Results

For this particular example, which is a base case with equal demands and capacities for each compound, the result of the objective function, which is equal to the total profit obtained from the system is 79262,45 €.

The numerical results obtained with respect to the waste streams that have to enter the system is shown in the following table:

Table 7. Molar flow of waste streams obtained in particular example of Model 1

Waste	CH3COOH	C6H6	Cl2	C2H4	C2H4Cl2	HCl	O2	H2O
Molar flow [mol/h]	100,00	100,00	100,00	100,00	100,00	100,00	0,00	0,00

From the results obtained regarding the obtained waste compounds, it can be observed how the compounds that fill their whole capacity are those that have the biggest amount of atoms to build the required raw materials. In this sense, it is relevant to outline the fact that neither oxygen nor water are consumed, this is because these compounds do not contain carbon and there are no demanded raw materials not containing carbon. Therefore, what the optimization does is prioritizing and filling the whole capacity for those inlet waste compounds that have the biggest amount of building blocks to conform the raw materials required. In this sense, the following figure depicts the relationship between the molar flow of the waste compounds obtained and the capacity for each of them:

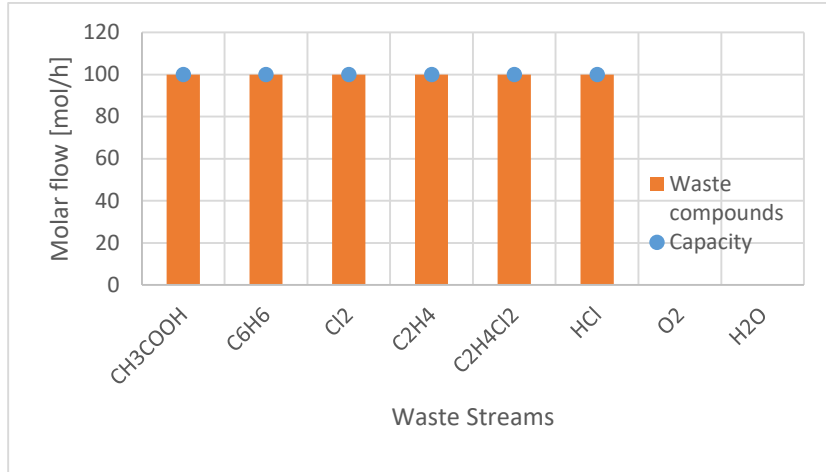


Figure 20. Obtained waste streams and capacity comparison in particular example of Model 1

On the other hand, the results regarding the obtained raw materials are shown in the table below:

Table 8. Molar flow of raw material streams obtained in particular example of Model 1

Raw Material	C <sub>2</sub> H <sub>3</sub> Cl	CH <sub>3</sub> CH <sub>2</sub> OH	C <sub>6</sub> H <sub>5</sub> C <sub>2</sub> H <sub>5</sub>	CH <sub>2</sub> OCH <sub>2</sub>	C <sub>2</sub> Cl <sub>4</sub>	C <sub>2</sub> HCl <sub>3</sub>	CH <sub>3</sub> CO <sub>2</sub> CHC <sub>2</sub>
Molar flow [mol/h]	100,00	100,00	68,75	0,00	25,00	100,00	0,00

As it can be seen in the table above, VCM, ethanol and trichloroethylene are the compounds that are produced until covering the demand completely. On the other hand, the demand of ethylbenzene is almost covered up to a 70% and the demand of PERC is covered up to a 25%. The rest of raw materials involved are not obtained. The relationship between the molar flow obtained for each raw material and the demand of each of them is depicted in the figure below:

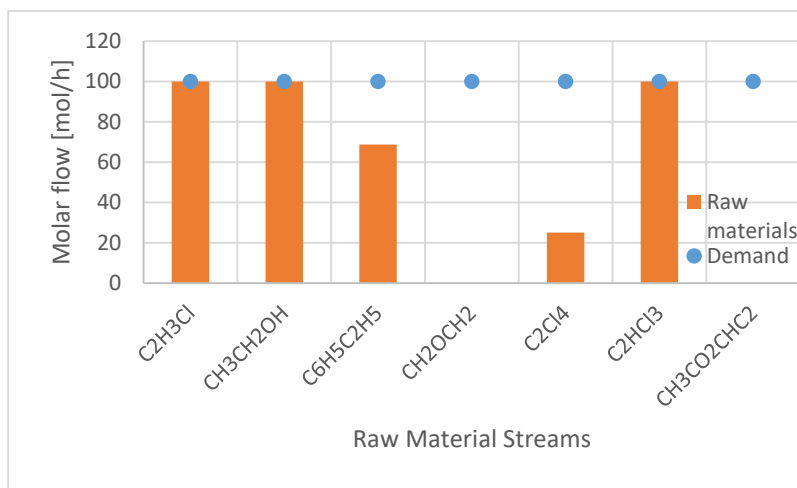


Figure 21. Obtained raw materials and demand comparison in particular example of Model 1

In line with this, it is relevant to outline that VCM and ethanol are the raw materials that present a highest selling price, this is the reason why their demands are covered. On the other hand, the next most profitable raw material is ethylbenzene, whose demand is covered up to a 70%. It may seem



weird that the demand of trichloroethylene is covered up to a 100% when its selling price is not so high in comparison to other compounds. However, there is an explanation for this and is the fact that a big amount of chlorine atoms available to build raw materials but are not used to the fullest when producing VCM and ethanol. Thus, what the system does is using them to produce this trichloroethylene until it covers its demand. Then, PERC, which has 4 atoms of chlorine in its composition, is formed with the rest of chlorine atoms.

In line with all of this, it is relevant to present a global atomic balance of the system. This can be seen in the figure below:

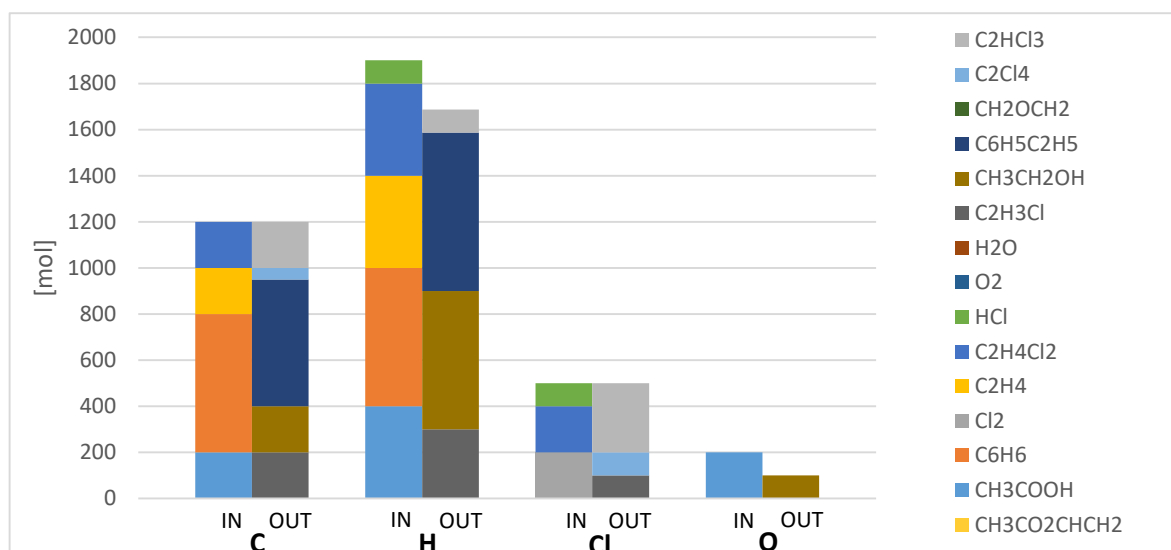


Figure 22. Comparison between inlet and outlet atoms in particular example of Model 1

Figure 22 shows a global atomic balance of the system, considering both inlet waste compounds and outlet raw materials. For each atom type, which are carbon (C), hydrogen (H), chlorine (Cl) and oxygen (O), the stacked column in the left shows the amount of atoms available in the inlet waste streams. On the other hand, the stacked column in the right side shows the amount of atoms that compose each of the demanded raw materials. Thus, this allows seeing how inlets are converted into outlets, which are added value raw materials.

In this sense, Figure 22 shows that in the case of carbon and chlorine, the amount of atoms forming inlets and outlets is the same. On the contrary, in the case of hydrogen and oxygen, the amount of atoms that conform the inlet compounds exceeds the amount of them that compose the outlets. It may seem that they do not fit the atomic balance. However, this unbalance of atoms is related with the atoms to be disposed. Therefore, for a given compound the difference between inlet moles of atoms that were composing waste streams minus the atoms composing raw material streams equals the amount of atoms that could not form any raw material and have to be sent to disposal.

So, the numerical results for the disposed moles of atoms is shown in the table below:

**Table 9. Disposed atoms in particular example from Model 1**

Atom	C	H	Cl	O
[mol]	0	212,5	0	100

As a conclusion for this particular example of Model 1, it could be stated that what the optimal solution for this situation represents is the fact that the best alternative is using the necessary amount of waste streams that allow generating the most profitable products. Thus, the most profitable raw material according to the parameters set, is formed until all its demand is covered. Then, the second most profitable raw material is formed and so on. Then, the rest of available atoms compose the raw material whose composition contains them. Finally, all the atoms that were not able to form a raw material exit the system in the disposal stream.

### 7.1.5. Model limitations

At this point, it is essential to outline the limitations of the present model so that they can be overcome in the next step. These limitations are listed below:

- The fact that the waste stream is just characterized by leftover unbounded atoms does not hold from a chemical perspective.
- The characterization of the compounds involved in the model is limited to their chemical formula.
- The system does not resemble nature chemical reactions or the chemical or technological paths to achieve the desired outcomes. Thus, it does not reflect the transformations that are feasible or affordable.
- Streams formed by mixtures of components have not been taken into account. This is not accurate because in general, waste streams will be composed by mixtures of compounds.
- Only mass balances have been taken into account, no energy balances have been considered.
- No possible external supply has been considered.
- Inlet waste streams enter the system completely, there is not the possibility to accept some streams just partially.

However, this first black box model is relevant because it depicts the best of all the possible solutions for the stated problem and it can be useful as “upper-bound” in order to compare further models with this one.

In order to overcome some of the limitations that this first model presents, Model 2 was developed.

## 7.2. Model 2: Industrial symbiosis LP model considering mass balances

### 7.2.1. Problem Statement

The problem statement exposed in this second model is the same as in the first model that has just been explained. However, the main limitation that is overcome is the fact that the waste stream was just characterized by leftover unbounded atoms. The disposal in this new system is defined by streams of compounds that have to be sent to be further treated. It should be outlined that this problem is represented by a LP. So, the figure below depicts this new system's scheme:

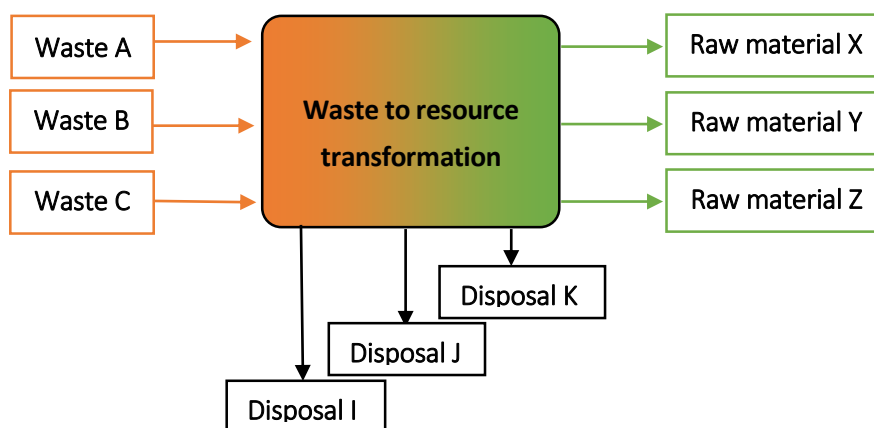


Figure 23. Problem scheme example in Model 2

As it can be seen in figure 20, the compounds to be disposed now appear in different streams and not only as unbounded atoms (Disposal I, disposal J and disposal K).

The assumptions that have been considered for this second model are listed below:

- The system works in continuous mode.
- Any chemical reaction is considered. Thus, any transformation from one compound to another is possible as long as it meets the atomic balance.
- The presence of any catalyzers that would allow or facilitate the conversion of one compound into another has not been considered.
- No equipment considerations have been taken into account.
- In order to convert one or more compounds into a different one, a mere balance of the atoms present in them has been done.
- All the compounds involved in the model are pure and have a chemical formula.

Then, in order to define this problem completely the data that has to be given is listed below:

- Chemical composition of each compound involved, for waste inlets, disposal outlets and raw materials required.
- Molar weight of each compound.

- Associated cost or selling price for waste inlets, disposal compounds and desired raw materials.
- Maximum flow capacity for each of the input waste compounds.
- Required demand for each of the output raw materials.

Therefore, the variables that have to be computed starting with the data that has just been defined are the following ones:

- Total economic profit obtained from the system.
- Amount of raw materials obtained.
- Amount of waste that has to be introduced in the system.
- Amount of compounds that have to be sent to disposal for their further treatment.

In the following subsection, the mathematical formulation of this second model is clearly stated.

## 7.2.2. Mathematical Formulation

The mathematical formulation regarding to this first black box model is described in this section, this includes an explanation of the sets, parameters, variables, equations and objective function that define the studied model.

### 7.2.2.1. Sets

The sets involved in the model are shown below:

- Atoms ( $i$ )
- Waste input compounds ( $j$ )
- Raw materials output streams ( $k$ )
- Disposal output streams ( $l$ )

### 7.2.2.2. Parameters

The parameters that are defined in the present model are these:

- Cost of each of the involved waste input compounds ( $C_j$ )
- Selling price of each of the demanded raw materials or output compounds ( $C_k$ )
- Selling price of each of the disposal compounds ( $C_l$ )
- Chemical composition of each of the involved waste input compounds ( $M_{j,i}^{in}$ )
- Chemical composition of each of the output raw materials ( $M_{k,i}^{out}$ )
- Chemical composition of each of the disposal compounds ( $M_{l,i}^{disp}$ )
- Molecular weight of the involved waste input compounds ( $MW_j$ )
- Molecular weight of the output raw materials ( $MW_k$ )
- Molecular weight of the disposal compounds ( $MW_l$ )

- Capacity of each of the involved waste input compounds ( $Q_j$ )
- Demand of each of the output raw materials ( $D_k$ )
- Annual working hours ( $H$ )

### 7.2.2.3. Variables

The variables that are included in the model are defined below:

- Molar flow from the waste supply that enters the system to be processed ( $F_j^{in}$ )
- Molar flow from the processed raw materials that exit the system to satisfy the demand of raw materials. ( $F_k^{out}$ )
- Molar flow from the compounds sent to disposal. ( $F_l^{disp}$ )
- Mass flow from the waste supply that enters the system to be processed ( $MF_j^{in}$ )
- Mass flow from the processed raw materials that exit the system to satisfy the demand of raw materials. ( $MF_k^{out}$ )
- Mass flow from the compounds sent to disposal. ( $MF_l^{disp}$ )
- Profit obtained ( $B$ )

From all these variables, it is worth noting that the ones that refer to flows, whether they are mass or molar, are positive variables.

### 7.2.2.4. Equations

At this point, it is crucial to define the equations behind the model. These equations consist of mass balances with respect to the atoms that enter and exit in the inlets and the outlets of the system. The first of these is shown below:

$$\sum_j F_j^{in} \cdot M_{j,i}^{in} = \sum_k F_k^{out} \cdot M_{k,i}^{out} + \sum_l F_l^{disp} \cdot M_{l,i}^{disp} \quad \forall i \quad (\text{Eqn. 18})$$

Equation 18 represents a decomposition the waste inlets that enter the system into atoms. Then, it equates the fact that all the atoms entering the system must be the same as the addition of the atoms that exit the system both composing raw materials and as disposal streams. Finally, it implies a conversion of the outlet atoms in outlet raw materials. Briefly, this equation represents a mass balance of the whole system.

Then, the next three equations represent the change of units between molar flow and mass flow with respect to input waste streams, output disposal streams and output raw materials:

$$MF_j^{in} = F_j^{in} \cdot MW_j \quad \forall j \quad (\text{Eqn. 19})$$

$$MF_k^{in} = F_k^{in} \cdot MW_k \quad \forall k \quad (\text{Eqn. 20})$$

$$MF_l^{disp} = F_l^{disp} \cdot MW_l \quad \forall l \quad (\text{Eqn. 21})$$

Then, two constraints have been set in order to define the system completely. They are explained below:

$$F_k^{out} \leq D_k \quad \forall k \quad (\text{Eqn. 22})$$

$$F_j^{in} \leq Q_j \quad \forall j \quad (\text{Eqn. 23})$$

Equation 22 represents the fact that the amount of raw materials obtained should be less or equal than the demand. On the other hand, equation 23 involves that the amount of waste inlets used should be less or equal than the system's capacity.

#### 7.2.2.5. Objective Function

Finally, the objective function that has to be maximized is defined by the profits obtained from the system, which take into account the cost of the waste inlets and the waste atoms and the profit derived from the raw materials obtained:

$$B = \sum_k MF_k^{out} \cdot C_k - \sum_j MF_j^{in} \cdot C_j - \sum_l MF_l^{disp} \cdot C_l \quad (\text{Eqn. 24})$$

Once the mathematical formulation defining the model has been presented, a particular example is developed in order to appreciate in a more intuitive way the way this first model behaves.

### 7.2.3. Particular Example

After describing the mathematical formulation of this model, now a particular example is presented.

The particular example that is now analyzed shares many similarities with the one explained in Model 1. Just as before, this example considers each of the compounds that were presented in the Case Study section.

With respect to the atoms involved in the system, they are the same as in Model's 1 particular example. The same happens with waste input streams (set  $j$ ) and raw material streams (set  $k$ ). However, in this model the disposal is defined not as unbounded atoms but as a set  $l$ , which is formed by the same compounds present in the set  $j$ .

Then, there are several parameters that are equal to the ones defined in the particular example of Model 1. These are the following:  $C_j$ ,  $C_k$ ,  $M_{j,i}^{in}$ ,  $M_{k,i}^{out}$ ,  $H$ ,  $D_k$  and  $Q_j$ . It is important to mention that the particular values of this parameters can be found in the example of Model 1.

On the other hand, this model includes the parameter  $C_l$ , which is the cost of sending to further treatment each disposal compound. The values for each compound are shown in the table below:

Table 10. Values of parameter  $C_l$  in particular example of Model 2

Disposal compound	Cost [€/kg]
CH3COOH	0,0084
C6H6	0,0065
Cl2	0,0950
C2H4	0,4923
C2H4Cl2	0,0084
HCl	0,7919
O2	0,0005
H2O	0,0001

In this sense, it is relevant to explain that these costs have been taken to be a 10% of the selling price of the compounds found in literature.

Once the particular example has been clearly defined, the optimization results are discussed in the following subsection.

### 7.2.4. Results

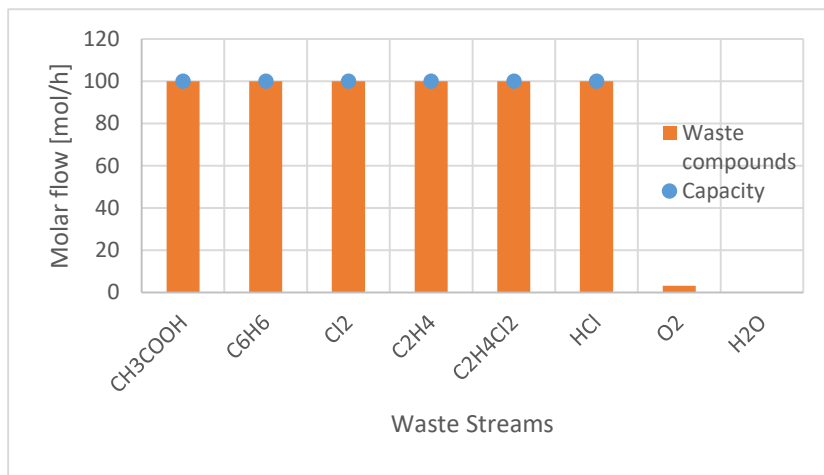
For this particular example, the final result of the objective function, which is the total profit obtained once the optimization has been developed is 79261,87 €.

The numerical results obtained regarding waste streams entering the system are shown in the table below:

**Table 11. Molar flow of waste streams obtained in particular example of Model 2**

Waste	CH <sub>3</sub> COOH	C <sub>6</sub> H <sub>6</sub>	Cl <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	HCl	O <sub>2</sub>	H <sub>2</sub> O
<b>Molar flow [mol/h]</b>	<b>100,00</b>	<b>100,00</b>	<b>100,00</b>	<b>100,00</b>	<b>100,00</b>	<b>100,00</b>	<b>3,10</b>	<b>0,00</b>

They are almost the same as the ones obtained in the particular example of Model 1, except from the fact that there is a small amount of oxygen entering the transformation system, as is better depicted in the figure below:



**Figure 24. Obtained waste streams and capacity comparison in particular example of Model 2**

In this sense, the same explanation that was done in Model 1 particular example works for this model as well: the compounds that fill their whole capacity are those that have the biggest amount of atoms to build the required raw materials, what the optimization does is prioritizing and filling the whole capacity for those inlet waste compounds that have the biggest amount of building blocks to conform the raw materials required

On the other hand, results regarding the obtained raw materials are the same shown in Table 8: VCM, ethanol and trichloroethylene are the compounds that are produced until covering the demand completely. On the other hand, the demand of ethylbenzene is almost covered up to a 70% and the demand of PERC is covered up to a 25%. The rest of raw materials involved are not obtained. Thus, the same explanation that was performed in the previous case is also applicable here.



The global atomic balance for this case is shown next:

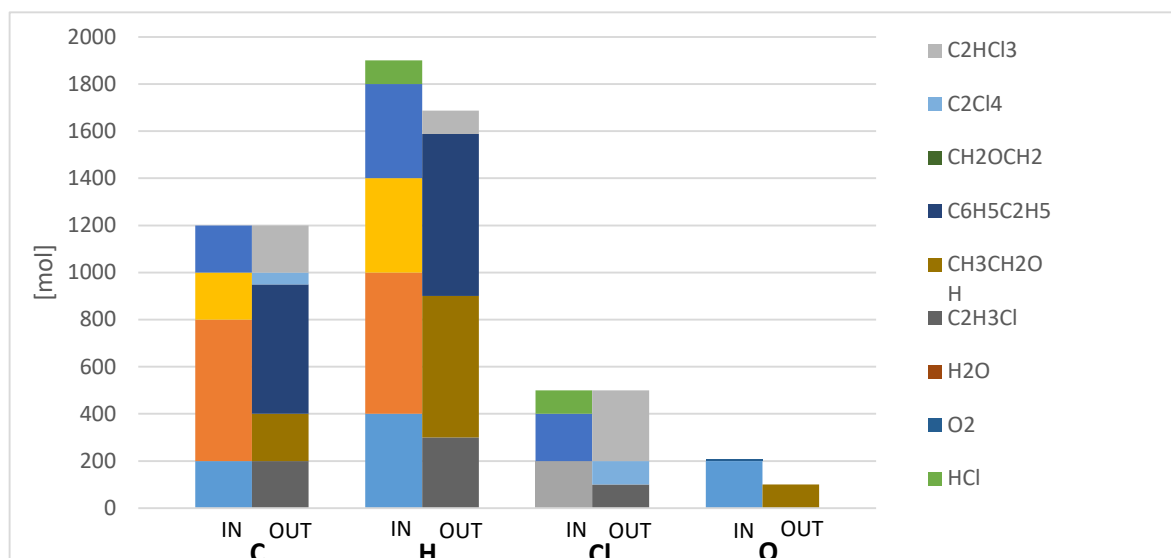


Figure 25. Comparison between inlet and outlet atoms in particular example of Model 2

With respect to figure 25, it is relevant to remark the added presence of oxygen atoms in the inlet coming from this amount of oxygen in the waste streams.

