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MULTI-SCALE MODELLING AND OPTIMISATION OF SUSTAINABLE CHEMICAL PROCESSES

by

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DECLARATION

I herewith declare that this dissertation is the result of my own work and has not been previously submitted for consideration to any other degree or qualification at this or any other university. The work which is not my own has been properly acknowledged.

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ABSTRACT

This dissertation explores the process modelling and optimisation of chemical processes under sustainability criteria. Resting on process systems engineering techniques combined with life cycle assessment (LCA), we present implementation strategies to improve flowsheet performance and reduce environmental impacts from early design stages.

We first address the relevance of sustainability assessments in the sector and present process and environmental modelling techniques available. Under the observation that chemical processes are subject to market, technical, and environmental fluctuations, we next present an approach to account for these uncertainties. Process optimisation is then tackled by combining surrogate modelling, objective-reduction, and multi-criteria decision analysis tools. The framework proved the enhancement of the assessments by reducing the use of computational resources and allowing the ranking of optimal alternatives based on the concept of efficiency. We finally introduce a scheme to assess sustainable performance at a multi-scale level, from catalysis development to planet implications. This approach aims to provide insights about the role of catalysis and establish priorities for process development, while also introducing absolute sustainability metrics *via* the concept of 'Planetary boundaries'. Ultimately, this allows a clear view of the impact that a process incurs in the current and future status of the Earth.

The capabilities of the methods developed are tested in relevant applications that address challenges in the sector to attain sustainable performance. We present how concepts like circular economy, waste valorisation, and renewable raw materials can certainly bring benefits to the industry compared to their fossil-based alternatives. However, we also show that the development of new processes and technologies is very likely to shift environmental impacts from one category to another, concluding that cross-sectorial cooperation will become essential to meet sustainability targets, such as those determined by the Sustainable Development Goals.

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Don't turn your back on wisdom, for she will protect you. Love her, and she will guard you.

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NOMENCLATURE

Abbreviations

AEC	Alkaline electrolysis cells
AP	Acidification potential
AR	Assurance region in DEA
BAU	Business as usual
CAPEX	Capital expenses
CCU	Carbon capture utilisation
CEPCI	Chemical engineering process cost indexes
DAC	Direct air capture
DALY	Disability-adjusted life years
DAR	Depletion of abiotic resources
DEA	Data envelopment analysis
DMU	Decision making units
DPG	Dipropylene glycol
EA	Evolutionary algorithms
EG	Ethylene glycol
EP	Eutrophication potential
FAET	Fresh aquatic ecotoxicity
GWP	Global warming potential
HEN	Heat exchanger network
HT	Human toxicity
ISBL	Inside battery limits
ISO	International Organisation of Standardisation
LCA	Life cycle assesment
LCIA	Life cycle impact assessment
MAET	Marine aquatic ecotoxicity
MCDA	Multi-criteria decision analysis
MILP	Mixed integer linear programming
MINLP	Mixed integer nonlinear programming

	MOGA	Multi-objective Genetic Algorithm
	MOO	Multi-objective optimisation
	NG	Natural gas
	NLP	Nonlinear programming
	OLD	Ozone layer depletion
	OPEX	Operational expenses
	OR	Objective reduction
	OSBL	Off-site battery limits
	PB	Planetary boundary
	PE	Polyethylene
	PEMEC	Proton-exchange electrolysis cells
	PG	Propylene glycol
	PO	Photochemical oxidation
	PSE	Process systems engineering
	SD	Sustainable development
	SDG	Sustainable development goals
	SM	Surrogate model
	SOEC	Solid-oxide electrolysis cells
	SUSCAPE	Sustainable chemical processes
	TE	Terrestrial ecotoxicity
	TPG	Tripropylene glycol
	TRL	Technology readiness levels
	TWI2050	The World in 2050 Initiative
	UN	United nations
	WAR	Waste reduction algorithm
(Greek symbol	ls
δ	5	Upper bound in approximation error $\delta_{s,s',i}$
δ	p,p',i	Approximation error between solution s and s' in objective i
е	θ _o , θ _j	Technical efficiency of DMU _{o/j}
е) _{SE,j}	Super-efficiency score of DMU j
λ	'n	Linear weights of inefficient unit j to project it in the efficient frontier

 μ_i Relative error of the surrogate in objective f_i

φ	Non-Archimedean infinitesimal value
σ^2	Standard deviation of environmental inventories
Variables	
а	Cost constant of purchase equipment cost
А	Matrix of multipliers preferences in dual model of DEA for outputs y_{ro}
ACC	Annualised capital cost
ACCR	Annual capital charge
b	Cost constant of purchase equipment cost
В	Matrix of multipliers preferences in dual model of DEA for inputs x_{lo}
BOUND _i	bound value defining a given uncertainty region for PB i
с	Number of decision-making units in DEA model
C _e	Purchase equipment cost of unit e
CF _{cat,es}	Characterisation factor of substance es
D	Matrix of multipliers preferences in dual model of DEA
EI _{cat}	Environmental impact indicator of category cat
f _i	Function to evaluate sustainability metric i
f _{imax}	Maximum value of objective f _i
f _{imin}	Minimum value of objective f _i
f _{ni}	Normalised value of f _i
$f_{p^\prime,i},f_{p,i}$	Value of objective i in solution p'/p
FCOP	Fixed costs of operation
i	Number of objectives to optimise
if _{ie}	installation factor of equipment ie
IMPBAU _i	impact on a PB i exerted by the total production of the BAU process
IMPT _i	impact referred to the functional unit
IMPTOT _i	Current total level of impact in PB i subtracting the natural background level
int	interest rate
j	DMU index
k	Objectives in the reduced space
К	Objectives in the full space
l	Index for inputs x in DEA model
LCI	Life cycle inventory

m	Total number of inputs x in DEA model
n	Number of decision variables in design problem
N _{cat}	Normalised environmental impact of category cat
NB _i	Natural background level of PB i
Р	Pareto set of design problem
PSHARE _i	Share of the safe operating space according to sharing principle
p, p′	Pareto solution of set P
r	Index for outputs y in DEA model
r ²	Correlation coefficient
R _{cat}	Reference values to normalise Environmental Impacts in category cat
RMSE	Root mean squared error
S	Total number of outputs y in DEA model
S	Size of the equipment e to calculate purchase equipment cost
s _r ⁺	Output slack variable
s	Input slack variable
SHARE _i	Share of the safe operating space associated with BAU process
SOS_i	safe operating space in PB i
TAC	Total annualised cost
TCC	Total Capital Cost
t	Equipment size exponent in purchase equipment cost
TI	Environmental single impact indicator
TT _i	level of transgression in a PB i
tol	Tolerance error for surrogate model in objective function f_i
u _r	Multiplier for output y _{ro}
U _{Dx}	Uncertain parameters of environmental inventories
vl	Multiplier for input x _{lo}
VCOP	Variable costs of operation
W _{cat}	Environmental weight of category cat
X	DEA inputs expressing multipliers preferences in inputs x_{lo}
x _{lj} , x _{lo}	Input value of $DMU_{j/o}$ in input i
\overline{Y}	DEA outputs expressing multipliers preferences in outputs y_{ro}
y _{si}	Scalar output at observation si

\hat{y}_{si}	Surrogate output of observation si
yr	years of compound interest
y _{rj} , y _{ro}	Output value of $DMU_{j/o}$ in output r
YP _{p,p',i}	Binary parameter to denote dominance between solution s and s' in objective i
Z	Set of samples to evaluate in original model
ZD _{p,p} ,	Binary variable to denote dominance between solution s and s' in the reduced
	space
ZO _i	Binary variable to denote is objective i is omitted
$\text{ZOD}_{p,p',i}$	Binary variable to denote if error $\delta_{s,s',i}$ is accounted

Chapter 1 INTRODUCTION

Human activities have become a major driving force of the environment and have pushed the Earth system into previously unknown states. Human progress has caused the physical, chemical and biological global-scale cycles and energy fluxes of the planet to significantly depart from natural behaviour. Although pre-industrial human activities certainly showed impact from local to continental levels in earlier societies, the power of human activities to modify the Earth's natural behaviour is associated to the start of the Industrial Revolution. Particularly, the increase in energy consumption favoured by technology developments of the age. An industrialised society consumed four to five times more energy than an agrarian one. According to Steffen *et al.* (2007), a demographic explosion from a billion people in 1820 to more than six billion in 2000 would be inconceivable without energy availability. This increase in population also opened an era of intensified human influence upon the Earth.

The emergence of the chemical industry is also associated to the Industrial Revolution, when the development of the textile and glass industries spurred the sector. One of the most prominent processes came from the patent by Nicolas Leblanc in 1791 to produce soda ash from sea salt. Despite this process was patented in France, it was in Britain where it really took off in 1824. The British soda production reached 200,000 tons by the 1870s, exceeding the production of the rest of the world combined. The Leblanc process was environmentally noxious, releasing large quantities of hydrochloric acid fumes to the environment, and the Alkali Act forced an absorption of at least 95% of the fume acid in 1863. From these early stages, the chemical industry started to face social and environmental challenges.

1.1 The great acceleration

As the Industrial Revolution matured, so did the chemical industry and its portfolio increased after the successful isolation of compounds such as naphthalene, phenol, benzene, and toluene in the early 19th century. During the period of World War II, the petrochemicals started to become the driving force of the industry, and after the war, the industry shifted almost entirely its production from coal to petrochemicals.

The use of oil also brought additional and accelerated changes in human activities, doubling the global population in only 50 years and increasing the global economy by more than 15-fold. Urban areas concentrated more than 50% of the world's population, as they became the centre of technological innovation and engines of economic growth. Yet, the global impact of the chemical industry and human activities in the environment started to be noticed by the early to mid-20th century. In this period, the global land use passed from 1.35 Mha from around 1800 to 4.92 Mha by 1950. The flux of nitrogen increased more than 10 times in the coastal zone of the planet, and the global concentration of CO_2 went from 270-275 ppm to 310 ppm in the same period (Steffen *et al.*, 2007).

The chemical industry by itself has dealt with additional challenges related to social and environmental concerns. One of the most dramatic cases was the 'Bhopal disaster' in 1984, in which 3,000 residents in Bhopal, India, died after a leak of toxic chemicals from a Union Carbide plant. The disaster prompted stricter regulatory measures in the face of public hostility. In 1988, the Chemicals Manufacturers Association adopted codes and performance goals, addressing topics such as pollution prevention, safe operation and distribution of products, and community involvement in the case of disasters. The program resulted successful in reestablishing the legitimacy of the sector. However, it failed to address the fundamental problem of the chemical industry: energy and resources intensive, release of pollutants, and toxicity of many of its products. As pointed by Hart and Milstein (1999), this caused an 'incremental' improvement of the chemical industry, meaning that companies focused on existing products and processes aiming for a continuous improvement of the industry. This resulted in smaller companies following the practices of the most established ones and significantly reduced the opportunity for fundamental innovation.

Since its origins, the chemical sector has become an important part of the economy. In 2017, the sector generated global annual sales for \$3,920 billion, representing 7% of the world's gross domestic product (GDP). If we consider its supply chain and payroll-induced impacts, this value increases to an estimated of \$5,700 billion, 120 million jobs supported, and expected sales growth to \$7,450 billion in 2030. In this context, classical economics viewed natural resources as external to the market, and essentially free. Similarly, there was no penalty associated to industrial waste, on the assumption that natural systems were resilient and would simply absorb them. However, these assumptions have also changed the world's ecosystem more rapidly and extensively than any other comparable period in human history. Steffen et al. (2007) marks this period as the sixth great extinction, with a high rate of species loss, a significant increase on greenhouse gases (GHG), and more nitrogen being converted to reactive forms from fertilisers and fuel combustion than from all the natural processes combined. One of the most plausible examples is the concentration of atmospheric CO₂ in the planet, which passed from 310 ppm in 1950 to 380 ppm in 2000. Figure 1.1 shows the GHG emissions released by the industry from 1970 to 2010, year in which the chemical industry was responsible for approximately 7% of global anthropogenic GHG (around 15% of industrial GHG emissions) and approximately 10% of the global energy consumption (IPCC, 2014).







1.2 The response of the chemical industry

The development of strategies to ensure the sustainability of the Earth have become a priority and one of the main challenges that we face. However, arguing that sustainable development is ill-defined, many companies resisted sustainability as a business driver, without realising that sustainable development offers one of the biggest opportunities in the history of commerce. Established companies now have the chance to lead the redefinition and shaping of the industry while innovators and entrepreneurs seek to incorporate into an entirely new market (Hart and Milstein, 1999). The new 'ecological economics', incorporates environmental and social capitals as part of a larger industrial ecosystem (Bakshi and Fiksel, 2003). However, to be able to properly incorporate environmental and social factors as business drivers, a clear definition of sustainability is required. Furthermore, the sustainability of a process has to be measured according to the 'three pillars of sustainability', where economic, environmental and social objectives are simultaneously accomplished.

As defined by the Brundtland Report in 1987 (WCED, 1987), 'sustainable development is development that meets the needs of the present without compromising the ability of future generations to meet their own needs'. The Brundtland report was intended to address the exacerbation of global environmental burdens and social problems as a result from the industrial revolution. The response of the society created public pressure over environmental issues to stimulate the incorporation of sustainable development into decision-making in process industries. However, the chemical sector, as many other industries and activities, were lacking of clear performance objectives to be achieved.

In 2015, this problem was partially solved by the United Nations (UN), who announced the 17 Sustainable Development Goals (SDGs) (UN, 2019). The SDGs have been adopted by all of the UN Member States, and establish 169 associated targets to be achieved by 2030. The goals are integrated and inseparable, and harmonise the Triple Bottom Line of sustainability (Azapagic and Perdan, 2000): people (social), planet (environmental), and prosperity (economic). They also aim to improve the standard of living, reduce the inequality gap, preserve the environment, promote sustainable thinking and foster innovation. More recently, 'The World in 2050 Initiative' (TWI2050), published the six transformations that will allow the achievement of the SDGs and long term sustainability to 2050 and beyond. These transformations include: i) human capacity and demography; ii) consumption and production; iii) decarbonisation and energy; iv) food, biosphere and water; v) smart cities; and vi) digital revolution.

The implementation of these transformations to achieve the SDGs within the chemical sector can be translated into particular challenges, as it seeks to satisfy the world's chemicals demand in the global market. In a developed economy, consisting of 1 billion customers, the main challenge of the sector is to minimise its footprint, on the basis of a stable market and infrastructure availability. In an emerging economy, with approximately 2 billion people, the main challenge is to avoid collision between a rapid industrialisation and an increasing demand for additional products and services. Development in emerging countries has resulted in largescale pollution and the question to address is how to meet the growing needs without exacerbating urban problems. Finally, in a surviving economy, formed by 3 billion customers, the main challenge is to meet the basic needs of largely rural and poor customers, where no infrastructure is available and few companies dare to invest in what they perceive as risky.

Organisations like the World Business Council for Sustainable Development, which is formed by more than 200 leading companies, constantly demonstrate the value of sustainable practices. According to Fiksel (2002), sustainable development creates shareholder value-added through enabling growth (e.g. product innovation and new markets), reducing costs (e.g. resource conservation and energy efficiency), conserving capital (e.g. process simplification, supply chain), and decreasing risks (e.g. incident prevention). Additional intangible assets also benefit from sustainable practices, such as innovation within own processes, or creating value for society and external stakeholders.

1.3 Sustainable evaluation of chemical processes

The main challenges that the chemical industry faces to implement sustainable development are depicted in Figure 1.2 (Poliakoff and Licence, 2007). The first is to identify renewable feedstocks that allow the replacement of fossil fuels as the source of carbon for the production of chemicals. The second is to devise reactions and catalytic pathways that minimise the environmental impact. The third arises in the engineering of processes, in which the generation of waste and energy consumption should be minimised. Finally, the fourth challenge refers to the impact caused to the environment by the chemical being produced, where less toxic and biodegradable products should be pursued.



Fig. 1.2 Challenges at the multi-scale level for the development of a sustainable chemical industry (Poliakoff and Licence, 2007).

The incorporation of SD in the chemical industry also includes multiple scales. At the molecular scale, the concept of 'Green Chemistry' (Anastas and Kirchhoff, 2002) presents a useful framework to efficiently develop new products by utilising (preferable renewable) raw materials, eliminating waste, and avoiding the use of toxic/hazardous agents. At the engineering and macro-scale levels, the framework of 'Green Engineering' (Anastas and Zimmerman, 2003) also provides meaningful principles for the selection and design of technologies aiming to maximise the efficiency of a process while minimising waste generation and energy consumption. These guidelines certainly help to incorporate sustainable thinking in the development of a process at a multi-scale level. However, it is not expected that all new

processes fulfil these criteria, not to mention that the level of sustainable attained by a process remains unknown. This raises the need for sustainability metrics, such as the E-factor (Sehldon, 2017), life cycle assessment (LCA) (Azapagic, 1999), or the waste reduction algorithm (WAR) (Cabezas *et al.*, 1999).

Given its natural link between fundamental science, engineering and industrial practice, Process Systems Engineering (PSE) plays a key role in meeting the challenges of sustainable development (Narodoslawsky, 2013). Over the last 60 years, PSE has aimed to improve the performance of chemical processes through the development of models and optimisation algorithms. However, the new quest for sustainability presents increasing challenges and opportunities for the community, as the understanding of the complex interactions between industry, society, and ecosystems is essential to achieve sustainable development.

1.4 Research objectives and thesis overview

This thesis addresses emerging global sustainability challenges in a transition toward a sustainable chemistry industry. It endeavours to promote sustainability practices in the sector through a proactive response to the key transformations to achieve the SDGs defined by the UN. The main contributions that lie at its heart cover both methodological aspects deriving from mathematical techniques and life cycle methods, and prominent applications to promote sustainable development in the sector. The general research objectives that this thesis aims to achieve are as follows:

- To enhance process and life cycle modelling techniques during the assessment of chemical processes in order to understand interactions among them at the local and global level from early design stages.
- To develop a systematic approach to assess and optimise a chemical process according to sustainability criteria, merging process design and optimisation techniques, sustainability metrics, and multi-criteria decision analysis tools.

- To assess the role of catalysis during the process modelling and optimisation of chemical processes, providing guidance into research areas focused on the development and/or enhancement of processes and technologies.
- To explore relevant applications of the methods developed to attain a sustainable industry. The attention has been drawn to the most relevant TWI2050 key transformations for the chemical sector: consumption and production, decarbonisation and energy, and food, biosphere and water.

The rest of this thesis is organised as follows. In Chapter 2, we present an extensive literature review about the assessment of sustainability performance of chemical processes. The focus of this chapter is to present a background of current methods available to perform technoeconomic and environmental assessments and the methodological implications and limitations still to be addressed. The end of the chapter discusses the main contributions of this work. In Chapter 3, we present the methodology applied for the modelling and assessment of chemical processes along with a relevant case study focused on circular economy. This chapter aims to lay the foundations for the further discussion of the contributions achieved in this work, which include the modelling of uncertainties in Chapter 4, process optimisation in Chapter 5, and a multi-scale assessment in Chapters 6. These contributions and their application are briefly discussed in section 2.8. Chapter 7 puts forward the conclusions and future directions of the research. Supplementary information for Chapters 4 to 6 is included in the Appendices.

Chapter 2 BACKGROUND

2.1 Measuring sustainability in the chemical industry

Chemical processes have been traditionally assessed in terms of economic criteria. The new pursuit of sustainability requires the incorporation of additional sustainable metrics, for which a wide variety of methods have emerged over the last decades. In 1992, Sheldon (2017) introduced the E-factor to relate the amount of waste and products in a process. Later on, in a pioneer work, Azapagic (1999) showed the application of life cycle assessment (LCA) in the selection, design and optimisation of chemical processes. At the same time, Cabezas *et al.* (1999) introduced the waste reduction algorithm (WAR), focused on the minimisation of waste and harmful substances. From this time on, a myriad of alternatives started to emerge (Gong and You, 2017; Hui Liew *et al.*, 2016; Khila *et al.*, 2016; Ruiz-Mercado *et al.*, 2016; Siew Ng and Martinez Hernandez, 2016).

When assessing a chemical process or product, we must recall that sustainable development can only be achieved when considering the full environmental impact caused across all the stages in the product's life cycle. Among the multiple approaches to address the level of sustainability in a process, LCA offers a holistic approach for the quantitative evaluation of a system through its entire life cycle. In addition, it also combines the different impacts to evaluate, the place where the process is carried out, and the time scale into one consistent framework (Guinée *et al.*, 2002). This kind of approach avoids the risk of solving one environmental problem by shifting the environmental burdens to another stage in the life cycle of the process. This makes LCA unique compared to other environmental analysis tools, as LCA defines the system's boundaries so as to include the whole material and energy supply chains instead of focusing only in the manufacturing stage (Azapagic & Clift, 1999).

The sustainability of a process has to be measured according to the knowledge and understanding of the current level of sustainability according to the 'three pillars of sustainability', where economic, environmental and social objectives are simultaneously accomplished. According to Azapagic and Perdan (2000), three major phases can be summarised to achieve it: i) the assessment of environmental burdens of the products or processes of interest, ii) the evaluation of their sustainable performance and the establishment of improvement targets, and iii) the identification of approaches towards the sustainable improvement of those systems.

The translation of these phases within chemical process design is reflected in three similar stages. The first one is related to the modelling and assessment of the process under study. Here, sustainability metrics are selected and incorporated in the process model. In a second stage, the design task is posed as an optimisation problem that seeks to minimise (or maximise) the sustainability metrics previously defined. Due to the existence of inherent trade-offs between them, these metrics tend to be in conflict with each other. In a third stage, a post-optimal analysis is carried out to select the best design among a set of optimal solutions. This analysis is usually performed by stakeholders who are assisted by multi-criteria decision analysis (MCDA) tools.

2.2 Economic assessment

The economic feasibility of a chemical process is given by the potential profit of the design considering the investment required and cost of production. The different elements that constitute the total cost of a product include fixed capital investment, variable costs of production, fixed costs of production, and revenues. The fixed capital investment required for a new design can be broken down in four elements:

- Inside battery limits (ISBL): major process equipment
- Off-site battery limits investment (OSBL): modifications and improvements that must be made to the site infrastructure
- Engineering and construction costs: home office costs or contractor charges, including the costs of detailed design and other engineering services
- Contingency charges: costs added into the budget project to allow for variations in the cots estimate

An approximation to the OSBL investment, engineering and construction costs, and contingency charges can be calculated from the ISBL investment (Towler and Sinnott, 2013), also referred as Total Capital Cost (TCC).

The individual capital cost of a major equipment can be calculated using standard correlations of the form:

$$C_e = a + bS^t \tag{2.1}$$

Where C_e is the purchase equipment cost; a and b are cost constants; S refers to the size of the equipment, and t accounts for the equipment cost exponent. Constants and exponential factors are obtained from the literature (Seider *et al.*, 2009; Smith, 2016; Towler and Sinnott, 2013), while the size of the equipment is calculated from the simulation. The TCC is determined from the sum of the individual equipment purchase cost $C_{e,ie}$ and the corresponding installation factors:

$$TCC = \sum_{ie} C_{e,ie} i f_{ie}$$
(2.2)

All the costs can be extrapolated to the corresponding year using Chemical Engineering Process Cost Indexes (CEPCI).

Variable costs of production (VCOP) refer to costs that are proportional to the plant output or operation rate. These include raw materials, utilities, consumables, waste management, and packaging and shipping. Fixed costs of production (FCOP) relate to costs that are incurred regardless of the plant operation or output. They include labour, maintenance, land, insurance, interest payments, overhead, license fees and royalties, which can also be calculated as a function of the capital investment (Towler and Sinnott, 2013). Finally, the revenues refer to the income earned from the sales of main products and byproducts.

There are multiple metrics to assess the economic performance of a product, such as cash flow diagrams, pay-back time, return on investment, net present value, or total annualised cost. One of the most common metrics refers to the total annualised cost (TAC):

$$TAC = FCOP + VCOP + ACC$$
(2.3)

Where FCOP are the fixed costs of production, VCOP are the variable costs of production and ACC refers to the annual capital charge.

To translate the capital investment TCC of a process into current value, an annual capital charge ratio ACCR is defined, according to the following expression:

ACCR =
$$\frac{[int(1 + int)^{yr}]}{[(1 + int)^{yr} - 1]}$$
(2.4)

Where int represents the interest rate and yr the years of compound interest. The annualised capital cost ACC is given by:

$$ACC = TCC \cdot ACCR \tag{2.5}$$

2.3 Life cycle assessment (LCA)

The International Organisation of Standardisation (ISO) defines LCA as the 'compilation and evaluation of the inputs, outputs and potential environmental impacts of a product system throughout its life cycle' (ISO, 2006). Broadening this definition, LCA is a product-oriented tool that evaluates environmental burdens across its life cycle, which means that takes into

consideration the impact over the natural resources when raw materials are obtained, the management of the waste generated during the production process and the final disposal of the product (Baumann and Tillman, 2004). The structure defined by ISO to implement an LCA includes: goal and scope definition, inventory analysis, impact assessment, and improvement assessment or interpretation.

2.3.1 Goal and scope definition

The first step defines the aim of the study, from which functional unit, spatial location, and system boundaries are defined. The functional unit allows a fair comparison among systems by defining an equivalent amount of goods or services to be provided by the systems. The spatial location helps to locate the area of study so as to identify and evaluate the specific inventory data of processes as well as the environmental challenges of the region.

The system boundaries of an LCA rely heavily on the practitioner's subjectivity, and must be selected in accordance to the general goal of the study in order to carry out a meaningful assessment. System boundaries are traditionally defined as cradle-to-gate, cradle-to-grave, and cradle-to-cradle. While the cradle-to-gate analysis includes the activities from resources extraction to factory gate, the cradle-to-grave approach expands the analysis until the waste disposal. The cradle-to-cradle analysis can be considered a special case of the cradle-to-grave approach, in which waste products are recycled to the process. The cradle-to-gate approach is mainly applied in cases where only the production process of a product is to be modified, keeping the same use and final disposal. This approach allows for a direct comparison of the change of technologies and the potential savings that can be attained, which is the reason to be the most applied approach while assessing a chemical process. The cradle-to-grave approach accounts for the full life cycle of the system under study, and finds most of its applications when not only the production process is modified but also characteristics of its supply chain and final disposal. The cradle-to-cradle approach relates to the circular

economy concept, in which the product is entirely or partially recycled to the production process.

While system boundaries for single-product processes can be relatively easy to define, their selection when dealing with multiproduct processes can be more complex, as environmental burdens can be distributed among different products. This raises the concern of omitting potential interactions with other processes outside the boundaries defined, transferring impacts to systems that are not being analysed. When recycling or multiproduct processes are considered, the ISO standard leaves a large degree of freedom to allocate environmental burdens, being allocation and system expansion the most popular approaches.

Allocation methods distribute the environmental impact of a process among the different products according to different basis. Here, three different methods arise: main product allocation, mass or volume-based, physical allocation, and economic allocation. In main product allocation, the total environmental impact of a process is assigned to the main product, while the byproducts are considered burden free. Mass or volume-based, physical allocation distributes the burdens according to the corresponding share of the property used as basis for the allocation. Economic allocation follows the same principle as physical allocation, using as basis the revenues generated by the different products. Despite the ISO standard puts allocation as the last resort to allocate environmental burdens, economic allocation has traditionally been one of the most applied methods in practice. As stated by Ardente and Cellura (2012), the cause is not only its simplicity but also the ability of prices to encapsulate complex attributes of a system. However, these prices can also present large variability and low correlation with physical flows. Despite its limitations, economic allocation has certain qualities that make it flexible and potentially suitable for different contexts, such as those when large quantities of byproducts with low economic value are produced.

In system expansion, byproducts are considered as an alternative to those on the global market. Under this assumption, the main product takes all the impact of the process, but credits are given to the byproducts according to the environmental impact attached to their production using the technologies available in the current global market. Although this approach aims to avoid the subjectivity attached to allocation methods, it can also underestimate the impact of a process if the consumption of the byproducts generated is not guaranteed.

2.3.2 Inventory analysis

The second step quantifies all the material and energy flows (LCI) that have an impact on the environment within the boundaries of the system. This step requires the compilation of data about the system and the calculation of mass and energy balances to quantify resources consumed and emissions released. The collection of data at this stage is burdensome and time-consuming, not to mention that, in many cases, this information is unavailable. A common practice to avoid this task, is the use LCA databases to get approximated inventories for reference processes of our system. While some LCA databases are sector specific, such as Agrifoodprint (Blonk Consultants, 2019), others cover a broader range of processes and activities, such as Ecoinvent (Wernet *et al.*, 2016) or GaBi (Think Step, 2015). These databases usually provide average inventory data based on know-how industrial processes as well as patent, technical and scientific literature.

When making use of environmental databases, differences in inventories are evident between the process being analysed and the one available in the database. This results in a certain degree of uncertainty given by the reliability of the source (experimental, model, and estimated), completeness of the data (number of samples), temporal, geographic and technological differences. To address these uncertainty, Weidema and Wesnaes (1996) proposed a method for data quality management. In this approach, the uncertain life cycle entries are modelled as lognormal distributions whose mean value is obtained from the database, and the standard deviation is calculated using the Pedigree matrix according to Eq. 2.6:

$$\sigma^{2} = \exp\left\{ \sqrt{[\ln(U_{Db})]^{2} + \sum_{i=1}^{5} [\ln(U_{Di})]^{2}} \right\}$$
(2.6)

Where U_D are parameters based on the reliability of source, completeness of the data, temporal, geographic and technological differences (U_{Di}). These parameters also include uncertainty dependent on the specific emissions being modelled (U_{Db}). Although useful, the approach still presents challenges at the conceptual and methodological level, such as if the Pedigree matrix is actually the best way to account for the uncertainties, its definition, and the way in which scores U_{Di} are assigned.

2.3.3 Impact assessment

In the third step, the inventory is translated into environmental impact indicators (EI) across multiple categories aiming to facilitate the interpretation of LCA studies. These indicators determine the severity of the impact caused by the system into the environment. According to the standard ISO 14042, the definition and characterisation of impact categories are mandatory steps to perform the impact assessment, while normalisation and weighting are optional.

Definition and characterisation of environmental categories. The definition of impact categories (EI_{cat}) aims to describe the environmental damage caused by the consumption of natural resources and release of emissions according to the inventory (LCI_{es}). This is achieved by using characterisation factors ($CF_{cat,es}$), which indicate the environmental impact per unit of stressor (e.g. per kg of resource or emission released). The total impact on each category (EI_{cat}), is calculated from Eq. 2.7:

$$EI_{cat} = \sum_{es} LCI_{es} \cdot CF_{cat,es}$$
(2.7)
Where EI_{cat} represents the environmental category c being assessed, LCI_{es} represents the amount of substance es in the inventory, and $CF_{c,es}$ is the characterisation factor of substance es in category cat. Eq. 2.7 assumes a linear relationship between the environmental impact EI_{cat} and the inventory LCI_{es} , which is referred as average modelling. However, this is not necessarily true when scaling processes. Instead, a marginal approach can be adopted to account for the change of the environmental impact with regards to the inventory (Goedkoop *et al.*, 2008).

Characterisation factors can be derived at the midpoint or endpoint level, depending on the stage where the cause-effect chain is analysed. While midpoint indicators typically address the direct impact on the environmental categories, endpoint indicators assess the final consequence of such an impact. For instance, in the release of CO_2 to the environment, a midpoint indicator would measure the concentration of CO_2 in the atmosphere while the endpoint indicator would measure the effects on human health caused by the CO_2 . These approaches are complementary in that the midpoint characterisation has a stronger relation to the environmental flows and a relatively low uncertainty, while the endpoint characterisation provides better information about the environmental relevance of the environmental flows (Huijbregts *et al.*, 2017).

Typical midpoint categories include climate change, stratospheric ozone depletion, ionizing radiation, fine particulate matter formation, photochemical ozone formation, terrestrial acidification, freshwater eutrophication, toxicity, water use, land use, and mineral and fossil resources consumption. Some of the most common methods available are CML 2001 and ReCiPe midpoint. CML 2001 is a methodology developed by the Centre of Environmental Science (CML) of Leiden University in The Netherlands. The characterisation factors developed are representative for the European scale, although they can be extended to the global scale. It evaluates 11 environmental categories in its baseline, referring to the most applied midpoints previously described, and 50 categories in its extended version, which includes

alternative impact categories recommended for extended LCA's (PRé Consultants, 2019). ReCiPe 2016 provides characterisation factors that are representative for the global scale, while maintaining the possibility for a number of impact categories to implement characterisation factors at a country and continental scale, assessing 12 different categories (Huijbregts *et al.*, 2017). In addition, characterisation factors are developed according to three different perspectives or scenarios: the individualistic perspective, the hierarchist perspective, and the egalitarian perspective. In the individualistic perspective, it is assumed a short-term interest, impact types that are undisputed, and technological optimism. The hierarchist approach is based on scientific consensus with regard to the time frame and plausibility of impact mechanisms. Finally, the egalitarian perspective is the most precautionary perspective, taking into account the longest time frame and all impact pathways for which data is available.

Endpoint indicators measure the impact on different areas of protection, such as human health, natural environment, and resource scarcity. At these level, most of the midpoint impact categories are further converted and aggregated into the endpoint indicators. One of the most popular methods at the endpoint level is ReCiPe 2016, which measures the environmental impact in terms of damage to human health, damage to ecosystem quality, and damage to resource availability (Goedkoop *et al.*, 2008; Huijbregts *et al.*, 2017). ReCiPe 2016, as most life cycle assessment methods, assesses damage to human health using the concept of 'disability-adjusted life years' (DALY). The DALY of a disease is derived from human health statistics on life years both lost and disabled, and values for disability-adjusted life years have been reported for a wide range of diseases, including various cancer types, vector-borne diseases and non-communicable diseases. Ecosystems quality can be described in terms of energy, matter and information flows. When such flows are used to characterise ecosystem quality, it can be said that a high ecosystem quality is the condition that allows flows to occur without noticeable disruption by anthropogenic activities. In contrast, a low ecosystem quality

is the condition in which these flows are disrupted by anthropogenic activities. Consequently, it is the level of the disruption that is the most important parameter when ecosystem quality is being measured. It is quite evident that all of these attributes cannot be modelled on all of these levels and dimensions. In the ReCiPe 2016 model, a focus is given to the flows at the species level. This assumption implies that that the diversity of species adequately represents the quality of ecosystems, and the quality of ecosystems is therefore reflected by the species loss during a certain time in a certain area as the basis for the endpoint indicator. The depletion of resources defines the basic needs of future societies as a starting point to determine if there will be sufficient resources in the future. In ReCiPe 2016, this is measured according to the geological distribution of mineral and fossil resources and assesses how the use of these resources causes marginal changes in the efforts to extract future resources.

Normalisation. In the normalisation step, the impacts EI_{cat} are divided by reference values R_{cat} , in order to prioritise or resolve trade-offs between different product alternatives according to Eq. 2.8:

$$N_{cat} = EI_{cat}/R_{cat}$$
(2.8)

This optional step indicates which categories have a major contribution to the overall environmental problem, so attention can be focused on them. Reference values R_{cat} are expressed in equivalent units determined on the basis of region, temporal scale, and capita in the area of study (e.g. CO₂-eq/capita/year).

Weighting. During the weighting, the relative importance of the environmental categories cat is incorporated by the use of weights W_{cat} which allow the aggregation of the normalised impacts N_{cat} into a single indicator TI:

$$TI = \sum_{cat} N_{cat} \cdot W_{cat}$$
(2.9)

This step is highly controversial given the subjectivity used to determine the significance of the environmental categories (Azapagic, 1999). In this category, some methods report the impact in terms of scores or points, such as the Ecoindicator 99, or ReCiPe. Using a different approach, the environmental indicators can be translated into monetary values, resulting in the potential cost to fix the impact caused by a given product or process, also referred as externalities. This approach applies a cost benefit analysis to enable the cross-comparison between different impacts and/or with other economic costs and benefits (Pizzol *et al.*, 2015).

2.3.4 Interpretation

The fourth phase of LCA interprets the impact assessment results in order to suggest modifications that aim for environmental improvements. According to the ISO standard, these improvements are obtained from process innovation, identification of hot spots, and/or sensitivity and uncertainty analysis. When multiple alternatives are being considered, inherent trade-offs among environmental categories difficult the selection of the 'best' process, as it is very unlikely that one option outperforms the rest in all the categories. In section 2.6 we address the use of multi-criteria decision making tools to provide further insights in the comparison and help in the raking of alternatives.

LCA has become one of the main tools in the identification of sustainable processes in the chemical industry and the literature regarding the application of LCA in process design is vast. Examples include the creation of new facilities or the retrofitting of the existing ones in areas like bioprocesses (Van Boxtel *et al.*, 2015), cement and concrete (Chen *et al.*, 2010), the pharmaceutical industry (Jimenez-Gonzalez and Overcash, 2014), and energy supply technologies (Varun *et al.*, 2009), (Gerber *et al.*, 2011), among many others. Yet, it still presents some limitations related to the subjectivity in aspects like the system boundaries, the goal definition and scope as well as the fact that the LCA impacts are often determined by data with unknown reliability (Pieragostini *et al.*, 2012).

2.4 Process modelling

PSE has played a significant role in the development of decision-making tools for the chemical supply chain, from the molecular to the enterprise level (Grossmann and Westerberg, 2000). The quest for sustainability, as expressed by Bakshi and Fiksel (2003), requires a broadening of this definition from the 'chemical supply chain' to the 'chemical value chain'.

Process modelling started as an entirely experienced-based approach to then evolve to a heuristics-based process. As the computational power increased, sophisticated modelling and optimisation methods were developed, supplementing the previous practices and making the use of computational tools a common practice. Among them, process simulators became a standard tool for process engineers during the modelling of current and new processes. Two main approaches are identified in commercial process simulators: sequential modular and equation-oriented.

The sequential modular approach is the most popular method used in process simulators, and implies the use of stand-alone blocks that define a unit or operation, and which outputs are used as inputs for the next block. This approach enables the use of tailored initialisation techniques for each module that facilitate the convergence of the entire flowsheet (Caballero *et al.*, 2005; Skiborowski *et al.*, 2015). Their methodology presents a natural and efficient way to model an acyclic process, being easy to construct, debug, and understand. Its downside, however, is that the algebraic expressions on which it is based are seldom explicitly available, forcing to treat the simulation as a black box model (e.g. Aspen-HYSYS, Pro II, etc.). This makes this approach very inefficient when recycling streams are included, as some level of iteration is required for its solution and the most efficient methods rely on the full derivative information (Biegler, 1983). Since process modules are essentially input-output black boxes, the gradients are often calculated by perturbing the simulation model in a given point, which creates numerical noise

and convergence problems as iterations proceed. In addition, this approach is time-consuming and potentially inaccurate since modules contain function and derivative discontinuities.

The equation-oriented approach has proved to be more efficient than the sequential-modular, as it offers more flexibility in the definition of degrees of freedom, multiple recycles do not slow down convergence, and powerful optimisation techniques are available (Biegler et al., 1997). The availability of first and second derivatives enables the use of very efficient nonlinear programming (NLP) algorithms capable to handle more than 100,000 equations (Dowling and Biegler, 2015). The inclusion of discrete variables also represents an advantage over the sequential modular approach, as they can be embedded in equation-oriented frameworks using disjunctive programming or mixed integer nonlinear programming (MINLP) algorithms. The limitations related to this approach are that it typically requires a deep understanding of the model by the process engineer, can be difficult to debug and may fail to find a solution if initial guesses are poor, making the optimisation task challenging (Pattison et al., 2017; Steimel and Engell, 2016). These characteristics have hindered the broad spread of equation-oriented methods in process simulation, although great progress is being achieved through their incorporation in software such as Aspen Plus (AspenTech, 2014), gPROMS (PSE Limited, 2019), or the recently launched and open-source modelling software IDAES PSE Framework (2019).

2.5 Flowsheet optimisation

Given a process flowsheet conformed by multiple unit operations and connecting streams, flowsheet optimisation aims to identify the values for which the design and operating variables minimise an objective. The sustainable process design problem is further complicated by the need to incorporate multiple sustainability criteria into the analysis (Guillén-Gosálbez *et al.*, 2008). A typical optimisation problem in sustainable problems can be written as:

$$\min[f_1(\mathbf{w}), f_2(\mathbf{w}), \dots, f_i(\mathbf{w})]$$
(2.10)

s.t.
$$g(\mathbf{w}) \le 0$$
 (2.11)

$$\mathbf{h}(\mathbf{w}) = \mathbf{0} \tag{2.12}$$

$$\mathbf{c}(\mathbf{w}) = \mathbf{0} \tag{2.13}$$

Where **w** represents all the variables of the process, $f_i(\mathbf{w})$ represents the objectives to be minimised (economic and environmental performance), the inequality constraints $g(\mathbf{w})$ represent limits on process operation, $h(\mathbf{w})$ are the equations simulated by the process, and $c(\mathbf{w})$ are the conditions imposed by the designer. In addition, variables **w** are typically divided in **w1** and **w2**, where **w1** represents process decisions (degrees of freedom), and **w2** is calculated from c and h after **w1** has been defined. The optimisation problem in Eqs. 2.10-2.13 typically results in NLPs, which are nonconvex and exhibit multiple (suboptimal) solutions even when dealing with simple flowsheets (Bongartz and Mitsos, 2019).

Simulation-optimisation approaches offer an appealing framework to decouple the sequential-modular modelling task from the optimisation (Caballero *et al.*, 2005; Ibrahim *et al.*, 2017; Skiborowski *et al.*, 2015). Following this approach, an optimisation algorithm interrogates the simulator to get the value(s) of the objective function(s) and check that all the constraints are satisfied. After a set of iterations, a solution is finally reported when a termination criterion is met. In this context, derivative-free optimisation algorithms are particularly appealing, as they are known to perform well in problems where discontinuous, nondifferentiable, or highly nonlinear expressions are present. In addition, certain algorithms can guarantee an 'exact' optimal solution using methods such as trust-region, or the modified Nelder-Mead simplex algorithm (Rios *et al.*, 2013). Even when these techniques are not applied to guarantee optimality, the computational performance of derivative-free algorithms without sacrificing much in terms of the accuracy of the final solution (Coello Coello *et al.*, 2007).