Next, the numerical results for the disposed compounds are shown in the table below:

Table 12. Molar flow of disposal streams obtained in particular example of Model 2

Waste	CH <sub>3</sub> COOH	C <sub>6</sub> H <sub>6</sub>	Cl <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	HCl	O <sub>2</sub>	H <sub>2</sub> O
Molar flow [mol/h]	0,00	0,00	0,00	0,00	0,00	0,00	0,00	106,25

Thus, it can be seen that there is water being disposed. Then, it makes sense that there was an extra input of oxygen entering the system, due to the fact that there were plenty of leftover hydrogen atoms that could not compose any raw material compound. Therefore, oxygen has been consumed from the waste inlet streams in order to build water, which is the cheapest disposal compound from all the possible alternatives.

In this case, just as in Model 1, the optimal solution for this situation uses the necessary amount of waste streams that allow generating the most profitable products. Thus, the most profitable raw material according to the parameters set, is formed until all its demand is covered. Then, the second most profitable raw material is formed and so on. Then, the rest of available atoms compose the raw material whose composition contains them. Finally, all the atoms that were not able to form a raw material are coupled together with other atoms coming from different compounds in order to generate the cheapest disposal compound.

### 7.2.5. Model limitations

The limitations of this second model are listed below:

- The characterization of the compounds involved in the model is limited to their chemical formula.
- The system does not resemble nature chemical reactions or the chemical or technological paths to achieve the desired outcomes. Thus, it does not reflect the transformations that are feasible or affordable.
- The model does not take into account the existence of compounds that are isomeric or share the same chemical formula but their atoms are arranged in a different way.
- Streams formed by mixtures of components have not been taken into account. This is not accurate because in general, waste streams will be composed by mixtures of compounds.
- Only mass balances have been taken into account, no energy balances have been considered.
- No possible external supply has been considered.
- Inlet waste streams enter the system completely, there is not the possibility to accept some streams just partially.

Furthermore, a big limitation that has been observed is the fact that having the demand as a constraint may limit the solution obtained.

Thus, in order to overcome some of the limitations that this model presents, Model 3 was developed.

### 7.3. Model 3: Industrial symbiosis MILP model considering mass balances

#### 7.3.1. Problem Statement

The particular problem statement in Model 3 is the same as in Model 2. In this sense, the main limitation that is overcome in this new model is the fact that the demand should not be a constraint. Instead, it should appear in the objective function, not to limit the optimal solution.

In order to accomplish this, a MILP has been developed where binary variables have been introduced using big Ms as a tool to linearize the problem. In this sense, it must be noted that one of the biggest differences this model presents with respect to the two previous models is the fact that it considers a cost of disposing all those raw materials that can not be covered by the demand. Thus, as those raw materials cannot be sold, they must be further treated, which has a derived cost, regarding the fact that no storage possibilities have been taken into account. Thus, this new model does not limit the obtained solution in terms of how this demand is defined.

In this sense, the following figure represents a scheme of the particular problem stated in this model:

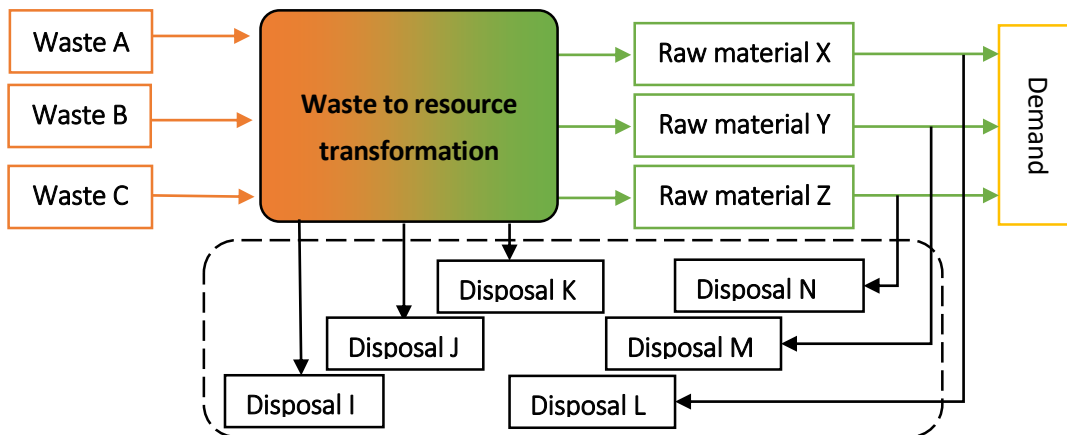


Figure 26. Problem scheme in Model 3

The following subsection discusses the changes added with respect to the mathematical formulation of this new model.

#### 7.3.2. Mathematical Formulation

As it was just stated, this third model is very similar to the second one, the only difference is the addition of binary variables, resulting this in a change of program from LP to MILP. In order to do so, a

part from all the information with respect to sets, variables and equations included in Model 2, the particularities that are now explained were added.

### 7.3.2.1. Sets

The sets defined in this model are the same as in Model 2.

### 7.3.2.2. Parameters

Apart from each one of the parameters presented in section 7.2.2.2, the following ones are added:

- Cost of disposing over demanded raw materials ( $C_k^{disp}$ )

### 7.3.2.3. Variables

Apart from the variables considered in Model 2, these new variables are also taken into account:

- Binary variable representing if demand has been covered. ( $z_k$ )
- Function representing the case where demand has been covered ( $f_k^1$ )
- Function representing the case where demand has not been covered ( $f_k^2$ )

### 7.3.2.4. Equations

Apart from the equations 18 to 21 and 23, already explained in Model 2, the following equations have been added:

First, the two following equations use a big M and define the binary variable  $z_k$  representing if demand has or has not been covered:

$$D_k \cdot z_k \leq F_k^{out} \quad \forall k \quad (\text{Eqn. 25})$$

$$F_k^{out} - D_k \leq 10^8 \cdot z_k \quad \forall k \quad (\text{Eqn. 26})$$

In this sense, it is relevant to outline that the term  $10^8$  is an arbitrary Big M.

Once the binary variable  $z_k$  has been added and defined using a big M, two more functions showing whether the demand has or has not been covered are defined by means of another big M. Thus, the two following equations represent the case where the demand has been covered. Moreover, it is

important to point out that in equation 28, there is a term representing a penalization derived from producing more than the demand, as was explained in the problem statement:

$$f_k^1 \leq 10^8 \cdot z_k \quad \forall k \quad (\text{Eqn. 27})$$

$$f_k^1 \leq D_k \cdot MW_k \cdot C_k - C_k^{disp} \cdot (F_k^{out} - D_k) \cdot MW_k \quad \forall k \quad (\text{Eqn. 28})$$

On the other hand, the next two equations represent the case where the demand has not been covered:

$$f_k^2 \leq 10^8 \cdot (1 - z_k) \quad \forall k \quad (\text{Eqn. 29})$$

$$f_k^2 \leq MF_k^{out} \cdot C_k \quad \forall k \quad (\text{Eqn. 30})$$

### 7.3.2.5. Objective function

The objective function to be maximized in this model is the following one:

$$B = \sum_k f_k^1 + \sum_k f_k^2 - \left( \sum_j MF_j^{in} \cdot C_j \right) - \left( \sum_l MF_l^{disp} \cdot C_l \right) \quad (\text{Eqn. 31})$$

Where the first term of the function refers to the profit obtained from the selling of the raw material streams when the demand has been covered, the second term refers to the profit obtained in case the demand has not been covered. Then, the third and fourth terms refer to the cost of the waste inlets and the compounds sent to disposal, respectively.

### 7.3.3. Particular Example

The particular example that has been considered in this case is exactly the same one considered as a particular example of Model 2. Therefore, if the exact values for the parameters taken into account can be seen in section 7.2.3.

### 7.3.4. Results

Regarding the results for the particular example established in this model, it is worth mentioning that in this case the results obtained are exactly the same as in Model 2 shown in section 7.2.4., with respect to the total profit obtained from the system, composition and flow of waste inlets, raw material and disposal outlets.

However, the novelty that this model offers has to do with the addition of binary variables. In this sense, the obtained results for variable  $z_k$  are shown in the table below:

Table 13. Results of  $z_k$  in particular example of Model 3

Raw material (k)	C2H3Cl	CH3CH2OH	C6H5C2H5	CH2OCH2	C2Cl4	C2HCl3	CH3CO2CH2
$z_k$	1	1	0	0	0	1	0

So, this binary variable should indicate whether a demand for a given raw material has been covered or not. Thus,  $z_k$  should take a value of 1 when the demand is covered and a value of 0 otherwise. This is clearly depicted in the figure below, which shows the results obtained regarding the molar flow in the raw material streams, the demand and the value the variable  $z_k$  takes for each raw material. Thus, only in the case of VCM, ethanol and trichloroethylene the binary variable has taken a value of 1:

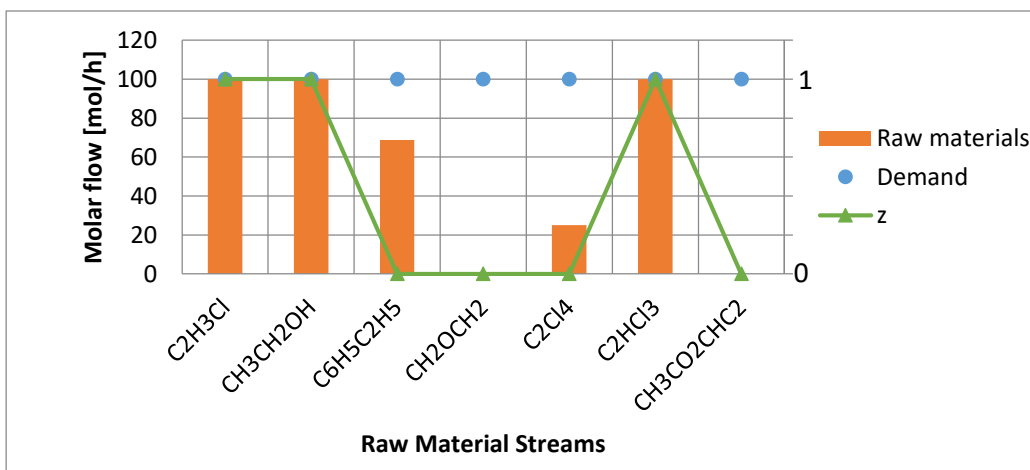


Figure 27. Obtained raw material streams molar flow and  $z_k$  in particular example of Model 3

The conclusion that can be extracted from this model is similar to that extracted in Model 2. This means that the optimal solution for the example analyzed uses the amount of waste from each particular stream that allows obtaining the most profitable raw materials until the demand is covered and with

respect to the atoms that cannot conform any raw material compound, they form the cheapest disposal stream. In this case, there is no production of over demanded raw materials that have to be further disposed.

### **7.3.5. Model limitations**

The limitations of this third model are listed below:

- Only mass balances have been taken into account, no energy balances have been considered.
- The characterization of the compounds involved in the model is limited to their chemical formula.
- The system does not resemble nature chemical reactions or the chemical or technological paths to achieve the desired outcomes. Thus, it does not reflect the transformations that are feasible or affordable.
- The model does not take into account the existence of compounds that are isomeric or share the same chemical formula but their atoms are arranged in a different way.
- Streams formed by mixtures of components have not been taken into account.
- No possible external supply has been considered.
- Inlet waste streams enter the system completely, there is not the possibility to accept some streams just partially.

In order to overcome some of the limitations that this first model presents, Model 4 was developed.

## 7.4. Model 4: Industrial symbiosis MILP model considering mass and energy balances

### 7.4.1. Problem Statement

This fourth model, which is developed as a MILP, represents the same system defined in Models 2 and 3. However, the important novelty it presents has to do with considering energy balances in the system. This allows a more realistic approach of the system in comparison to the former models developed as it considers the energy that has to be added or subtracted to the system to allow each transformation. Thus, this model includes both energy and mass balances to transform inlet waste streams into outlet raw materials that are required to feed other processes. In this sense, energy considerations allow to set a new limit to the transformations. The following figure depicts a scheme of the particular problem this model aims to solve.

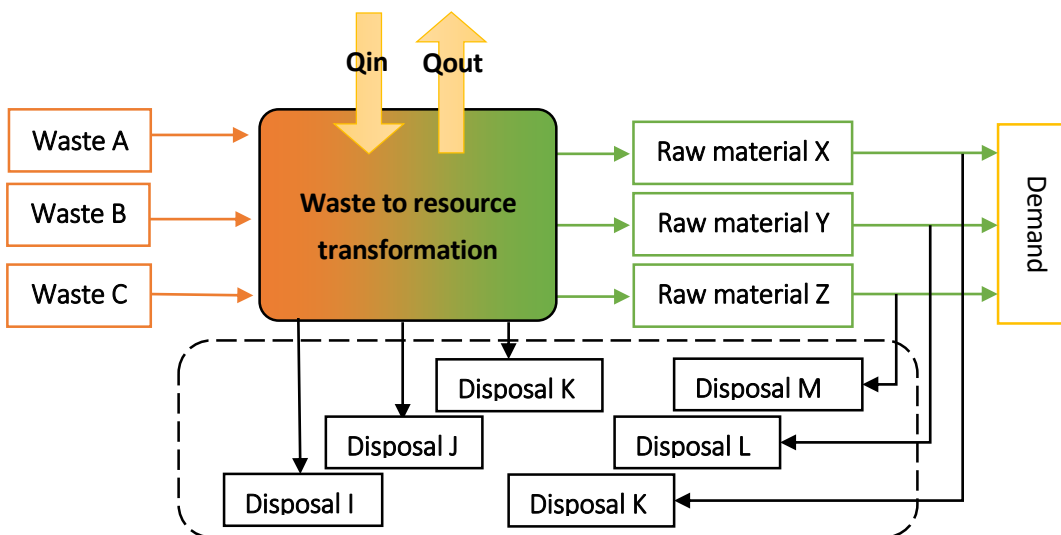


Figure 28. Problem scheme in Model 4

In the following subsections this third model is defined in a more exhaustive way.

### 7.4.2. Mathematical Formulation

With respect to the mathematical formulation of this model, it is relevant to remark that most of the parameters, variables and equations are 70ret h with model 3. However, it presents differences that are now explicated.



#### 7.4.2.1. Sets

The sets defined in this model are the same as in Model 2 and Model 3.

#### 7.4.2.2. Parameters

Apart from all the parameters considered in Model 3, this model also takes into account the following ones:

- Molar enthalpy of inlet waste compounds ( $H_j$ )
- Molar enthalpy of outlet raw material compounds ( $H_k$ )
- Molar enthalpy of outlet compounds sent to disposal ( $H_l$ )
- Molar entropy of inlet waste compounds ( $S_j$ )
- Molar entropy of outlet raw material compounds ( $S_k$ )
- Molar entropy of outlet compounds sent to disposal ( $S_l$ )
- Cost of heat addition ( $CQ_{in}$ )
- Cost of heat subtraction ( $CQ_{out}$ )
- Working temperature of the system ( $T$ )

It is relevant to outline that all these parameters related to energy are obtained from HYSYS through VBA and exported to Excel. Once in Excel, they are exported through GAMS using the GDX utility, as it has been explained in the Tools & Software section.

#### 7.4.2.3. Variables

Apart from all the variables considered in Model 3, the following variables are also considered in this new model:

- Heat added or subtracted from the system ( $Q_{exc}$ )
- Binary variable representing whether heat is added or extracted from the system ( $y$ )
- Function representing the case where heat has to be added to the system ( $f_3$ )
- Function representing the case where heat has to be extracted from the system ( $f_4$ )

#### 7.4.2.4. Equations

The equations that are considered in this model are presented in this section. First, it should be outlined that equations 18 to 21 that were presented in Model 2 and 3 are also taken into account in this model. Furthermore, all the equations defining the binary variable  $z_k$ ,  $f_k^1$  and  $f_k^2$  also apply to this model (equations 25 to 30). Apart from these, the following ones are considered:

First, equation 32 represents an enthalpy balance between all the streams entering and exiting the system. The global balance equates the heat that must be added or extracted from the system:

$$\sum_j F_j^{in} \cdot H_j - \sum_k F_k^{out} \cdot H_k - \sum_l F_l^{disp} \cdot H_l = Q_{exc} \quad (\text{Eqn. 32})$$

So, once the enthalpy balance has been presented, it is time to define the binary variable representing heat addition or subtraction. This is done using a big M, as can be seen below:

$$Q_{exc} \leq 10^8 \cdot y \quad (\text{Eqn. 33})$$

$$-Q_{exc} \leq 10^8 \cdot (1 - y) \quad (\text{Eqn. 34})$$

In this sense, it is relevant to outline that the term  $10^8$  is an arbitrary Big M and that the procedure that was followed in order to find the functions defining the binary variable can be seen in one of the attached MS Excel files.

Then, once binary variable  $y$  has been defined, different functions are built with it. These functions are now explained.

Thus, the next four equations refer to the heat exchanged and to the binary variable  $y$ . The following two equations represent the case where heat has to be extracted from the system (equations 34 and 35) and afterwards, two more equations representing the case where heat has to be added to the system.

$$f^3 \leq 10^8 \cdot y \quad (\text{Eqn. 35})$$

$$-f^3 \leq Q_{exc} \cdot CQ_{out} \quad (\text{Eqn. 36})$$

As it has been stated, the equations 37 and 38 refer to the case where heat has to be extracted from the system:

$$f^4 \leq 10^8 \cdot (1 - y) \quad (\text{Eqn. 37})$$

$$-f^4 \leq -Q_{exc} \cdot C Q_{in} \quad (\text{Eqn. 38})$$

Then, the capacity constraint that was already presented in previous models is still included in this one, as it can be seen below:

$$F_j^{in} \leq Q_j \quad \forall j \quad (\text{Eqn. 39})$$

#### 7.4.2.5. Objective function

Finally, the objective function to be maximized in this model is defined below:

$$B = \sum_k f_k^1 + \sum_k f_k^2 - \left( \sum_j MF_j^{in} \cdot C_j \right) - \left( \sum_l MF_l^{disp} \cdot C_l \right) - f^3 - f^4 \quad (\text{Eqn. 40})$$

Where the first term of the function refers to the profit obtained from the selling of the raw material streams when the demand has been covered, the second term refers to the profit obtained in case the demand has not been covered. Then, the third and fourth terms refer to the cost of the waste inlets and the compounds sent to disposal, respectively. Finally, the last two terms refer to the cost related to the heat added or subtracted from the system, respectively.

#### 7.4.3. Particular Example

The particular example that has been considered in this case contains the same values for parameters  $C_j, C_k, C_l, C_d, M_j, M_k, M_l, MW_j, MW_k, MW_l, Q, D$  and  $H$ .

On the other hand, with respect to the new energy-related parameters that have been introduced in this model, the values for each of them are now shown.

First of all, regarding enthalpies, the following two tables show the values that have been obtained from HYSYS at 1 atm of pressure and 293,15 K regarding inlet waste streams, outlet raw material and outlet disposal compounds:

Table 14. Values for parameter  $H_j$  and  $H_l$  in particular example of Model 4

j/l	H(j/l) [J/mol]
CH3COOH	-460557,20
C6H6	49761,03
Cl2	0,00
C2H4	52329,80
C2H4Cl2	-165089,38
HCl	-92359,00
O2	0,00
H2O	-284902,93

In this sense, it is worth noting that the values in table 14 represent both  $H_j$  and  $H_l$ . On the other hand, the values for  $H_k$  are shown in the table below:

Table 15. Values for parameter  $H_k$  in particular example of Model 4

k	H(k) [J/mol]
C2H3Cl	35169,00
CH3CH2OH	-278143,08
C6H5C2H5	-11558,18
CH2OCH2	-52670,00
C2Cl4	-51414,31
C2HCl3	-40125,25
CH3CO2CHCH2	-354796,23

Once the values related to enthalpy have been presented, entropy-related parameters are now shown:

Table 16. Values for parameter  $S_j$  and  $S_l$  in particular example of Model 4

j/l	S(j/l) [J/mol·C]
CH3COOH	70,88
C6H6	-125,51
Cl2	232,95
C2H4	214,67
C2H4Cl2	160,20
HCl	209,65
O2	183,42
H2O	6,56

In this case, the entropy defining both  $S_j$  and  $S_l$  is the same, too. On the contrary, the entropy values extracted from HYSYS at 1 atm and 293,15 K for  $S_k$  are shown in the table below:

Table 17. Values for parameter  $S_k$  in particular example of Model 4

k	S(k) [J/mol·C]
C2H3Cl	150,24
CH3CH2OH	12,88
C6H5C2H5	-80,54
CH2OCH2	62,11
C2Cl4	353,99
C2HCl3	247,52
CH3CO2CHCH2	166,11

Moreover, the price that has been considered for heat addition (heating) is  $1,13 \cdot 10^{-4} \frac{\text{€}}{\text{J}\cdot\text{h}}$ , which has been found in (Eurostat 2017). On the other hand, the price for heat subtraction (cooling) is  $6,21 \cdot 10^{-3} \frac{\text{€}}{\text{J}\cdot\text{h}}$  and has been obtained in ("Comparing Fuel Costs of Heating and Cooling Systems" 2003).

Thus, with all the values that have just been presented, the results that were obtained are shown next.

#### 7.4.4. Results

In this case, the value obtained for the objective function, which equals the profit obtained from the system, is 79194,76€.

The composition and flow of each raw material outlet is shown in the table below:

Table 18. Molar flow of raw material streams obtained in particular example of Model 4

Raw material	C2H3Cl	CH3CH2OH	C6H5C2H5	CH2OCH2	C2Cl4	C2HCl3	CH3CO2CHCH2
Molar flow [mol/h]	100,00	100,00	67,80	0,00	25,00	100,00	0,00

Moreover, the results of the binary variable  $z_k$ , which indicates if the demand of a given raw material is covered or not, is shown below:

Table 19. Results of  $z_k$  in particular example of Model 4

Raw material (k)	C2H3Cl	CH3CH2OH	C6H5C2H5	CH2OCH2	C2Cl4	C2HCl3	CH3CO2CHCH2
$z_k$	1	1	0	0	0	1	0

In this sense, the following figure shows a comparison between the demand of each raw material compound or stream, the value of the binary variable  $z_k$  and the result obtained in the optimization:

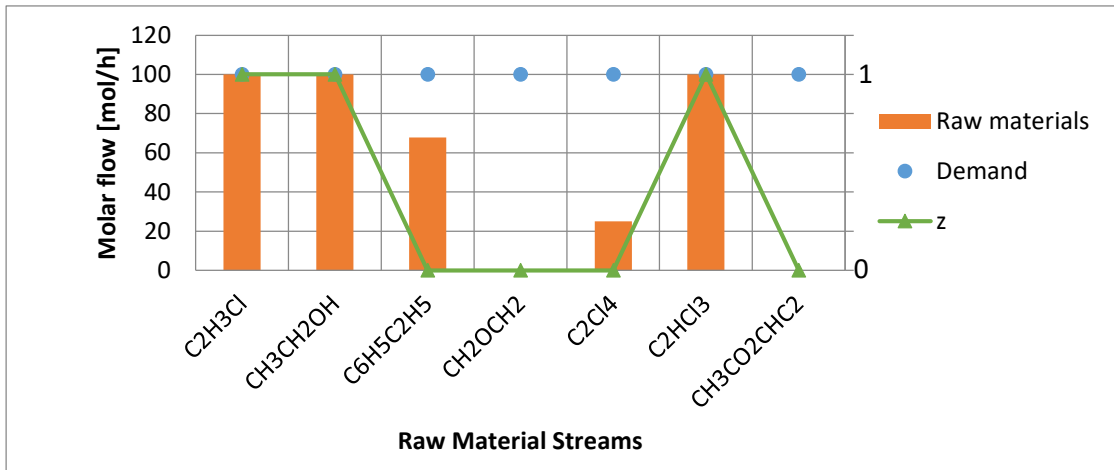


Figure 29. Obtained raw material streams molar flow and  $z_k$  in particular example of Model 4

From the figure above, it can be seen that the raw materials obtained are pretty much the same as in the previous cases, the only difference is that the amount of ethylbenzene obtained is slightly smaller. In this sense, the raw materials obtained are the most profitable ones (VCM and ethanol), then ethylbenzene is obtained as much as possible. On the other hand, trichloroethylene is also obtained, which is due to the fact that chlorine atoms coming from waste inlet streams have to be used as much as possible to obtain profit instead of sending them to the disposal stream. Thus, trichloroethylene is produced until its whole demand is covered and then PERC, as the first is more profitable than the latter.