Among them, evolutionary algorithms (EA) are the most well-known techniques (Skiborowski et al., 2015). EA fall within the category of stochastic algorithms, which rely on a set of points to explore the design space. These methods require a function assigning a fitness value to every solution, also referred as individual. According to the evaluation of the fitness function, the algorithm modifies the initial set of individuals (population) using mutation and crossover functions, and determines which individuals will survive in the next generation. Given that the 'starting point' of the algorithm is the initial population, the quality of the solution generated depends on the initial individuals generated; nevertheless, the mutation and crossover functions attempt to improve the fitness of the individuals after each generation, making the algorithm less sensitive to the initial population. When multiple objectives are considered, the evaluation of the population allows to find several members of the Pareto frontier in a single 'run' of the algorithm. The initial population is then modified as iterations proceed according to the internal ranking of the population, which is modified by the mutation and crossover functions (Coello Coello *et al.*, 2007). The application of EA algorithms in process design has increased over the last years, mainly due to their appealing properties when coupled with process simulators (Coello Coello et al., 2007; Henao and Maravelias, 2011; Ibrahim et al., 2017; Otte et al., 2016; Skiborowski et al., 2015; Valadi and Siarry, 2014). However, when complex processes are analysed, care must be placed on several issues. These include the handling of constraints that cannot be included explicitly in the simulation, the selection of the decision variables and their boundaries, and the initialisation of the entire flowsheet. Additionally, this approach can be hard to apply when the flowsheet requires a long time to converge or fails to do so for some values of the decision variables proposed by the optimisation algorithm as iterations proceed (Ibrahim et al., 2017; Skiborowski et al., 2015).

The MINLPs arising in the equation-oriented approach are typically solved via deterministic optimisation approaches based on branch and bound and outer approximation. These methods

cannot guarantee convergence to the global optimum due to the non-convexities in the MINLP. When the global optimum is desired, deterministic global optimisation methods shall be applied, such as spatial branch and bound. The main characteristic of this algorithm is the tight relaxations of the functions, which converge to the original functions when increasingly smaller partitions of the domain are considered (Bongartz and Mitsos, 2019). In this approach, convex and concave relaxations are constructed using methods such as interval extensions or McCormick relaxations, to then solve an optimisation problem which provides a lower bound. Using the solution of this problem as starting point, the original problem is solved and an upper bound is generated. When the lower and upper bound are within a tolerance ε , the search is finished. Otherwise, the search space is partitioned and the process repeated. Recent advances in global optimisation for solving MINLPs are presented by Boukouvala et al. (2016). When the models are multi-objective, they are first reformulated using an auxiliary single-objective formulation, which is solved iteratively for a set of values of the auxiliary parameters (weights on objectives in the weighted-sum method and epsilon parameters in the epsilon-constraint algorithm). A disadvantage of deterministic algorithms is that the demand of computational resources increases exponentially with the number of objectives. An additional challenge when using these algorithms concerns the need to devise a proper initialisation scheme to identify feasible solutions.

2.6 Surrogate modelling

This approach presents an appealing alternative to overcome some of the limitations of simulation-based or equation-oriented optimisations that arise when dealing with complex and computationally expensive systems (Biegler *et al.*, 2014; Boukouvala *et al.*, 2015; Caballero and Grossmann, 2008; Cozad *et al.*, 2014). A surrogate model aims to learn a mapping $y = f(\mathbf{w})$ based on known observations, which can be derived from computer or physical experiments/measurements. These surrogates make the optimisation task easier at the expense

of sacrificing, to some extent, the accuracy of the model and quality of the final solution (Biegler *et al.*, 2014; Boukouvala *et al.*, 2015). A second application of surrogate models arise when physical models are not available (or fail) to represent a system but data are at disposal to obtain a desired scalar output y from a vector of inputs \mathbf{w} . The construction of a surrogate model typically involves three stages: data collection and preparation, parameter estimation and training, and model testing (Forrester *et al.*, 2008).

The procedure for the data collection and preparation is dependent on the source of data. While experiment-based data require the use of adequate sampling methods to generate the set of inputs and outputs across the design space, measurement-based models have to deal with issues like missing data and identification of outliers. An additional challenge in both cases is the noise of the data.

When dealing with the structure of the surrogate, different approximations have been proposed in literature: linear, polynomial, kriging, support vector regression or artificial neural networks (Gonzalez-Garay and Guillen-Gosalbez, 2018). Although any such procedure involves the solution of an optimisation problem, the approach and the corresponding algorithms are rather diverse. For instance, some advantages of linear models are that the user can observe the interactions between the different inputs, resulting in models that are easy to analyse and interpret. Moreover, calculation time for such models is rather low. However, a linear combination of inputs may not be the most adequate way to model complex functions. Thus, the results of such models on complex functions may not be satisfying. Another method refers to neural networks, which are models from the field of computational intelligence mimicking natural systems and processes. The neurons of these models are weighted transformation functions and the ability to model complex structures is given by the connectivity among them. In the simplest structure, neurons are ordered in layers and neurons within layers are connected forward and/or backward to other layers. Several algorithms for

learning the weights of neurons are available to achieve the best fit from the input (layer) to the output (layer). Neural networks produce excellent results in approximation and especially classification tasks. However, they also provide results that are comparably complex and thus difficult to interpret. In the case of Kriging, its outstanding features are an uncertainty measure for the prediction and its suitability for complex functions. However, due to the computational effort needed, Kriging models do not perform well for high dimensional data. Although the selection of the surrogate model depends on the nature of the problem and sampled points, Bartz-Beielstein *et al.* (2016) present some useful guidelines for their selection. For instance, linear models may easily do overfitting of the data when the number of samples is low, and also may not be sufficient to model highly nonlinear problems. Kriging is recommended for problems with less than 20 variables, continuous problems, and not very high number of samples. If the cost of evaluations is rather high, a complex and powerful model should be used, such as Kriging, support vector machine, or neural networks. If it is low, cheaper models could be more appropriate, such as linear and polynomial models.

Any model structure, $\hat{f}(\mathbf{w})$, represents a parameter estimation problem. The most well-known criteria for the fitting of the data is given by the least squares criterion:

$$\min \sum_{si} (y_{si} - \hat{f}(\mathbf{w}))^2$$
(2.14)

Where si represents the number of observations, y_{si} the scalar output at each observation, and **w** the vector of parameters in the model. Modifications of this method include the maximum likelihood estimation and cross-validation (Forrester *et al.*, 2008).

The final stage related to the construction of the surrogate is the testing of the model. Here, a randomly selected subset of the observations n_t should be set aside for model testing, where the

root mean squared error (RMSE) and correlation coefficient (r^2) are the most common metrics to measure the accuracy of the model:

RMSE =
$$\sqrt{\frac{\sum_{i=0}^{n_{t}} (y_{si} - \hat{y}_{si})^{2}}{n_{t}}}$$
 (2.15)

$$r^{2} = \left(\frac{n_{t} \sum_{i=0}^{n_{t}} y_{si} \cdot \hat{y}_{si} - \sum_{i=0}^{n_{t}} y_{si} \sum_{si=0}^{n_{t}} \hat{y}_{si}}{\sqrt{\left[n_{t} \sum_{si=0}^{n_{t}} y_{si}^{2} - \left(\sum_{si=0}^{n_{t}} y_{si}\right)^{2}\right] \left[n_{t} \sum_{si=0}^{n_{t}} \hat{y}_{si}^{2} - \left(\sum_{si=0}^{n_{t}} \hat{y}_{si}\right)^{2}\right]}}\right)^{2}$$
(2.16)

The optimisation of surrogate models presents multiple challenges, such as multimodality during the optimisation given its typical non-convexity form, the inclusion of constraints, or the inherent noise in functions and/or constraints. Multiple authors have proposed alternatives to tackle these problems. In an aim to reduce the complexity of the surrogates without sacrificing its accuracy, Cozad et al. (2014) presented their approach 'Automated Learning of Algebraic Models for Optimisation' (ALAMO). In their method, an initial low complexity model is built and its accuracy is further improved through adaptive sampling including polynomial, multinomial, exponential, and logarithmic basis functions. Caballero and Grossman (2008) presented an algorithm for the use of surrogate models in modular flowsheet optimisation, focusing on noisy implicit functions based on a kriging estimator. A similar approach was later applied by Ouirante et al. (2015) in the modelling of distillation columns. In their ARGONAUT framework, Boukouvala and Floudas (2016) addressed the global optimisation of constrained systems incorporating model structures such as linear, quadratic, signomial, radial basis, and kriging. In the optimisation of crude oil distillation units, Ibrahim et al. (2018) presented a model based on artificial neural networks, feasibility constraints constructed using a support vector machine, and pinch analysis for heat integration. Mogilicharla et al. (2015) provided an example of surrogate-based multi-objective optimisation in the polymerisation of vinyl acetate. Their approach uses a population-based optimisation algorithm (NSGA-II) with kriging as the model structure to optimise the performance of the reactor. Henao and Maravelias (2011), presented a superstructure-based strategy where unit models were replaced using surrogate models built from data generated via commercial process simulators. Despite the progress in the area and the multiple applications within the chemical sector, surrogates are still scarcely applied with a sustainability focus.

2.7 Multi-criteria decision-making

The solution of a Multi-Objective Optimisation (MOO) problem is given by a Pareto frontier rather than by one single optimal solution, the latter being the case in single-objective problems. All the solutions contained in the Pareto frontier are optimal and have the property that one objective cannot be improved without worsening another one. The last step in the MOO of sustainable chemical processes is the selection of the best solution among the Pareto set, a step that requires ranking the different criteria considered. Since these criteria tend to be different in dimension and units of measure, it is necessary to resort to decision-analysis tools. Multi-criteria decision analysis tools (MCDA) offer a systematic analysis and modelling of the different objectives and provide guidance to decision-makers in the selection of the most suitable option.

One way to tackle multi-criteria decision-making problems is articulating the preferences and assigning weights of importance to the sustainability indicators (i.e. economic, environmental and social). This framework consists of four main steps: i) criteria selection, ii) criteria weighting, iii) evaluation and iv) aggregation. Three main approaches are considered in this category (Huang *et al.*, 2011): Multi-attribute utility theory (MAUT), outranking approaches, and the Analytical Hierarchy Process (AHP). All of them require the same mathematical inputs: scores in a number of dimensions on the basis of which the different alternatives are assessed and weights related to the different criteria among the dimensions. The differences arise in how

the values are assigned and combined. Additionally, there are different data requirements based on the knowledge of the process so the final values have different mathematical properties.

Different MCDA approaches are available to select the best option among the Pareto points (Azapagic *et al.*, 2016; Bortz *et al.*, 2014; Huang *et al.*, 2011; Miettinen and Hämäläinen, 1997), which often rank the alternatives on the basis of weights that reflect the decision-makers' preferences. Although the previous methods are relatively easy to implement, they present difficulties at philosophical and conceptual levels. One of them is the fact that in many cases, the assessment considered to determine the preferences lacks of strong technical foundations. This could mislead the results or make them meaningless, thereby interfering the process among stake-holders which is crucial to decision making (Galán-Martín *et al.*, 2016).

A different method to analyse the Pareto frontier is Data Envelopment Analysis (DEA), which is a mathematical programming technique that identifies the best practices across similar Decision Making Units (DMUs) converting multiple inputs into multiple outputs. DEA links the outputs generated by each DMU to its corresponding inputs to determine efficiency scores and improvement targets. The first step of the methodology is to build a convex envelope of the entire set of DMUs being assessed. This envelope is also known as 'efficient frontier' or best 'practice frontier', and all the DMUs lying on this frontier are classified as 'efficient', while the rest are identified as 'inefficient'. The level of 'efficiency' is given by the calculated scores for each DMU, which quantify the ratio of weighted outputs to weighted inputs. In a second step, DEA determines targets for the 'inefficient' units to become 'efficient' via its projection to the efficient frontier (Charnes *et al.*, 1978). In the context of chemical process design, a DMU refers to one process design analysed under multiple sustainability criteria such as total cost, global warming potential, human toxicity, etc. DEA provides efficiency scores for all the DMUs. Those with an efficiency of one are deemed efficient and ideally represent the best practices. defined such that, if attained, would make them optimal. DEA also allows to rank the efficient units by applying the concept of super-efficiency. These characteristics allow the use of DEA to: i) filter and rank the optimal solutions of the Pareto frontier, and ii) to determine improvement targets of a given process identified as inefficient (in terms of sustainability performance).

As described, the model of DEA is based on the concept of efficiency, which is defined as the ratio between the weighted sum of s outputs y_{rj} (r = 1, ..., s) and the weighted sum of m inputs x_{lj} (l = 1, ..., m):

$$\max \theta_{o} = \frac{\sum_{r=1}^{s} u_{r} y_{ro} - u_{o}}{\sum_{l=1}^{m} v_{l} x_{lo}}$$
(2.17)

Where multipliers u_r and v_l denote weights given to inputs x_{lo} and outputs y_{ro} , respectively; u_o is a variable that imposes a convexity condition. To enforce the productivity ratio to be less or equal to 1, constraint 2.18 is included in the model:

$$\sum_{r=1}^{s} u_r y_{rj} / \sum_{l=1}^{m} v_l x_{lj} - u_o \le 1; \quad j = 1, ..., n$$
(2.18)

$$u_r, v_l \ge \varphi; \quad \forall l, r; \quad \theta_o, u_o \text{ unconstrained}$$
 (2.19)

In the model, multipliers u_r and v_l are optimised in order to maximise the efficiency value of DMU_o, hence, weights are optimised rather than given by decision-makers. As formulated by Charnes *et al.* (1978), Eq. 2.19 forces them to be strictly positive using the 'non-Archimedean infinitesimal' value φ , which is smaller than any positive real number, and, in fact, the product of φ by any real number remains smaller than any positive number. A more detailed treatment of these non-Archimedean elements can be found in Arnold *et al.* (1998).

The technical efficiency of a DMU, θ_0 (o = 1, ..., c), is obtained by solving Eqs. 2.17-2.19, also referred as the BCC model (Banker, 1984). This nonlinear model assumes variable returns to scale (VRS), which implies that changes in outputs are not proportional to changes in inputs.

From the solution of the model, those designs with an efficiency $\theta_0 = 1$ are considered efficient, while those with an efficiency $\theta_0 < 1$ are considered inefficient.

DEA can be applied using either input or output oriented models (Cook and Seiford, 2009). The input-oriented model aims to minimise the inputs (e.g. total annualised cost, global warming potential, etc.) while maintaining the same level of outputs (e.g. profit, amount of products and by-products produced, etc.). The models here described refer to the input oriented approach. The nonlinear model in Eqs. 2.17-2.19 can be reformulated into its equivalent linear program by setting to one the denominator of the efficiency in 2.17 (Banker, 1984):

$$\max \sum_{r=1}^{s} u_r y_{ro} - u_o \tag{2.20}$$

$$\sum_{l=1}^{m} v_l x_{lo} = 1$$
 (2.21)

$$\sum_{r=1}^{s} u_r y_{rj} - u_o - \sum_{l=1}^{m} v_l x_{lj} \le 0; \quad j = 1, ..., n$$
(2.22)

 $u_r, v_l \ge \varphi; \quad \forall l, r; \quad \theta_o \text{ unconstrained}$ (2.23)

Improvement targets. Similarly, model in Eqs. 2.20-2.23 can be reformulated into a partner dual problem, which provides both, the efficiency scores and improvement targets for the inefficient units. The dual problem is expressed as follows (Banker, 1984):

$$\min \theta_{o} - \varphi \left(\sum_{r} s_{r}^{+} + \sum_{l} s_{l}^{-} \right)$$
(2.24)

$$\sum_{j} \lambda_{j} x_{lj} + s_{l}^{-} = \theta_{0} x_{lo}; \quad l = 1, ..., m$$
 (2.25)

$$\sum_{j} \lambda_{j} y_{rj} - s_{r}^{+} = y_{ro}; \quad r = 1, ..., s$$
 (2.26)

$$\sum_{j=1}^{n} \lambda_j = 1 \qquad j = 1, \dots, n \tag{2.27}$$

$$\lambda_{j}, s_{l}^{-}, s_{r}^{+} \ge 0; \quad \forall i, j, r; \quad \theta_{o} \text{ unconstrained}$$
 (2.28)

Where s_r^+ is a slack variable representing the additional amount of output r required by DMU_o to become efficient; s_1^- is a slack variable denoting the amount of input l to be reduced to become efficient; and λ_j are the linear weights used to project the inefficient units onto the efficient frontier using a combination of efficient units. When $\theta_o = 1$ and $(\sum_i s_i^- + \sum_r s_r^+) =$ 0, the DMU is said to be strongly efficient. If $\theta_o = 1$ but $(\sum_i s_i^- + \sum_r s_r^+) \neq 0$, the DMU is deemed as weakly efficient. If $\theta_o < 1$, the DMU is inefficient.

In DEA, the improvement target for input l in a given DMU is expressed as:

$$\sum_{j=1}^{n} \lambda_j x_{lj} = \theta_o x_{lo} - s_l^-$$
(2.29)

Multipliers preferences. DEA also allows to define constraints on multipliers u_r and v_l according to the decision-makers' preferences. These constraints can be included directly in the primal model described in Eqs. 2.20-2.23. However, to include such constraints in the dual model and obtain the improvement targets, it is necessary to determine an Assurance Region (AR) (Cook and Seiford, 2009). The AR is defined as the feasible region in which the multipliers u_r and v_l will satisfy the new constraint. A technique to determine AR is the coneratio method (Thompson *et al.*, 1995), where a polyhedral convex cone is defined to restrict the efficient frontier. The concept of cone-ratio method is shown in Figure 2.1.

This cone is mathematically expressed as a matrix D, which contains the preferences on the multipliers for the original inputs and outputs:

$$D = \begin{pmatrix} A & 0\\ 0 & B \end{pmatrix}$$
(2.30)

Where A defines the constraints imposed on the multipliers of inputs x_{lo} , while B defines constraints imposed on the multipliers of outputs y_{ro} . The cone-ratio, expressed as matrix D, is further used to transform the original inputs and outputs of the model as follows:

$$D\begin{pmatrix} x_{lo} \\ y_{ro} \end{pmatrix} = \begin{pmatrix} Ax_{lo} \\ By_{ro} \end{pmatrix} = \begin{pmatrix} \overline{X} \\ \overline{Y} \end{pmatrix}$$
(2.31)

By substituting Eq. 2.30 in 2.31, the original inputs x_{lo} and outputs y_{ro} are transformed into \overline{X} and \overline{Y} , respectively. Eqs. 2.24-2.28 are then solved by replacing x_{lo} and y_{ro} by \overline{X} and \overline{Y} . The solution of the model indicates the efficient units.



Fig. 2.1 Graphical representation of the assurance region in DEA. The assurance region is determined by the blue region and reflects the preferences on the multipliers. Units falling out of the efficient frontier contained in the assurance region are inefficient. This also applies to units identified as efficient by model in Eqs. 2.20-2.23 without considering the assurance region, such as units A and D.

Ranking of efficient units. DEA can also be applied to further rank the Pareto points of the model. This is achieved by using a super-efficiency model (Andersen and Petersen, 1993), which is essentially the same as the one described in Eqs. 2.24-2.28, but in which the summation of lambdas excludes the efficient unit being assessed:

$$\sum_{j=1,j\neq j'}^{m} \lambda_j x_{lj} + s_l^- = \theta_j x_{lj'},; \quad l = 1, ..., m$$
 (2.32)

$$\sum_{j=1,j\neq j'}^{s} \lambda_{j} y_{rj} - s_{r}^{+} = y_{rj'}; \quad r = 1, ..., s \tag{2.33}$$

In an input-oriented model, the super-efficiency can be seen as the input savings achieved by an efficient DMU, which are measured by the extent to which the efficient frontier changes when such unit is removed. The modified DEA model provides a super-efficiency score $\theta_{SE,j'}$ that is always greater or equal to one and can be used to further discriminate among efficient solutions.

2.8 Literature gaps

The modelling and optimisation of chemical processes using sustainable indicators present multiple challenges. At the LCA level, limitations are related to the subjectivity in aspects like the system boundaries, the goal definition and scope, as well as the fact that the LCA impacts are often determined by data with unknown reliability. A limitation at the conceptual level, is that standard LCAs are useful to compare and rank alternatives, but cannot determine whether they are truly sustainable because there are no reference values available to interpret the results. Therefore, they fail to evaluate the global implications of technologies on the environment.

With regard to the process modelling, we observe a trade-off between the equation-oriented and sequential modular approaches. While the equation-oriented approach has generally proved to be more powerful than the sequential modular, as it allows the use of powerful optimisation techniques, its use is typically restricted to experts. In addition, good initial estimates are required to reach a feasible solution. In the case of the sequential modular approach, despite their formulation is still non-convex and nonlinear, they enable the use of tailored initialisation techniques and solution algorithms that facilitate the convergence of the flowsheet. This, combined with its easy application, make it the most widely approach used in commercial simulators. Their downside, however, is that the algebraic expressions on which they are based are seldom explicitly available, hampering the direct application of deterministic derivativebased optimisation solvers.