In this sense, the composition and flow of the waste streams entering the system is shown in the table below:

Table 20. Molar flow of waste streams obtained in particular example of Model 4

Waste	CH <sub>3</sub> COOH	C <sub>6</sub> H <sub>6</sub>	Cl <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	HCl	O <sub>2</sub>	H <sub>2</sub> O
Molar flow [mol/h]	96,19	100,00	100,00	100,00	100,00	100,00	5,51	0,00

These results regarding waste streams are compared with the capacity in the figure below:

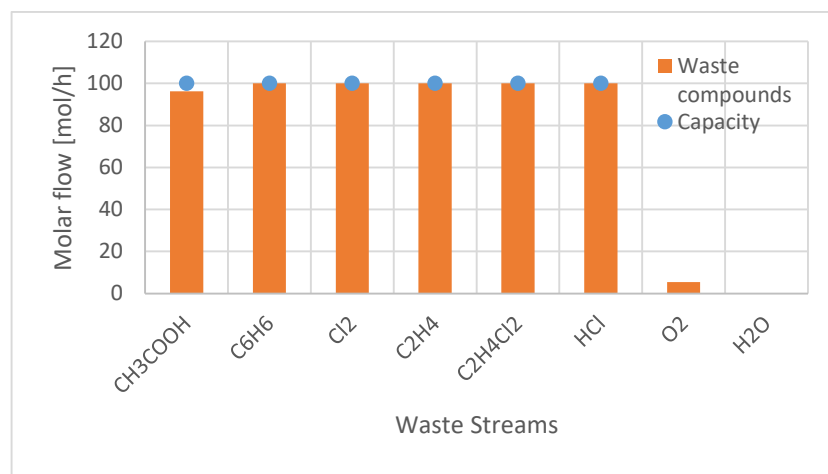


Figure 30. Waste streams molar flow and capacity comparison in particular example of Model 4

From these results it can be observed that almost all of the waste streams are taken, but it is noticeable that oxygen, water and acetic acid streams do not overpass their capacities. The explanation for this is later explained.

At this point it is relevant to present a global atomic mass balance of the system under study. The image below depicts it:

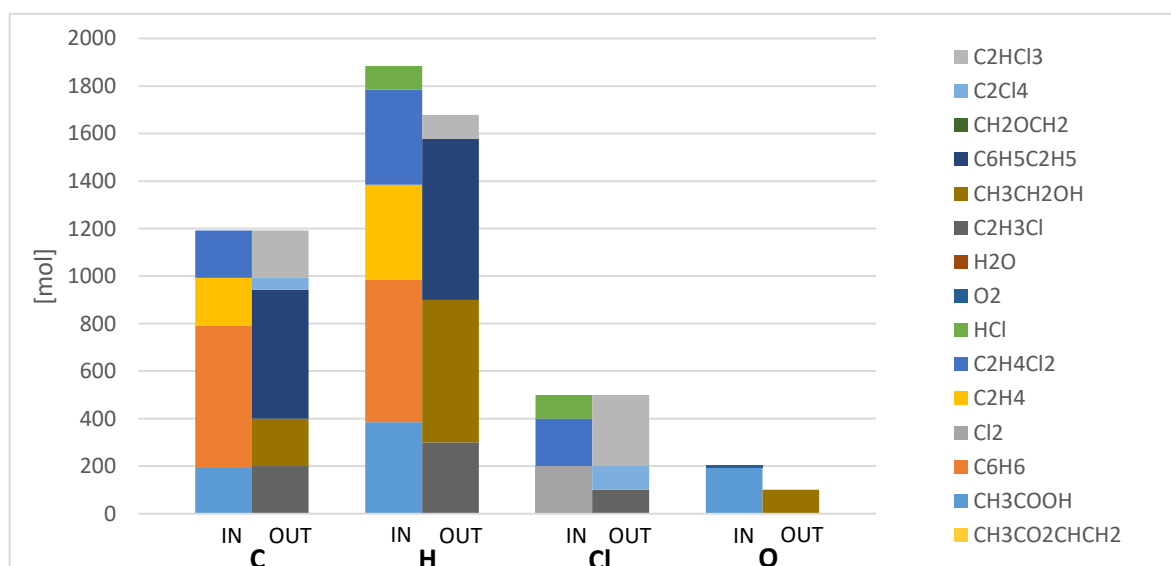


Figure 31. Global atomic mass balance in particular example of Model 4

From the figure above, it can be seen that the global atomic mass balance for carbon and chlorine is accomplished. However, with respect to hydrogen and oxygen, this is not done. This can be explained if one takes a look at the disposal streams obtained in this optimization. Thus, with respect to the disposal streams obtained, the results can be seen below:

Table 21. Disposal streams molar flow in particular example of Model 4

Waste	CH <sub>3</sub> COOH	C <sub>6</sub> H <sub>6</sub>	Cl <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	HCl	O <sub>2</sub>	H <sub>2</sub> O
Molar flow [mol/h]	0,00	0,00	0,00	0,00	0,00	0,00	0,00	103,39

Therefore, it can be seen that the amount of hydrogen and oxygen not included in the global atomic mass balance between waste streams and raw material streams has been sent to disposal forming water, which according to the case study established is the cheaper compound to dispose.

With respect to energy-related terms, the heat added or subtracted in this particular example equals zero. Therefore, both the variables  $f_3$  and  $f_4$  are zero too. This is due to the fact that the cost to be paid for adding or subtracting energy is so high that it makes the objective function to get a worse result. Therefore, what GAMS does is balancing the molar flows so that the global heat exchange in the system equals to zero and the objective function is not affected by heat or cooling costs. A further explanation of these results is done in the Results and Discussion section.

#### 7.4.5. Model limitations

The limitations of this model are listed below:

- The characterization of the compounds involved in the model is limited to their chemical formula.
- The system does not resemble nature chemical reactions or the chemical or technological paths to achieve the desired outcomes. Thus, it does not reflect the transformations that are feasible or affordable.
- The model does not take into account the existence of compounds that are isomeric or share the same chemical formula but their atoms are arranged in a different way.
- Streams formed by mixtures of components have not been taken into account.
- In spite of the fact that energy balances were added, the fact that there is only a heat exchanged for the whole system makes that sometimes, if for a given compound energy has to be added and for another energy has to be subtracted, the result shown, as it is global, makes that positive and negative values cancel each other.

In order to overcome the limitations of this model, Model 5 was developed.



## 7.5. Model 5: Industrial symbiosis MILP model considering mass & energy balances, chemical reactions and partial flows

### 7.5.1. Problem Statement

This model has been designed to overcome the limitations that the former approaches presented.

This approach represents a system that presents different waste input streams from external sources. Each of these streams is a mixture of different compounds and the objective is to transform these compounds into added value raw materials, which are the outputs of the system. In this model, the inlet partial flows for each stream are known, and waste supply may be used as a resource only partially. Furthermore, in this case the transformation from waste inputs to output raw materials is done by means of a set of potential chemical reactions. Thus, in order to obtain an output raw material, given compounds from the waste streams have to react. In this case, the non-desired compounds or the disposal ones are defined by the set of chemical reactions. Apart from this, not only do inputs and outputs have a related economic cost but also each chemical reaction does. Moreover, the demand of each raw material is limited. Moreover, this model also takes into account the possibility to obtain some compounds from an external supply. Furthermore, it should also be pointed out the fact that not only mass balances but energy balances have also been taken into account.

This model shares similar aspects to the previous models. The main similarity is that in this case each of the involved compounds is characterized by a given chemical composition, just as before. On the other hand, there is an important difference that should be noted: in this approach, each of the waste streams involved is now a mixture of different compounds, whereas in the approaches before there was just one compound present in each stream. This change allows a more realistic representation of waste, due to the fact that in most cases, waste is characterized as a mixture of different compounds, not just as a pure one.

This optimization problem is a MILP, just as in the previous case. The objective is to maximize the profit obtained from the system by means of finding the maximum amount of waste that can be processed and cover as much as possible the raw material demand considering all the costs derived both from the compounds and from the reactions taking place.

In this context, the following figure shows a scheme of the problem stated in this case:

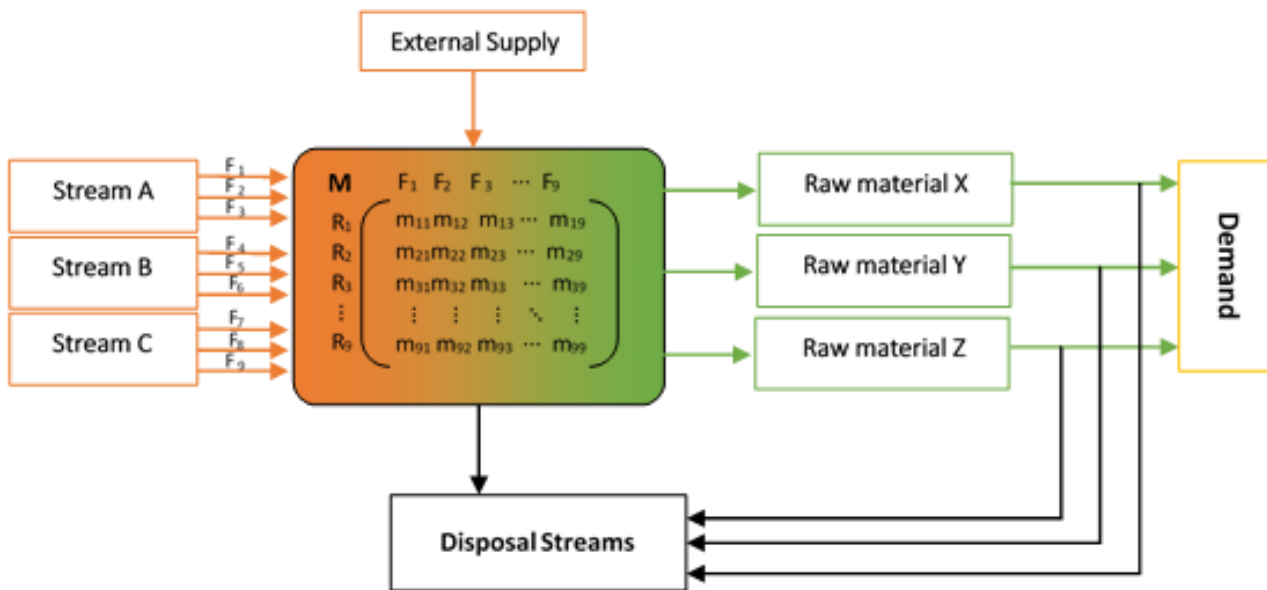


Figure 32. Problem scheme in model 5

As depicted in the figure above, there are different streams (A, B and C in the figure) entering the system, each of which is a mixture of compounds ( $F_1$  to  $F_9$ ). Then, these different compounds react following the stoichiometry of different established reactions, forming the different raw materials demanded. In this sense, just as in the case of the two previous models, if there are more raw materials produced than the demand, the excess of raw materials that cannot be sold has to be disposed.

The points that have been assumed during the development of this model are pointed below:

- The system works in continuous mode.
- The composition of each inlet waste stream is known.
- Each involved compound is defined by an exact chemical formula.
- The chemical reactions taken into account do not need the presence of any catalyser in order to take place.
- No equipment details have been considered.

Apart from the assumptions considered in the model, another important topic to point out is the main data that has to be given in order to completely define the problem. It is listed below:

- Chemical composition of each compound involved, both waste inlets and raw materials required.
- Associated cost or selling price for both waste inlets and desired raw materials.
- Partial flow of each of the input waste compounds.
- Required demand for each of the output raw materials.

Thus, the most relevant variables that can be computed with the data that has just been defined are the next ones:

- Total economic profit obtained from the system.
- Amount of raw materials that are obtained from the system.
- Amount of waste that has to be introduced in the system from all the available one.
- Amount of compounds generated from each chemical reaction.

In the following sections, this model is defined in a more exhaustive way.

## 7.5.2. Mathematical Formulation

### 7.5.2.1. Sets

First, the sets involved in the model are the following ones:

- Compounds ( $i$ )
- Waste streams ( $j$ )
- Raw material streams ( $k$ )
- Disposal streams ( $l$ )
- Reactions ( $m$ )

### 7.5.2.2. Parameters

The parameters involved in this approach are these:

- Available waste partial molar flow inlet ( $W_{j,i}$ )
- Demand of each raw material compound for each given stream ( $D_{k,i}$ )
- Stoichiometry of each potential chemical reaction in the system ( $R_{m,i}$ )
- Cost associated to the input waste streams ( $C_j$ )
- Cost associated to each of the involved raw material streams ( $C_k$ )
- Cost associated to the treatment of each stream sent to disposal ( $C_l$ )
- Cost of disposing over demanded raw materials ( $C_k^{disp}$ )
- Cost associated to the compounds obtained from an external supply ( $C_i^{es}$ )
- Cost associated to the potential chemical reactions taking place ( $C_m^r$ )
- Molecular weight of each compound involved ( $MW_i$ )
- Molar enthalpy of each compound ( $H_i$ )
- Molar entropy of each compound ( $S_i$ )
- Cost of heat addition ( $CQ_{in}$ )
- Cost of heat subtraction ( $CQ_{out}$ )
- Annual working hours of the system ( $AH$ )
- Working temperature of the system ( $T$ )

### 7.5.2.3. Variables

The variables involved in this model are defined below:

- Input waste partial molar flow entering the system ( $F_{j,i}$ )
- Fraction per unit of the total waste available that enters the system ( $fF_j$ )
- Total waste input for each given compound ( $W_i^{in}$ )
- Total amount of compounds obtained from an external supply ( $ES_i$ )
- Total input compounds entering the system ( $F_i^{in}$ )
- Molar flow of each compound obtained from each chemical reaction ( $F_m^{gen}$ )
- Output molar flow of each compound ( $F_i^{out}$ )
- Partial output molar flow in each raw material stream ( $F_{k,i}^{rm}$ )
- Partial output molar flow in each disposal stream ( $F_{l,i}^d$ )
- Heat that has to be exchanged with the system in each reaction ( $Q_m^{exc}$ )
- Enthalpy associated to each reaction taking place ( $H_m^{react}$ )
- Entropy associated to each reaction taking place ( $S_m^{react}$ )
- Gibbs free energy associated to each reaction taking place ( $G_m^{react}$ )
- Binary variable representing if demand has been covered. ( $z_{k,i}$ )
- Binary variable representing whether heat has to be added or extracted in each reaction ( $y_m$ )
- Function representing the case where demand has been covered ( $f_{k,i}^1$ )
- Function representing the case where demand has not been covered ( $f_{k,i}^2$ )
- Function representing the case where heat has to be added to the system ( $f_m^3$ )
- Function representing the case where heat has to be extracted from the system ( $f_m^4$ )
- Profit obtained from the system ( $B$ )

It is important to outline the fact that all the variables that refer to a flow are strictly positive variables. Moreover, it is also relevant to outline that  $fF_j \in [0,1]$ , being it the amount of part per units with respect to the total available waste to be treated.

### 7.5.2.4. Equations

At this point, it is important to mention and explain the equations that define the model. They are presented in this section.

First, equation 40 presents  $F_{j,i}$ , which is the waste that is actually entering the system, expressed as partial molar flows, as a fraction of all the available waste that could potentially be treated. Thus, this equation offers the possibility that the waste supply is only used partially:

$$F_{j,i} = fF_j \cdot W_{j,i} \quad \forall j, i \quad (\text{Eqn. 41})$$

Subsequently, it is relevant to define all the different flows in the system. In this sense, equation 42 shows that the sum of all the waste input molar flows for all the waste streams is the total waste input flow for a given compound. This is shown in the equation below:

$$\sum_j F_{j,i} = W_i^{in} \quad \forall i \quad (\text{Eqn. 42})$$

At this point is where the external supply of compounds is included. The following equation shows that the total input compounds in the system is the addition of the compounds obtained from the available waste streams and the amount of compounds obtained from an external supply:

$$W_i^{in} + Es_i = F_i^{in} \quad \forall i \quad (\text{Eqn. 43})$$

Once these previous equations have been defined, it is time to present equation 44, which refers to a mass balance including the chemical reactions taking place in the system. This equation implies that the input molar flow for all the compounds plus the amount of moles of compound that are consumed or generated inside the system equates the output molar flow of all the compounds defined in the system:

$$F_i^{in} + \left( \sum_m R_{m,i} \cdot F_m^{gen} \right) = F_i^{out} \quad \forall i \quad (\text{Eqn. 44})$$

Then, it is relevant to define that the total output compounds obtained are separated into raw materials output partial flows and the rest of leftover compounds are then sent to disposal:

$$F_i^{out} = \sum_k F_{k,i}^{rm} + \sum_l F_{l,i}^d \quad \forall i \quad (\text{Eqn. 45})$$

All the equations presented until this moment regarded material balances. On the contrary, the next equation refers to an energy balance where the heat exchanged in each reaction is computed:

$$\left( \sum_i R_{m,i} \cdot F_m^{gen} \cdot H_i \right) = Q_m^{exc} \quad \forall m \quad (\text{Eqn. 46})$$

Apart from that last equation, reaction enthalpies entropies and Gibbs free energy are computed as follows.

$$\left( \sum_i R_{m,i} \cdot H_i \right) = H_m^{react} \quad \forall m \quad (\text{Eqn. 47})$$

With respect to reaction entropies, the equation can be defined as follows:

$$\sum_i R_{m,i} \cdot S_i = S_m^{react} \quad \forall m \quad (\text{Eqn. 48})$$

Finally, having the enthalpy, the entropy and the working temperature of the system, reaction Gibbs free energy can be computed as shown below:

$$G_m^{react} = H_m^{react} - T \cdot S_m^{react} \quad \forall m \quad (\text{Eqn. 49})$$

Afterwards, just as in Model 4, different big Ms are used in order to define the binary variables that appear in the model.

Firstly, in order to define the binary variable  $z_{k,i}$ , which has to do with the demand, two equations have been build, which follows a similar logic as the ones presented in Model 4:

$$D_{k,i} \cdot z_{k,i} \leq F_{k,i}^{rm} \quad \forall k, i \quad (\text{Eqn. 50})$$

$$F_{k,i}^{rm} - D_{k,i} \leq 10^8 \cdot z_{k,i} \quad \forall k, i \quad (\text{Eqn. 51})$$

In this sense, it is relevant to remind that the term  $10^8$  is an arbitrary Big M.

After the definition of the binary variable representing demand, the binary variable representing heat addition or subtraction is now defined. Again, the logic that has been followed is very similar to that followed in Model 4 (equation 31):

$$Q_m^{exc} \leq 10^8 \cdot y_m \quad \forall m \quad (\text{Eqn. 52})$$

$$-Q_m^{exc} \leq 10^8 \cdot (1 - y_m) \quad \forall m \quad (\text{Eqn. 53})$$

Then, once the binary variables  $z_{k,i}$  and  $y_m$  have been defined, different functions are built with them. These functions are now explained.

The following four equations refer to the binary variable representing the demand. Two of them represent the case where the demand has been covered and the other to represent the case where the demand has not been covered.

First, the two following equations represent the case where the demand has been covered. Moreover, in equation 54, there is a term representing a penalization derived from producing more than the demand:

$$f_{k,i}^1 \leq 10^8 \cdot z_{k,i} \quad \forall k \quad (\text{Eqn. 54})$$

$$f_{k,i}^1 \leq (D_{k,i} \cdot C_k \cdot MW_i) - C_k^{disp} \cdot MW_i \cdot (F_{k,i}^{rm} - D_{k,i}) \quad \forall k, i \quad (\text{Eqn. 55})$$

On the other hand, the next two equations represent the case where the demand has not been covered:

$$f_{k,i}^2 \leq 10^8 \cdot (1 - z_{k,i}) \quad \forall k, i \quad (\text{Eqn. 56})$$

$$f_{k,i}^2 \leq (MW_i \cdot F_{k,i}^{rm} \cdot C_k) \quad \forall k, i \quad (\text{Eqn. 57})$$

Apart from this, the next four equations refer to the heat exchanged and to the binary variable  $y_m$ . The following two equations represent the case where heat has to be extracted from the system (equations 58 and 59) and afterwards, two more equations representing the case where heat has to be added to the system.

$$f_m^3 \leq 10^8 \cdot y_m \quad \forall m \quad (\text{Eqn. 58})$$

$$-f_m^3 \leq Q_m^{exc} \cdot CQ_{out} \quad \forall m \quad (\text{Eqn. 59})$$

As it has been stated, the equations 60 and 61 refer to the case where heat has to be added to the system:

$$f_m^4 \leq 10^8 \cdot (1 - y_m) \quad (\text{Eqn. 60})$$

$$-f_m^4 \leq -Q_m^{exc} \cdot CQ_{in} \quad (\text{Eqn. 61})$$

Apart from all of this, there is one constraint in the system, which is the following:

$$\sum_i W_{j,i} \leq Q_j \quad \forall j \quad (\text{Eqn. 62})$$

It implies that in all cases, the total flow of each waste stream should always be less or equal than an established capacity.

#### 7.5.2.5. Objective function

Finally, the objective function that has to be maximized is now defined. It is an economic approach that takes into account a monetary balance derived from the system:

$$\begin{aligned}
 P = & -AH \cdot \left( \sum_i \sum_l F_{l,i}^d \cdot C_l \cdot MW_i \right) - AH \cdot \left( \sum_i \sum_j F_{j,i} \cdot C_j \cdot MW_i \right) \\
 & - \left( \sum_m F_m^{gen} \cdot C_m^R \right) - \left( \sum_i ES_i \cdot C_i^{es} \cdot MW_i \right) + \sum_k \sum_i f_{k,i}^1 \\
 & + \sum_k \sum_i f_{k,i}^2 - \left( \sum_m f_m^3 + \sum_m f_m^4 \right)
 \end{aligned} \quad (\text{Eqn. 63})$$



The first term in the objective function represents the losses derived from the output streams that are sent to disposal for their further treatment. Then, the second term refers to the cost derived from the waste streams that enter the system for their transformation into more valuable products. Subsequently, the third term refers to the cost associated to each one of the reactions that are taking place in the system. Next, the fourth term refers to the cost derived from obtaining resources from an external supply. Fifth and sixth terms refer to the profit obtained from the selling of the raw materials, depending if the demand has been covered or not. Finally, the seventh and eighth term refer to the cost derived when having to pay money for adding or subtracting heat in each reaction.

### 7.5.3. Particular Example

Once the mathematical formulation of this fifth model has been presented, a particular example in line with all those presented in the previous models is now shown.

First, the compounds involved are the following:

$$i = \langle \text{CH}_3\text{COOH}, \text{C}_6\text{H}_6, \text{Cl}_2, \text{C}_2\text{H}_4, \text{C}_2\text{H}_4\text{Cl}_2, \text{HCl}, \text{O}_2, \text{H}_2\text{O}, \text{C}_2\text{H}_3\text{Cl}, \text{CH}_3\text{CH}_2\text{OH}, \text{C}_6\text{H}_5\text{C}_2\text{H}_5, \text{CH}_2\text{OCH}_2, \text{C}_2\text{Cl}_4, \text{C}_2\text{HCl}_3, \text{CH}_3\text{CO}_2\text{CHCH}_2 \rangle$$

Then, the ten waste input streams that have been considered are the following, were each of them has an associated composition with respect to each compound:

$$j = \langle W_1, W_2, \dots, W_{10} \rangle$$

Whilst the raw material streams considered are:

$$k = \langle \text{RM}_1, \text{RM}_2, \dots, \text{RM}_{10} \rangle$$

Regarding the disposal output streams, the ones in this particular example are:

$$l = \langle D_1, D_2, \dots, D_{10} \rangle$$

Finally, the set of potential chemical reactions considered is:

$$m = \langle R_1, R_2, \dots, R_9 \rangle$$

Then, once the sets involved in the system have been presented, the parameters involved are now shown.

First, the waste input partial molar flow taken into account is shown in the table below:

Table 22. Input waste partial molar flows  $W_{j,i}$  [mol/h] in particular example of Model 5

$W_{j,i}$	CH3COOH	C6H6	Cl2	C2H4	C2H4Cl2	HCl	O2	H2O
W1	100,00	0	0,00	0,00	0,00	0,00	0,00	0,00
W2	0,00	100,00	0,00	0,00	0,00	0,00	0,00	0,00
W3	0,00	0,00	100,00	0,00	0,00	0,00	0,00	0,00
W4	0,00	0,00	0,00	100,00	0,00	0,00	0,00	0,00
W5	0,00	0,00	0,00	0,00	100,00	0,00	0,00	0,00
W6	0,00	0,00	0,00	0,00	0,00	100,00	0,00	0,00
W7	0,00	0,00	0,00	0,00	0,00	0,00	100,00	0,00
W8	0,00	0,00	0,00	0,00	0,00	0,00	0,00	100,00
W9	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
W10	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00

It is worth noting that only compounds until water are presented in the table above, and the rest of compounds included in the set  $i$  are not shown in the table because they are not considered to be present in the waste inlet streams and thus their input partial molar flows were zero. This is done in order to apply this parameter in the most similar way as it was applied in the previous model, for a better further results comparison between all models.

Moreover, it is relevant to outline that in the MS Excel file where all the data is exported to GAMS, the partial flow entering has been computed as a total molar flow in each given stream times the composition as shown below:

$$W_{j,i} = W_j^F \cdot x_{j,i} \quad (\text{Eqn. 64})$$

Where  $W_j^F$  is the total molar flow in a given stream and  $x_{j,i}$  is the molar fraction of a given compound in each given stream. This was done this way in order to introduce the partial molar flow of each compound in each stream directly in GAMS and thus avoid non-linearity.

Then, the parameter of the demand of each compound in each raw material stream is shown below:

Table 23. Raw material streams demand  $D_i^j$  [mol/h] in particular example of Model 5

$D_i^j$	C2H3Cl	CH3CH2OH	C6H5C2H5	CH2OCH2	C2Cl4	C2HCl3	CH3CO2CHCH2
RM1	100,00	0,00	0,00	0,00	0,00	0,00	0,00
RM2	0,00	100,00	0,00	0,00	0,00	0,00	0,00
RM3	0,00	0,00	100,00	0,00	0,00	0,00	0,00
RM4	0,00	0,00	0,00	100,00	0,00	0,00	0,00
RM5	0,00	0,00	0,00	0,00	100,00	0,00	0,00
RM6	0,00	0,00	0,00	0,00	0,00	100,00	0,00
RM7	0,00	0,00	0,00	0,00	0,00	0,00	100,00

In this case, the values have been set in order to follow the same data handled in previous models. In this sense, the compounds appearing before VCM are not shown in the table because they do not appear in the raw material streams. The same happens with raw material streams 8 to 10.

Then, the maximum capacities ( $Q_j$ ) for each waste inlet stream have been set to 100 mol/h.

Furthermore, another relevant parameter that is first introduced in this model are the stoichiometry of the potential chemical reactions that can take place in the system. These are defined with parameter  $R_{m,i}$ , which is shown in the table found in the next page:

Table 24. Stoichiometry of the potential chemical reactions considered in particular example of Model 5

$R_{m,i}$	CH <sub>3</sub> COOH	C <sub>6</sub> H <sub>6</sub>	Cl <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	HCl	O <sub>2</sub>	H <sub>2</sub> O	C <sub>2</sub> H <sub>3</sub> Cl
R1			-1	-1	1				
R2			-3		-1	4			
R3				-2	2	-4	-1	2	
R4					-1	1			1
R5			-1		-1	3			
R6				-1				-1	
R7				-1			0,5		
R8	-1			-1			-0,5	1	
R9		-1		-1				1	
$R_{m,i}$	CH <sub>3</sub> CH <sub>2</sub> OH	C <sub>6</sub> H <sub>5</sub> C <sub>2</sub> H <sub>5</sub>	CH <sub>2</sub> OCH <sub>2</sub>	C <sub>2</sub> Cl <sub>4</sub>	C <sub>2</sub> HCl <sub>3</sub>	CH <sub>3</sub> CO <sub>2</sub> CHCCH <sub>2</sub>			
R1									
R2				1					
R3									
R4									
R5					1				
R6	1								
R7			1						
R8								1	
R9		1							

Regarding the table above, it should be stated that chemical reactions are represented as a bill of materials where reagents have a minus sign in front of them and products a positive sign. Moreover, the values of each of the numbers that appear are equivalent to the stoichiometric coefficient of each of the compounds involved.

Then, regarding thermodynamic parameters, both enthalpies and entropies have been obtained from Aspen HYSYS. In this sense, the values for each compound are the same ones that were shown in Model 4.

With respect to the costs, the parameters  $C_j$ ,  $C_l$ ,  $C_k^{disp}$  have the same values for each compound already shown in Model 4 particular example. However, it should be noted that the parameter  $C_k$  is now computed considering the cost of each compound times the molar fraction of them in a given stream. Thus, it is related to the composition of the stream.

Moreover, regarding the external supply cost ( $C_i^{es}$ ), the values that have been considered are shown in the next table:

Table 25. External supply cost ( $C_i^{es}$ ) in particular example of Model 5

i	Ces(i) [€/kg]
CH3COOH	0,084
C6H6	0,065
Cl2	0,950
C2H4	4,923
C2H4Cl2	0,084
HCl	7,919
O2	0,005
H2O	0,001
C2H3Cl	2,173
CH3CH2OH	1,347
C6H5C2H5	0,189
CH2OCH2	0,001
C2Cl4	0,057
C2HCl3	0,094
CH3CO2CHCH2	0,013

These values have been found in the following sources: (“Acetic Acid Cost” 2017; “Benzene Cost” 2017; “Chlorine Cost” 2017; “Ethylene Cost” 2017; “EDC Cost” 2017; “Oxygen Cost” 2017; “Water Cost” 2017; “VCM Cost” 2017; “Ethanol Cost” 2017; “Ethylbenzene Cost” 2017; “Epoxyethane Cost” 2017; “PERC Cost” 2017; “Trichloroethylene Cost” 2017; “Vinyl Acetate Cost” 2017)

Finally, regarding the reaction costs ( $C_m^r$ ), they have been estimated in terms of the Gibbs free energy of each reaction. Gibbs free energy indicates the spontaneity of a reaction or in other words, how easy it is to happen. Therefore, it has been assumed that the producing costs were higher if the Gibbs free energy was higher and vice versa. Thus, the function that is represented in the figure below was used in order to determine the cost of each reaction:

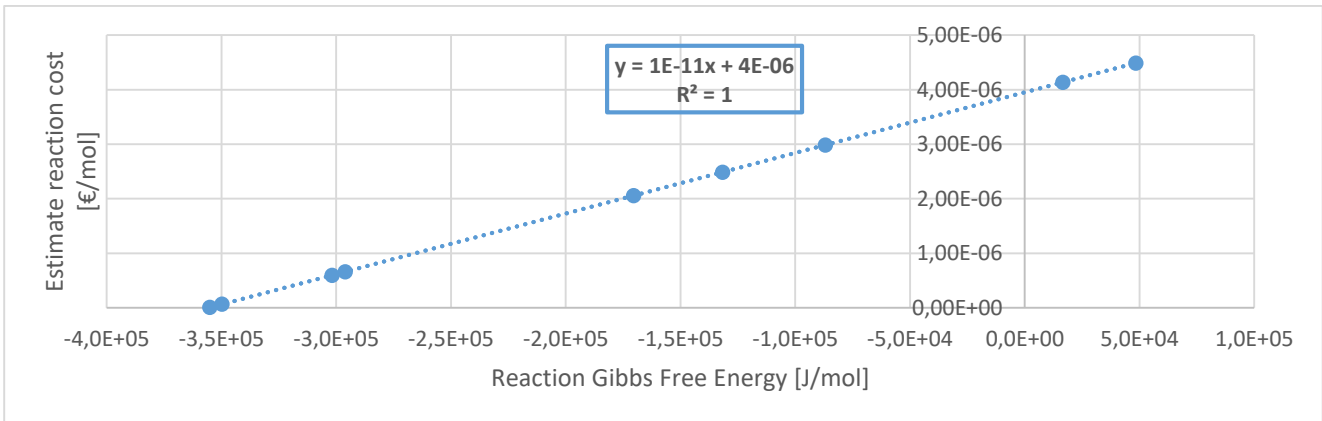


Figure 33. Reaction cost estimation ( $C_m^r$ ) as a function of Gibbs Free Energy

Therefore, the values obtained for parameter  $C_m^r$  are shown below:

Table 26. Reaction cost ( $C_m^r$ ) estimated parameters

m	$C_r(m)$ [€/mol]
R1	2,49E-06
R2	3,28E-09
R3	5,95E-07
R4	4,49E-06
R5	6,59E-07
R6	4,13E-06
R7	2,98E-06
R8	2,06E-06
R9	6,21E-08

At this point, it should be pointed out that these reaction costs also contain the energy related cost for the reaction to take place. Therefore, in this particular example the costs for both adding and subtracting heat are directly included in  $C_m^r$ .

Thus, once the parameters considered in this particular example have been shown, the results obtained are now presented.

#### 7.5.4. Results

The results obtained in the particular example applied to Model 5 are presented in this section. First of all, it is worth noting that in this case two possibilities were considered: the first one does not include the possibility to obtain certain compounds from an external supply while the second does.

Moreover, it should be remarked that in order to make these optimization results comparable with those obtained in previous models, the way of showing them will be the same as before. Then, it should always be reminded that in this case a stream does not have to particularly contain just one compound but also a mixture of them. Moreover, in this model there is not a particular set for inlet waste compounds and another for outlet raw material compounds, but an only set that contains all the compounds involved in the system. Thus, in order to make results easily understandable and not redundant, sometimes only some compounds will be presented.

#### 7.5.4.1. Not considering the external supply

The results of the example that does not consider the possibility of obtaining some compounds from an external supply are now presented.

First of all, the profit that is obtained from the system equals 69255,94€.

The fraction of input waste that enters the system is now shown:

Table 27. Fraction of input waste entering the system  $fF_j$

Stream	W1	W2	W3	W4	W5	W6	W7	W8	W9	W10
Fraction	0	0	0	1	1	0	0	1	0	0

Thus, the only waste streams entering the system are W4, W5 and W8, which are completely composed by ethylene, ethylene dichloride and water.

Results regarding compounds entering the system and capacity can be seen in the figure below:

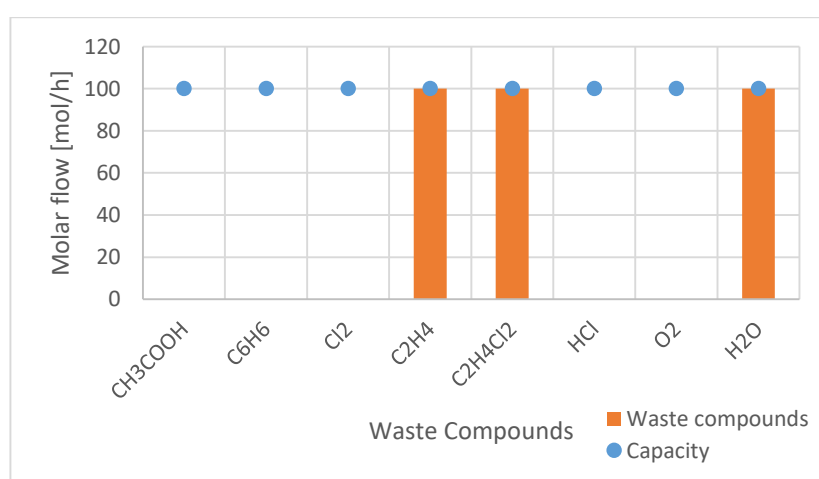


Figure 34. Waste compounds and capacity in particular example without external supply of Model 5

Then, regarding to the transformations taking place in the system there are two reactions R4 and R6 that generate 100 moles as a basis. These reactions are VCM synthesis and ethanol synthesis, respectively. The stoichiometry of these two reactions can be found in equations 6 and 8.

Therefore, once these two reactions have taken place, the obtained raw materials are shown below:

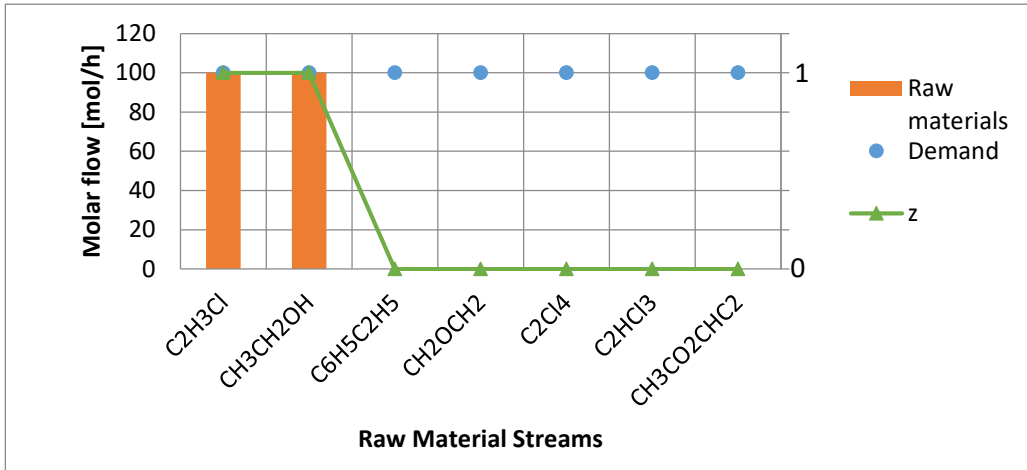


Figure 35. Raw material compounds and demand in particular example without external supply of Model 5

Thus, it can be seen that VCM and ethanol are obtained and completely cover the demand. In this sense, it is important to outline that VCM is obtained in stream RM1 and ethanol in stream RM2. Moreover, the binary variable  $z_{k,i}$  can also be seen in the figure, depicting when the demand has been covered and when not.

Regarding the obtained disposal streams, the results show that 100 moles of HCl are disposed in stream D1. This is due to the fact that VCM synthesis presents HCl as a subproduct and as there is no demand for it, it must be disposed.

Moreover, the results regarding the heat exchanged in each reaction are shown in the table below:

Table 28. Heat exchanged in each reaction  $Q_m^{exc}$  in particular example without external supply of Model 5

Reaction	R1	R2	R3	R4	R5	R6	R7	R8	R9
Qexc [MJ/h]	0	0	0	10,79	0	-4,56	0	0	0

Thus, only in the reactions that are taking place there is a heat exchange. In R6, there is heat to be added while in R4 it must be subtracted.

Finally, a global atomic mass balance of inlet waste compounds and outlet raw materials is shown below:



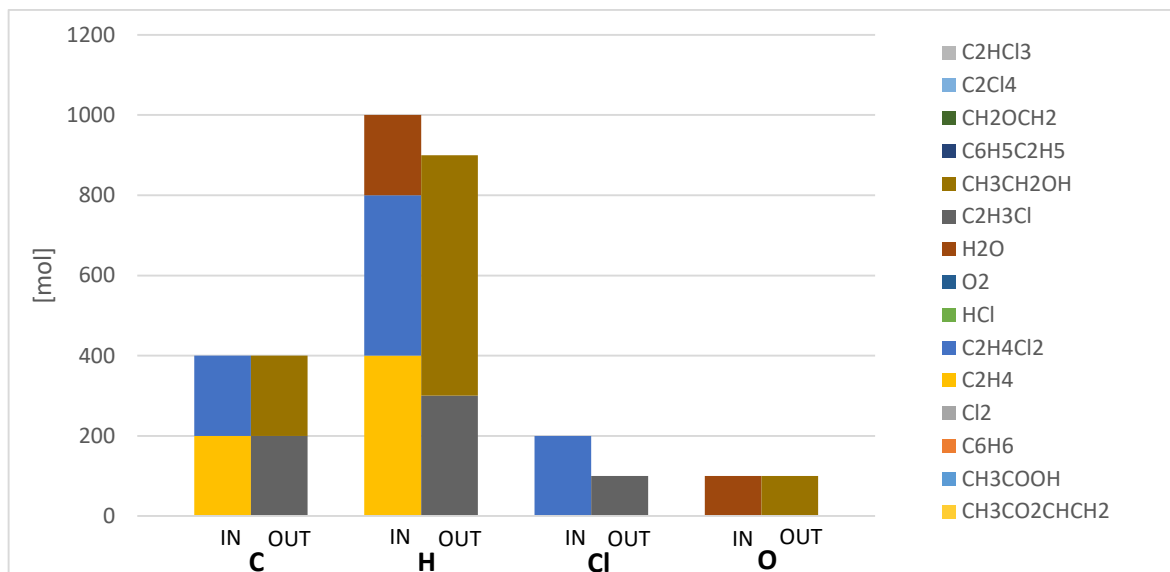


Figure 36. Global atomic mass balance in particular example without external supply of Model 5

As shown in the figure above, the only atoms where there is an imbalance are H and Cl, which precisely form HCl, which is the compounds that is disposed.

Now, the results regarding the case that takes into account the external supply is presented.

#### 7.5.4.2. Considering the external supply

For this example, the obtained value for the system’s profit is 84363,03€, which is considerably bigger than in the example that has just been explained.

The fraction of input waste that enters the system is the following:

Table 29. Fraction of input waste entering the system  $fF_j$

Stream	W1	W2	W3	W4	W5	W6	W7	W8	W9	W10
Fraction	0	0	0	1	0,5	0	0,25	0	0	0

Thus, the stream W4, composed by ethylene, enters completely into the system. Then, the streams W5 and W7, composed by ethylene dichloride and oxygen only enter the system partially. Results regarding waste entering the system and capacity can be seen in the figure below:

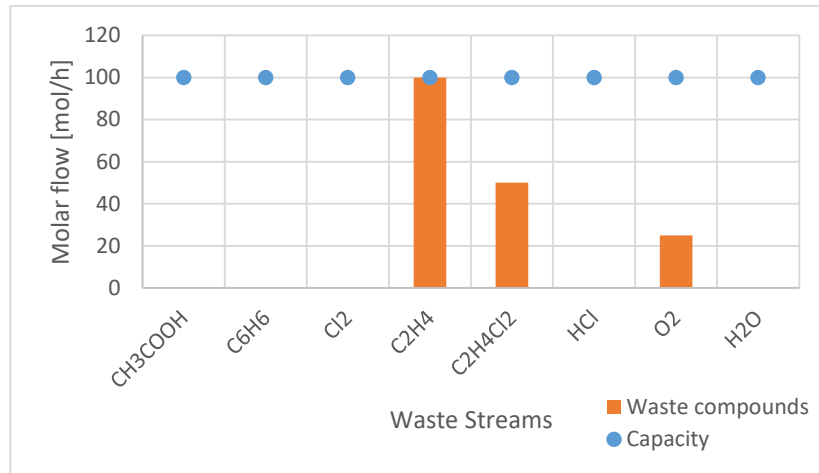


Figure 37. Molar flow of waste compounds entering the system and capacity in particular example considering external supply of Model 5

Thus, ethylene enters the system until filling its maximum capacity while EDC and O<sub>2</sub> only enter partially.

Now, the external supply consumed is shown in the table below:

Table 30. External supply consumed in particular example of Model 5

Compound	CH <sub>3</sub> COOH	C <sub>6</sub> H <sub>6</sub>	Cl <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	HCl	O <sub>2</sub>	H <sub>2</sub> O
mol/h	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
Compound	C <sub>2</sub> H <sub>3</sub> Cl	CH <sub>3</sub> CH <sub>2</sub> OH	C <sub>6</sub> H <sub>5</sub> C <sub>2</sub> H <sub>5</sub>	CH <sub>2</sub> OCH <sub>2</sub>	C <sub>2</sub> Cl <sub>4</sub>	C <sub>2</sub> HCl <sub>3</sub>	CH <sub>3</sub> CO <sub>2</sub> CHCH <sub>2</sub>	
mol/h	0,00	50,00	100,00	100,00	100,00	100,00	100,00	

Then, regarding to the transformations taking place in the system, there are three reactions taking place. These are R3, R4 and R6. These are the oxychlorination of ethylene, VCM synthesis and ethanol synthesis. The basis amount of moles produced in each of them is 25, 100 and 50 respectively.

Therefore, once these reactions have taken place and considering the compounds obtained from an external supply, the obtained raw materials are shown below:

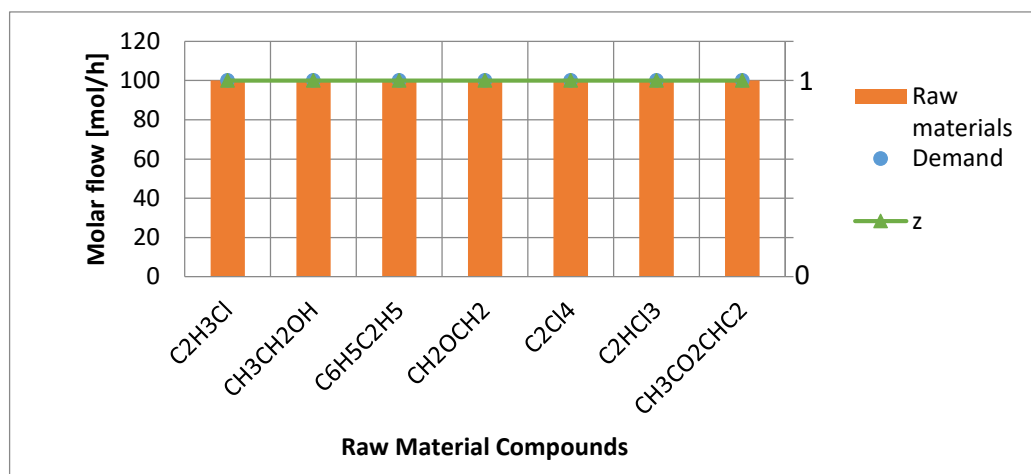


Figure 38. Obtained raw material compounds in particular example considering external supply of Model 5

Thus, it can be seen that the demand for each raw material stream is covered. Moreover, the binary variable  $z_{k,i}$  can also be seen in the figure, depicting when the demand has been covered and when not.

Regarding the obtained disposal streams, results show that in this case there are no compounds sent to disposal.

Moreover, the results regarding the heat exchanged in each reaction are shown in the table below:

Table 31. Heat exchanged in each reaction  $Q_m^{exc}$  in particular example without external supply of Model 5

Reaction	R1	R2	R3	R4	R5	R6	R7	R8	R9
$Q_{exc}$ [MJ/h]	0	0	-15,88	10,79	0	-2,28	0	0	0

Thus, only in the reactions that are taking place there is a heat exchange. In R3 and R6, there is heat to be added while in R4 it must be subtracted.

What can be concluded from this particular example considering an external supply possibility, is the fact that it allows to obtain more profit from the system, as all the raw material demands can be fully covered. Moreover, this external supply possibility also permits obtaining just the exact amount of compounds to be transformed so that no compounds have to be further disposed.

In general terms, it can be said that this final model overcomes most of the limitations stated in previous models.

## 8. Comparison and Discussion

The topic of this section is comparing and discussing each one of the models that were developed in the scope of this project.

In order to do so, first it is relevant to sum up all the systematic that was followed in the modelling process and the decisions that were taken at each step. The following scheme shows an overview of that:

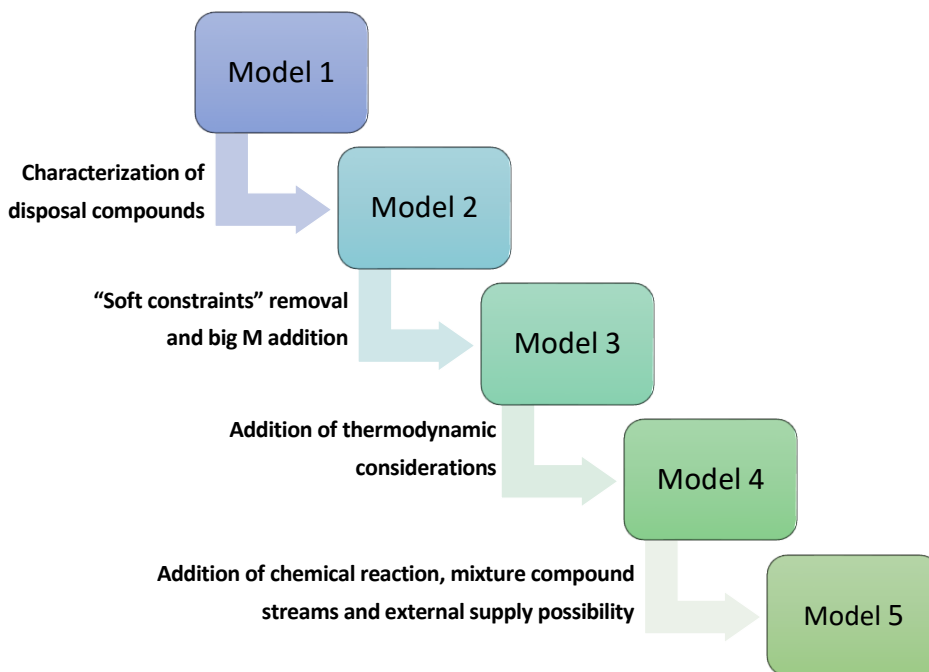


Figure 39. Overview of the models developed

Thus, as depicted in the figure above, the first model presented had no characterization of disposal compounds, being the disposal composed by unbounded atoms. Then, the first change to be implemented in a second model was the fact of better characterizing these disposal streams, turning them into a list of compounds instead of a set of atoms.