An appealing alternative to overcome these limitations is the use of surrogate models, which are built from data generated with the original simulation or coming from experiments or plant measurements. These surrogates make the optimisation task easier at the expense of sacrificing, to some extent, the accuracy of the model and quality of the final solution. Despite the progress in the area and the multiple applications within the chemical sector, surrogates are still scarcely applied with a sustainability focus.

The sustainable process design problem is further complicated by the need to incorporate multiple sustainability criteria into the analysis, which leads to MOO problems whose complexity grows as the number of objectives increases. A natural conflict arises at this point between an easier solution procedure and interpretation of results when omitting indicators, and more complex calculations and analysis when considering more sustainability criteria. The solution of a MOO is given by a Pareto which has to be further analysed in order to determine the option with the best performance. MCDA tools provide methods relatively easy to implement, although they present difficulties at philosophical and conceptual levels. One of them is the fact that in many cases, the assessment considered to determine the preferences lacks of strong technical foundations.

In recent years, different frameworks have emerged that differ in the modelling approach and solution procedure. Some make use of simplified expressions based on rigorous thermodynamic models (surrogate models) (Boukouvala *et al.*, 2015; Boukouvala and Floudas, 2016; Lin *et al.*, 2017; Quirante *et al.*, 2017; Ye and You, 2016). Other works focus on single-objective optimisation, trying to improve the conceptual design of the flowsheets by identifying 'hotspots' and replacing the units responsible for most of the impact (Bertran *et al.*, 2017; Babi *et al.*, 2015; Tula *et al.*, 2017). Other frameworks focus on multi-objective optimisation,

providing a Pareto frontier which has to be further analysed to identify the most promising designs (Azapagic and Clift, 1999; Helmdach *et al.*, 2017; Yue *et al.*, 2016). In these methodologies, the analysis of the Pareto frontier is typically omitted. An exception is the work by Bortz *et al.*(2014), where the approach presented includes the modelling, MOO and analysis of the Pareto frontier.

From the different approaches presented in the literature, we identified a clear need for methods capable of accurately evaluate and optimise the sustainable performance of chemical processes while making an efficient use of computational resources.

The sustainable development of the sector has become a priority, and strong efforts are required from industry and academics to identify the most viable pathways and focus efforts to reach the SDGs. However, efforts at the basic science level seem to be decoupled from process modelling during the development of new technologies and improvement of others. While new and innovative processes will come only through a paradigm shift at the basic-science or engineering level, the incorporation of process modelling and optimisation to assess new developments in these fields is crucial to understand the complex interactions between industry, society, and ecosystems. Despite collaborations between basic sciences and engineering have become more popular, the use of these mathematical tools to inform and guide research efforts and policymaking in the transition toward a sustainable industry is still limiting in various areas.

2.9 Thesis contributions

In this thesis, we address sustainable development in the chemical industry through the application of mathematical programming techniques and life cycle methods. The main objective of this project is to develop a systematic approach to design sustainable chemical processes by adopting life cycle thinking while guiding research efforts from catalysis to plant to policymaking. The methods and contributions presented focus mainly on the use of commercial process simulators coupled to LCA and mathematical programming tools to

quantitatively determine the sustainability level of a process in terms of economic and environmental criteria. The methods developed are applied in relevant case studies that promote sustainability in the sector. In this context, we address concepts such as circular economy in Chapter 3, waste chemicals valorisation in Chapter 4, and the use of renewable raw materials in Chapters 5 and 6.

Chapter 3 presents the methodology applied in the remaining chapters for the technoeconomic and environmental assessment of chemical processes. This approach consists in the use of heuristics and energy integration (heat waste recovery and heat integration) to enhance flowsheet performance. The solution of energy and mass balances is done through commercial process simulators, which allows the further economic and environmental assessment. We present the application of the methodology in a novel case study analysing the potential benefits of the circular economy in the plastics sector. The process studied refers to the recovery of ethylene from the pyrolysis of waste polyethylene. The material of this chapter heavily relies on the contribution submitted to the following peer-reviewed journal, in which the candidate assessed and discussed the overall process model, modelled the refrigeration cycle, performed the environmental assessment and contributed in the generation of Figures and writing of the manuscript. A statement declaring equal contributions between first author and the candidate has been included in the original manuscript:

Somoza-Tornos, A., Gonzalez-Garay, A., Pozo, C., Graells, M., Espuña, A., Guillén-Gosálbez, G. Realizing the Potential High Benefits of Circular Economy in the Chemical Industry: Ethylene Monomer Recovery *via* Polyethylene Pyrolysis. *ACS Sustainable Chemistry and Engineering*.

Chapter 4 addresses the importance of including process and environmental uncertainties to traditional assessments. In this chapter, we perform flowsheet optimisation using heat integration and a sensitivity analysis on distillation columns and recycling streams. The uncertainty modelling is done *via* Monte Carlo analysis, and the approach is automated by coupling a process simulator with external routines to solve the heat integration problem and modify the uncertain parameters accordingly. The methodology is presented in a relevant case study for the valorisation of a waste chemical to boost the bioeconomy in the sector. The process analysed is the production of propylene glycol from waste biodiesel glycerol. The material of this chapter is based on the following peer-reviewed publication:

Gonzalez-Garay, A., Gonzalez-Miquel, M., & Guillen-Gosalbez, G. (2017). High-Value Propylene Glycol from Low-Value Biodiesel Glycerol: A Techno-Economic and Environmental Assessment under Uncertainty. *ACS Sustainable Chemistry and Engineering*, *5*(7), 5723–5732.

Chapter 5 presents a general famework for the modelling and optimisation of chemical processes. This chapter extends on the modelling presented in Chapters 3 and 4 by including surrogate modelling to enhance the optimisation stage. To attain the best performance of the process, multi-objective optimisation is included usign a genetic algorithm. An objective-reduction technique is incorporated to reduce the computational effort without loss of information. Finally, the Pareto front generated during the optimisation is further analysed using Data Envelopment Analysis (DEA) as multi-criteria decision analysis tool. One of the main advantages of this technique is the optimisation of the weights of each indicator, avoiding the subjectivity typical in this assessments. The capabilites of the framework are demonstrated in a case study for the production of methanol from CO₂ and hydrogen. The material of this chapter appears in the following peer-reviewed publication:

Gonzalez-Garay, A., & Guillen-Gosalbez, G. (2018). SUSCAPE: A framework for the optimal design of SUStainable ChemicAl ProcEsses incorporating data envelopment analysis. *Chemical Engineering Research and Design*, *137*, 1711–1716.

In Chapter 6, we extend the framework introduced in Chapter 5 to a multi-scale model. In this approach, we propose the use of an ideal catalytic model during the process modelling and compare its performance against a catalyst-based process. The primary objective of this comparison is to identify potential catalyst improvements and direct research efforts on the basis of an entire flowsheet performance and not only on the reactor. In addition, we also introduce the application of 'Planetary boundaries' in the assessment of chemical processes. The main contribution of this concept is to allow an absolute quantification of the environmental performance at a global scale while providing limits that should not be transgressed to preserve the Earth's natural behaviour. Overall, the work presented in this chapter allows an assessment from catalysis development to plant design to planet impact. The framework is presented in the same case study as Chapter 5, but addressing now the global environmental implications that the use of CO₂ and renewable hydrogen play to achieve sustainable development in the sector. The material of this chapter is based on the contribution published in the following peer-reviewed journal:

Gonzalez Garay, A., Frei, M., Alqahtani, A., Mondelli, C., Guillen-Gosalbez, G., Perez-Ramirez, J., 2019. Plant-to-planet analysis of CO2-based methanol processes. *Energy & Environmental Science*. doi:10.1039/C9EE01673B

Chapter 7 presents the overall conclusions of this thesis and potential future directions.

Chapter 3 METHODOLOGY AND CIRCULAR ECONOMY IN THE PLASTICS SECTOR

This chapter presents the methodology followed for the coupling of process modelling and optimisation with Life Cycle Assessment (LCA) during the evaluation of chemical processes. The methodology is applied in a relevant case study based on the concept of circular economy, in which we analyse the potential benefits of recovering ethylene from waste polyethylene (PE). This illustrates the capabilities of combining process systems engineering tools with LCA to measure the level of sustainability of emerging technologies to finally attain sustainable development within the sector.

3.1 Background and problem statement

The need to develop a sustainable chemical industry has spurred substantial research for replacing petroleum-based feedstocks by renewable ones (Clark *et al.*, 2015). Several studies have already demonstrated that bio-based chemicals can meet the quality standards required within the industry while at the same time bringing significant environmental benefits (Farrán *et al.*, 2015; Isikgor and Becer, 2015). As a result, economies around the world are implementing policies and legislations to promote more sustainable practices on the basis of these and similar concepts (European Commission, 2012; The White House, 2012). In addition,

the use of waste products in the chemical sector, such as plastics or captured CO₂, offers the opportunity to reduce environmental impacts while keeping profit margins high.

The development of a sustainable sector requires the assessment of alternative technologies and their impact within the chemical industry. Process systems engineering enables the understanding of sustainability performance in chemical processes *via* techno-economic and environmental assessments, coupling process modelling techniques and optimisation with Life Cycle Assessment (LCA) (Azapagic, 1999; Adisa Azapagic and Clift, 1999). When coupled with process modelling and optimisation, LCA provides a full representation and scaling of a process across economic and environmental dimensions, rendering insights about the improvement of sustainability performance in a process or product.

In this chapter, we aim to present the state of the art methodology followed by practitioners in the coupling of process modelling and optimisation with LCA to assess chemical processes. The methods presented in this chapter also lay the foundation to discuss the contributions achieved in this thesis during the following chapters. This approach is further clarified in Section 3.3, where we present a relevant case study focused on circular economy, which analyses ethylene recovery from waste polyethylene (PE). The study compares the PE pyrolysis against both, the business as usual (BAU) process for the production of ethylene, and two conventional end-of-life alternatives for the treatment of waste PE.

The rest of this chapter is organised as follows. In section 3.2, we present in detail the methodology followed in the process, economic and environmental modelling of chemical processes. In Section 3.3, we apply this methodology in the production of ethylene from waste PE and show the potential benefits of the circular economy in the chemical sector. Finally, the conclusions of this contribution are addressed section 3.4.

3.2 Methodology

Figure 3.1 summarises the methodology followed to perform a techno-economic and environmental assessment. In essence, a chemical process is developed using traditional equipment models and standard heuristics, heat waste recovery techniques, and heat integration. Flowsheet optimisation, focusing on a sequential modular approach, is addressed at different levels in each chapter of this thesis. In particular, the use of advanced flowsheet optimisation techniques is addressed in Chapter 5. To assess the sustainability of a process, we focus on economic and environmental criteria. While the economic performance of a process is measured using the total annualised cost (TAC) (Towler and Sinnott, 2013), the environmental performance is assessed following the LCA standard described by the International Organisation for Standardisation (ISO, 2006).



Fig. 3.1 General methodology to assess the techno-economic and environmental performance of chemical processes.

3.2.1 Process modelling and energy integration

The desire to achieve sustainable development in the sector has motivated scientists to explore alternative routes for the production of chemicals, ideally following the 12 principles for green chemistry. After a potential sustainable route has been identified at the lab scale, we

built a rigorous process simulation adhering to the 12 principles of green engineering, where process integration is essential to attain sustainable designs. To do so, the process is modelled using commercial simulators based on a sequential modular approach, such as Aspen and Aspen-HYSYS. Thermodynamic packages are selected according to the operating conditions of the processes and the nature of the chemical components present in the simulation. A crucial section of the flowsheet corresponds to the modelling of the reactor, where a detailed kinetic model is highly desired to get a deeper understanding of the process. However, these models are often missing in the literature and yield estimations have to be made from either approximated models using parameter estimation or by directly applying the yields reported at the experimental stage. Despite these approaches increase the uncertainty of the results, they still allow a meaningful estimation of the sustainable performance of the alternative proposed.

As a standard practice, we addressed process integration by using standard heuristics (Seider *et al.*, 2009), heat waste recovery techniques (Smith, 2016), and heat integration (Smith, 2016; Yee and Grossmann, 1990). Examples of design heuristics include recycling streams, favouring the direct sequence in distillation trains, or using short cut methods to find the number of trays and minimum reflux ratio in distillation columns. Heat waste recovery is mainly considered by using steam Rankine cycles to generate electricity and burning purge streams to generate high pressure steam. Finally, heat integration is carried out using either the pinch analysis and composite curve (Smith, 2016), the MINLP approach developed by Yee and Grossmann (1990) or models based on the same strategy, which involve the development of a stage-wise superstructure. In the pinch analysis, the minimum energy consumption of a process is calculated on the basis of thermodynamically feasible targets. An advantage of this method, is that energy performance can be addressed without the need to design a detailed heat exchanger network (HEN). However this characteristic also results in an underestimation of energy consumption and capital investment, as the ultimate HEN design will typically consume more

utilities and require more heat exchangers. The MINLP used to design the detailed HEN optimise simultaneously operation and capital costs of the network. In this model, a superstructure is generated given hot and cold streams, their corresponding duties, temperature targets, and the number of stages in which heat transfer is allowed. The superstructure allows then the heat exchange between all cold and hot streams during each stage. The solution of the problem provides the utilities required, stream matches, flows of streams and splits, network configuration and number of heat exchangers with their corresponding heat load, area and operating temperatures.

3.2.2 Sustainability Assessment

We estimate the economic performance using the total annualised cost per kg of main product (TAC) as referred in section 2.2. The environmental performance is quantified applying life cycle assessment (LCA) in accordance to the standard ISO 14040:2006 (ISO, 2006).

The main objective in the case studies analysed in this thesis is to measure the sustainability level of alternative chemical routes and compare their performance against conventional technologies, mostly based on fossil fuels. Assuming that the use and disposal stages will not vary for the same chemical, we generally define the system boundaries from cradle-to-gate, and the functional unit as 1 kg of the main product. The process inventory (LCI) considers both process flows (i.e. raw materials, utilities, products and waste) and the manufacture of the general equipment (i.e. reactors, distillation towers, flash separators and heat exchangers). Mass flowrates and electricity consumption are retrieved from the simulation, while heating and cooling requirements are obtained from the solution of the heat integration problem. The impact associated to the equipment is determined from the total amount of steel calculated from the sizing specifications in the simulation model. Entries for the streams outside the boundaries of the plant are retrieved from environmental databases, such as Ecoinvent (Wernet *et al.*, 2016), GaBi (Think Step, 2015), or Agri-foodprint (Blonk Consultants, 2019). In this thesis, the

translation of the inventory (LCI) into environmental indicators (EI) is made using both midpoint and endpoint methods, and their benefits and challenges are discussed in each chapter. In particular, we applied the methods CML 2001 and ReCiPe 2016, which are briefly discussed in section 2.3.3. Finally, the economic and environmental results are analysed and discussed in the context of the corresponding application within the chemical sector.

3.3 Case study: Circular economy in the plastics sector

In order to provide a deeper understanding of the procedure followed to perform a technoeconomic and environmental assessment, this contribution assesses the emerging technology for recovering ethylene from waste polyethylene (PE) following the principles of the circular economy. The procedure followed is shown in Figure 3.2.



Fig. 3.2 Methodology applied for the techno-economic and environmental assessment of ethylene recovery from waste polyethylene (PE).

This case study is motivated by the relevance of plastics within the chemical sector and society. The annual production of plastic materials, which amounted 60 million tons in 2016 in Europe, is expected to increase in the short and mid-term (Plastics-Europe, 2018). Among them, PE is at present the most widely demanded, representing 30% of the total production when considering all its varieties: high, medium, low and linear low-density polyethylene (Plastics-Europe, 2018). Currently, the main use of PE is packaging in the form of films, bottles or bags,

which are nearly always single-use and result in thousands of tons of plastic waste. Around 72% of plastic packaging is not recovered at all, with 40% being landfilled and 32% mismanaged (Ellen MacArthur Foundation, 2016). This percentage of inadequately managed plastic causes severe environmental problems, being the deterioration of marine ecosystems and microplastics contamination some of the most debated (Hoornweg *et al.*, 2013; Jambeck *et al.*, 2015). Recent studies have shown that problems related to plastic-waste accumulation are increasing dramatically, and that the main polymers responsible for this are by far PE and polypropylene (PP), the two most common polyolefins (Lebreton *et al.*, 2018).

The recycling of PE and PP is difficult to handle, as they degrade during melting. For this reason, some researchers have proposed the upcycling of polymers into quality plastics again as the way forward (Lacy *et al.*, 2019). The treatment of waste polymers calls for adequate technologies that, in the case of PE, are at a very early development stage and show low Technology Readiness Levels (TRLs). Different reviews on chemical technologies that would enable the transformation of PE into reusable monomers point toward pyrolysis as a promising alternative (Hong and Chen, 2017; Ragaert *et al.*, 2017). Recently, Fox and Stacey (2019) compared PE pyrolysis and gasification, concluding that while pyrolysis is environmentally friendlier, gasification leads to higher revenues. However, the positive effect of closing material cycles stresses the need to keep exploring pyrolysis as a way to upcycle the building blocks of plastics.

Some attempts to model the pyrolysis of PE include the development of kinetic models (Gascoin *et al.*, 2012) and process simulations (Vargas Santillán *et al.*, 2016). However, a further technical, economic and environmental analysis is still required to assess the implications of industrialising this process. In order to provide a deeper assessment in terms of both economic and environmental criteria, this contribution assesses the emerging technology for recovering ethylene from waste PE pyrolysis following the principles of the circular

economy. The analysis compares the PE pyrolysis against both, the business as usual (BAU) process for the production of ethylene based on naphtha, and two conventional end-of-life alternatives for the treatment of waste PE according to Figure 3.2.

3.3.1 Process description

Figure 3.3 depicts the process flowsheet for ethylene production from PE pyrolysis. The process was simulated in Aspen Plus v10 using the POLYNRTL fluid package to model the thermodynamic properties of the components and their mixtures. Van Krevelen's group contribution method was implemented to estimate the properties of the polymer (Van Krevelen and Te Nijenhuis, 2009).

The process starts feeding 18,900 kg/h of purified waste PE. This amount is the equivalent to the daily PE waste generated by 8 million people, corresponding to a big city such as London, or an average European region such as Catalonia in Spain. The feed of PE enters a furnace operating at 1000°C and 1 bar, where the pyrolysis takes place. The furnace has a total heat duty of 27.8 MW, which is provided burning a mixture of hydrocarbons that come from one of the streams of the process, avoiding the consumption of natural gas. The distribution of the products follows Eq. 3.6, which represents a global reaction whose stoichiometric coefficients were adjusted according to the data reported by Kannan *et al.* (2014):

$$PE \rightarrow 4.62 C_2 H_4 + 1.17 C_3 H_6 + 0.07 C_3 H_4 + 0.09 C_4 H_8 + 0.59 C_4 H_6$$
(3.6)
+ 0.45 C_6 H_6 + 1.66 CH_4

The gas leaving the reactor is sent to the evaporator of a steam Rankine cycle to generate electricity from the heat generated during the pyrolysis. The gas stream is cooled down to 60 °C in the evaporator. After the evaporator, the reactor outlet stream enters a series of three compressors before being sent to the distillation train. After each compression stage, the gas is cooled down to reduce the temperature and the electricity consumption of the next compression stage. The gas stream enters the distillation train at 30 bar and 40 °C.



Fig. 3.3 Flowsheet for the waste PE pyrolysis with heat integration and steam Rankine cycle.

Column T1 recovers 99% of methane from the hydrocarbons mixture with a purity of 99.5 wt%. The column has 25 trays and operates with a reflux ratio of 15.4. The bottoms of column T1 enter T2 after reducing the pressure to 25 bar in valve V1. In this column, 99.9% of C_2H_4 is recovered at the top of the column with a purity of 99.5 wt%. The high recovery of C_2H_4 aims to increase the purity of propylene to polymer-grade in the next column. The column has 20 trays and operates with a reflux ratio of 2.3. The pressure of the bottoms stream leaving T2 is

reduced to 10 bar and then fed to T3, which recovers 99% of propylene at the top with a purity of 99.5 wt%. The column has 30 stages and operates with a reflux ratio of 4.2. The final column, T4, operates at atmospheric pressure and recovers 99% of benzene at the bottoms with a mass purity of 99.5 wt%. T4 has 12 stages and operates with a reflux ratio of 0.2. A mixture of propylene, propyne, 1-butene, 1,3-butadiene, and benzene is obtained at the top of the column. Some of these products have an aggregated value; however, the separation process is complex and the revenues would probably fail to offset the costs of the separation. Instead, this stream is used to satisfy the entire fuel demand of the pyrolysis furnace.

Heat integration was carried out using Aspen Energy Analyser v10, which suggests to use the heat generated by compressors K1 to K3 to heat the reboilers of columns T1 and T2. This arrangement could be difficult to implement directly in the facilities, as it would require an intermediate circuit in order to transfer the heat from the compressor to the corresponding reboilers. Although this would incur in additional costs and environmental impact, the configuration retrieved from Aspen Energy Analyser is still considered to provide a good approximation of the energy savings and environmental potential of the process.