Afterwards, it became clear that that the raw material demand should not be a constraint, as it is a wish and not a physical or chemical impairment or in other words a “hard constraint”. Therefore, what was done was enforcing the objective function to take care of the demand, which was then represented using binary variables and the big M method to avoid non linearity. In this sense, it was introduced that if any raw material flow went over the demand, there would be a penalization cost for it, as there is no possibility to sell it or store it, having it to be further treated. Thus, “soft constraints” were removed as much as possible and were reflected in the objective function instead, transforming the program from LP to MILP, because of the binary variables added.

Then, energy balances were implemented so that conservation principles were better explored. Thus, when introducing energy, there was a related cost to it, depending on if this energy had to be added or subtracted from the system. So, energy was considered as a limit or additional element that would allow to improve the characterization of the described network.

Afterwards, the characterization of each stream was improved by adding compound mixtures. In the first models developed there was an analogy between stream and compound, due to the fact that each stream contained just one compound. However, this did not represent reality because generally waste or even raw materials are defined by mixtures of compounds in a given composition.

Additionally, the possibility to obtain compounds from an external supply was also added, which allows to cover more the raw material demand or even allows some transformations to happen when they need a compound that is not present in the inlet waste streams.

Moreover, a set of specific chemical reactions was introduced in the system, in order to describe better feasible transformations or nature or achievable technological paths. An associated cost for each of these reactions was estimated as a function of each reaction's Gibbs free energy, which indicates the spontaneity or easiness for it to happen. Thus, reactions with a smaller Gibbs free energy were cheaper than the ones with a bigger one.

Once this overview of the developed models has been made, a comparison between the results obtained in each model regarding the particular example is now done.

On the first place, the results of the optimized objective function in each model for the same particular example are graphed below:

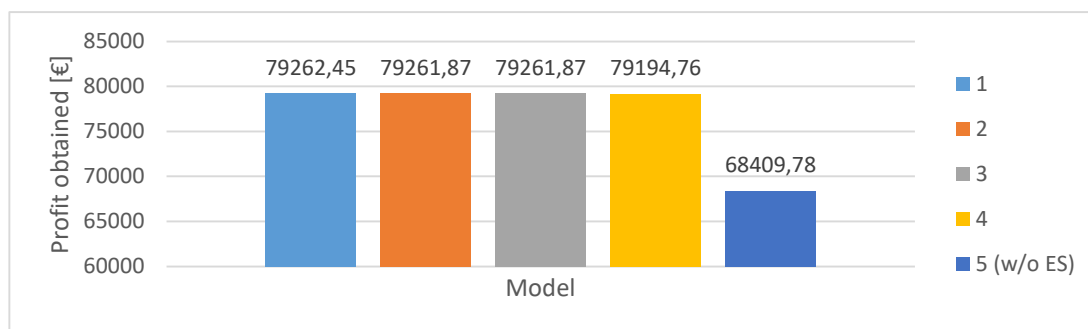


Figure 40. Results objective function optimized in each model developed

From the figure above, it can be seen that the profit obtained each time a new model was developed was progressively decreasing.

However, it is worth to mention that the profit obtained in Model 2 and Model 3 are the same due to the fact that the changes implemented from one model to the other did not reflect in the objective function.

Furthermore, as showed the results obtained in the particular example solved with Model 4, when adding energy and related costs to the system, the optimization resulted in no energy-derived costs. Thus, in order to prove that the result with respect to heat addition or subtraction in the system was right, the procedure now explained was followed. First, the solution with energy costs 0 was obtained, which was equal to the solution obtained when not considering energy balances. Then, the energy cost associated to it was computed. Thus, this made the final profit to diminish. Therefore, the solution considering energy tends to avoid this cost. So, it is better to reduce the profit obtained from raw materials selling and force the energy balance to be zero instead of having to pay for the energy.

Regarding to the last model, where the possibility to obtain compounds from an external supply was addressed, results show the potential of this external supply, as it allows the network to completely cover the raw materials' demand and thus increment the profit obtained. Comparing the results obtained in the example solved in Model 5 when it was not possible to acquire certain compounds from an external supply and when it was possible, it can be seen that having an external supply incremented the profit a 21,8%.

Apart from comparing the values of the objective functions once each model has been optimized, something that must be noted regarding each of the models develop is the way compounds and streams were defined. The approach followed in each model considered to treat compounds and streams as a bill or materials. In the first models developed, this bill of material approach was considered from the atomic level. For example, in order to produce a compound  $H_2O$ , 2 atoms of H and 1 atom of O are needed. This way, a matrix was created in order to define every compound. On the contrary, in the last models, this bill of material approach when further than the atomic level to a compound level, taking into account stoichiometry. For example, in order to obtain 1 mole of a raw material  $CH_3CH_2OH$ , 1 mole of  $C_2H_4$  and 1 mole of  $H_2O$  are needed. This allowed to create a matrix that characterized each chemical reactions. Thus, these interpretations of bill of materials applied to a chemical example were crucial in terms of the mathematical formulation of each model.

Additionally, the following figure aims to represent how complexity and solution feasible area change along with each model developed. The addition of new features and considerations in each model provides a more accurate description of the symbiosis network. Due to this, more realistic bounds can be exploited in the next optimization step. Therefore, the feasible area for the solution narrows each time. In other words, the more complex a model is, the smaller feasible area it presents. Thus, this is what the results obtained show.

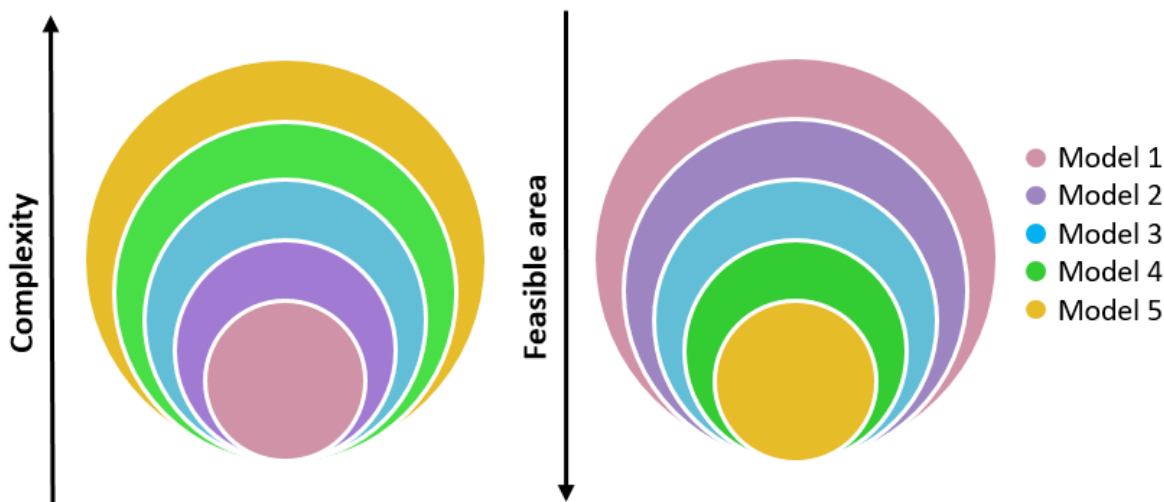


Figure 41. Comparison between complexity and feasible area in the models developed

## 9. Economic Analysis

The present section consists of the analysis of the economic aspects related to this project. It is divided in first an economic evaluation of all the costs derived from the project, and then a part in which the potential economic profits of this project are discussed.

In order to evaluate the total costs derived from the development of this project, the costs that are listed below have been taken into account:

- Software
- Hardware
- Personnel

First, the software costs are shown in the table below:

**Table 32. Economic evaluation. Software costs**

<b>Software</b>		
Microsoft Office Professional 2016 [€]		539
ASPEN-HYSYS v3.2 [€]		32098,31
GAMS v24.0.2	Base Module [\$]	640
	Solvers [\$]	17280
	Solver-Links [\$]	2880
	<i>GAMS Subtotal [\$]</i>	20800
	<i>GAMS Subtotal [€]</i>	19075,57
<i>Total [€]</i>		19614,57
<i>Total with usage factor [€]</i>		10342,58

With respect to the software costs shown above, it must be taken into account that the software costs include the licenses needed for Microsoft Office® Professional 2016, ASPEN-HYSYS® v3.2 and GAMS® v24.0.2 (General Algebraic Modelling System).

Regarding Microsoft Office®, the cost has been extracted from the official Microsoft Store (“Microsoft Store - Office Professional 2016” 2017)

On the other hand, with respect to ASPEN-HYSYS®, no more information apart from an approximate cost of 20000-50000 \$/year has been found. Thus, an average price in euros has been taken into account.



With respect to the GAMS® license, the cost has been computed from the data extracted from (“GAMS Academic Price List” 2016) as the summation of the cost of the base module, plus the cost of all the available solvers, plus the cost of the link between GAMS® and each of the solvers. In this sense, the license that has been considered is an academic one, which applies only for teaching and academic research at degree granting institutions. Moreover, for the conversion between euros and dollars, an amount of 1,0902 \$/€ has been considered. This amount was obtained from (“El Economista - EUR-USD” 2017) on 27/4/17.

Moreover, it must be outlined that an usage factor of 0,2 has been considered. This is because the license was shared between approximately five people and thus, the cost should be split too.

As for the hardware costs, the summary of these can be seen below:

**Table 33. Economic evaluation. Hardware costs**

<b>Hardware</b>	
Computer and peripherals [€]	46,43
<b>Total [€]</b>	<b>46,43</b>

The hardware costs take into account the physical material that has been used. In this sense, it is relevant to outline that as this project consists on modelling networks, the only material used is a computer and its peripherals, namely the screen, the keyboard and the mouse. Thus, the obtained cost of 92,86€ has been computed considering a base price of 1000€ for both the computer and the peripherals, a lifespan of 7 years and a residual or salvage value of 350€, being the latter the estimated value that the assets will realize upon their sale at the end of their lifespan. In this sense, the amortization expense for year can be computed as follows:

$$Amortization\ expense\ \left[ \frac{\text{€}}{\text{year}} \right] = \frac{Purchase\ price\ [€] - Salvage\ value[€]}{Lifespan\ [years]} \quad (2)$$

Then, the amortization expense has been multiplied by 0,5 years, which has approximately been the duration of this end of degree thesis.

With respect to the hardware costs, a usage factor of 1 has been taken into account.

With respect to the personnel costs, it has been considered that this project was developed by a process engineer with no working experience.

According to (PagePersonnel 2016), the yearly gross salary of this kind of engineering without occupational experience is between 20.000 and 25.000 €, so an average salary of 22.500€ per year has been considered. Thus, taking into account that there are 52 weeks per year and that 8 hours 5 days per week are worked, there are 2080 working hours (or hours that should be paid) per year. Thus, a salary of 10.82 €/h is obtained. The total dedications hours to this project are approximately 740. This number of hours has been computed taking into account the number of working days between 1/11/16 and 6/6/17, which is 148 in Catalonia and a dedication of 5 hours per day. Then, the total cost designated to the process engineer is computed as a product of these values. Moreover, the social security contribution has also been taken into account and a contribution rate of 23,6% has been established according to (“Seguridad Social - Bases Y Tipos de Cotización 2017” 2017)

Then, the personnel working costs are shown in the table below:

**Table 34. Economic analysis. Personnel costs**

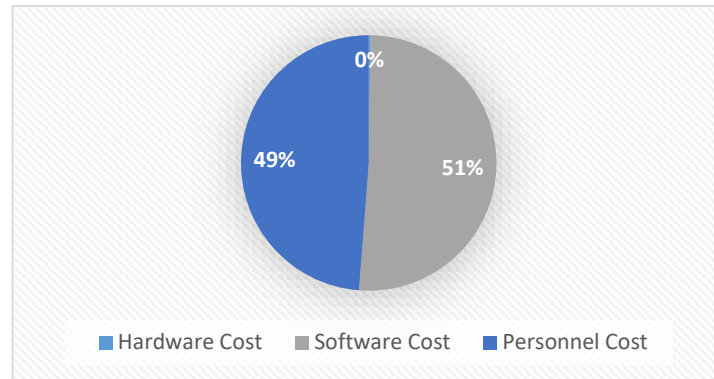
<b>Personnel</b>	
Process Engineer [€]	8004,81
Social Security (23.6%) [€]	1889,13
<b>Total [€]</b>	<b>9893,94</b>

Finally, taking into account the software, hardware and personnel costs a subtotal has been computed. Moreover, an overhead of 10% of the total cost has been taken into account in order to account the cost of intangible assets such as electricity, internet connection, literature, etc. Then, the total costs have been computed and can be seen below:

**Table 35. Final cost computation**

<b>Subtotal [€]</b>	20282,95
<b>Overhead (10%) [€]</b>	2028,29
<b>TOTAL [€]</b>	<b>22311,24</b>

Once the total costs have been computed, the figure below shows a graphic summary of all the costs that have been considered in the project:



**Figure 42. Summary of the project costs**

As depicted in the figure above, it can be said that the costs related to this project are basically personnel and hardware derived. In this sense, it should also be noted that the software cost are slightly higher than the personnel ones but they share the same order of magnitude.

Moreover, it is important to note that the potential economic profits that could be obtained from this project are related to the usage of waste, which is way cheaper than using virgin resources, and transforming it into an added-value raw material from which economic profit is obtained too. Having these developed models represents a good way to confront a targeting problem in order to decide in which direction a given industrial symbiosis network should be build.

## 10. Environmental Impact Analysis

As posed in (Sánchez et al. 2015) “Future will be sustainable or it won't be at all”. This is the reason why it is relevant to include an environmental impact analysis in any end of degree thesis. This type of analysis have a remarkable importance in every scientific discipline, but especially in all those related to information technology (IT) and engineering, for they can significantly make a positive impact regarding sustainability in other scientific fields.

As this project was completely developed digitally, it is relevant to discuss the environmental effects of the assets that have been used. In this sense, it must be outlined that the manufacturing of computers and peripherals can harm the environment in the following ways:

- Air, water, heat and noise pollution. In this sense, carbon emissions and the generation of greenhouse gases are one effect of the manufacturing of these devices that leads to global warming.
- Consumption of non-renewable resources, such as several metals and other compounds used in the manufacturing of computers. This consumption of natural resources can be indirectly related to the sources to obtain the electricity needed to run each device, for example coal.
- The manufacturing of technology generates large amounts of waste. In this sense, it must be said that all used computers and electronics get thrown out when break or become outdated. All these devices contain materials that are hazardous for the environment and that are difficult to treat for their further disposal.
- The manufacturing of these types of technology can lead to disrupting ecology, which means that a given land where there is a natural ecosystem is cleared to install factories thus allowing pollution to enter the trophic chain and affect natural cycles.
- Using specific type of compounds or materials can lead to health hazards.

In contraposition, while some of the impact of computers and information technologies has been negative, there are many ways in which this type of technology is helping to improve the environment, as it allows the development and production of new materials and technologies that are sustainable so that those which harm it can stop being used. This last fact can be clearly depicted analysing the concepts behind this project.

In this sense, this project aims to show that there are several disciplines aiming to disassociate unlimited resource consumption and our progress as a collective. Thus, there are many solutions being developed which offer sustainable values for industry, governments and society.

One of these is exhaustively explored in this thesis, and it is the fact of conceiving waste from one process as a potential resource that, if transformed, can turn into added value raw materials for another process. This can help reducing the consumption of virgin raw materials and thus, diminishing many of the environmental problems that are being faced nowadays.

As it can be extracted from the obtained results, the targeting approach developed in the context of this project allows a systematic identification and assesment of promising industrial symbiosis opportunities, which helps substantially in the decision-making process, allowing the efficient management of industrial symbiosis networks in chemical process industries.

Thus, it could be concluded that although there is indeed an environmental impact related to the manufacturing and use of the assets that were needed to develop this project, it is trivial in comparison to the potential that the developed tools offer to reduce many environmental concerns and advance towards a more sustainable society in harmony with nature.

## 11. Conclusions

Once the discussion of the obtained results during the development of this project has taken place, the points that are now explained have been concluded:

- Industrial symbiosis and related concepts have been studied and shown as an alternative to confront 21st century environmental problems while addressing industry economic and production needs.
- Five linear programming (LP) and mixed-integer linear programming (MILP) models of increasing complexity have been developed for chemical based industrial symbiosis and closed-loop supply chain concepts:
  - An initial LP considered atomic mass balances and pure compound streams with a poor characterization of the disposals.
  - Another LP was developed to further improve the characterization of the disposals.
  - A MILP was build in order to include soft constraints such as the demand in the objective function. The big M method was used for this purpose.
  - Energy balances were next added to expand this MILP.
  - Then, a final MILP model was developed that included mixed streams, chemical reactions, and the possibility to acquire certain compounds from an external supply.
- A case study involving ethylene, chlorine and related chemicals that represented the system was selected and solved by each model. Thus, different scenarios were studied to better understand and analyze the models developed. Finally, a particular example was presented that allowed to compare the results obtained in each model.
- Each model provides a more accurate description of the symbiosis network and more realistic bounds that can be exploited in the next optimization step. Accordingly, the economic objective function values diminish at each optimization step. Results show that the systematic used is effective as a targeting procedure to evaluate promising industrial symbiosis opportunities (i.e. it allows finding the most promising symbiosis opportunities in a given network, which should be next further investigated and eventually optimized).
- This project was addressed using math programming techniques (i.e. linear programming (LP), mixed-integer linear programming (MILP) or Big M methods) and implemented using general optimization tools (General Algebraic Modelling System (GAMS). Finally, Visual Basic for Applications (VBA) was used to obtain thermodynamic data from the Aspen HYSYS v7.3 database and export these parameters to MS Excel. Furthermore, MS Excel was connected to GAMS for both reading data and exporting optimization results with the GAMS's GDX utility.

## 12. Future Work

On the basis of the models developed and the above conclusions, some future work and recommendations are now proposed:

- To take into consideration other thermodynamic concepts such as exergy, which would allow to see the maximum useful work possible of the system under study. In order to do so, the models should be expanded in order to consider the system's surroundings.
- To include a specific definition of the equipment used to transform waste inlets into raw material outlets, such as splitters, mixers, chemical reactors or distillation columns. This would imply a more accurate simulation of a real case, which would lead to more reliable optimization results.
- To include several characteristics of the chemical reactions considered, such as side reactions, yields, conversions, catalysts, etcetera would allow a more precise definition of what would happen in industrial practice.
- To pose a multiobjective model that considers not only economical aspects but also other reasonable non-economic objectives such as safety or environmental impact.
- To state the problem as a supply chain, where there are specific locations related to each stream and the transformation system and distribution costs to connect one stream with another.
- To assess multiple actors and stakeholders decision making problems in the context of industrial symbiosis.

Therefore, all these further developments would allow to build a more systematic and realistic decision-making support to the efficient management of industrial symbiosis networks in the chemical process industries.

## 13. Bibliography

- “Acetic Acid Cost.” 2017. Accessed June 2.  
<http://www.sigmaaldrich.com/catalog/product/sial/ark2183?lang=es&region=ES>.
- Akdoğan, M.Şükrü, and Aysen Coşkun. 2012. “Drivers of Reverse Logistics Activities: An Empirical Investigation.” *Procedia - Social and Behavioral Sciences* 58: 1640–49.  
 doi:10.1016/j.sbspro.2012.09.1130.
- “Benzene Cost.” 2017. Accessed June 2.  
[http://www.sigmaaldrich.com/catalog/product/sial/401765?lang=es&region=ES&gclid=CjwKEA\\_jwu4\\_JBRDpqs2RwsCbt1MSJABOY8anAeZ6Ub\\_vD\\_qVzSqmj\\_WhHuUmlG1irf1MtvkhKMJ-\\_BoCRgDw\\_wcB](http://www.sigmaaldrich.com/catalog/product/sial/401765?lang=es&region=ES&gclid=CjwKEA_jwu4_JBRDpqs2RwsCbt1MSJABOY8anAeZ6Ub_vD_qVzSqmj_WhHuUmlG1irf1MtvkhKMJ-_BoCRgDw_wcB).
- Biegler, L. T. 2010. “Introduction to Process Optimization.” *Nonlinear Programming: Concepts, Algorithms, and Applications to Chemical Processes*, 1–16.  
 doi:<http://dx.doi.org/10.1137/1.9780898719383.ch1>.
- Boix, Marianne, Ludovic Montastruc, Catherine Azzaro-Pantel, and Serge Domenech. 2015. “Optimization Methods Applied to the Design of Eco-Industrial Parks: A Literature Review.” *Journal of Cleaner Production* 87 (1). Elsevier Ltd: 303–17. doi:10.1016/j.jclepro.2014.09.032.
- Bonciu, F. 2014. “The European Economy: From a Linear to a Circular Economy.” *Romanian J. Eur. Aff.*, no. 14: 78–91.
- Brito, Marisa P. de, and Rommert Dekker. 2003. “A Framework for Reverse Logistics.” Erasmus University Rotterdam.
- Brundtland, G. 1987. “Report of the World Commission on Environment and Development: Our Common Future.” *Oxford Paperbacks* Report of: 400. doi:10.2307/2621529.
- Chertow, Marian R. 2000. “Industrial Symbiosis : Literature and Taxonomy.” *Annual Review of Energy and the Environment* 25 (1): 313–37. doi:10.1146/annurev.energy.25.1.313.
- “Chlorine Cost.” 2017. Accessed June 2.  
<http://www.sigmaaldrich.com/catalog/product/aldrich/295132?lang=es&region=ES>.
- “Comparing Fuel Costs of Heating and Cooling Systems.” 2003.  
[https://engext.engg.ksu.edu/files/engext/publications/space/Heat\\_Cool\\_Costs.pdf](https://engext.engg.ksu.edu/files/engext/publications/space/Heat_Cool_Costs.pdf).
- “Daily Optimization.” 2017. Accessed May 22. <https://thoughtburner.org/about/daily-optimization/>].
- “Data Exchange with Excel.” 2017. Accessed May 22.  
[https://www.gams.com/latest/docs/userguides/userguide/\\_u\\_g\\_data\\_exchange\\_excel.html](https://www.gams.com/latest/docs/userguides/userguide/_u_g_data_exchange_excel.html).
- Dobbyn, Tyrone. 2015. “Linear Programming: The Simplex Method.”  
<http://slideplayer.com/slide/3758802/>].
- “EDC Cost.” 2017. Accessed June 2.