The cooling requirements in the condensers of the four columns cannot be met with cooling water. To satisfy this service, a two-stage refrigeration cycle reported by Luyben (2017) was implemented, as depicted in Figure 3.3. The first stage of the cycle uses a flowrate of 92.7 ton/h of propylene in a closed loop. In this stage, compressor K2 operates at 21 bar and discharges the gas at 112 °C. Propylene is then condensed at 50 °C and depressurised to 3 bar in valve V4, reaching -26°C. At this point, the stream is used to reduce the temperature of the fluid in the second stage of the cycle, condensers of columns T2 (-19°C), T4 (-9°C), and T3 (20°C), respectively. The second stage of the refrigeration cycle uses 32.3 ton/h of ethylene also in a closed loop, which is pressurised to 25 bar in K3, cooled down to 50°C in C3 and then cooled down further with the propylene of the first stage to -21°C in C4. After reducing the pressure

to 1 bar in V5, ethylene reaches -104 °C, which is enough to satisfy the required temperature of -94°C in the condenser of T1. The refrigerants of both sections have a lifetime of 8 years.

Concept	Cost (€/unit)	Process taken from Ecoinvent v3.4
Products		
Methane (kg)	0.334	* Market for natural gas, high pressure, Europe without Switzerland.
Ethylene (kg)	1.075	**Ethylene production, average, Europe without Switzerland.
Propylene (kg)	0.875	*Production of propylene, Europe.
Benzene (kg)	0.994	*Production of benzene, Europe.

Table 3.1 Costs and environmental entries for the inputs in the process.

* Considered as avoided products in the LCA assessment.

** Process for the BAU production method of ethylene.

Raw materials

Polyethylene (kg)	0.315	Treatment of waste polyethylene, for recycling, unsorted, sorting, Europe.	
Utilities			
Electricity (kWh)	0.110	Market group for electricity, high voltage, Europe.	
Cooling water (kW)	4.38.10-3	Market group for electricity, high voltage, Europe.	
		Cooling duty is replaced by the electricity required to pump water within the cooling cycle.	
Low pressure steam (1,000 kg)	7.820	Market for heat, from steam, in chemical industry, Europe.	
Fuel (kW)	-	No cost or impact considered as stream from top of T4 is used as fuel, avoiding the consumption of any additional fuel.	
Equipment			
Steel (kg)	-	Steel production, converter, chromium steel 18/8, Europe. Compressors and turbines are not considered. Impact amortised considering 25 years of lifetime.	
Furnace (1 piece)	-	Industrial furnace, natural gas, Europe. Impact amortised considering 25 years of lifetime.	
Polyethylene end-life treatment			
Municipal incineration (kg)	-	Treatment of waste polyethylene, municipal incineration Europe without Switzerland	
Landfill (kg)	-	Treatment of waste polyethylene, sanitary landfill Europe without Switzerland	
Heat (MJ)		Market for heat, district or industrial, natural gas, Europe without	
(credit for incineration)		Switzerland	

3.3.2 Sustainability assessment

The economic performance was quantified using the total annualised cost per kg of ethylene (TAC/kg of C₂H₄) as described in section 3.2.2. The plant is located in Europe, meaning that a regional factor of 1.1 was considered in the capital costs estimation. Capital costs were annualised considering 330 operational days per year and a 10 years linear depreciation scheme with a fixed interest rate of 15% (Seider *et al.*, 2009). All the costs were extrapolated to 2019 using the Chemical Engineering Process Cost Index (CEPCI). In addition, costs retrieved in USD were converted to Euros (\in) using a factor of 1.13 USD/ \in . The costs of raw materials, utilities, and products used in the analysis are reported in Table 3.1.The environmental performance was quantified applying LCA in accordance to the ISO 14040:2006 standards (ISO, 2006), as reported in section 3.2.3.

The goal of the LCA in this assessment is twofold. First, to assess the environmental impact of the C_2H_4 produced *via* pyrolysis of PE, and compare it against the naphtha-based business as usual (BAU) process in Europe. The functional unit was set to 1 kg of C_2H_4 produced. Second, our analysis compares the environmental impact of processing 1 kg of waste PE against two conventional end-of-life stages of PE: incineration with power generation and landfill. For the latter case, the functional unit was set as the treatment of 1 kg of waste PE. In the first case, we applied a cradle-to-gate scope, considering the burdens embodied in raw materials and energy inputs, while disregarding the end-of-life phase of the monomer according to the flowsheet presented in Figure 3.3. In the second case, we considered a gate-to-grave scope, where the end-of-life phase of PE was accounted for in the calculations. In the analysis, we apply the system expansion method, in which environmental credits are associated to byproducts for avoiding their production using conventional routes.

The inventory within the boundaries of the system, i.e., foreground system, was obtained from the material and energy balances of the simulation. The entries beyond these boundaries,
i.e., background system, were retrieved from the Ecoinvent database v3.4 (Wernet *et al.*, 2016), accessed via SimaPro (Goedkoop *et al.*, 2016). Table 3.1 presents the entries considered in the assessment. ReCiPe 2016 (Huijbregts *et al.*, 2017) at the endpoint level is used to evaluate the environmental impact of the processes.

The feed of waste PE has assigned the cost and impact of sorting, given that after common industrial or urban use, waste PE may be mixed with other plastic, metallic or organic materials. The impact of cooling water is calculated from the electricity required to pump the water that satisfies the heat demand. As for the fuel, given that we make use of a process stream, the only impact considered for its use is related to the direct emissions of CO₂ during the combustion. The environmental flows associated to the equipment units were estimated from the corresponding steel requirements of distillation columns, heat exchangers and industrial furnace. The impact of the equipment was amortised using a lifetime of 25 years.

When comparing the different end-of-life processes of waste polyethylene, the burdens of the use and collection stages are neglected due to lack of information and potential variability of the results according to the different waste management policies. However, this level of detail can be omitted for comparative LCAs, where identical processes and life-cycle stages can be excluded. As stated by the European Commission – Joint Research Centre (2010), only differences between the compared systems are relevant to discriminate between them. In the gate-to-cradle analysis, landfilling does not produce any valuable product, receiving no credits caused by avoided products. As for incineration, credits are assigned for heat generation to reflect the burden avoided by replacing the market source of heating. The heating source considered refers to high-pressure steam generated by burning low density PE with a heating value of 42.83 MJ/ kg in a boiler with 60% efficiency (Grosso *et al.*, 2010).

3.3.3 Results and discussion

Process modelling. The net flows of the process per kg of C_2H_4 are reported in Table 3.2, while the sizing parameters of the equipment are reported in Table 3.3. Equipment sizing was carried out in 'Aspen Plus v10' and 'Aspen Energy Analyser v10', while capital costs were calculated as described in section 2.2.

Concept	Amount per kg/h of C ₂ H ₄
Products	
Methane (kg)	0.204
Propylene (kg)	0.378
Benzene (kg)	0.287
Raw materials	
Polyethylene (kg)	2.17
Utilities	
Net electricity consumption (kW)	0.454
Electricity main process (kW)	0.231
Electricity refrigeration cycle (kW)	0.839
Electricity generated Rankine cycle (kW)	0.615
Cooling water (kW)	2.447
Low pressure steam (kW)	0.222
Fuel (kW)	3.201
Water (kg) (steam Rankine cycle)	2.69.10-5
Ethylene (kg) (refrigeration cycle)	1.64.10-4
Propylene (kg) (refrigeration cycle)	5.80.10-5
Equipment	
Steel (kg)	9.63.10-5
Direct emissions (fuel combustion)	
CO ₂ (kg)	0.986

Table 3.2 Net flows of the process per kg of C₂H₄/h produced (no allocation considered).

The pyrolysis of waste PE is a highly energy-intensive process, as observed from the fuel, cooling water and electricity requirements in Table 3.2. A total of 2.17 kg of PE are required to produce 1 kg of ethylene, 0.2 kg of methane, 0.4 kg of propylene, and 0.3 kg of benzene. A great advantage of the process is the reduction of electricity consumption by 60% through the incorporation of a steam Rankine cycle, which allows the generation of 5.3 MW of electricity

(efficiency of 36%). Similarly, the process avoids the use of natural gas or any other fuel in the furnace by using the stream leaving the top of T4 as fuel, which contains mainly C3's and C4's. This, however, increases the CO₂ emissions with respect to natural gas by 31.7%. A total of 0.986 kg of CO₂/kg of C₂H₄ are released directly to the atmosphere due to fuel combustion. Heat integration also allowed a reduction of heating and cooling demand by 66% and 36%, respectively.



Fig. 3.4 Capital costs breakdown for the PE pyrolysis.

Economic assessment. Figure 3.4 shows the capital costs of the process. The pyrolysis reactor contributes with 12% to the TAC, while the compressors of the main process represent 18%, and the heat exchanger network (HEN) represents 15%. The need for cryogenic temperatures, provided by the refrigeration cycle, contributes significantly to the total capital cost of the process (32%). The cost per kJ of the cycle is $0.44 \in$, considering both the annualised capital cost and energy consumption. Luyben (2017) reported a value of $0.48 \in (0.54 \text{ USD})$ per kJ generated in the second stage of the cycle. The difference in cost comes from the additional provision of cooling utilities in the first stage of our cycle, together with the use of different cost correlations and depreciation scheme. Finally, the Rankine cycle represents 19% of the cycle saves $4.71 \cdot 10^6 \notin$ per year, which is four times larger than the annualised cost of the cycle, clearly offsetting the investment.

Equipment	Sizing parameter	Installed Cost (€)	
Main process			
Furnace F1	27.8 MW	$3.55 \cdot 10^{6}$	
Compressor K1	797 kW	$1.80 \cdot 10^{6}$	
Compressor K2	743 kW	$1.74 \cdot 10^{6}$	
Compressor K3	769 kW	$1.44 \cdot 10^{6}$	
Column T1	25 stages, diameter: 1.676 m Mass shell: 5,304 kg	5.77·10 ⁵	
Column T2	20 stages, diameter: 1.372 m Mass shell: 3,543 kg	meter: 1.372 m 4.31·10 ⁵ 543 kg	
Column T3	30 stages, diameter: 0.914 m Mass shell: 2,329 kg	3.25·10 ⁵	
Column T4	12 stages, diameter: 0.762 m Mass shell: 885 kg	1.85·10 ⁵	
Heat Exchanger	C5 (2.45 MW, 1,511 m ²)	$3.89 \cdot 10^4$	
Network	C6 (1.65 MW, 1,599 m ²)	$4.12 \cdot 10^4$	
	C7 (0.78 MW, 219 m ²)	$5.69 \cdot 10^3$	
	C8 (0.38 MW, 169 m ²)	$4.15 \cdot 10^3$	
	H1 (0.71 MW, 31 m ²)	$1.11 \cdot 10^{3}$	
	H2 (0.02 MW, 4 m ²)	$3.69 \cdot 10^3$	
	H3 (1.20 MW, 119 m ²)	$2.78 \cdot 10^3$	
	HX1 (0.99 MW, 314 m ²)	$8.09 \cdot 10^{3}$	
	HX2 (0.61 MW, 76 m ²)	$2.01 \cdot 10^3$	
	HX3 (0.53MW, 76 m ²)	$2.01 \cdot 10^{3}$	
	HX4 (1.58 MW, 179 m ²)	$4.15 \cdot 10^3$	
Rankine cycle			
Turbine T1	5,352 kW	$5.09 \cdot 10^{6}$	
Pump P1	84 kW	$1.25 \cdot 10^{5}$	
Condenser C1	315 m ² (9.7 MW)	$3.10 \cdot 10^5$	
Evaporator E1	103 m ² (14.9 MW)	1.59.105	
Refrigeration cycle			
Compressor K2	4,537 kW	$4.75 \cdot 10^{6}$	
Compressor K3	2,761 kW	$3.49 \cdot 10^{6}$	
Condenser C2	224 m ² (10.5 MW)	2.42·10 ⁵	
Cooler C3	107 m ² (1.15 MW)	$1.62 \cdot 10^5$	
Condenser C4	997 m ² (3.9 MW)	9.18·10 ⁵	
Total		2.99 ·10 ⁷	

Table 3.3 Equipment sizing and installation cost of the process.

Figure 3.5 shows the total cost of production per kg of C_2H_4 . Following the procedure described by Towler and Sinnott (2013), the revenues obtained from the byproducts are

subtracted from the VCOP, resulting in a total production cost of 0.386 \notin /kg of C₂H₄. The main contributor to the costs of production is waste PE with a share of 64% (0.684 \notin /kg of C₂H₄), which comes from the cost of sorting the waste PE. It is worth noting that this contribution could increase if additional treatment of waste PE is required. The second largest contributor are the capital and fixed costs, with a share of 30% (0.239 and 0.084 \notin /kg of C₂H₄, respectively), while utilities represent the remaining 6% (0.062 \notin /kg of C₂H₄). The sales of byproducts represent 64% of the total costs of production, which equals the contribution of waste PE. As a result, the TAC/kg of C₂H₄ is mainly given by the cost of utilities and annualised capital costs. Among the byproducts, methane contributes with 0.068 \notin /kg of C₂H₄, propylene with 0.331 \notin /kg of C₂H₄, and benzene with 0.285 \notin /kg of C₂H₄.



Fig. 3.5 Total cost of production per kg of ethylene from naphtha (BAU) and PE pyrolysis.

In a different configuration, methane could be burned to generate steam used in a Rankine cycle. Considering a boiler and steam Rankine cycle efficiency of 75% and 30%, respectively, this configuration would generate 0.643 kW/kg of C₂H₄. As a result, the process would be self-sufficient in terms of electricity and would still generate a surplus of 0.189 kW/kg of C₂H₄. This electricity surplus represents 0.021 €/kg of C₂H₄, which almost offsets the capital costs of the steam Rankine cycle (0.023 €/kg of C₂H₄). At the market conditions considered, it is still more

profitable to sell the methane and pay for the electricity, which generates a profit of $0.018 \notin$ /kg of C₂H₄, in contrast to the self-sufficient configuration, in which no profit is generated.

As observed from Figure 3.5, the TAC/kg of C_2H_4 is reduced by half compared to the cost of 0.835 \notin kg of C_2H_4 for the BAU process reported by Spallina *et al.*(2017). These results clearly show a high economic potential, particularly given by the revenues of the byproducts. In this context, methane shows an increasing market and price stability (IEA, 2019), although its contribution to the revenues of the process is very low. In the case of propylene, there is also a vast an increasing market, guaranteeing its allocation within the sector. However, the different technologies available, production, and demand result in a varying market price (ICIS, 2017), which could increase the cost of ethylene in the pyrolysis process. Something similar happens with benzene, whose price seem to be in constant fluctuation as the global production increases (ICIS, 2018). An additional factor that could play a significant role, is the identification, modelling, and optimisation of the product's distribution in the reactor at different operating conditions.

Under the market assumptions considered in this assessment, the introduction of waste PE pyrolysis in the ethylene market seems feasible. However, it is not expected that this technology will fully substitute ethylene production from naphtha, and therefore, the total production cost of $0.386 \notin$ kg of C₂H₄ only represents a lower bound.

Environmental assessment: Cradle-to-gate. Figure 3.6 shows the environmental impact of 1 kg of C₂H₄ for both, the BAU and PE pyrolysis processes. We can observe that the categories of human health and ecosystems quality behave similarly in the waste PE pyrolysis scenario. In both cases, the emissions of CO₂ from the fuel combustion (direct emissions) show the largest contribution to the negative impact, with shares of 47% in human health and 58% in ecosystems quality (9.15 \cdot 10⁻⁷ DALYs/kg of C₂H₄ and 2.76 \cdot 10⁻⁹ Species \cdot yr/kg of C₂H₄, respectively). The high energy requirements of the process lead to contributions of 26% in human health and 24%

in ecosystems quality $(5.16 \cdot 10^{-7} \text{ DALYs/kg} \text{ of } \text{C}_2\text{H}_4 \text{ and } 1.16 \cdot 10^{-9} \text{ Species} \cdot \text{yr/kg} \text{ of } \text{C}_2\text{H}_4,$ respectively). Waste PE, the raw material carrying the impact embodied in sorting, contributes with 27% of the impact in human health and 18% in ecosystems quality $(5.26 \cdot 10^{-7} \text{ DALYs/kg} \text{ of } \text{C}_2\text{H}_4 \text{ and } 8.70 \cdot 10^{-10} \text{ Species} \cdot \text{yr/kg} \text{ of } \text{C}_2\text{H}_4$, respectively). In the category of resources scarcity, the impact related to waste PE, utilities, emissions and equipment is negligible (0.016 USD/kg of C₂H₄).





As mentioned in section 2.3, the byproducts are considered as avoided products, while credits are taken from their production according to the processes described in Table 3.1. From Figure 3.6, we observe that these credits almost offset the impact of the process activities in the categories of human health and ecosystems quality. The net impact value of the process is $2.67 \cdot 10^{-7}$ DALYs/kg of C₂H₄ in human health, $5.57 \cdot 10^{-10}$ Species·yr/kg of C₂H₄ in ecosystems quality, and $-3.85 \cdot 10^{-1}$ USD/kg of C₂H₄ in resources scarcity. In the case of human health, methane reduces the impact by $4.30 \cdot 10^{-10}$ DALYs/kg of C₂H₄, propylene by $8.31 \cdot 10^{-7}$ DALYs/kg of C₂H₄, and benzene by $8.60 \cdot 10^{-7}$ DALYs/kg of C₂H₄. In the ecosystems quality category, methane reduces the impact by $1.03 \cdot 10^{-12}$ Species·yr/kg of C₂H₄, propylene by $2.10 \cdot 10^{-9}$ Species·yr/kg of C₂H₄, and benzene by $2.13 \cdot 10^{-9}$ Species·yr/kg of C₂H₄. The impact

in the resources scarcity category is reduced to $2.47 \cdot 10^{-4}$ USD/kg of C₂H₄ by methane, $2.31 \cdot 10^{-1}$ USD/kg of C₂H₄ by propylene, and $1.70 \cdot 10^{-1}$ USD/kg of C₂H₄ by benzene.

As in the economic analysis, these results present a lower bound on the environmental impact of ethylene production, as it is not expected that waste PE pyrolysis fully replaces ethylene production from naphtha. Similarly, the use of a different allocation method could vary the results. For instance, the use of economic allocation would assign around 50% of the impact to ethylene, resulting in 9.73.10⁻⁷ DALYs/kg of C₂H₄ in human health versus the 2.67.10⁻⁷ DALYs/kg of C₂H₄ obtained using system expansion. As observed, with economic allocation, or even when the full impact of the pyrolysis of waste PE is considered, that is, no credits are assumed, the value in all the categories is still lower than the BAU. In this case, the fluctuating prices of ethylene and byproducts render economic allocation as a poor method to distribute the environmental impact of waste PE pyrolysis. It could be argued that as the market adapts to new technologies, the environmental impact for the production of the byproducts is very likely to be reduced as more stringent regulations are applied worldwide (UN, 2019). As a result, the credits accounted from the byproducts would be reduced, increasing the total impact of ethylene. However, these changes in technologies will take place throughout the years, resulting in less volatile changes in the assessment. Regardless of the allocation method used, waste PE pyrolysis can bring significant environmental benefits to ethylene production, in addition to the economic advantages discussed in the previous section.

Environmental assessment: Gate-to-cradle. Figure 3.7 shows the comparison between the two most common end-of-life processes for waste PE with the pyrolysis process. The functional unit for this case is the treatment of 1 kg of waste PE. Here, credits of ethylene are also accounted for, as it is a byproduct in this case.



Fig. 3. 7 Environmental impact of end-of-life alternatives for waste PE.

In the category of human health, the pyrolysis of PE represents the best option with a negative impact of -0.86 · 10⁻⁶ DALYS/kg of waste PE. The negative value is given by the credits of byproducts. Incineration represents the second best alternative with a net impact value of 0.64 · 10⁻⁶ DALYS/kg of waste PE considering credits for the heat cogenerated. Landfill has the largest impact, with a value of 0.80 · 10⁻⁶ DALYS/kg of waste PE. Pyrolysis also represents the best alternative in the category of ecosystems quality, with a net value of $-0.23 \cdot 10^{-8}$ Species yr /kg of waste PE, followed by landfill and incineration $(0.06 \cdot 10^{-8} \text{ and } 0.14 \cdot 10^{-8} \text{ Species} \cdot \text{yr /kg})$ of waste PE, respectively). Finally, we can observe that the contribution to the category of resources scarcity is significantly low in all the end-of-life alternatives given that no mineral or fossil resources are being consumed. PE pyrolysis has the lowest impact with a value of -0.45 USD/kg of waste PE, followed by incineration with -0.34 USD/kg of waste PE, and landfill with $0.02 \cdot 10^{-1}$ USD/kg of waste PE. Given the valorisation of waste PE in the pyrolysis, it is evident that the process would render the best performance for its end-of-life stage. However, it must be considered that the byproducts will still generate an impact in downstream processes and, consequently, care should be placed in their management to ensure a sustainable performance in the entire cycle.

From the environmental assessment at both, the cradle-to-gate and gate-to-grave systems, we observe that the three main contributors to the negative impact are electricity, direct emissions (CO_2) , and the sorting of waste PE. In terms of electricity, the alternative configuration proposed in the economic analysis, where methane is burned to cogenerate electricity, would certainly avoid the impact caused by electricity consumption. However, methane combustion would generate 0.56 kg of CO_2/kg of C_2H_4 , which is more than half of the emissions already released by the process. These results reinforce that, under the assumptions proposed, selling methane represents the best alternative from the cradle-to-gate perspective. In addition, it is also expected that the electricity mix will continue to decarbonise, reducing the environmental impact attached to this entry. As for the CO₂ emissions coming from the fuel combustion in the furnace, carbon capture techniques could be analysed to be incorporated and reduce the impact of the process although an economic penalty would be included. A proved and efficient way to reduce the cost and impact attached to the sorting or pre-treatment of waste PE is the adoption of additional policies in the collection of the polymer after use. This would not only reduce the cost and impact of this stage but also would allow a higher recycling ratio. An example of these policies and their results is Switzerland, country which recycles 51% of its municipal waste and 83% of PET bottles (SWI, 2016).

3.4 Conclusions

In this chapter, we introduced the methodology followed in this thesis to assess the economic and environmental performance of a chemical process. The methodology was then applied to evaluate the potential benefits of circular economy through the recovery of ethylene from waste PE. A process flowsheet was proposed according to standard heuristics and energy integration, including heat integration and the use of a steam Rankine cycle to generate electricity. The analysis of the process considered economic and environmental criteria based on the total annualised cost and endpoint environmental indicators from the LCIA method ReCiPe 2016 (Huijbregts *et al.*, 2017). The process was finally compared against the business as usual (BAU) process for the production of ethylene and two traditional end-of-life alternatives for waste PE.

The process modelled required a total of 2.17 kg of waste PE to produce 1 kg of ethylene, 0.2 kg of methane, 0.4 kg of propylene, and 0.3 kg of benzene. The process was highly energyintensive given the need to operate at 1,000 °C in the furnace and the use of cryogenic temperatures in the distillation columns. However, the use of a process stream as fuel avoided the consumption of external heating sources. Similarly, the incorporation of a steam Rankine cycle reduced by 60% the electricity consumption of the process. The final energy savings were provided by heat integration, from which heating and cooling demand decreased by 66% and 36%, respectively. The total cost of production per kg of ethylene was $0.386 \in$, which represents half of the cost of the BAU process ($0.835 \in$) reported by Spallina *et al.* (2017).

The environmental performance of the PE pyrolysis was made using a system expansion approach to account for byproducts, and presented clear advantages over the BAU process. The impacts assessed at the endpoint categories of human health and ecosystems quality was close to zero given the credits given from the byproducts. Environmental improvements are particularly appealing in the category of resource scarcity, where a negative impact was observed in the waste PE process as no mineral or fossil resources are consumed. In the comparison of the end-of-life processes, PE pyrolysis also showed a better performance than landfill and incineration. This becomes evident given the valorisation of waste PE into multiple products. Despite the good environmental performance exhibited by the PE pyrolysis, it must be recalled that byproducts will still generate an impact in downstream processes and care should be placed in their management to ensure a sustainable performance in the entire cycle.

Overall, the economic and environmental results reported should be considered as a lower bound, as it is not considered full replacement of the current technology. In addition, the fluctuating costs of byproducts could also increase the cost of ethylene production from waste PE pyrolysis as the market adapts to emerging technologies, global production and demand. This fluctuation of prices also reinforces the use of system expansion modelling to distribute environmental impacts among the main product and byproducts.

The results presented in this case study showed waste PE pyrolysis as an appealing route to close the loop in the ethylene production process and enhance the development of circular economy within the plastics and chemical sector. The results also incentive research in the field to generate kinetic data to properly identify, model, and optimise the distribution of the products obtained in the reactor. In this context, pre-treatment processes of waste PE should also be studied and integrated in the model to guarantee the feasibility of the process.

The fluctuations of the market, lack of detailed kinetic models, among other technical variations, generate uncertainties that are usually neglected during the assessment of chemical processes. The incorporation of these uncertainties is required to provide robust results that allow the incorporation not only of market and technical uncertainties but also environmental ones, related to the information retrieved from databases. In addition, despite techniques such as heuristics and energy integration certainly improve the process performance, it is still clear the need for more rigorous techniques to optimise the entire process in terms of sustainability criteria. Finally, as observed form the environmental assessment presented in this chapter, despite PE pyrolysis presents clear advantages over its fossil-based counterpart, it is still difficult to indicate the real level of sustainability that can be attained with this or any other new technology. This calls for the need of improved impact assessment methodologies that can guide the development of the industry and its impact to the planet and society.

Chapter 4 MODELLING OF UNCERTAINTIES AND WASTE

VALORISATION

In this chapter, we address the importance of including process and environmental uncertainties to traditional assessments. The uncertainty modelling is done *via* Monte Carlo analysis, and the approach is automated by coupling a commercial process simulator with external software to solve the heat integration problem and modify the uncertain parameters accordingly. The methodology is tested in the valorisation of waste biodiesel glycerol to produce propylene glycol.

4.1 Background and problem statement

LCA quantifies all the material and energy flows taking place across the product's supply, avoiding the shift of environmental burdens between different stages (Azapagic, 1999). However, this only holds true when the entire supply chain of the process is being considered and adequate system boundaries are determined. This is particularly important when byproducts are generated in large-scale processes, as the behaviour of the chemical sector might be disrupted by the surplus of specific chemicals and their demand in the market. In contrast, the exploitation of these byproducts represents an opportunity to enhance the bioeconomy.

This relationship between availability and demand of a product generates market uncertainties. By nature, chemical processes are subject to additional sources of uncertainty that introduce variability into the decision-making problem, such as product and byproducts yields, energy consumption, or streams concentrations. In terms of the environmental assessment, uncertainties mainly derive from differences in LCA inventories between the process under study and data retrieved from environmental databases. These uncertainties relate to the reliability of the source, completeness of the data, and temporal, geographical or technological differences. Both, process and environmental uncertainties, certainly affect the performance of chemical processes, and the proper understanding of their impact becomes essential for the success of a sustainable design. Yet, many practitioners still neglect uncertainties and report nominal values for the economic and environmental performance.

Focusing on the enhancement of the bioeconomy and the provision of robust results through the use of PSE techniques, this chapter presents a techno-economic and environmental analysis incorporating uncertainty analysis and sensitivity-based flowsheet optimisation. The aim of this contribution is to strengthen traditional assessments by incorporating process and environmental uncertainties while accounting for flowsheet optimisation techniques. In this chapter, we follow the methodology described in sections 3.2.1 and 3.2.2 to build a simulation model and optimise it through standard heuristics (De Meyer *et al.*, 2008; Seider *et al.*, 2009), sensitivity analysis and heat integration (Yee and Grossmann, 1990). The economic performance and life cycle impact were both assessed afterward considering process and environmental uncertainties modelled *via* Monte Carlo sampling. The assessment is achieved by coupling a sequential modular process simulator with external sequences to simultaneously solve the process flowsheet and heat integration MINLP problem for each scenario, allowing an automation of the Monte Carlo sampling and final evaluation of the processes. The methodology proposed is presented through a case study that aims to boost the bioeconomy in the chemical sector through the valorisation of potential waste byproducts. In this case study, we address the valorisation of glycerol generated as byproduct in the production of biodiesel. In particular, we analyse the production of propylene glycol from biodiesel glycerol. To this end, the conventional industrial process for propylene glycol production is compared against three different hydrogenolysis routes based on biodiesel glycerol.

The rest of the chapter is organised as follows. Section 4.2 presents the methodology followed to address the process and environmental uncertainties in the assessment of chemical processes. In section 4.3, we present the case study analysed and discuss the benefits in the valorisation of waste biodiesel glycerol. Finally, the conclusions of the chapter are drawn in section 4.4.

4.2 Methodology

Figure 4.1 summarises the methodology applied. Building on the methods presented in Chapter 3, we now incorporate a sensitivity analysis over distillation columns and recycling streams to identify better economic performance conditions and include process and environmental uncertainties in the assessment *via* Monte Carlo sampling.



Fig. 4.1 Methodology applied for the incorporation of uncertainties in the economic and environmental assessment of chemical processes.

4.2.1 Process modelling and optimisation

An initial base case model is built following the procedure described in sections 3.2.2 and 3.2.3. In this chapter, flowsheet optimisation is performed through standard heuristics (De Meyer *et al.*, 2008; Seider *et al.*, 2009), one-at-a-time parametric (sensitivity) analysis and heat integration (Yee and Grossmann, 1990). The use of advanced optimisation techniques for flowsheet optimisation is addressed in Chapter 5. Following this approach, the number of trays in each distillation column is selected by running different simulations for an increasing number of trays to ultimately identify the alternative with minimum total cost. Recycle streams are in turn optimised through sensitivity analysis by varying the amount of material being recycled to the process. Finally, heat integration was carried out solving the MINLP approach developed by Yee and Grossmann (1990), which optimises simultaneously the operation and capital costs of the network. After the model is optimised, the economic and environmental assessments are conducted using the data retrieved from the simulation.

To automate the entire analysis, a function in MATLAB was built to perform the economic and environmental assessment. In this approach, we used MATLAB to send the vector containing process variables to Aspen-HYSYS v8.8 according to the samples generated. After solving the model, MATLAB retrieved the data required for the economic and environmental assessment. These data include the information of hot and cold streams, which were used to build and solve the heat integration problem via GAMS v24.5.6. The solution of both, the process simulation and heat integration problem, provided the final inventories required for the assessment.

4.2.2 Sustainability Assessment

The economic performance is now quantified using the total annualised cost (TAC) and economic potential (EP) per kg of main product. The economic potential is included given that

the selling prices of products and byproducts are also uncertain. The TAC is calculated using the method described in section 2.2, while the EP is calculated using Eq. 4.1:

$$EP = Revenue - TAC - taxes$$
(4.1)

Where the Revenue is calculated from the sales of products, and taxes represent 35% of the gross profit of the process (Towler and Sinnott, 2013). The environmental performance was quantified following the method described in section 3.2.3.

4.2.3 Uncertainty analysis

Chemical processes are affected by multiple technical and environmental uncertainties. To handle them, we first perform a sensitivity analysis over the technical parameters in order to identify those with the highest impact on the economic and environmental performance. These parameters include prices of products and raw materials, operating pressures and temperatures, and process yields. The most influential parameters are then chosen to generate a set of samples using Monte Carlo sampling. The nominal value is taken as the mean and a probability distribution assumed if historical data are not available (Biwer *et al.*, 2005).

As discussed in section 2.3.2, environmental uncertainties refer to the data reported in the inventories of LCA databases, and depend on the reliability of source (experimental, model, and estimated), completeness of the data (number of samples), temporal, geographic and technological differences. To deal with these uncertainties, we follow a simplification of the approach proposed by Weidema and Wesnaes (1996) based on the Pedigree matrix. In this approach, the uncertain life cycle entries are modelled as lognormal distributions whose mean value is obtained from the database, and the standard deviation (SD) is calculated with the Pedigree matrix according to Eq. 2.6. The use of lognormal distributions is the default assumption in LCA because it is strictly non-negative, positive skewed, and captures a large range of values. This distribution is also useful to model pollutant releases and model energy consumption and emissions.

In our case, we assume that the impact categories themselves follow lognormal distributions (rather than the emissions values). This assumption is motivated by the observation that most of the impacts are caused by a reduced number of emissions. Hence, for each impact, we use the U_{Db} value of the most predominant emission causing such impact together with the remaining entries of the Pedigree matrix. After obtaining the mean and SD for the parameters considered, Monte Carlo sampling was applied to generate a set of samples, each entailing a specific set of values of the uncertain parameters. The total number of samples ensures that the mean relative error of the economic and environmental performance indicators would fall below 5% for a confidence level of 95%, following the statistical test described by Law (2015).

4.3 Case study

The methodology proposed is presented through a case study that aims to boost the bioeconomy in the chemical sector through the valorisation of potential waste byproducts. As presented in the previous chapter, byproducts can become an additional source of pollution if they are not properly managed. However, they also represent opportunities to enhance the bioeconomy and sustainability in the sector. In this context, biofuels production has been one of areas with large potential to contribute toward the development of a more sustainable society. The many regulations seeking to promote their industrialisation and commercialisation has resulted in large amounts of biofuels being manufactured over the last years, opening up new opportunities to use their byproducts in other chemical routes. One of these byproducts is glycerol, a highly active molecule generated as byproduct in the transesterification of vegetable oils during the production of biodiesel (10 wt. % of total biodiesel production).

Before the biodiesel market took off, glycerol was an expensive chemical seldom used as feedstock. However, the large amounts of biodiesel glycerol produced in the last decade caused a drastic price drop from 380 USD/ton in 2002 to less than 100 USD/ton in 2012 (Quispe *et al.*, 2013), stimulating its use as platform chemical. In fact, the fast growth of biodiesel production

has resulted in 88% of the global glycerol demand being supplied by this process in 2013 (Quispe *et al.*, 2013). Considering that biodiesel production is expected to grow at an estimated annual rate of 10% (BP, 2015), there will be soon a surplus of glycerol supply that the current market cannot accommodate. As a result, exploitation of glycerol as inexpensive, abundant feedstock is receiving increasing attention as an strategy to develop more sustainable processes and products, including valuable bio-based chemicals and novel bio-renewable solvents (Esteban *et al.*, 2015, 2014; López-Porfiri *et al.*, 2016).

In this case study, we address the production of high-value bio-based propylene glycol as an alternative chemical route to revalorise biodiesel glycerol. The conversion of biodiesel glycerol to propylene glycol (PG) emerges as an appealing alternative, since the market demand of PG can absorb large quantities of glycerol (Dasari et al., 2005). PG is a major commodity across the world having an annual production over 2.18 million tons in 2014 and annual growth of 8% (Merchant Research & Consulting ltd, 2014). PG is traditionally produced from propylene oxide (PO), a petroleum-based chemical that reacts with water to produce PG along with diand tripropylene glycols, which are products with industrial application and additional value (McKetta and Cunningham, 1993; Wittcoff et al., 2013). Over the last decade, different studies have analysed the production of PG from renewable sources such as glycerol, sorbitol or biomass (Adom et al., 2014; Gong and You, 2015; Merchant Research & Consulting ltd, 2014). Among these options, catalytic hydrogenolysis of glycerol to PG has been put forward as a sustainable production route and studied under several operating conditions. Some of the alternatives evaluated include systems at high or atmospheric pressure (Dasari et al., 2005; Wang et al., 2015; Zhou et al., 2010), isothermal or non-isothermal conditions (Akiyama et al., 2009; Dasari et al., 2005; Maglinao and He, 2012; Wang et al., 2015; Zhou et al., 2010), external or in situ generated hydrogen (Akiyama et al., 2009; Chen et al., 2015; Maglinao and He, 2012, 2011; Martin *et al.*, 2013; Seretis and Tsiakaras, 2016) and liquid or vapour phase reactions (Dieuzeide *et al.*, 2016; Harisekhar *et al.*, 2015; Vasiliadou and Lemonidou, 2013).

Some authors have also studied the industrial production of PG from biodiesel glycerol. Posada *et al.* (2012) analysed the economic performance of chemical and biochemical processes that convert glycerol into six different valuable products, concluding that the production of PG represents the best economic option, with a 'sale price/total cost of production' ratio of 1.57. In the environmental context, Adom *et al.* (2014) found that savings of 60% in energy consumption and greenhouse gas emissions could be attained in the production of PG by replacing the conventional process with the hydrogenolysis of bio-based glycerol. Following a different approach, and considering another biomass-source of glycerol, Gong and You (2015) developed a superstructure to assess the use of microalgae as raw material in the production of biodiesel, hydrogen, PG, glycerol-tert-butyl ether and poly-3-hydroxy-ybutyrate. The authors found that when PG is the only bio-product generated, 1.82 kg of CO₂ equivalent per kg of PG produced are generated, which represents a reduction of 51.5% compared to the propylene oxide technology. The economic results for this case are nevertheless not reported. None of the previous studies included uncertainty in their assessments.

Focusing on the enhancement of the bioeconomy and the replacement of petroleum-based compounds by renewable feedstocks, we here address the economic and environmental assessment under uncertainty for different routes in the production of PG from biodiesel glycerol. The results of these alternatives are compared against a benchmark industrial PG technology based on the use of petroleum-derived propylene oxide.

4.3.1 Process modelling

Crude glycerol, produced in the transesterification of vegetable oils in biodiesel plants, usually contains water, methanol, salts and other organic material. In this study, we assume that crude glycerol is purified before being fed to our processes by removing methanol, salts and organics. The purified stream contains 90 wt. % glycerol and 10 wt. % water (Xiao *et al.*, 2013). The liquid feed stream of propylene oxide/glycerol has a flow rate of 75 kmole/h in all the cases. Propylene glycol is produced with 99.5 wt. % purity. A description of the alternatives proposed along with the mechanisms considered for each route is presented next.

Route business as usual (BAU): Propylene oxide conversion. In this process, propylene glycol (PG) is produced from liquid-phase hydrolysis of propylene oxide (PO) under a non-catalytic reaction according to Eq. 4.3 (McKetta and Cunningham, 1993). Secondary reactions take place in the process, since PG reacts with PO to produce dipropylene glycol (DPG) (Eq. 4.4), which in turn reacts with PO to generate tripropylene glycol (TPG) (Eq. 4.5).

$$C_3H_6O + H_2O \to C_3H_8O_2$$
 (4.3)

$$C_3H_6O + C_3H_8O_2 \to C_6H_{14}O_3 \tag{4.4}$$

$$C_3H_6O + C_6H_{14}O_3 \to C_9H_{20}O_4 \tag{4.5}$$

Figure 4.2 provides a flow diagram of the process. PO and water are mixed according to the ratio 1:15 (McKetta and Cunningham, 1993) (an excess of water is required to limit the generation of byproducts). The resulting stream is pressurised to 18.25 bar and heated to 190 °C. The reaction takes place in the liquid phase and full conversion of PO is achieved with a yield of 85 % to PG, 10 % to DPG and 5% to TPG. The pressure of the products leaving the reactor is reduced to 1 bar before they are fed into a flash separator, where the vapour phase (containing mainly water) is recycled to the process. The liquid phase (mixture of glycols and water) is sent to a train of distillation columns operating under vacuum at 0.1 bar to avoid decomposition of the products. The remaining water is recovered in the top of the first distillation column (VC-1) and is fully recycled to the process. The bottoms of the first column are sent to the second column (VC-2), where PG glycol is recovered as overhead product with 99.5 wt. % purity. The bottoms of the second column are fed into a third column (VC-3), where

Water Wastewater Propylene Wate Glycol Dipropylene Glycol Wate Propylene oxide Tripropylene Glycol Vacuum column 2 Flash Vacuum Vacuum Reactor column 1 column 3

DPG and TPG are further separated to obtain valuable products with 99.5 wt. % purity in both cases.

Fig. 4.2 Production of PG from propylene oxide conversion (BAU).

Route glycerol-based 1 (GB-1): Isothermal hydrogenolysis at high pressure and external hydrogen. This alternative follows the two-step mechanism introduced by Pudi *et al.*(2015). In the first stage, dehydration of glycerol takes place to produce acetol and water (Eq. 4.6), followed by hydrogenation of acetol to generate PG (Eq. 4.7). A secondary reaction is presented when glycerol reacts directly with hydrogen to produce ethylene glycol (EG) and methanol (Eq. 4.8).

$$C_3 H_8 O_3 \to C_3 H_6 O_2 + H_2 O$$
 (4.6)

$$C_3H_6O_2 + H_2 \to C_3H_8O_2$$
 (4.7)

$$C_3H_8O_3 + H_2 \rightarrow C_2H_6O_2 + CH_3OH$$
 (4.8)

Typical operating conditions for the process vary from 20 to 50 bar and from 200 to 350 °C. Operating conditions for the simulation were taken from Wolosiak-Hnat *et al.* (2013), who performed a statistical experimental design, concluding that the optimal production of propylene glycol is achieved at 205 °C, 20 bar and a mixture glycerol-water at the entrance of the reactor having a concentration 75 wt. % glycerol. Reported glycerol conversion is 88.7 % with a selectivity toward propylene glycol of 94.3%. This reaction is generally performed over

a Cu/Al₂O₃ catalyst, where the acidic function is modified to favour the selectivity over propylene glycol.

Figure 4.3 shows the flowsheet of the process. Freshwater and glycerol are mixed, pressurised to 20 bar and heated to 205 °C. Separately, hydrogen is also heated to 205 °C and fed into the reactor. A molar ratio hydrogen/glycerol 5:1 is used in the simulation (Zhou *et al.*, 2010). The gas stream from the reactor is cooled down to 30 °C and then sent to a flash unit to separate the hydrogen from the products that are dragged in the gas stream. The gas phase of the flash unit, containing mainly hydrogen, is recycled into the process while the liquid stream is mixed with the liquid stream of the reactor. The pressure of the mixed stream is reduced to 0.1 bar and sent to the distillation train, where water with methanol is recovered at the top of the first column (VC-1). This stream is further separated in an atmospheric column (DC-1), where methanol is recovered having a purity of 99.5 wt. %. A fraction of the water recovered is returned to the reactor, while the remaining part is sent to wastewater treatment. The bottoms of the first column (VC-1) are sent to a second column (VC-2), where glycerol is recovered and recycled to the process. PG and EG are separated in a third column (VC-3), obtaining 99.5 wt % purity in both cases.