- <http://www.sigmaaldrich.com/catalog/product/sial/284505?lang=es&region=ES>.
- “El Economista - EUR-USD.” 2017. <http://www.eleconomista.es/cruce/EURUSD>.
- Ellen MacArthur Foundation. 2014. “Towards the Circular Economy: Accelerating the Scale-up Across Global Supply Chains.” Geneva.
- “Epoxyethane Cost.” 2017. Accessed June 2. <https://www.intratec.us/chemical-markets/ethylene-oxide-price>.
- “Ethanol Cost.” 2017. Accessed June 2. <http://www.sigmaaldrich.com/catalog/product/aldrich/v1503?lang=es&region=ES>.
- “Ethylbenzene Cost.” 2017. Accessed June 2. [http://www.sigmaaldrich.com/catalog/product/sial/296848?lang=es&region=ES&gclid=CjwKEAjuw4\\_JBRDpg](http://www.sigmaaldrich.com/catalog/product/sial/296848?lang=es&region=ES&gclid=CjwKEAjuw4_JBRDpg).
- “Ethylene Cost.” 2017. Accessed June 2. <http://www.sigmaaldrich.com/catalog/substance/ethylene28057485111?lang=es&region=ES>.
- Eurostat. 2017. “Natural Gas Prices for Industrial Consumers.” Accessed June 2. [http://ec.europa.eu/eurostat/statistics-explained/index.php/Energy\\_price\\_statistics#Natural\\_gas\\_prices\\_for\\_industrial\\_consumers](http://ec.europa.eu/eurostat/statistics-explained/index.php/Energy_price_statistics#Natural_gas_prices_for_industrial_consumers).
- Frosch, Robert a., and Nicholas E. Gallopoulos. 1989. “Strategies for Manufacturing.” *Scientific American* 261 (3): 144–52. doi:10.1038/scientificamerican0989-144.
- “GAMS - Cutting Edge Modeling.” 2017. Accessed May 22. <https://www.gams.com/>.
- “GAMS Academic Price List.” 2016. <https://www.gams.com/fileadmin/academicp.pdf>.
- Garner, Andy. 1995. “Industrial Ecology: An Introduction,” no. November.
- Geng, Yong, and Brent Doberstein. 2008. “Developing the Circular Economy in China: Challenges and Opportunities for Achieving ‘Leapfrog Development.’” *International Journal of Sustainable Development & World Ecology* 15 (3): 231–39. doi:10.3843/SusDev.15.3:6.
- “Getting Started with VBA in Office 2010.” 2016. [https://msdn.microsoft.com/en-us/library/office/ee814735\(v=office.14\).aspx](https://msdn.microsoft.com/en-us/library/office/ee814735(v=office.14).aspx).
- Govindan, Kannan, Hamed Soleimani, and Devika Kannan. 2015. “Reverse Logistics and Closed-Loop Supply Chain: A Comprehensive Review to Explore the Future.” *European Journal of Operational Research* 240 (3). Elsevier B.V.: 603–26. doi:10.1016/j.ejor.2014.07.012.
- Graedel, T., and B. Allenby. 1995. *Industrial Ecology*. Englewood Cliffs, NJ: Prentice Hall.
- Harriss Olson, Molly. 1996. “The U.S. President’s Council on Sustainable Development.” *Global Environmental Change* 6 (1): 63–65.
- “History of Excel - Excel Chronology.” 2015. <http://www.whatisexcel.net/excel-history.html>.

- “HYSYS and UniSim.” 2017. Accessed May 22.  
<http://people.clarkson.edu/~wwilcox/Design/refhysys.htm>.
- Kuhlman, Tom, and John Farrington. 2010. “What Is Sustainability?” *Sustainability* 2 (11): 3436–48.  
 doi:10.3390/su2113436.
- Lifset, Reid, and Thomas E Graedel. 2002. “Industrial Ecology: Goals and Definitions.” *A Handbook of Industrial Ecology*, 3–15.
- Lu, Dawei. 2011. *Fundamentals of Supply Chain Management*. doi:10.1007/978-3-540-24816-3\_1.
- McDonough, William, Michael Braungart, Paul T. Anastas, and Julie B. Zimmerman. 2003. “Peer Reviewed: Applying the Principles of Green Engineering to Cradle-to-Cradle Design.” *Environmental Science & Technology* 37 (23): 434A–441A. doi:10.1021/es0326322.
- “Microsoft Store - Office Professional 2016.” 2017. Accessed May 22.  
[https://www.microsoftstore.com/store/mseea/es\\_ES/pdp/Office-Profesional-2016/productID.324451100](https://www.microsoftstore.com/store/mseea/es_ES/pdp/Office-Profesional-2016/productID.324451100).
- “Oxygen Cost.” 2017. Accessed June 2.  
<http://www.sigmaaldrich.com/catalog/product/sial/00476?lang=es&region=ES>.
- PagePersonnel. 2016. “Estudios de Remuneración 2016 Ingenieros Y Técnicos.”
- Pearce, David. 1992. “Green Economics.” *Environmental Values* 1 (1): 3–13.  
 doi:10.3197/096327192776680179.
- “PERC Cost.” 2017. Accessed June 2.  
<http://www.sigmaaldrich.com/catalog/product/sial/371696?lang=es&region=ES>.
- Ping-Qi, Pan. 2014. *Linear Programming Computation*. Springer Science & Business Media.
- Preston, F. 2012. *A Global Redesign? Shaping the Circular Economy*. London: Chatham House Briefing Paper.
- Rahman, Farhadur Md, Kamrul Islam, and Nazrul Kazi Islam. 2016. “Industrial Symbiosis : A Review on Uncovering Approaches , Opportunities , Barriers and Policies.” *Journal of Civil Engineering and Environmental Sciences* 2 (April): 011–019. doi:10.17352/2455-488X.000008.
- “Residuo-Recurso.” 2017. Accessed May 22. <http://www.residuorecurso.com/en/inici>.
- Rezaei, Jafar. 2015. “A Systematic Review of Multi-Criteria Decision-Making Applications in Reverse Logistics.” *Transportation Research Procedia* 10 (July). Elsevier B.V.: 766–76.  
 doi:10.1016/j.trpro.2015.09.030.
- Sánchez, Fermín, Jordi Garcia, Eva Vidal, David López, Jose Cabré, Helena García, and Marc Alier. 2015. “Guía Y Evaluación de La Sostenibilidad En Los Trabajos de Fin de Grado,” 34–41.
- Sauvé, Sébastien, Sophie Bernard, and Pamela Sloan. 2016. “Environmental Sciences, Sustainable Development and Circular Economy: Alternative Concepts for Trans-Disciplinary Research.”

*Environmental Development* 17. Elsevier: 48–56. doi:10.1016/j.envdev.2015.09.002.

“Seguridad Social - Bases Y Tipos de Cotización 2017.” 2017. Accessed May 22. [http://www.seg-social.es/Internet\\_1/Trabajadores/CotizacionRecaudaci10777/Basesytiposdecotiza36537/index.htm](http://www.seg-social.es/Internet_1/Trabajadores/CotizacionRecaudaci10777/Basesytiposdecotiza36537/index.htm).

Stahel, W R. 1997. “The Service Economy: ‘wealth without Resource Consumption’?” *Philosophical Transactions of the Royal Society of London. Series A: Mathematical, Physical and Engineering Sciences* 355 (1728): 1309 LP-1319.  
<http://rsta.royalsocietypublishing.org/content/355/1728/1309.abstract>.

“The Big M Method.” 2017. Accessed May 22.  
<http://businessmanagementcourses.org/Lesson09TheBigMMethod.pdf>.

“The Simplex Method. Maximization and Minimization with Problem Constraints. Introduction to the Big M Method.” 2017. Accessed May 22.  
<http://www.pstcc.edu/facstaff/jwlamb/Math1630/6.4.pdf>.

“Trichloroethylene Cost.” 2017. Accessed June 2.  
<http://www.sigmaaldrich.com/catalog/product/sial/372145?lang=es&region=ES>.

“VCM Cost.” 2017. Accessed June 2.  
[http://www.sigmaaldrich.com/catalog/product/aldrich/744484?lang=es&region=ES&cm\\_sp=Insite\\_-\\_prodRecCold\\_xviews\\_-\\_prodRecCold10-1](http://www.sigmaaldrich.com/catalog/product/aldrich/744484?lang=es&region=ES&cm_sp=Insite_-_prodRecCold_xviews_-_prodRecCold10-1).

“Vinyl Acetate Cost.” 2017. Accessed June 2.  
<http://www.vidrafoc.com/vidrafoc/Store/Product.aspx?LanguageID=es&ProductID=141086.1211>.

“Water Cost.” 2017. Accessed June 2. [https://www.promofarma.com/alvita-agua-destilada-1l?bpp=1&gclid=CjwKEAjwu4\\_JBRDpgs2RwsCbt1MSJABOY8anjGWQ3wlziT4arfKf8mstvOAmxT71psNfEFTuoxH\\_8xoCBLPw\\_wcB#ectrans=1](https://www.promofarma.com/alvita-agua-destilada-1l?bpp=1&gclid=CjwKEAjwu4_JBRDpgs2RwsCbt1MSJABOY8anjGWQ3wlziT4arfKf8mstvOAmxT71psNfEFTuoxH_8xoCBLPw_wcB#ectrans=1).

Webster, K, and C Johnson. 2010. *Sense & Sensibility: Educating for a Circular Economy*. 2nd editio. Isle of Wight: Ellen MacArthur Foundation.

Wolf, Anna, and Magnus Karlsson. 2008. “Evaluating the Environmental Benefits of Industrial Symbiosis: Discussion and Demonstration of a New Approach.” *Progress in Industrial Ecology* 5 (5–6): 502–17. doi:10.1504/PIE.2008.023413.

## 14. Annexes

### 14.1. GAMS codes of each model developed

#### 14.1.1. Model 1

\$ontext

-----  
Model 1 Industrial Symbiosis Problem Black Box First Approach

\$offtext

\*First, the data of the problem, which is in an Excel file, must be called

```
$call gdxxrw.exe Model1_Data.xlsx output=data.gdx set=i cdim=1 rng=Mj!B2:Z2 set=j rdim=1
rng=Mj!A3:A50 set=k rdim=1 rng=Mk!A3:A50
```

```
$call gdxxrw.exe Model1_Data.xlsx output=data1.gdx par=Cj rng=Cj!A3:B50 rdim=1 par=Ck
rng=Ck!A3:B50 rdim=1 par=Cw rng=Cw!A2:B50 rdim=1
```

```
$call gdxxrw.exe Model1_Data.xlsx output=data2.gdx par=Mj rng=Mj!A2:Z50 rdim=1 cdim=1 par=Mk
rng=Mk!A2:Z50 rdim=1 cdim=1
```

```
$call gdxxrw.exe Model1_Data.xlsx output=data3.gdx par=MWj rng=MWj!A3:B50 rdim=1 par=MWk
rng=MWk!A3:B50 rdim=1
```

```
$call gdxxrw.exe Model1_Data.xlsx output=data4.gdx par=Q rng=Q!A3:B50 rdim=1 par=D
rng=D!A3:B50 rdim=1 par=H rng=Others!E3 rdim=0
```

Sets i(\*) Atoms

$j(*)$  Reagents

$k(*)$  Products ;

\$gdxin data.gdx

\$load i j k

\$gdxin

Parameters

$C_j(j)$  Cost of each one of the involved reagents

$C_k(k)$  Cost of each one of the involved products

$C_w(i)$  Cost of each one of the leftover or waste atoms

$MW_j(j)$  Molar weight of the reagents

$MW_k(k)$  Molar weight of the products

$Q(j)$  Storage capacity for the reagents

$D(k)$  Demand of each one of the products

$M_j(j,i)$  Matrix defining the composition of each one of the reagents

$M_k(k,i)$  Matrix defining the composition of each one of the products

H Annual working hours;

\$gdxin data1.gdx

\$load  $C_j$   $C_k$   $C_w$

\$gdxin

\$gdxin data2.gdx

\$load Mj Mk

\$gdxin

\$gdxin data3.gdx

\$load MWj MWk

\$gdxin

\$gdxin data4.gdx

\$load Q D H

\$gdxin

display i, j, k, Cj, Ck, Cw, Mj, Mk, Q, D, H;

\*\$ontext

Variables

Fin(j) Reagent's molar flow [mol per h]

Fout(k) Product's molar flow [mol per h]

MFin(j) Reagent's mass flow [kg per h]

MFout(k) Product's mass flow [kg per h]

W(i) Leftover atoms

B Benefits

Positive variables Fin, Fout, W;

Equations

Eqn1(i)

Eqn2(j)

Eqn3(k)

Benefits

Constr1(k)

Constr2(j);

\*Equations

Eqn1(i) ..  $\sum(j, Fin(j) * Mj(j,i)) = E = \sum(k, Fout(k) * Mk(k,i)) + W(i)$  ;

Eqn2(j) ..  $MFin(j) = E = Fin(j) * MWj(j)$  ;

Eqn3(k) ..  $MFout(k) = E = Fout(k) * MWk(k)$  ;

\*Constraints

Constr1(k) ..  $Fout(k) = L = D(k)$  ;

Constr2(j) ..  $Fin(j) = L = Q(j)$  ;

\*Objective function

Benefits .. B =E=  $H \cdot \sum(k, MFout(k) \cdot Ck(k)) - H \cdot \sum(j, MFin(j) \cdot Cj(j)) - \sum(i, W(i) \cdot Cw(i))$  ;

Model Model1 /All/ ;

Solve Model1 using LP maximizing B ;

\*Results in Excel worksheet

FILE ID /Model1\_Results.xls/;

PUT ID;

ID.pc = 6;

ID.pw = 32767;

PUT 'Black Box Results' PUT/ PUT/ ;

PUT 'Total profit'/;

PUT '-----'PUT/;

PUT 'Benefits [€/year]', PUT B.I PUT/ PUT/ PUT/;

PUT 'Obtained Raw Material Outlets' PUT/;

PUT '-----'PUT/;



```
PUT 'Raw Material Stream',loop(k, PUT k.tl)PUT /;  
PUT 'Mass Flow [kg/h]' ,loop(k, PUT MFout.l(k)PUT ,) PUT/;  
PUT 'Molar Flow [mol/h]' ,loop(k, PUT Fout.l(k)PUT ,);  
PUT/ PUT/ PUT/;
```

```
PUT 'Obtained Waste Inlets' PUT/;  
PUT '-----'PUT/;  
PUT 'Waste Stream',loop(j, PUT j.tl)PUT /;  
PUT 'Mass flow [kg/h]' ,loop(j, PUT MFin.l(j)PUT ,) PUT/;  
PUT 'Molar flow [mol/h]' ,loop(j, PUT Fin.l(j)PUT ,);  
PUT/ PUT/ PUT/;
```

```
PUT 'Left over from each compound'/;  
PUT '-----'PUT/;  
PUT 'Atom',loop(i, PUT i.tl)PUT /;  
PUT '[mol/h]' ,loop(i, PUT W.l(i)PUT ,) PUT/ PUT/ PUT/;
```

\*\$OFFTEXT

### 14.1.2. Model 2

\$ontext

-----  
Industrial Symbiosis Black-Box LP Approach Considering Mass Balances

\$offtext

\*First, the data of the problem, which is in an Excel file, must be called

```
$call gdxrw.exe Model2_Data.xlsm output=data.gdx set=i cdim=1 rng=Mj!B2:Z2 set=j rdim=1
rng=Mj!A3:A50 set=k rdim=1 rng=Mk!A3:A50 set=l rdim=1 rng=Cl!A3:A50
```

```
$call gdxrw.exe Model2_Data.xlsm output=data1.gdx par=Cj rng=Cj!A3:B50 rdim=1 par=Ck
rng=Ck!A3:B50 rdim=1 par=Cl rng=Cl!A2:B50 rdim=1
```

```
$call gdxrw.exe Model2_Data.xlsm output=data2.gdx par=Mj rng=Mj!A2:Z50 rdim=1 cdim=1 par=Mk
rng=Mk!A2:Z50 rdim=1 cdim=1 par=MI rng=MI!A2:Z50 rdim=1 cdim=1
```

```
$call gdxrw.exe Model2_Data.xlsm output=data3.gdx par=MWj rng=MWj!A3:B50 rdim=1 par=MWk
rng=MWk!A3:B50 rdim=1 par=MWI rng=MWI!A3:B50 rdim=1
```

```
$call gdxrw.exe Model2_Data.xlsm output=data5.gdx par=Q rng=Q!A3:B50 rdim=1 par=D
rng=D!A3:B50 rdim=1 par=H rng=Others!E3 rdim=0
```

\*Now, the sets involved in the system are defined

Sets i(\*) Atoms involved in the system

j(\*) Waste input streams

k(\*) Raw material output streams

l(\*) Disposal output streams ;

\$gdxin data.gdx

\$load i j k l

\$gdxin

\*Then, the parameters are defined

Parameters

Cj(j) Cost of each one of the involved waste inputs

Ck(k) Cost of each one of the involved raw material outputs

Cl(l) Cost of each one of the disposal compounds

Mj(j,i) Matrix defining the composition of each one of the waste inputs

Mk(k,i) Matrix defining the composition of each one of the raw material outputs

MI(l,i) Matrix defining the composition of each one of the disposal compounds

MWj(j) Molar weight of the waste inputs

MWk(k) Molar weight of the raw material outputs

MWl(l) Molar weight of the disposal compounds

Q(j) Storage capacity for the reagents

D(k) Demand of each one of the products

H Annual working hours ;

\*These commands below load the information from the data Excel into GAMS

\$gdxin data1.gdx

\$load Cj Ck Cl

\$gdxin

\$gdxin data2.gdx

\$load Mj Mk MI

\$gdxin

\$gdxin data3.gdx

\$load MWj MWk MWI

\$gdxin

\$gdxin data5.gdx

\$load Q D H

\$gdxin

\*Now, the order display is used to check if the sets and parameters read from Excel are the right ones

display i, j, k, l, Cj, Ck, Cl, Mj, Mk, MI, MWj, MWk, MWI, Q, D, H;

\*Then, the system variables are defined

\*\$ontext

Variables

Fin(j) Waste molar flow [mol per h]

Fout(k) Raw material molar flow [mol per h]

$F_d(l)$  Disposal molar flow [mol per h]

$M_{Fin}(j)$  Waste mass flow [kg per h]

$M_{Fout}(k)$  Raw material mass flow [kg per h]

$M_{Fd}(l)$  Disposal mass flow [kg per h]

B Benefits

B1

B2

B3

Positive variables  $F_{in}$ ,  $F_{out}$ ,  $F_d$ ;

\*Once the variables have been defined, the equations of the system are presented

Equations

Eqn1(i)

Eqn2(j)

Eqn3(k)

Eqn4(l)

Constr1(k)

Constr2(j)

EqnB1

EqnB2

EqnB3

Benefits ;

\*Mass balance

$$\text{Eqn1}(i) \dots \sum((j), \text{Fin}(j) * \text{Mj}(j,i)) = E = \sum((k), \text{Fout}(k) * \text{Mk}(k,i)) + \sum((l), \text{Fd}(l) * \text{Ml}(l,i)) ;$$

$$\text{Eqn2}(j) \dots \text{MFin}(j) = E = \text{Fin}(j) * \text{MWj}(j) ;$$

$$\text{Eqn3}(k) \dots \text{MFout}(k) = E = \text{Fout}(k) * \text{MWk}(k) ;$$

$$\text{Eqn4}(l) \dots \text{MFd}(l) = E = \text{Fd}(l) * \text{MWl}(l) ;$$

\*Constraints

$$\text{Constr1}(k) \dots \text{Fout}(k) = L = D(k) ;$$

$$\text{Constr2}(j) \dots \text{Fin}(j) = L = Q(j) ;$$

\*Objective function

$$\text{EqnB1} \dots B1 = E = -H * \sum((j), \text{MFin}(j) * \text{Cj}(j)) ;$$

$$\text{EqnB2} \dots B2 = E = -H * \sum((l), \text{MFd}(l) * \text{Cl}(l)) ;$$

$$\text{EqnB3} \dots B3 = E = H * \sum((k), \text{MFout}(k) * \text{Ck}(k)) ;$$

$$\text{Benefits} \dots B = E = B1 + B2 + B3 ;$$

Model Model2 /All/ ;

Solve Model2 using LP maximizing B ;

\*Results are exported to a new Excel spreadsheet from GAMS

FILE ID /Model2\_Results.xls/;

PUT ID;

ID.pc = 6;

ID.pw = 32767;

PUT 'Results Industrial Symbiosis Black-Box LP Approach Considering Mass Balances' PUT/ PUT/ ;

PUT 'B1', PUT B1.I PUT/ PUT/ PUT/;

PUT 'B2', PUT B2.I PUT/ PUT/ PUT/;

PUT 'B3', PUT B3.I PUT/ PUT/ PUT/;

PUT 'Total profit obtained'/;

PUT '-----'PUT/;

PUT 'Benefits [€/year]', PUT B.I PUT/ PUT/ PUT/;

PUT 'Raw materials obtained' PUT/;

PUT '-----'PUT/;

```
PUT 'Raw material',loop(k, PUT k.tl)PUT /;  
PUT 'Mass Flow [kg/h]' ,loop(k, PUT MFout.l(k)PUT ,) PUT/;  
PUT 'Molar Flow [mol/h]' ,loop(k, PUT Fout.l(k)PUT ,);  
PUT/ PUT/ PUT/;
```

```
PUT 'Waste compounds obtained' PUT/;  
PUT '-----'PUT/;  
PUT 'Waste',loop(j, PUT j.tl)PUT /;  
PUT 'Mass flow [kg/h]' ,loop(j, PUT MFin.l(j)PUT ,) PUT/;  
PUT 'Molar flow [mol/h]' ,loop(j, PUT Fin.l(j)PUT ,);  
PUT/ PUT/ PUT/;
```

```
PUT 'Disposal obtained'/;  
PUT '-----'PUT/;  
PUT 'Disposal',loop(l, PUT l.tl)PUT /;  
PUT 'Mass flow [kg/h]' ,loop(l, PUT MFd.l(l)PUT ,) PUT/;  
PUT 'Molar flow [mol/h]' ,loop(l, PUT Fd.l(l)PUT ,);  
PUT/ PUT/ PUT/;
```



### 14.1.3. Model 3

\$ontext

-----  
Industrial Symbiosis Black-Box MILP Approach Considering Mass Balances

\$offtext

\*First, the data of the problem, which is in an Excel file, must be called

```
$call gdxrw.exe Model3_Data.xlsm output=data.gdx set=i cdim=1 rng=Mj!B2:Z2 set=j rdim=1  
rng=Mj!A3:A50 set=k rdim=1 rng=Mk!A3:A50 set=l rdim=1 rng=Cl!A3:A50
```

```
$call gdxrw.exe Model3_Data.xlsm output=data1.gdx par=Cj rng=Cj!A3:B50 rdim=1 par=Ck  
rng=Ck!A3:B50 rdim=1 par=Cl rng=Cl!A2:B50 rdim=1 par=CD rng=Cd!A3:B50 rdim=1
```

```
$call gdxrw.exe Model3_Data.xlsm output=data2.gdx par=Mj rng=Mj!A2:Z50 rdim=1 cdim=1 par=Mk  
rng=Mk!A2:Z50 rdim=1 cdim=1 par=MI rng=MI!A2:Z50 rdim=1 cdim=1
```

```
$call gdxrw.exe Model3_Data.xlsm output=data3.gdx par=MWj rng=MWj!A3:B50 rdim=1 par=MWk  
rng=MWk!A3:B50 rdim=1 par=MWl rng=MWl!A3:B50 rdim=1
```

```
$call gdxrw.exe Model3_Data.xlsm output=data6.gdx par=Q rng=Q!A3:B50 rdim=1 par=D  
rng=D!A3:B50 rdim=1 par=H rng=Others!E3 rdim=0
```

\*Now, the sets involved in the system are defined

Sets i(\*) Atoms involved in the system

j(\*) Waste input streams

k(\*) Raw material output streams

l(\*) Disposal output streams ;

\$gdxin data.gdx

\$load i j k l

\$gdxin

\*Then, the parameters are defined

Parameters

$C_j(j)$  Cost of each one of the involved waste inputs

$C_k(k)$  Cost of each one of the involved raw material outputs

$C_l(l)$  Cost of each one of the disposal compounds

$CD(k)$  Cost of disposing over demanded raw materials

$M_j(j,i)$  Matrix defining the composition of each one of the waste inputs

$M_k(k,i)$  Matrix defining the composition of each one of the raw material outputs

$M_l(l,i)$  Matrix defining the composition of each one of the disposal compounds

$MW_j(j)$  Molar weight of the waste inputs

$MW_k(k)$  Molar weight of the raw material outputs

$MW_l(l)$  Molar weight of the disposal compounds

$Q(j)$  Flow capacity for the reagents

$D(k)$  Demand of each one of the products

$H$  Annual working hours

;