Fig. 4.3 Hydrogenolysis of glycerol at high pressure and isothermal conditions with external hydrogen (GB-1).

Route glycerol-based 2 (GB-2): Non-isothermal hydrogenolysis at ambient pressure and external hydrogen. This alternative is based on the work by Akiyama *et al.* (2009), where the

conversion of glycerol takes place at ambient hydrogen pressure and gradient temperatures, following the two-step mechanism presented in alternative GB-1. The approach proposed exploits the catalytic activity of Cu/Al₂O₃ to favour the conversion of glycerol above 200 °C and the hydrogenation of acetol at lower temperatures (100-150 °C). Akiyama *et al.* (2009) proposed a gradient temperature reactor where the temperature of the reactor varies from 170 to 230 °C at the entrance, and from 135 to 190 °C in a second reaction stage. In the process, we considered temperatures of 200 and 120 °C at the top and bottoms of the reactor, respectively, since these conditions result in full conversion of glycerol with the highest yield toward PG (96.9%). The reactor was modelled using a conversion reactor and adjusting input and output temperatures accordingly, given that kinetic data were not available. The results obtained by Akiyama *et al.* (2009) also showed that the concentration of glycerol has no impact on the conversion. Hence, the fresh glycerol stream is not diluted.

Figure 4.4 displays the flowsheet of the process. The glycerol and hydrogen streams are heated to 200 °C and fed to the reactor. The molar ratio hydrogen/glycerol is 5:1 (Zhou *et al.*, 2010). The gas phase products are cooled down to 30 °C and sent to a flash unit where most of the gas stream is recycled to the process and the rest is discharged to avoid the accumulation of products in the process. The liquid phase of the flash unit is mixed with the liquid stream of the reactor and sent to the distillation columns, which operate at atmospheric pressure. PG and EG are recovered in the bottoms of the first column (DC-1) and separated in a second column (DC-2), obtaining both products with 99.5 wt. % purity. Water, acetol and methanol (recovered at the top of the first column) are sent to a third column (DC-3), where methanol with 99.5 wt. % purity is recovered. The bottoms stream, containing water and acetol, is sent to a fourth distillation column (DC-4), where acetol is recycled to the process while water is sent to a wastewater treatment facility.



Fig. 4.4 Hydrogenolysis of glycerol at ambient pressure and non-isothermal conditions with external hydrogen (GB-2).

Route glycerol-based 3 (GB-3): Isothermal hydrogenolysis at high pressure and *in situ* generated hydrogen. The use of external hydrogen may lead to high operation costs as well as higher environmental impact because most of it is produced from fossil fuel in refineries. In order to circumvent this limitation, we considered as third alternative hydrogenolysis using *in situ* generated hydrogen. The mechanism of this route is not well defined, with different mechanisms available in the literature (Maglinao and He, 2012, 2011; Martin *et al.*, 2013; Seretis and Tsiakaras, 2016). In this analysis, we applied the mechanism reported by Maglinao *et al.* (2012, 2011), based on a thermodynamic analysis that accounts for all the products detected in both gas and liquid phases.

As in the previous alternatives, PG is produced by a two-step mechanism (Eq. 4.9), where glycerol is dehydrated to acetol, which is further hydrogenated to PG (Eq. 4.12). Hydrogen is produced by two different reactions. In Eq. 4.10, acetol reacts with water to generate hydrogen and CO₂. A second route is shown in Eq. 4.11, where glycerol reacts directly with water to produce hydrogen, CO₂ and methanol. Secondary reactions are given in Eqs. 4.13 and 4.14, where PG reacts with hydrogen to produce propanol, ethanol, methane and water. The reaction takes place at 240 °C, 20 bar and a glycerol solution 50 wt. %, in accordance with the experiments performed by Maglinao and He (2012). The reaction is performed over a Nickel-Raney catalyst.

$$C_3 H_8 O_3 \to C_3 H_6 O_2 + H_2 O \tag{4.9}$$

$$C_3H_6O_2 + 4H_2O \rightarrow 3CO_2 + 7H_2$$
 (4.10)

$$C_3H_8O_3 + 2H_2O \rightarrow 2CO_2 + 4H_2 + CH_3OH$$
 (4.11)

$$C_3H_6O_2 + H_2 \to C_3H_8O_2$$
 (4.12)

$$C_3H_8O_2 + H_2 \rightarrow C_3H_7OH + H_2O$$
 (4.13)

$$C_3H_8O_2 + 2H_2 \rightarrow C_2H_5OH + CH_4 + H_2O$$
 (4.14)

Figure 4.5 shows the flowsheet of the process. The glycerol stream is diluted with water to 50 wt. % concentration. The pressure of the stream is increased to 20 bar and the temperature to 240 °C. The reaction takes place in the gas phase with a glycerol conversion of 96% and 33% yield to PG. Products are cooled down to 30 °C and sent to a flash unit where the gas phase is released to the atmosphere. The pressure of the liquid phase is reduced to 1 bar and sent to a second flash unit where most of the remaining gases are purged. The liquid stream of the second flash unit is sent to a distillation column (DC-1) where methanol, ethanol, and propanol are recovered along with water at the top of the first column, while acetol, glycerol, PG, and the remaining water are obtained in the bottoms. The stream with the heavy alcohols is sent to a vacuum column (VC-1) to avoid degradation of the glycols. In the top of VC-1, acetol and water are recovered and part of this stream is recycled to the reactor while the rest is sent to treatment. The bottoms of VC-1 are sent to a second vacuum distillation column (VC-2) where PG is recovered at the top with 99.5 wt. % purity, while glycerol is recovered at the bottoms. The process to purify the stream containing the light alcohols (top of VC-1) involves the use of four distillation columns, given the existence of an ethanol/propanol/water azeotrope. As a first step, the stream is sent to a distillation column (DC-2) where the azeotropic point is achieved. The water recovered at the bottoms of the column is sent to wastewater treatment while the alcoholswater mixture is sent to a new distillation column (DC-3). In this column, methanol with 99.5

wt. % purity is recovered in the top of the column. The mixture ethanol/propanol/water is further sent to an extractive distillation column (EC-1), where the glycerol recovered in the second vacuum distillation (VC-2) is used as separating agent. Gil *et al* (2014) reported that purification of ethanol above 99.5 % mole could be achieved by using 0.8 moles of solvent (60 % mole ethylene glycol and 40 % mole glycerol) per mole of azeotropic feed. In this work, we only use the glycerol recovered in the VC-2 as separating agent. Under this assumption, 0.45 moles of solvent per mole of azeotropic feed are fed to the column, removing 94 % of the water present in the azeotropic mixture. The mixture glycerol/water is recycled to the reactor while the mixture ethanol-propanol is separated in a fourth distillation column DC-4, where propanol 99.5 wt. % and ethanol 99.3 wt. % are produced.



Fig. 4.5 Isothermal hydrogenolysis of glycerol at high pressure with in situ generated hydrogen (GB-3).

4.3.2 Sustainability performance

We first present the results for the flowsheet obtained after performing the sensitivity analysis and heat integration of each alternative, to later on discuss the uncertainty attached to the models. Energy and mass balances per kg of PG are summarised in Table 4.1.

Economic Assessment. Figure 4.6 displays the contribution to the TAC and the economic potential per kg of PG produced for the alternatives proposed. Detailed information on the

operating and capital costs is reported in Tables A12-A14. As observed from the EP in Figure 4.6, all the alternatives generate profit, being alternatives GB-1 and GB-2 the routes with the best economic performance.

Concept	BAU	GB-1	GB-2	GB-3		
Raw materials						
Propylene oxide (kg)	0.9034	-	-	-		
Glycerol solution 90 wt. % (kg)	-	1.4238	1.3707	3.7300		
Hydrogen (kg)	-	0.0297	0.0321	-		
Water (kg)	0.2165	0.0093	-	0.5687		
Waste streams						
Gas Purge (kg)	-	0.0052	0.0071	2.7926		
Wastewater (kg)	-	0.4305	0.3798	0.3205		
Products						
By-products (kg)	DPG: 0.1326	Me: 0.0111	Me: 0.0080	Me: 0.0325		
	TPG: 0.0087	EG: 0.0178	EG: 0.0146	Et: 0.1316		
				Pr: 0.0165		
Energy consumption						
Electricity (kWh)	0.1229	0.0578	0.0582	0.1214		
Heating demand (MJ)	11.231	4.635	4.819	16.707		
Cooling demand (MI)	12,640	5 970	6 157	12 288		

DPG: Dipropylene glycol; TPG: Tripropylene glycol; EG: Ethylene glycol; Me: Methanol; Et: Ethanol; Pr: Propanol.

In terms of TAC per kg of PG produced, both options present significant reductions when compared to the BAU case (0.679 USD/kg of PG for GB-1 and 0.636 USD/kg of PG for GB-2 versus 1.781 USD/kg of PG in the BAU case). The main reason behind such savings is the difference in price between propylene oxide and glycerol. In the BAU case, the cost of propylene oxide (1.53 USD/kg of PG) is already higher than the total cost reported for either process GB-1 or GB-2. The profit obtained in alternative GB-2 is 1.33 USD/kg of PG, which represents an increase of 90% compared to the BAU case. Alternative GB-1 generates a profit of 1.30 USD/kg of PG, representing an increase of 86% compared to the BAU case. In contrast, the low yield of PG attained in alternative GB-3 increases the cost per kg of PG to 2.06 USD/kg of PG, which represents 19% more than the BAU case. Consequently, GB-3 shows a significant

decrease in economic potential, generating only 0.25 USD/kg of PG, which corresponds to 36% of the EP obtained in the BAU case (0.70 USD/kg of PG).

In our assessment, no subsidies nor incentives were considered. However, the significant improvements attained in the economic performance of alternatives GB-1 or GB-2, certainly promote the shift from the current process to the glycerol-based options on a long term basis. In addition, the aim of the industry to boost the bioeconomy and the increasing demand of PG (resulting in the generation of more plants), can further favour the incorporation of the glycerol-based options to the current market.



Fig. 4.6 Contribution to the total annualised cost and economic potential per kg of PG generated.

Environmental assessment. To quantify the environmental performance of each alternative, we applied a cradle-to-gate approach following the life cycle impact assessment (LCIA) methodology CML 2001, which is described in section 2.3.3. Glycerol is considered to be produced from the transesterification of soybean oil in the US. An analysis to validate the impact loads attached to glycerol in the Ecoinvent database is presented in Tables A3-A6 in Appendix A. Environmental impacts are evaluated per kilogram of PG produced while economic allocation is applied to distribute the total impact of the processes among products

and byproducts. The Ecoinvent database v3.2 (Wernet *et al.*, 2016) is used to obtain the impact data of streams located beyond the plant boundaries. The purge gas streams are burned to generate high pressure steam, which is used to satisfy the demand of the plant. The liquid waste is immediately sent to a wastewater treatment plant. Entries taken from the Ecoinvent database are displayed in Table A2.

Figure 4.7 shows the environmental impact of the different alternatives proposed. As in the economic analysis, alternatives GB-1 and GB-2 have the best performance. When comparing any of these two options against the propylene oxide case, we observe a significant reduction in the environmental impact. The greatest improvement is achieved in the category of ozone layer depletion, with reductions of 89% (1.67 · 10⁻⁶ kg CFC-11-eq/kg of PG in the BAU case versus 1.82·10⁻⁷ and 1.78·10⁻⁷ kg CFC-11-eq/kg of PG for alternatives GB-1 and GB-2, respectively). This category is mainly affected by substances with chlorine or bromine groups in their molecules that interact with ozone in the stratosphere (Huijbregts et al., 2017). The significant savings in this category can be attributed to the reduction in chlorine substances (chlorine and sodium chloride) consumed in the production of propylene oxide compared to those in biodiesel glycerol. Ultimately, this savings help to reduce UVB-radiation, which is related to skin cancer and cataracts. The lowest improvement is shown in photochemical oxidation. This environmental category quantifies the creation of reactive substances (mainly ozone) at ground-level by nitrogen oxides and volatile organic compounds, and relates to problems such as respiratory diseases in humans or reduction of growth and seed production in vegetation. While the main contributor in the BAU case is the release of propane to the environment during the propylene oxide production, in the glycerol-based options the main contributor is hexane released during the biodiesel production process. The category presents a drop of 60% in GB-1 and GB-2 $(2.38 \cdot 10^{-3} \text{ kg CFC}-11 \cdot \text{eq/kg of PG in BAU versus } 9.78 \cdot 10^{-4} \text{ kg})$ CFC-11-eq/kg of PG in GB-1 and 9.43.10⁻⁴ kg CFC-11-eq/kg of PG for GB-2). All the

categories are improved on average by 73% in GB-1 and 74% for GB-2. Alternative GB-3 shows the highest environmental impact among the glycerol-based options. The main reasons for this are i) the low yield of PG (35% versus 98% in GB-2 and 96 in GB-1), ii) the large amount of emissions generated, and iii) the utilities and equipment necessary to carry out the reaction and separation steps.



Fig. 4.7 Environmental life cycle assessment results for the production of PG from PO and glycerol. Impacts expressed per kg of PG. AP: Acidification potential; GWP: Global warming potential; DAR: Depletion of abiotic resources; FAET: Fresh aquatic ecotoxicity; MAET: Marine aquatic ecotoxicity; TE: Terrestrial ecotoxicity; EP: Eutrophication potential; HT: Human toxicity; OLD: Ozone layer depletion; PO: Photochemical oxidation].

The potential benefits of these savings on the planet are hard to define since they depend on the extent to which the new technologies might be deployed, their location, transportation routes, logistics, etc. In an attempt to achieve a better appreciation of these savings, we focus on the category of global warming potential, for which specific targets have been pledged to reduce the greenhouse gas emissions by 2020. If we take the production of PG in the US during 2014 from the BAU process, the total contribution of PG to the CO₂ emissions accounted for 3.10 million tons of CO₂-eq. If instead, we analyse the production of PG from processes GB-1 or GB-2, the CO₂ emissions would account for 1.21 million tons of CO₂-eq. Hence, the production of PG from GB-1 or GB-2 could reduce the CO₂ emissions of the chemical sector in the US by 3%, according to the emissions reported in 2005. The reduction of the total GHG emissions in the US would represent 0.1%. Despite the global benefits are related to global warming mitigation, we would certainly benefit in turn from lower levels of atmospheric pollution causing local impacts.

Looking deeper into the main contributors of the impacts, raw materials entail 94% of the total environmental impact in the BAU case, from which propylene oxide contributes with 99% and water accounts for the remaining 1%. Utilities are responsible for the other 6% of the impact, being the heating demand responsible for 80% of the utilities impact. In options GB-1 and GB-2, based on external hydrogen, raw materials account for 89% of the total impact. In these alternatives, glycerol represents 98% of the raw materials impact, while hydrogen is responsible for the remaining 2%. As for alternative GB-3, based on the *in situ* generation of hydrogen, the contribution of raw materials is 75%, while utilities represent 21%, steel 1% and waste 3%.

It is worth noting that the total reductions in GHG emissions in GB-1 and GB-2 compared to the propylene oxide case are above those described by Adom *et al.*(2014). In their analysis, values of 8 and 4.5 kg CO₂-eq/kg of PG were reported for the propylene oxide case and glycerol option, respectively, in a cradle-to-grave approach. In this work, values of 4.80 and 1.85 kg CO₂-eq/kg of PG are reported using a cradle-to-gate approach. The difference in system boundary definition might explain the discrepancy between the total values reported in both assessments. While the cradle-to-grave approach reported by Adom *et al.* (2014) accounts for the end of life stage *via* landfill and CO₂ released upon degradation, the assessment presented here does not include such stage. However, the net difference in CO₂ emissions between the BAU case and the glycerol-based option results in similar values for both assessments. In our case, a reduction of 2.95 kg CO₂-eq/kg of PG is achieved by the glycerol-based option, versus 3.5 kg CO₂-eq/kg of PG in the results reported by of Adom *et al.* (2014). For option GB-2, the value of 1.85 kgCO₂-eq reported is close to the one reported by Gong and You (2015) (1.82 kgCO₂-eq), who applied a similar cradle to gate LCA study, although in their assessment microalgae were considered as raw material (as opposed to the biodiesel glycerol used in ours). Of course, the use of different raw materials does not allow a direct comparison. However, it indicates that biodiesel glycerol can achieve similar environmental advantages to raw materials such as algae, while remaining cost competitive.

Despite obtaining results of the same order of magnitude as other studies, caution must be placed concerning the source of biomass used during the assessment. The use of different types of biomass and/or logistics (e.g. locations of the facilities for the production of soybean oil) may lead to different results. In Table A6 of the Appendix, we further assess alternative GB-1 considering five different sources of biomass, showing how drastically different conclusions might be reached depending on the assumptions made.

4.3.3 Uncertainty analysis

To handle the technical and environmental uncertainties, we first performed a sensitivity analysis over the technical parameters (Tables A7 and A8) in order to identify those with the highest impact on the economic and environmental performance. The most critical parameters were found to be the prices of products and raw materials, process conversions and raw materials flowrates. These parameters were then modelled via normal distributions using the mean values and data variation shown in Table A8. Normal distribution was chosen as a given value of the uncertain variables is the most likely (mean value), variations could equally occur above and below the mean, and the uncertain variable is more likely to be in the vicinity of the mean than further away (Mun, 2015). Environmental uncertainties associated with the data retrieved from Ecoinvent (Wernet *et al.*, 2016) were modelled using a lognormal distribution

following a simplified version of the approach proposed by Weidema and Wesnaes (1996), as described in section 4.2.3 (Table A10).

After modelling all the uncertain parameters, Monte Carlo sampling was applied to generate a set of samples, each entailing a specific set of values of the uncertain parameters and for which the calculations were repeated iteratively. A total of 3,000 samples were generated, ensuring that the mean relative error of the economic and environmental performance indicators would fall below 5% for a confidence level of 95% following the statistical test presented by Law (2015) (see details in appendix A).



Fig. 4.8 Total annualised cost and economic potential per kg of PG generated under uncertainty.

In terms of the mass and energy flows, the uncertainty analysis reveals fluctuations of up to 10% in variables such as PG production and utilities consumption, while byproducts and waste streams are more sensitive (from 5% up to 70%). Figure 4.8 presents the EP/kg of PG and TAC/kg of PG evaluated considering the different uncertainties reported in Table A8. Results are displayed using box plots, where the central mark indicates the mean and the bottom and top edges indicate the 25th and 75th percentiles, respectively. The whiskers extend to the most extreme data points within ± 2.7 standard deviations, representing approximately and 99.3 percent coverage data. The results show that the TAC/kg of PG falls in the interval 1.79 $\pm 15\%$

for the BAU case, 0.70±9% in GB-1, 0.67±12% in GB-2 and 1.89±21% in GB-3. The EP/kg of PG falls in the interval 0.67±35% for the BAU case, 1.29±23% in GB-1, 1.34±22% in GB-2 and 0.39±106% in GB-3. In GB-3, the high fluctuation of EP/kg of PG makes the process economically unappealing in some scenarios. As in the deterministic evaluation, the economic indicators present alternatives GB-1 and GB-2 as the options with the best performance, followed by the BAU and GB-3 options. The overall mass and energy balances for all the alternatives under uncertainty are presented in Table A11.



Fig. 4.9 Environmental life cycle assessment results under uncertainty for the production of PG from PO and glycerol. Impacts expressed per kg of PG.

The full LCA results are presented in Figure A6 of the Appendix. In Figure 4.9, we display the results of the categories with the largest uncertainty. Overall, the trend of the deterministic evaluation remained. The results presented glycerol-based options GB-1 and GB-2 as the best

alternatives with less variation against the uncertainties considered in this study. However, a closer performance with the BAU case is observed in five of the ten categories. In the deterministic evaluation of the environmental performance, alternative GB-2 shows the lowest impact in the ten categories evaluated. However, when uncertainty in the processes is considered, it is not possible to distinguish a better alternative among them. The BAU case and alternative GB-3 show the largest environmental impact and larger uncertainty among the scenarios generated. In addition, their performance is now similar and within their uncertainty range in eight of the ten environmental categories. In the BAU case, the variation of the results is attributed mainly to the uncertainty of the data retrieved from the Ecoinvent database. As for alternative GB-3, the high variation in the environmental categories is attributed mainly to the impact of the conversion in the process. Among all the categories, global warming potential shows the lowest variation from its corresponding mean (17 % in BAU, 6 % in GB-1, 6% in GB-2 and 9% in GB-3). The largest variation is identified in the category of marine aquatic ecotoxicity (186 % in BAU, 171 % in GB-1, 176% in GB-2 and 169 % in GB-3).

4.4 Conclusions

Herein, we introduced an approach to combine a commercial process simulator with MINLP techniques, LCA, and external functions to assess four different processes economically and environmentally under uncertainty. This approach aimed to provide simple optimisation techniques able to improve flowsheet performance while allowing a deeper understanding of process behaviour through the analysis of technical and environmental uncertainties.