\*These commands below load the information from the data Excel into GAMS

\$gdxin data1.gdx

\$load Cj Ck Cl CD

\$gdxin

\$gdxin data2.gdx

\$load Mj Mk MI

\$gdxin

\$gdxin data3.gdx

\$load MWj MWk MWI

\$gdxin

\$gdxin data6.gdx

\$load Q D H

\$gdxin

\*Now, the order display is used to check if the sets and parameters read from Excel are the right ones

display i, j, k, l, Cj, Ck, Cl, Mj, Mk, MI, MWj, MWk, MWI, Q, D, H;

\*Then, the system variables are defined

\*\$ontext

## Variables

$F_{in}(j)$  Waste molar flow [mol per h]

$F_{out}(k)$  Raw material molar flow [mol per h]

$F_d(l)$  Disposal molar flow [mol per h]

$M_{Fin}(j)$  Waste mass flow [kg per h]

$M_{Fout}(k)$  Raw material mass flow [kg per h]

$M_{Fd}(l)$  Disposal mass flow [kg per h]

$B$  Benefits

$z(k)$  Binary variable representing if suppliers' demand has been covered

$B_1$

$B_2$

$B_3$

$B_4$

$B_5$

$f_1(k)$

$f_2(k)$

$f_3(k);$

Positive variables  $F_{in}, F_{out}, F_d;$

Binary variables  $y, z;$

## Equations

Eqn1(i)

Eqn2(j)

Eqn3(k)

Eqn4(l)

Eqn6(k)

Eqn7(k)

Benefits

Constr2(j)

Eqn9(k)

Eqn10(k)

Eqn11(k)

Eqn12(k)

\*Eqn13(k)

\*Eqn14(k)

EqnB1

EqnB2

EqnB3

EqnB4;

\*EqnB5;

\*Mass balance

$$\text{Eqn1}(i) \dots \sum(j), \text{Fin}(j) * \text{Mj}(j,i) = E = \sum(k), \text{Fout}(k) * \text{Mk}(k,i) + \sum(l), \text{Fd}(l) * \text{Ml}(l,i) ;$$

$$\text{Eqn2}(j) \dots \text{MFin}(j) = E = \text{Fin}(j) * \text{MWj}(j) ;$$

$$\text{Eqn3}(k) \dots \text{MFout}(k) = E = \text{Fout}(k) * \text{MWk}(k) ;$$

$$\text{Eqn4}(l) \dots \text{MFd}(l) = E = \text{Fd}(l) * \text{MWl}(l) ;$$

\*Demand represented as a binary variable

$$\text{Eqn6}(k) \dots \text{D}(k) * z(k) = L = \text{Fout}(k) ;$$

$$\text{Eqn7}(k) \dots \text{Fout}(k) - \text{D}(k) = L = 100000000 * z(k) ;$$

\*Demand constraint in objective function using a Big M

\*Eqn 9 and Eqn 10 represent the case where the demand has been covered

$$\text{Eqn9}(k) \dots f1(k) = L = 100000000 * z(k) ;$$

$$\text{Eqn10}(k) \dots f1(k) = L = \text{D}(k) * \text{MWk}(k) * \text{Ck}(k) - \text{CD}(k) * (\text{Fout}(k) - \text{D}(k)) * \text{MWk}(k) ;$$

\*Eqn 11 and Eqn 12 represent the case where the demand has not been covered

$$\text{Eqn11}(k) \dots f2(k) = L = 100000000 * (1 - z(k)) ;$$

$$\text{Eqn12}(k) \dots f2(k) = L = \text{MFout}(k) * \text{Ck}(k) ;$$

\*Constraints

$$\text{Constr2}(j) \dots \text{Fin}(j) = L = \text{Q}(j) ;$$

\*Objective function

Benefits .. B =E= B1+B2+B3+B4;

EqnB1 .. B1 =E= -H\*sum((j),MFin(j)\*Cj(j));

EqnB2 .. B2 =E= -H\*sum((l),MFd(l)\*Cl(l));

EqnB3 .. B3 =E= H\*sum(k,f1(k));

EqnB4 .. B4 =E= H\*sum(k,f2(k));

Model Model3 /All/ ;

Solve Model3 using MIP maximizing B ;

\*Results in Excel worksheet

FILE ID /Model3\_Results.xls/;

PUT ID;

ID.pc = 6;

ID.pw = 32767;

PUT 'Results Industrial Symbiosis Black-Box MILP Approach Considering Mass Balances' PUT/ PUT/ ;

PUT 'B1', PUT B1.I PUT/ PUT/ PUT/;

PUT 'B2', PUT B2.I PUT/ PUT/ PUT/;

PUT 'B3', PUT B3.I PUT/ PUT/ PUT/;

PUT 'B4', PUT B4.I PUT/ PUT/ PUT/;

\*PUT 'B5', PUT B5.I PUT/ PUT/ PUT/;

PUT 'Total profit obtained'/;

PUT '-----'PUT/;

PUT 'Benefits [€/year]', PUT B.I PUT/ PUT/ PUT/;

PUT 'Raw materials obtained' PUT/;

PUT '-----'PUT/;

PUT 'Raw material',loop(k, PUT k.tl)PUT /;

PUT 'Mass Flow [kg/h]' ,loop(k, PUT MFout.l(k)PUT ,) PUT/;

PUT 'Molar Flow [mol/h]' ,loop(k, PUT Fout.l(k)PUT ,);

PUT/ PUT/ PUT/;

PUT 'Waste compounds obtained' PUT/;

PUT '-----'PUT/;

PUT 'Waste',loop(j, PUT j.tl)PUT /;



PUT 'Mass flow [kg/h]' ,loop(j, PUT MFin.l(j)PUT ,) PUT/;

PUT 'Molar flow [mol/h]' ,loop(j, PUT Fin.l(j)PUT ,);

PUT/ PUT/ PUT/;

PUT 'Disposal obtained'/;

PUT '-----'PUT/;

PUT 'Disposal',loop(l, PUT l.tl)PUT /;

PUT 'Mass flow [kg/h]' ,loop(l, PUT MFd.l(l)PUT ,) PUT/;

PUT 'Molar flow [mol/h]' ,loop(l, PUT Fd.l(l)PUT ,);

PUT/ PUT/ PUT/;

PUT 'Binary variable z'/;

PUT '-----'PUT/;

PUT 'Raw material',loop(k, PUT k.tl)PUT /;

PUT 'Units' ,loop(k, PUT z.l(k)PUT ,) PUT/ PUT/ PUT/;

\*\$OFFTEXT

#### 14.1.4. Model 4

\$ontext

-----

| Industrial Symbiosis Black-Box MILP Approach Considering Mass & Energy Balances |

-----

\$offtext

\*First, the data of the problem, which is in an Excel file, must be called

```
$call gdxrw.exe Model4_Data.xlsm output=data.gdx set=i cdim=1 rng=Mj!B2:Z2 set=j rdim=1
rng=Mj!A3:A50 set=k rdim=1 rng=Mk!A3:A50 set=l rdim=1 rng=Cl!A3:A50
```

```
$call gdxrw.exe Model4_Data.xlsm output=data1.gdx par=Cj rng=Cj!A3:B50 rdim=1 par=Ck
rng=Ck!A3:B50 rdim=1 par=Cl rng=Cl!A2:B50 rdim=1 par=CD rng=Cd!A3:B50 rdim=1
```

```
$call gdxrw.exe Model4_Data.xlsm output=data2.gdx par=Mj rng=Mj!A2:Z50 rdim=1 cdim=1 par=Mk
rng=Mk!A2:Z50 rdim=1 cdim=1 par=MI rng=MI!A2:Z50 rdim=1 cdim=1
```

```
$call gdxrw.exe Model4_Data.xlsm output=data3.gdx par=MWj rng=MWj!A3:B50 rdim=1 par=MWk
rng=MWk!A3:B50 rdim=1 par=MWI rng=MWI!A3:B50 rdim=1
```

```
$call gdxrw.exe Model4_Data.xlsm output=data4.gdx par=Hj rng=Hj!A3:B50 rdim=1 par=Hk
rng=Hk!A3:B50 rdim=1 par=HI rng=HI!A3:B50 rdim=1
```

```
$call gdxrw.exe Model4_Data.xlsm output=data5.gdx par=Sj rng=Sj!A3:B50 rdim=1 par=Sk
rng=Sk!A3:B50 rdim=1 par=SI rng=SI!A3:B50 rdim=1
```

```
$call gdxrw.exe Model4_Data.xlsm output=data6.gdx par=Q rng=Q!A3:B50 rdim=1 par=D
rng=D!A3:B50 rdim=1 par=H rng=Others!E3 rdim=0 par=T rng=Others!E6 rdim=0 par=CQin
rng=Others!E9 rdim=0 par=CQout rng=Others!E12 rdim=0
```

\*Now, the sets involved in the system are defined

Sets i(\*) Atoms involved in the system

j(\*) Waste input streams

$k^{(*)}$  Raw material output streams

$l^{(*)}$  Disposal output streams ;

\$gdxin data.gdx

\$load i j k l

\$gdxin

\*Then, the parameters are defined

Parameters

$C_j(j)$  Cost of each one of the involved waste inputs

$C_k(k)$  Cost of each one of the involved raw material outputs

$C_l(l)$  Cost of each one of the disposal compounds

$CD(k)$  Cost of disposing over demanded raw materials

$M_j(j,i)$  Matrix defining the composition of each one of the waste inputs

$M_k(k,i)$  Matrix defining the composition of each one of the raw material outputs

$M_l(l,i)$  Matrix defining the composition of each one of the disposal compounds

$MW_j(j)$  Molar weight of the waste inputs

$MW_k(k)$  Molar weight of the raw material outputs

$MW_l(l)$  Molar weight of the disposal compounds

$H_j(j)$  Specific molar heat waste inputs

$H_k(k)$  Specific molar heat raw material outputs

$H_l(l)$  Specific molar heat disposal compounds

Sj(j) Molar entropy waste inputs  
Sk(k) Molar entropy raw material outputs  
Sl(l) Molar entropy disposal compounds  
Q(j) Flow capacity for the reagents  
D(k) Demand of each one of the products  
H Annual working hours  
T Working temperature of the system  
CQin Cost of heat addition  
CQout Cost of heat subtraction;

\*These commands below load the information from the data Excel into GAMS

\$gdxin data1.gdx

\$load Cj Ck Cl Cd

\$gdxin

\$gdxin data2.gdx

\$load Mj Mk Ml

\$gdxin

\$gdxin data3.gdx

\$load MWj MWk MWl

\$gdxin

\$gdxin data4.gdx

\$load Hj Hk HI

\$gdxin

\$gdxin data5.gdx

\$load Sj Sk SI

\$gdxin

\$gdxin data6.gdx

\$load Q D H T CQin CQout

\$gdxin

\*Now, the order display is used to check if the sets and parameters read from Excel are the right ones

display i, j, k, l, Cj, Ck, Cl, Mj, Mk, Ml, MWj, MWk, MWl, Hj, Hk, HI, Sj, Sk, SI, Q, D, H, T, CQin, CQout;

\*Then, the system variables are defined

\*\$ontext

Variables

Fin(j) Waste molar flow [mol per h]

$F_{out}(k)$  Raw material molar flow [mol per h]

$F_d(l)$  Disposal molar flow [mol per h]

$M_{Fin}(j)$  Waste mass flow [kg per h]

$M_{Fout}(k)$  Raw material mass flow [kg per h]

$M_{Fd}(l)$  Disposal mass flow [kg per h]

**B** Benefits

$z(k)$  Binary variable representing if suppliers' demand has been covered

$Q_{exc}$  Heat added or extracted from the system [J per h]

$y$  Binary variable showing whether the heat is added or extracted from the system

B1

B2

B31

B32

B4

$f_1(k)$

$f_2(k)$

$f_3$

$f_4;$

Positive variables  $F_{in}, F_{out}, F_d, F_3, F_4;$

Binary variables  $y, z;$

## Equations

Eqn1(i)

Eqn2(j)

Eqn3(k)

Eqn4(l)

Eqn5

Eqn6(k)

Eqn7(k)

Eqn8

Eqn9

Eqn10(k)

Eqn11(k)

Eqn12(k)

Eqn13(k)

Eqn14

Eqn15

Eqn16

Eqn17

Constr2(j)

Benefits

EqnB1

EqnB2

EqnB31

EqnB32

EqnB4;

\*Mass balance

$$\text{Eqn1}(i) \dots \sum(j), \text{Fin}(j) * \text{Mj}(j,i) = E = \sum(k), \text{Fout}(k) * \text{Mk}(k,i) + \sum(l), \text{Fd}(l) * \text{Ml}(l,i) ;$$

$$\text{Eqn2}(j) \dots \text{MFin}(j) = E = \text{Fin}(j) * \text{MWj}(j) ;$$

$$\text{Eqn3}(k) \dots \text{MFout}(k) = E = \text{Fout}(k) * \text{MWk}(k) ;$$

$$\text{Eqn4}(l) \dots \text{MFd}(l) = E = \text{Fd}(l) * \text{MWl}(l) ;$$

\*Energy balance

$$\text{Eqn5} \dots \sum(j), \text{Fin}(j) * \text{Hj}(j) - \sum(k), \text{Fout}(k) * \text{Hk}(k) - \sum(l), \text{Fd}(l) * \text{Hl}(l) = E = \text{Qexc};$$

\*Demand represented as a binary variable

$$\text{Eqn6}(k) \dots \text{D}(k) * \text{z}(k) = L = \text{Fout}(k) ;$$

$$\text{Eqn7}(k) \dots \text{Fout}(k) - \text{D}(k) = L = 100000000 * \text{z}(k) ;$$

\*Heat addition or subtraction represented as a binary variable

$$\text{Eqn8} \dots \text{Qexc} = L = 100000000 * \text{y} ;$$

$$\text{Eqn9} \dots -\text{Qexc} = L = 100000000 * (1 - \text{y});$$



\*Demand constraint in objective function using a Big M

\*Eqn 10 and Eqn 11 represent the case where the demand has been covered and a term representing the penalization derived from producing more than the demand

$$\text{Eqn10}(k) \dots f1(k) = L = 100000000 * z(k);$$

$$\text{Eqn11}(k) \dots f1(k) = L = D(k) * MWk(k) * Ck(k) - CD(k) * (Fout(k) - D(k)) * MWk(k);$$

\*Eqn 12 and Eqn 13 represent the case where the demand has not been covered

$$\text{Eqn12}(k) \dots f2(k) = L = 100000000 * (1 - z(k));$$

$$\text{Eqn13}(k) \dots f2(k) = L = MFout(k) * Ck(k);$$

\*Heat exchanged (added or subtracted) represented using a Big M

\*Eqn 14 and Eqn 15 represent the situation where heat has to be extracted from the system

$$\text{Eqn14} \dots f3 = L = 100000000 * y;$$

$$\text{Eqn15} \dots -f3 = L = Qexc * CQout ;$$

\*Eqn 16 and Eqn 17 represent the situation where heat has to be added to the system

$$\text{Eqn16} \dots f4 = L = 100000000 * (1 - y);$$

$$\text{Eqn17} \dots -f4 = L = -Qexc * CQin ;$$

\*Constraints

$$\text{Constr2}(j) \dots Fin(j) = L = Q(j) ;$$

\*Objective function

Benefits .. B =E= B1+B2+B31+B32-B4;

EqnB1 .. B1 =E= -H\*sum((j),MFin(j)\*Cj(j));

EqnB2 .. B2 =E= -H\*sum((l),MFd(l)\*Cl(l));

EqnB31 .. B31 =E= H\*sum(k,f1(k));

EqnB32 .. B32 =E= H\*sum(k,f2(k));

EqnB4 .. B4 =E= f3+f4;

Model Model4 /All/ ;

\*Fin.fx(j)\$ord(j)=2)=100;

\*Fin.fx(j)\$ord(j)=1)=100;

\*Fin.fx(j)\$ord(j)=3)=100;

\*Fin.fx(j)\$ord(j)>3)=0;

Option Optcr=0;

Option Savepoint=1;

\$ontext

Execute\_load'Model4\_Hola2.gdx',Fin,Fout,Fd,MFin,MFout,MFd,y,z,Qexc,f1,f2;

B1.l = -H\*sum((j),MFin.l(j)\*Cj(j));

B2.l = -H\*sum((l),MFd.l(l)\*Cl(l));

$$B31.l = H * \text{sum}(k, f1.l(k));$$

$$B32.l = H * \text{sum}(k, f2.l(k));$$

$$f3.l = 0;$$

$$f4.l = -Q_{exc.l} * CQ_{in};$$

$$B4.l = f3.l + f4.l;$$

$$B.l = B1.l + B2.l + B31.l + B32.l - B4.l;$$

\$offtext

Solve Model4 using MIP maximizing B ;

\*Results in Excel worksheet

FILE ID /Model4\_Results.xls/;

PUT ID;

ID.pc = 6;

ID.pw = 32767;

PUT 'Results Industrial Symbiosis Black-Box MILP Approach Considering Mass & Energy Balances ' PUT/  
PUT/ ;

PUT 'B1', PUT B1.l PUT/ PUT/ PUT/;

PUT 'B2', PUT B2.l PUT/ PUT/ PUT/;

PUT 'B31', PUT B31.l PUT/ PUT/ PUT/;



PUT 'B32', PUT B32.I PUT/ PUT/ PUT/;

PUT 'B4', PUT B4.I PUT/ PUT/ PUT/;

PUT 'f3'/;

PUT '-----'PUT/;

PUT 'f3', PUT f3.I PUT/ PUT/ PUT/;

PUT 'f4'/;

PUT '-----'PUT/;

PUT 'f4', PUT f4.I PUT/ PUT/ PUT/;

PUT 'Total profit obtained'/;

PUT '-----'PUT/;

PUT 'Benefits [€/year]', PUT B.I PUT/ PUT/ PUT/;

PUT 'Raw materials obtained' PUT/;

PUT '-----'PUT/;

PUT 'Raw material',loop(k, PUT k.tl)PUT /;

PUT 'Mass Flow [kg/h]' ,loop(k, PUT MFout.l(k)PUT ,) PUT/;

PUT 'Molar Flow [mol/h]' ,loop(k, PUT Fout.l(k)PUT ,);

PUT/ PUT/ PUT/;

```
PUT 'Waste compounds obtained' PUT/;

PUT '-----'PUT/;

PUT 'Waste',loop(j, PUT j.tl)PUT /;

PUT 'Mass flow [kg/h]' ,loop(j, PUT MFin.l(j)PUT ,) PUT/;

PUT 'Molar flow [mol/h]' ,loop(j, PUT Fin.l(j)PUT ,);

PUT/ PUT/ PUT/;

PUT 'Disposal obtained';

PUT '-----'PUT/;

PUT 'Disposal',loop(l, PUT l.tl)PUT /;

PUT 'Mass flow [kg/h]' ,loop(l, PUT MFd.l(l)PUT ,) PUT/;

PUT 'Molar flow [mol/h]' ,loop(l, PUT Fd.l(l)PUT ,);

PUT/ PUT/ PUT/;

PUT 'Over demanded raw materials to be disposed';

PUT '-----'PUT/;

PUT 'Over Demanded Raw Material',loop(k, PUT k.tl)PUT /;

PUT 'Molar flow [mol/h]' ,loop(k, PUT (z.l(k)*(Fout.l(k)-D(k)))PUT ,);

PUT/ PUT/ PUT/;
```

PUT 'Binary variable z'/;

PUT '-----'PUT/;

PUT 'Raw material',loop(k, PUT k.tl)PUT /;

PUT 'Units' ,loop(k, PUT z.l(k)PUT ,) PUT/ PUT/ PUT/;

PUT 'Binary variable y'/;

PUT '-----'PUT/;

PUT 'Units', PUT y.l PUT/ PUT/ PUT/;

PUT 'Heat added or substracted'/;

PUT '-----'PUT/;

PUT '[J/h]', PUT Qexc.l PUT/ PUT/ PUT/;

\*\$OFFTEXT

### 14.1.5. Model 5

\$ontext

-----

| Industrial Symbiosis Model Partial Flows Approach |

-----

\$offtext

\*First, the data of the problem, which is in an Excel file, must be called

```
$call gdxrw.exe Model5_Data.xlsm output=data.gdx set=i cdim=1 rng=W(j,i)!C3:Z3 set=j rdim=1  
rng=W(j,i)!B4:B50 set=k rdim=1 rng=Ck(k)!B4:B50 set=l rdim=1 rng=Cl(l)!B4:B50 set=m rdim=1  
rng=CR(m)!B5:B50 set=n cdim=1 rng=MC!B2:Z2
```

```
$call gdxrw.exe Model5_Data.xlsm output=data1.gdx par=W rng=W(j,i)!B3:Z50 rdim=1 cdim=1 par=D  
rng=D(k,i)!B4:Z50 rdim=1 cdim=1 par=R rng=R(m,i)!B4:Z50 rdim=1 cdim=1 par=Q rng=Q(j)!B4:C50  
rdim=1
```

```
$call gdxrw.exe Model5_Data.xlsm output=data2.gdx par=Cj rng=Cj(j)!B4:C50 rdim=1 par=Ck  
rng=Ck(k)!B4:C50 rdim=1 par=Cl rng=Cl(l)!B4:C50 rdim=1 par=Cd rng=Cd(k)!B4:C50 rdim=1 par=Ces  
rng=Ces(i)!B4:C50 rdim=1 par=Cr rng=Cr(m)!B4:C50 rdim=1
```

```
$call gdxrw.exe Model5_Data.xlsm output=data3.gdx par=H rng=H!A3:B50 rdim=1
```

```
$call gdxrw.exe Model5_Data.xlsm output=data4.gdx par=S rng=S!A3:B50 rdim=1
```

```
$call gdxrw.exe Model5_Data.xlsm output=data5.gdx par=AH rng=Others!B9 rdim=0 par=T  
rng=Others!B12 rdim=0 par=CQin rng=Others!B15 rdim=0 par=CQout rng=Others!B18 rdim=0
```

```
$call gdxrw.exe Model5_Data.xlsm output=data7.gdx par=MW rng=MW(i)!A3:B50 rdim=1
```

Sets

i(\*) Compounds

j(\*) Waste input streams

$k(*)$  Raw materials output streams

$l(*)$  Disposal output streams

$m(*)$  Potential chemical reactions ;

\$gdxin data.gdx

\$load i j k l m

\$gdxin

Parameters

$W(j,i)$  Waste input partial molar flow

$D(k,i)$  Raw material output demand

$Q(j)$  Flow capacity for the input waste streams

$R(m,i)$  Potential chemical reactions in the system

$C_j(j)$  Cost of each of the involved waste inputs

$C_k(k)$  Cost of each of the involved raw material outputs

$C_l(l)$  Cost of each of the disposal outputs

$CD(k)$  Cost of disposing over demanded raw materials

$C_{es}(i)$  Cost associated to compounds' external supply

$C_r(m)$  Cost associated to each potencial chemical reaction



MW(i)

H(i) Molar enthalpy for each compound

S(i) Molar entropy for each compound

CQin Cost of heat addition

CQout Cost of heat subtraction

AH Annual working hours

T Working temperature of the system

HR(m) Reaction enthalpy

;

\$gdxin data1.gdx

\$load W D R Q

\$gdxin

\$gdxin data2.gdx

\$load Cj Ck Cl Ces Cd Cr

\$gdxin

\$gdxin data3.gdx

\$load H

\$gdxin

\$gdxin data4.gdx

\$load S

\$gdxin

\$gdxin data5.gdx

\$load AH T CQin CQout

\$gdxin

\$gdxin data7.gdx

\$load MW

\$gdxin

display i, j, k, l, m, W, D, R, Q, Cj, Ck, Cl, Ces, Cd, Cr, H, S, AH, T, CQin, CQout, MW ;

\*\$ontext

Variables

$fF(j)$

$F(j,i)$

$Win(i)$

$Es(i)$

$Fin(i)$

$Fgen(m)$

$Fout(i)$

$Frm(k,i)$

$Fd(l,i)$

$Qexc(m)$

$Hreact(m)$

$Sreact(m)$

$Greact(m)$

$z(k,i)$

$y(m)$

$f1(k,i)$

$f2(k,i)$



f3(m)

f4(m)

B1

B2

B31

B32

B4

B5

B6

B

overdisp(k,i)

;

Positive variables F, Win, ES, Fin, Fgen, Fout, Frm, Fd

Binary variables z, y

Equations

Eqn1(j,i)

Eqn2(i)

Eqn3(i)

Eqn4(i)

Eqn5(i)

Eqn6(m)

Eqn7(m)

Eqn8(m)

Eqn9(m)

Eqn10(k,i)

Eqn11(k,i)

Eqn12(m)

Eqn13(k,i)

Eqn14(k,i)

Eqn15(k,i)

Eqn16(k,i)

Eqn17(m)

Eqn18(m)

Eqn19(m)

Eqn20(m)

Eqn21(j)

Eqn22(m)

EqnB1

EqnB2

EqnB31

EqnB32

EqnB4

EqnB5

EqnB6

OF

;

\*Equations

$$\text{Eqn1}(j,i) \dots F(j,i) = F(j) * W(j,i);$$

$$\text{Eqn2}(i) \dots \sum(j, F(j,i)) = W_{in}(i);$$

$$\text{Eqn3}(i) \dots W_{in}(i) + E_s(i) = F_{in}(i);$$

$$*\text{Eqn3}(i) \dots W_{in}(i) = F_{in}(i);$$

$$\text{Eqn4}(i) \dots F_{in}(i) + \sum(m, R(m,i) * F_{gen}(m)) = F_{out}(i);$$

$$\text{Eqn5}(i) \dots F_{out}(i) = \sum(k, F_{rm}(k,i)) + \sum(l, F_d(l,i));$$

\*Enthalpy balance

$$\text{Eqn6}(m) \dots \sum(i, F_{gen}(m) * R(m,i) * H(i)) = Q_{exc}(m);$$

\*Reaction enthalpies, entropies and Gibbs free energies

$$\text{Eqn7}(m) \dots \sum(i, R(m,i) * H(i)) = H_{react}(m);$$

$$\text{Eqn8}(m) \dots \sum(i, R(m,i) * S(i)) = S_{react}(m);$$

$$\text{Eqn9}(m) \dots G_{react}(m) = H_{react}(m) - T * S_{react}(m);$$

\*Demand represented by a binary variable

$$\text{Eqn10}(k,i) \dots D(k,i) \cdot z(k,i) = L \cdot \text{Frm}(k,i);$$

$$\text{Eqn11}(k,i) \dots \text{Frm}(k,i) - D(k,i) = L \cdot 100000000 \cdot z(k,i);$$

\*Head addition or subtraction represented by a binary variable

$$\text{Eqn12}(m) \dots Q_{\text{exc}}(m) = L \cdot 100000000 \cdot y(m);$$

$$\text{Eqn22}(m) \dots -Q_{\text{exc}}(m) = L \cdot 100000000 \cdot (1 - y(m));$$

\*Demand constraint in objective function using a Big M

\*Eqn 13 and Eqn 14 represent the case where the demand has been covered and a term representing the penalization derived from producing more than the demand

$$\text{Eqn13}(k,i) \dots f_1(k,i) = L \cdot 100000000 \cdot z(k,i);$$

$$\text{Eqn14}(k,i) \dots f_1(k,i) = L \cdot (D(k,i) \cdot C_k(k) \cdot MW(i)) - (CD(k) \cdot MW(i) \cdot (\text{Frm}(k,i) - D(k,i)));$$

\*Eqn 15 and Eqn 16 represent the case where the demand has not been covered

$$\text{Eqn15}(k,i) \dots f_2(k,i) = L \cdot 100000000 \cdot (1 - z(k,i));$$

$$\text{Eqn16}(k,i) \dots f_2(k,i) = L \cdot \text{Frm}(k,i) \cdot C_k(k) \cdot MW(i);$$

\*Heat exchanged (added or subtracted) represented using a Big M

\*Eqn 17 and Eqn 18 represent the situation where heat has to be extracted from the system

$$\text{Eqn17}(m) \dots f_3(m) = L \cdot 100000000 \cdot y(m);$$

$$\text{Eqn18}(m) \dots -f3(m) = L = Q_{\text{exc}}(m) * CQ_{\text{out}};$$

\*Eqn 19 and Eqn 20 represent the situation where heat has to be added to the system

$$\text{Eqn19}(m) \dots f4(m) = L = 100000000 * (1 - \gamma(m));$$

$$\text{Eqn20}(m) \dots -f4(m) = L = -Q_{\text{exc}}(m) * CQ_{\text{in}};$$

\*Capacity constraint

$$\text{Eqn21}(j) \dots \sum(i, W(j,i)) = L = Q(j);$$

\*Objective Function

$$\text{EqnB1} \dots B1 = E = -AH * \sum(j, (\sum(i, F(j,i) * MW(i)) * Cj(j)));$$

$$\text{EqnB2} \dots B2 = E = -AH * \sum(l, i, Fd(l,i) * Cl(l) * MW(i));$$

$$\text{EqnB31} \dots B31 = E = AH * \sum(k, i, f1(k,i));$$

$$\text{EqnB32} \dots B32 = E = AH * \sum(k, i, f2(k,i));$$

$$\text{EqnB4} \dots B4 = E = \sum(m, f3(m) + f4(m));$$

$$\text{EqnB5} \dots B5 = E = -\sum(i, C_{\text{es}}(i) * E_{\text{s}}(i) * MW(i));$$

$$\text{EqnB6} \dots B6 = E = -\sum(m, F_{\text{gen}}(m) * Cr(m));$$

$$\text{OF} \dots B = E = B1 + B2 + B31 + B32 + B4 + B5 + B6;$$



Model Model5 /All/ ;

fF.lo(j)=0;

fF.up(j)=1;

\*z.fx(k,i) \$(ord(i)<11)=1;

Option Optcr=0;

Solve Model5 using MIP maximizing B ;

\*\$ontext

\*Results in Excel worksheet

FILE ID /Model5\_Results.xls/;

PUT ID;

ID.pc = 6;

ID.pw = 32767;

PUT 'Industrial Symbiosis Model Partial Flows Results' PUT/PUT/ ;

PUT 'B1', PUT B1.I PUT/ PUT/ PUT/;

PUT 'B2', PUT B2.I PUT/ PUT/ PUT/;

PUT 'B31', PUT B31.I PUT/ PUT/ PUT/;

PUT 'B32', PUT B32.I PUT/ PUT/ PUT/;

PUT 'B4', PUT B4.I PUT/ PUT/ PUT/;

PUT 'B5', PUT B5.I PUT/ PUT/ PUT/;

PUT 'B6', PUT B6.I PUT/ PUT/ PUT/;

PUT 'Total profit obtained, B'/;

PUT '-----'PUT/;

PUT 'Benefits [€/year]', PUT B.I PUT/ PUT/ PUT/;

PUT 'Fraction of input waste,  $fF(j)$ ' PUT/;

PUT '-----'PUT/;

PUT 'Stream', loop(j, PUT j.tl)PUT /;

PUT 'Fraction', loop(j, PUT fF.l(j)PUT ,);

PUT/ PUT/ PUT/;

PUT 'Waste entering the system,  $F(j,i)$ ' PUT/;

PUT '-----'PUT/;

PUT ' $F(j,i)$ ', loop(i, PUT i.tl)PUT /;

loop(j, PUT j.tl, loop(i, PUT F.l(j,i))PUT /);

PUT/ PUT/ PUT/;

PUT 'Raw materials in output streams, Frm(k,i)' PUT/;

PUT '-----'PUT/;

PUT 'Frm(k,i)',loop(i, PUT i.tl)PUT /;

loop(k, PUT k.tl, loop(i, PUT Frm.l(k,i))PUT /);

PUT/ PUT/ PUT/ ;

PUT 'Reaction basis Fgen(m)' PUT/;

PUT '-----'PUT/;

PUT 'Reaction', loop(m, PUT m.tl)PUT /;

PUT 'Fgen(m)' ,loop(m, PUT Fgen.l(m)PUT ,);

PUT/ PUT/ PUT/ ;

\*\$ONTEXT

PUT 'Consumed external supply Es(i)' PUT/;

PUT '-----'PUT/;

PUT 'Compound', loop(i, PUT i.tl)PUT /;

PUT 'Es(i)' ,loop(i, PUT Es.l(i)PUT ,);

PUT/ PUT/ PUT/ ;

\*\$OFFTEXT

```

PUT 'Compounds sent to disposal Fd(l,i)' PUT/;
PUT '-----'PUT/;
PUT 'Fd(l,i)',loop(i, PUT i.tl)PUT /;
loop(l, PUT l.tl, loop(i, PUT Fd.l(l,i))PUT /);
PUT/ PUT/ PUT/ ;

```

```

PUT 'z(k,i)' PUT/;
PUT '-----'PUT/;
PUT 'z(k,i)',loop(i, PUT i.tl)PUT /;
loop(k, PUT k.tl, loop(i, PUT z.l(k,i))PUT /);
PUT/ PUT/ PUT/ ;

```

```

PUT 'Binary variable y'/;
PUT '-----'PUT/;
PUT 'Reaction', loop(m, PUT m.tl)PUT /;
PUT 'y' ,loop(m, PUT y.l(m)PUT ,) PUT/ PUT/ PUT/;

```

```

PUT 'Heat added or substracted'/;
PUT '-----'PUT/;
PUT 'Reaction', loop(m, PUT m.tl)PUT /;
PUT 'Qexc [J/h]' ,loop(m, PUT Qexc.l(m)PUT ,);
PUT/ PUT/ PUT/ ;

```

```
PUT 'Gibbs free energy of each reaction'/;  
  
PUT '-----'PUT/;  
  
PUT 'Reaction', loop(m, PUT m.tl)PUT /;  
  
PUT 'G [J/mol]', loop(m, PUT Greact.l(m)PUT ,);  
  
PUT/ PUT/ PUT/ ;
```

\*\$offtext

## 14.2. Visual Basics for Applications (VBA) code to connect HYSYS with Excel

### 14.2.1. Model 4

Option Explicit

Sub HysysToExcel()

'-----

'Data reading from Hysys

'-----

Dim CaseStudy As SimulationCase 'CaseStudy declared as a  
simulation case in HYSYS

Set CaseStudy = GetObject("C:\Users\Valeria\Desktop\Model4\Case\_Study.hsc") 'The case  
Case\_Study.hsc is assigned to CaseStudy (call HYSYS and open .hsc)

Dim CaseStreams As Streams 'CaseStreams is defined as a list  
of streams

Set CaseStreams = CaseStudy.Flowsheet.MaterialStreams 'The stream list  
from CaseStudy is assigned to CaseStreams

'Temperature, pressure, enthalpies and entropies are declared as a real number

Dim Temperature As Double

Dim Pressure As Double

Dim Enthalpy1 As Double

Dim Enthalpy2 As Double

Dim Enthalpy3 As Double

Dim Enthalpy4 As Double

Dim Enthalpy5 As Double

Dim Enthalpy6 As Double

Dim Enthalpy7 As Double

Dim Enthalpy8 As Double

Dim Enthalpy9 As Double

Dim Enthalpy10 As Double

Dim Enthalpy11 As Double

Dim Enthalpy12 As Double

Dim Enthalpy13 As Double

Dim Enthalpy14 As Double

Dim Enthalpy15 As Double

Dim Enthalpy16 As Double

Dim Entropy1 As Double

Dim Entropy2 As Double

Dim Entropy3 As Double

Dim Entropy4 As Double

Dim Entropy5 As Double

Dim Entropy6 As Double

Dim Entropy7 As Double

Dim Entropy8 As Double

Dim Entropy9 As Double

Dim Entropy10 As Double

Dim Entropy11 As Double

Dim Entropy12 As Double

Dim Entropy13 As Double

Dim Entropy14 As Double

Dim Entropy15 As Double

Dim Entropy16 As Double

'Temperature, pressure, enthalpies and entropies take the value of the molar enthalpy of the streams in the HYSYS case

Temperature = CaseStreams.Item(0).TemperatureValue

Pressure = CaseStreams.Item(0).PressureValue

Enthalpy1 = CaseStreams.Item(0).MolarEnthalpyValue

Enthalpy2 = CaseStreams.Item(1).MolarEnthalpyValue

Enthalpy3 = CaseStreams.Item(2).MolarEnthalpyValue

Enthalpy4 = CaseStreams.Item(3).MolarEnthalpyValue

Enthalpy5 = CaseStreams.Item(4).MolarEnthalpyValue

Enthalpy6 = CaseStreams.Item(5).MolarEnthalpyValue



Enthalpy7 = CaseStreams.Item(6).MolarEnthalpyValue

Enthalpy8 = CaseStreams.Item(7).MolarEnthalpyValue

Enthalpy9 = CaseStreams.Item(8).MolarEnthalpyValue

Enthalpy10 = CaseStreams.Item(9).MolarEnthalpyValue

Enthalpy11 = CaseStreams.Item(10).MolarEnthalpyValue

Enthalpy12 = CaseStreams.Item(11).MolarEnthalpyValue

Enthalpy13 = CaseStreams.Item(12).MolarEnthalpyValue

Enthalpy14 = CaseStreams.Item(13).MolarEnthalpyValue

Enthalpy15 = CaseStreams.Item(14).MolarEnthalpyValue

Entropy1 = CaseStreams.Item(0).MolarEntropyValue

Entropy2 = CaseStreams.Item(1).MolarEntropyValue

Entropy3 = CaseStreams.Item(2).MolarEntropyValue

Entropy4 = CaseStreams.Item(3).MolarEntropyValue

Entropy5 = CaseStreams.Item(4).MolarEntropyValue

Entropy6 = CaseStreams.Item(5).MolarEntropyValue

Entropy7 = CaseStreams.Item(6).MolarEntropyValue

Entropy8 = CaseStreams.Item(7).MolarEntropyValue

Entropy9 = CaseStreams.Item(8).MolarEntropyValue

Entropy10 = CaseStreams.Item(9).MolarEntropyValue

Entropy11 = CaseStreams.Item(10).MolarEntropyValue

Entropy12 = CaseStreams.Item(11).MolarEntropyValue

Entropy13 = CaseStreams.Item(12).MolarEntropyValue

Entropy14 = CaseStreams.Item(13).MolarEntropyValue

Entropy15 = CaseStreams.Item(14).MolarEntropyValue

'-----

'Data writing to EXCEL

'-----

'Sheets declared as a spreadsheet in Excel

Dim GetData As Excel.Worksheet

Dim HJ As Excel.Worksheet

Dim HK As Excel.Worksheet

Dim HL As Excel.Worksheet

Dim SJ As Excel.Worksheet

Dim SK As Excel.Worksheet

Dim SL As Excel.Worksheet

'Sheets assigned to a given sheet in the Excel file

Set GetData = Sheets("Get Data From HYSYS")

Set HJ = Sheets("Hj")

Set HK = Sheets("Hk")

Set HL = Sheets("Hl")

Set SJ = Sheets("Sj")

Set SK = Sheets("Sk")

Set SL = Sheets("Sl")

'Temperature, pressure, enthalpies and entropies assigned to a given cell in the Excel sheets

'Temperature and pressure

GetData.Range("c7").Value = Temperature

GetData.Range("c8").Value = Pressure

'Enthalpies

HJ.Range("b3").Value = Enthalpy1

HJ.Range("b4").Value = Enthalpy2

HJ.Range("b5").Value = Enthalpy3

HJ.Range("b6").Value = Enthalpy4

HJ.Range("b7").Value = Enthalpy5

HJ.Range("b8").Value = Enthalpy6

HJ.Range("b9").Value = Enthalpy7

HJ.Range("b10").Value = Enthalpy8

HK.Range("b3").Value = Enthalpy9

HK.Range("b4").Value = Enthalpy10

HK.Range("b5").Value = Enthalpy11

HK.Range("b6").Value = Enthalpy12

HK.Range("b7").Value = Enthalpy13

HK.Range("b8").Value = Enthalpy14

HK.Range("b9").Value = Enthalpy15

HL.Range("b3").Value = Enthalpy1

HL.Range("b4").Value = Enthalpy2

HL.Range("b5").Value = Enthalpy3

HL.Range("b6").Value = Enthalpy4

HL.Range("b7").Value = Enthalpy5

HL.Range("b8").Value = Enthalpy6

HL.Range("b9").Value = Enthalpy7

HL.Range("b10").Value = Enthalpy8

'Entropies

SJ.Range("b3").Value = Entropy1

SJ.Range("b4").Value = Entropy2

SJ.Range("b5").Value = Entropy3

SJ.Range("b6").Value = Entropy4

SJ.Range("b7").Value = Entropy5

SJ.Range("b8").Value = Entropy6

SJ.Range("b9").Value = Entropy7

SK.Range("b10").Value = Entropy8

SK.Range("b3").Value = Entropy9

SK.Range("b4").Value = Entropy10

SK.Range("b5").Value = Entropy11

SK.Range("b6").Value = Entropy12

SK.Range("b7").Value = Entropy13

SK.Range("b8").Value = Entropy14

SK.Range("b9").Value = Entropy15

SL.Range("b3").Value = Entropy1

SL.Range("b4").Value = Entropy2

SL.Range("b5").Value = Entropy3

SL.Range("b6").Value = Entropy4

SL.Range("b7").Value = Entropy5

SL.Range("b8").Value = Entropy6

SL.Range("b9").Value = Entropy7

SL.Range("b10").Value = Entropy8

End Sub

## 14.2.2. Model 5

Option Explicit

Sub HsysToExcel()

'-----

'Data reading from Hsys

'-----

Dim CaseStudy As SimulationCase  
simulation case in HYSYS

'CaseStudy declared as a

Set CaseStudy = GetObject("C:\Users\Valeria\Desktop\Model5\Case\_Study.hsc")  
case Case\_Study.hsc is assigned to CaseStudy (call HYSYS and open .hsc)

'The

Dim CaseStreams As Streams  
of streams

'CaseStreams is defined as a list

Set CaseStreams = CaseStudy.Flowsheet.MaterialStreams  
from CaseStudy is assigned to CaseStreams

'The stream list

'Temperature, pressure, enthalpies and entropies are declared as a real number

Dim Temperature As Double

Dim Pressure As Double

Dim Enthalpy1 As Double

Dim Enthalpy2 As Double

Dim Enthalpy3 As Double

Dim Enthalpy4 As Double

Dim Enthalpy5 As Double

Dim Enthalpy6 As Double

Dim Enthalpy7 As Double

Dim Enthalpy8 As Double

Dim Enthalpy9 As Double

Dim Enthalpy10 As Double

Dim Enthalpy11 As Double

Dim Enthalpy12 As Double

Dim Enthalpy13 As Double

Dim Enthalpy14 As Double

Dim Enthalpy15 As Double

Dim Entropy1 As Double

Dim Entropy2 As Double

Dim Entropy3 As Double

Dim Entropy4 As Double

Dim Entropy5 As Double

Dim Entropy6 As Double



Dim Entropy7 As Double

Dim Entropy8 As Double

Dim Entropy9 As Double

Dim Entropy10 As Double

Dim Entropy11 As Double

Dim Entropy12 As Double

Dim Entropy13 As Double

Dim Entropy14 As Double

Dim Entropy15 As Double

'Temperature, pressure, enthalpies and entropies take the value of the molar enthalpy of the streams in the HYSYS case

Temperature = CaseStreams.Item(0).TemperatureValue

Pressure = CaseStreams.Item(0).PressureValue

Enthalpy1 = CaseStreams.Item(0).MolarEnthalpyValue

Enthalpy2 = CaseStreams.Item(1).MolarEnthalpyValue

Enthalpy3 = CaseStreams.Item(2).MolarEnthalpyValue

Enthalpy4 = CaseStreams.Item(3).MolarEnthalpyValue

Enthalpy5 = CaseStreams.Item(4).MolarEnthalpyValue

Enthalpy6 = CaseStreams.Item(5).MolarEnthalpyValue

Enthalpy7 = CaseStreams.Item(6).MolarEnthalpyValue



Enthalpy8 = CaseStreams.Item(7).MolarEnthalpyValue

Enthalpy9 = CaseStreams.Item(8).MolarEnthalpyValue

Enthalpy10 = CaseStreams.Item(9).MolarEnthalpyValue

Enthalpy11 = CaseStreams.Item(10).MolarEnthalpyValue

Enthalpy12 = CaseStreams.Item(11).MolarEnthalpyValue

Enthalpy13 = CaseStreams.Item(12).MolarEnthalpyValue

Enthalpy14 = CaseStreams.Item(13).MolarEnthalpyValue

Enthalpy15 = CaseStreams.Item(14).MolarEnthalpyValue

Entropy1 = CaseStreams.Item(0).MolarEntropyValue

Entropy2 = CaseStreams.Item(1).MolarEntropyValue

Entropy3 = CaseStreams.Item(2).MolarEntropyValue

Entropy4 = CaseStreams.Item(3).MolarEntropyValue

Entropy5 = CaseStreams.Item(4).MolarEntropyValue

Entropy6 = CaseStreams.Item(5).MolarEntropyValue

Entropy7 = CaseStreams.Item(6).MolarEntropyValue

Entropy8 = CaseStreams.Item(7).MolarEntropyValue

Entropy9 = CaseStreams.Item(8).MolarEntropyValue

Entropy10 = CaseStreams.Item(9).MolarEntropyValue

Entropy11 = CaseStreams.Item(10).MolarEntropyValue

Entropy12 = CaseStreams.Item(11).MolarEntropyValue

Entropy13 = CaseStreams.Item(12).MolarEntropyValue

```
Entropy14 = CaseStreams.Item(13).MolarEntropyValue
```

```
Entropy15 = CaseStreams.Item(14).MolarEntropyValue
```

```
'-----
```

```
'Data writing to EXCEL
```

```
'-----
```

```
'Sheets declared as a spreadsheet in Excel
```

```
Dim GetData As Excel.Worksheet
```

```
Dim H As Excel.Worksheet
```

```
Dim S As Excel.Worksheet
```

```
'Sheets assigned to a given sheet in the Excel file
```

```
Set GetData = Sheets("Get Data From HYSYS")
```

```
Set H = Sheets("H")
```

```
Set S = Sheets("S")
```

```
'Temperature, pressure, enthalpies and entropies assigned to a given cell in the Excel sheets
```

```
'Temperature and pressure
```

```
GetData.Range("c7").Value = Temperature
```

GetData.Range("c8").Value = Pressure

'Enthalpies

H.Range("b3").Value = Enthalpy1

H.Range("b4").Value = Enthalpy2

H.Range("b5").Value = Enthalpy3

H.Range("b6").Value = Enthalpy4

H.Range("b7").Value = Enthalpy5

H.Range("b8").Value = Enthalpy6

H.Range("b9").Value = Enthalpy7

H.Range("b10").Value = Enthalpy8

H.Range("b11").Value = Enthalpy9

H.Range("b12").Value = Enthalpy10

H.Range("b13").Value = Enthalpy11

H.Range("b14").Value = Enthalpy12

H.Range("b15").Value = Enthalpy13

H.Range("b16").Value = Enthalpy14

H.Range("b17").Value = Enthalpy15

'Entropies

S.Range("b3").Value = Entropy1

S.Range("b4").Value = Entropy2

S.Range("b5").Value = Entropy3

S.Range("b6").Value = Entropy4

S.Range("b7").Value = Entropy5

S.Range("b8").Value = Entropy6

S.Range("b9").Value = Entropy7

S.Range("b10").Value = Entropy8

S.Range("b11").Value = Entropy9

S.Range("b12").Value = Entropy10

S.Range("b13").Value = Entropy11

S.Range("b14").Value = Entropy12

S.Range("b15").Value = Entropy13

S.Range("b16").Value = Entropy14

S.Range("b17").Value = Entropy15

End Sub

### 14.3. Attached Annexes

Apart from all the annexes that can be found directly in this document, there is a list of files attached to this report. These files are described as follows:

- Model 1: File containing GAMS file, Excel data file and results sample for the particular example solved with model 1.
- Model 2: File containing GAMS file, Excel data file and results sample for the particular example solved with model 2.
- Model 3: File containing GAMS file, Excel data file and results sample for the particular example solved with model 3.
- Model 4: File containing Aspen HYSYS Case Study, GAMS file, Excel data file and results sample for the particular example solved with model 4.
- Model 5: File containing Aspen HYSYS Case Study, GAMS file, Excel data file and results sample for the particular example solved with model 5.
- Excel file containing the tests developed in order to find a valid equation that defined binary variables  $y$ ,  $z_k$ ,  $y_m$  and  $z_{k,i}$