The results presented for the deterministic evaluation of the alternatives showed that the use of an external source of hydrogen at atmospheric pressure and gradient of temperatures (GB-2) represents the best glycerol route. In fact, this route has the potential to increase profitability and reduce the environmental impact in all the categories evaluated compared to the BAU process. An additional benefit is the operation at atmospheric pressure through all the process.
The use of high pressure at isothermal conditions with an external hydrogen source (GB-1) is presented as the second best option, leading to a win-win scenario compared to the BAU case, but with slightly lower economic potential and environmental impact reduction than route GB-2. The assessment showed that hydrogen has a low contribution toward both the economic and environmental performance. Therefore, the use of *in situ* generated hydrogen at high pressure (GB-3) presents the worst performance given its low yield toward PG. The recovery of the byproducts generated has no significant impact either, while it requires an expensive and complex process configuration. All the routes evaluated have shown a high dependence on raw materials. From this, we can conclude that the use of biodiesel glycerol represents a more sustainable route for the production of PG, as long as the source of biomass has a low environmental impact embodied. Hence, the production of PG from biodiesel glycerol can represent not only a more sustainable option compared to the conventional process, but also an important route to overcome the surplus of glycerol.

The uncertainty analysis showed that the most critical parameters are the prices of products and raw materials, conversions of the process and feed flowrates. The economic indicators can vary in as much as 106% from the corresponding mean. As for the environmental indicators, variations in as much as 186% from the corresponding mean are observed. Among the alternatives, the results obtained for GB-1 and GB-2 appear less variable than those for the BAU and GB-3 options. Overall, the uncertainty analysis presented alternatives GB-1 and GB-2 as the most appealing routes to be further considered for industrial development. As for alternative GB-3, we advise improvement of the catalytic reaction prior further analysis.

Given that the alternatives are based on experimental studies and computer simulations, the results presented still carry a relatively high degree of uncertainty. While consistent with other reference studies, a more detailed assessment via kinetic data and/or pilot plants should be carried out before the scale up of the process. Ultimately, alternative processes like the ones

discussed in this chapter can contribute to boost the bioeconomy, ensure a more sustainable industrial development and address major social, environmental and economic challenges faced nowadays.

This Chapter presented simple optimisation techniques that improve flowsheet performance in economic terms. However, the optimisation of sustainability problems involve the consideration of multiple criteria that are often in conflict one with each other, raising the need for techniques that address this problem, such as multi-objective optimisation and multi-criteria decision analysis tools. As observed in the case study presented, various routes are being investigated to produce propylene glycol from waste glycerol. However, there is a lack of clear guidance to unveil the potential, or lack of it, of the processes under analysis. This is particularly relevant in the field of catalysis, where great efforts are conducted as to identify promising routes that help to boost the bioeconomy of the sector. From this, we identified the importance of using process modelling and optimisation to guide research efforts by identifying a hierarchy of priorities in process development, that ultimately lead to better process performance and use of available resources.

Chapter 5 MODELLINGANDOPTIMISATIONOFSUSTAINABLE

PROCESSES

This chapter presents a general famework for the modelling and optimisation of chemical processes. This chapter extends on the modelling presented in Chapters 3 and 4 by including surrogate modelling and objective-reduction techniques to enhance the optimisation stage, which is performed coupling the process simulator with a genetic algorithm. Finally, the Pareto front generated during the optimisation is further analysed using Data Envelopment Analysis (DEA) as multi-criteria decision analysis tool. The capabilites of the framework are demonstrated in a case study for the production of methanol from CO₂ and hydrogen.

5.1 Background and problem statement

Given its natural link between fundamental science, engineering and industrial practice, the chemical industry plays a key role in meeting the challenges of sustainable development (Narodoslawsky, 2013). In particular, process systems engineering (PSE) is at the core of sustainable development, as it assists in the identification of process alternatives showing better economic and environmental performance.

As presented in the previous chapters, techno-economic and environmental assessments provide a powerful set of tools to evaluate a chemical process. In this context, three main stages can be identified in the development of sustainable designs. The first stage is related to the modelling and assessment of the process under study. Here, sustainability metrics are selected and incorporated in the process model, which can be implemented following either equation-oriented or sequential modular approaches. In the second stage, the design task is posed as a multi-objective optimisation (MOO) problem that seeks to minimise (or maximise) the sustainability metrics previously selected. Due to the existence of inherent trade-offs between them, these metrics tend to be in conflict with each other. As a result, their optimisation results in a set of optimal points that form the so called Pareto front of the problem. In the third stage, a post-optimal analysis is carried out to select the best design from the set of Pareto alternatives. This analysis is usually performed by stakeholders who are assisted by multi-criteria decision analysis (MCDA) tools.

In this chapter, we present a framework for the optimal design of SUStainable ChemicAl ProcEsses (SUSCAPE), which combines life cycle assessment, surrogate modelling, objective-reduction techniques, multi-objective optimisation and multi-criteria decision analysis tools. The main novelty of SUSCAPE, additional to the integration of approaches, is the use of Data Envelopment Analysis (DEA) (Charnes *et al.*, 1978) to assess Pareto optimal designs. Based on the concept of efficiency, DEA classifies a set of units as efficient or inefficient, establishing targets for the improvement of the latter ones. This is particularly appealing in process design, as improvement targets can guide retrofit efforts in suboptimal technologies, classified as inefficient units, aiming for a more sustainable performance. Additionally, DEA allows filtering and ranking Pareto solutions, facilitating the post-optimal analysis of the Pareto frontier. Hence, our approach goes beyond the calculation of the Pareto front, where most of the works in the literature end the analysis, to further screen and rank alternatives without the need to define explicit weights on them. More precisely, in the context of process design, DEA serves two

main purposes: i) filtering and ranking of Pareto solutions, and ii) providing clear insight into how to make suboptimal solutions optimal through projections onto the efficient frontier.

The work introduced in this chapter is organised as follows. Section 5.2 explains in detail the methodology employed in SUSCAPE. In section 5.3, we present the capabilities of the framework in a case study based on the production of methanol from CO_2 and hydrogen. Finally, in Section 5.4 we present the conclusions of this contribution.

5.2 Methodology

The methodology proposed for sustainable process design is outlined in Figure 5.1. The first step in the framework is the definition of suitable metrics to quantify the economic and environmental performance. A process model is then implemented in a commercial process simulator. When complex or computationally demanding processes are analysed, surrogate models can be used to alleviate the computational. Prior to the MOO stage, an objective reduction analysis is performed to omit redundant criteria. To solve the MOO problem, a multi-objective genetic algorithm (MOGA) is coupled with the process simulator (or surrogate model). The Pareto frontier generated is finally analysed using DEA to rank the Pareto optimal solutions and establish improvement targets for the suboptimal alternatives, which may correspond to the business as usual design.

5.2.1 Sustainability assessment and flowsheet modelling

Sustainability assessment. While the framework is general enough to accommodate any metric, we focus here on economic and environmental criteria. Given that there is still a lack of general consensus into which social indicators could be included at the design stage, they have been omitted from the framework. Nevertheless, these could be easily added at the time they become available. Conventional economic indicators include total annualised cost, economic potential or net present value. As standard practice, we propose to use the total annualised cost (TAC), as presented in Section 2.2.



Fig. 5.1 Framework for the optimal design of SUStainable ChemicAl ProcEsses (SUSCAPE).

The environmental performance is assessed via LCA principles, as described in section 2.3. The entries exchanged between the main process and the surroundings (technosphere) are obtained from the simulation model. These include raw materials, energy, steel required for the equipment construction, emissions, and waste generated. The inventory entries for the elements outside the boundaries of the plant can be retrieved from available LCA databases (e.g. Ecoinvent, GaBi, ELCD, USDA, etc.). To translate the inventory data into impact categories, we can apply midpoint or endpoint life cycle impact assessment (LCIA) methodologies, such as TRACI, CML 2001, ReCiPe, etc. As presented in section 2.3.3, midpoint indicators typically address the direct impact on the environmental categories, while endpoint indicators assess the final consequence of such an impact. The use of one or the other strongly depends on the audience to be addressed as well as the goal and scope of the analysis. Depending on the scope of the analysis, the process can be assessed from cradle-to-gate, cradle-to-grave or cradle-to-cradle.

If the model boundaries are expanded, the additional stages have to be properly defined and incorporated to the flowsheet of the process (distribution, final disposal, recycling, etc.). Furthermore, allocation of environmental burdens might be required for those processes producing byproducts. The most common approach in traditional techno-economic and environmental analyses involves a cradle-to-gate system boundary using economic allocation. However, the increasing level of integration within the chemical industry calls for more rigorous allocation methods and wider system boundaries based on sound LCA principles.

Flowsheet modelling. In SUSCAPE, we primarily focus on commercial simulators based on the sequential modular approach. These software packages calculate the outputs of each unit from the input streams and a set of design parameters. The advantages of using sequential modular simulators include the easy implementation of unit operations and modelling of flowsheets, and the robust initialisation methods and tailored algorithms that facilitate the convergence of the model.

A fundamental part of process design and optimisation is heat integration. In SUSCAPE, we retrieve the hot and cold streams from the simulation and externally calculate the composite curve, which provides the minimum utilities consumption. The targets for the hot and cold utilities are then used to evaluate their cost and environmental impact. The detailed HEN design was therefore omitted, as it typically represents a small percentage of the total cost if a long period is chosen to annualise the capital cost (De Meyer *et al.*, 2008). If desired, the framework could be easily adapted to incorporate the design of the HEN using MINLP formulations or similar approaches to generate more accurate results. A brief description of these MINLP formulations is presented in section 3.2.1, while Chapter 4 provides an example of their application in the modelling of uncertainties. However, the incorporation of such methods might increase the complexity of the model, leading to use larger computational resources.

The overall optimisation is performed by decoupling the modelling step from the optimisation task. In the modelling step, the system of nonlinear equations is solved in the process simulator, while external functions calculate the composite curve and the values of the sustainability

indicators. During the optimisation, the solver seeks the best values for the design and operating variables by iteratively interrogating the simulator to obtain the objective function values and to check that the constraints are satisfied.

When complex or computationally expensive models are implemented in the simulator, the optimisation task becomes challenging, as convergence problems, numerical difficulties, or extremely large use of computational resources may arise. Examples of these systems include reactive distillation columns, reactors with complex kinetics, or flowsheets with several recycling streams (Skiborowski *et al.*, 2015). In such cases, surrogate models can be built to enhance the performance of the optimisation solver.



Fig. 5.2 Methodology for the generation of surrogate models.

Figure 5.2 shows a general methodology for the generation of surrogate models. To clarify the methodology, let us first consider a number of objective functions f_i dependent on n design variables w_n . The approach starts by generating an initial set of samples Z_0 used to fit the surrogate. A traditional rule of thumb dictates that at least 10n samples should be generated within the upper and lower bounds of the design variables. These boundaries are typically established by a previous exploration of the model. In our framework, we apply the Latin Hypercube Design them, as it shows good space-filling qualities (Mckay *et al.*, 1979) (left-hand side box in Figure 5.2). The simulator is then evaluated in the set Z_0 considering all the constraints of the process. As a result of the evaluation, feasible and infeasible samples will be identified (central box in Figure 5.2). Feasible samples are used to build and test the surrogate model, while infeasible and non-converged samples are discarded. Table 5.1 shows some of the most common forms of surrogates used in process design. At this stage, the boundaries of the decision variables can be further tightened to reduce the search space during the optimisation (Boukouvala et al., 2015; Boukouvala and Floudas, 2016). After fitting the surrogate, a relative error μ_i is evaluated for all the objective functions f_i . If this error is below a given tolerance, the surrogate is considered to have enough accuracy; otherwise, the model has to be recalibrated using more samples. To further improve accuracy, we propose to optimise the surrogate model using single-objective techniques according to the different metrics to be measured. This not only improves the performance of the surrogate in the optimal region of each objective but also provides optimal points that can be used during the objective reduction technique proposed in the framework. If the accuracy desired cannot be achieved, a different surrogate form has to be selected. The complexity of the surrogate model is related to the accuracy required and the number of variables to optimise. In practice, a proper balance between computational performance and accuracy has to be found based on engineering knowledge of the problem.

Note that a different set of samples may lead to significantly different results (Boukouvala *et al.*, 2015). Additionally, if the boundaries of the design variables are not well established, many of the sampled points might represent infeasible solutions (i.e. either because the constraints are violated or because the simulation model does not converge). The severity of this problem, which depends on the type of process being analysed, can be limited by increasing the number of samples. In some cases, the prediction error of the surrogate after the single-objective optimisation might be large; that is, the optimal solution found by optimising the surrogate leads to simulation results that do not match well the surrogate output. In such cases, the samples

the surrogate. This can be done in an iterative manner until the error of the surrogate in the optimal region falls below a given tolerance.

Modelling approach	Black box Explicit mode				
Simulator	х	Х			
Rigorous thermodynamic		х			
Surrogate models					
Linear		X			
Polynomial		Х			
Kriging		Х			
Neural networks	Х	Х			

Table 5.1 Typical modelling approaches used in process design for surrogate building

5.2.2 Multi-Objective Optimisation

Objective Reduction. This stage is particularly important, as the number of objectives significantly affects the performance of the optimisation solver and the quality of the solutions obtained (Brockhoff and Zitzler, 2006). To perform the OR, we use the MILP formulation introduced by Guillen-Gosalbez (2011), based on the approximation error presented by Brockhoff and Zitzler (2006).

In Figure 5.3, we present the overall stages of the process modelling and MOO stage. After selecting the modelling approach and metrics to assess in step 1, an approximation of the Pareto frontier is first generated. This can be done by optimising individually each objective separately or by optimising pairs of them (step 2a.1). The solutions obtained in these preliminary calculations are then normalised to build the Pareto frontier (step 2a.2). In the next stage, some objectives are removed iteratively, and the dominance relationships between solutions are checked in the reduced space of indicators (step 2a.3). An error is then calculated for each combination of objectives kept, which takes into account how the dominance structure of the Pareto changes compared to the full-space model. The method finishes when a maximum number of objectives has been removed while maintaining the error below a given tolerance.

When the boundaries of the system are modified and the modelling of the system rectified accordingly, the objective-reduction technique has to be repeated to capture the new interactions between indicators. The full objective reduction approach is explained in detailed in Appendix B.



Fig. 5.3 Interaction between the objective-reduction, multi-objective genetic algorithm and process modelling.MOO optimisation. The optimisation of a sustainable chemical process can be posed as an MOO problem of the following general form:

$$\min[f_1(\mathbf{w}), f_2(\mathbf{w}), \dots, f_i(\mathbf{w})] \quad \mathbf{w} \in \mathbf{W}$$
(5.2)

Where there are $i \ge 2$ objectives and **w** is the vector of decision variables contained in the feasible region W, which is defined by equality and/or inequality constraints.

In SUSCAPE, without loss of generality, we focus on the use of Multi-Objective Genetic Algorithms (MOGAs), as they can be easily coupled with process simulators/black-box models as well as explicit algebraic models (Coello Coello *et al.*, 2007; Ibrahim *et al.*, 2017; Konak *et al.*, 2006). MOGAs are particularly appealing as they handle simultaneously a set of points,

also referred as individuals in a population, which allows them to find several members of the Pareto frontier in a single 'run' of the algorithm (step 2b.1). Like any evolutionary algorithm, the initial population in MOGA is modified as iterations proceed according to the internal ranking of the population, which is modified by applying mutation and crossover functions (step 2b.2) (Coello Coello et al., 2007). To perform the optimisation, the MOGA evaluates a fitness function for the given number of individuals in the population and iterates until a convergence criterion is met (steps 2b.2-5). The fitness function contains all the information required to evaluate the sustainability metrics. When coupling the MOGA with commercial simulators, the fitness function is computed by calling the simulator and retrieving the mass and energy balances, sizes of the equipment units, and hot and cold streams, which are used to assess the sustainability metrics (step 2b.3). When surrogate models are implemented, the fitness function is already given by the surrogate. Penalties are employed to deal with the constraints that cannot be handled directly by the simulator or the surrogate (Ibrahim et al., 2017; Skiborowski et al., 2015). The solution of the algorithm provides the final Pareto frontier of the process (step 2b.6). Figure 5.3 shows the general optimisation procedure and its interaction with the modelling and objective-reduction stages.

5.2.3 Multi-Criteria Decision Making

Pareto frontier post-Analysis using Data Envelopment Analysis (DEA). The solution of the MOO problem provides a set of Pareto points. In SUSCAPE, we analyse such solutions using DEA, as described in section 2.7. The application of DEA within our framework allows to: i) filter and rank the optimal solutions of the Pareto frontier, and ii) to determine improvement targets of a given process identified as inefficient (in terms of sustainability performance).

To further illustrate and clarify the concepts of DEA in the context of process design, let us consider technologies A, B, C, D, E, and F producing the same amount of a given chemical

product. In the analysis, we aim to minimise the CO₂ emissions (modelled as an input), while maintaining the profit per kg of final product in each technology (modelled as an output). The graphical representation of the problem is shown in Figure 5.4. We can identify technologies A, B, C, and E as efficient, meaning that they lie in the convex envelope of the Pareto front and there are no better designs than these alternatives simultaneously in both criteria. Technologies D and F are instead classified as inefficient ($\theta_0 < 1$), as they are dominated by at least another design lying on the Pareto front.



Fig. 5.4 Graphical representation of DEA.

Filtering of Pareto solutions. As shown in Figure 5.4, the units identified as efficient by DEA form the convex envelope of the Pareto front. All those units which are not part of this efficient frontier are inefficient. DEA can therefore be used to filter out the points generated by any MOO algorithm, ultimately retaining only the ones lying on the convex envelope. This is shown for the case of technology F in Figure 5.4. Despite being Pareto optimal, it lies on the non-convex part of the Pareto front, so DEA would classify it as inefficient (with a θ_0 value close to one). This filtering step helps to narrow down the number of optimal designs, thereby

reducing the complexity of the post-analysis of the Pareto frontier. Additionally, we can further reduce the number of solutions kept by including a set of constraints reflecting priorities on sustainability metrics.

Enhancement of technologies. In Figure 5.4, technologies D and F can become efficient by projecting them onto the efficient frontier. As the reader may have noticed, there is an infinite number of potential projections, being the input-oriented and output-oriented projections the most common approaches. Here, we focus on the input-oriented approach, in which the DEA model determines the efficiency θ_0 as the ratio between the level of inputs of a given unit and the level of inputs in the efficient frontier. This means that inefficient units (D and F) can be enhanced by projecting them on the efficient frontier (i.e. points d and f, respectively). This model is presented in section 2.7. In contrast, the output-oriented model would require increasing the profit (output) for the same level of emissions (inputs). The maximum reduction in inputs necessary for DMUs D and F to become efficient is given by the difference between the observed point and its projection onto the frontier. Coming back to the example shown in Figure 5.4, the improvement targets for technology D are obtained using a linear combination of technologies A and B (d = $\lambda_{\rm B}B + \lambda_{\rm A}A$). In some cases, it might not be possible to practically achieve these targets, yet they allow identifying hotspots and sources of inefficiencies that can be employed to guide retrofit efforts toward more effective actions.

Ranking of efficient (optimal) solutions. To further rank the Pareto points obtained after the optimisation stage, we applied the super-efficiency model described in section 2.7. To exemplify this concept, let us consider the efficient technologies A, B, C, and E previously described and now shown in Figure 5.5. If we analyse solution B, we can see that the amount of CO_2 emissions released can increase until point b without the unit becoming inefficient. This hypothetical increase can be considered as an input saving when compared to the remaining technologies. Note that this analysis fails when we consider design E, as there are no technologies releasing more CO₂ emissions while achieving the same level of profit. Given that this technology has the largest emissions of CO₂, we denote $\theta_{SE,E} = 1$, indicating a zero input saving for design E.



Fig. 5.5 Graphical representation of the super-efficiency score.

5.3 Case study

To better illustrate the capabilities of SUSCAPE, we analyse the production of methanol from CO₂ and hydrogen, which has been identified as a promising route in carbon capture utilisation (CCU). The aim of the analysis is to optimise the process under sustainability criteria, obtaining a Pareto frontier which will be further analysed using DEA. A base case model is taken from Pérez-Fortes *et al.* (2016).



Fig. 5.6 Methanol production process.

5.3.1 Flowsheet modelling and assessment

The flowsheet of the process is shown in Figure 5.6, where CO₂ and hydrogen react to produce methanol and water. In a secondary reaction, the same reactants produce CO and water. CO₂ is obtained at 25 °C and 1 bar and is pressurised up to 78 bar through a series of four compressors. Hydrogen is available at 30 bar and is pressurised up to 78 bar. Both gases are heated to carry out the reaction in a PFR modelled according to the kinetics reported by Vanden Bussche and Froment (1996). The model assumes 44,500 kg of Cu-ZnO/Al₂O₃ catalyst.

Variable	Flow rate CO ₂ kmole/h	Flow rate H ₂ kmole/h	T _{in} reactor °C	Reactor vol. m ³	Recycling ratio	Heat recovery purge
BC	1,830	5,455	210	45	0.99	1
LB	1,500	4,500	180	20	0.950	0
UB	2,300	6,500	240	80	0.999	1
Variable	Pressure dist. kPa	T _{in} dist. °C	Reflux ratio	Methanol recovery	# of trays (Integer)	Feed tray (Integer)
BC	100	80	1.2	99.45	57	38
LB	100	40	0.8	90.00	10	15
UB	200	120	6.0	99.90	80	75

Table 5.2 Decision variables in the methanol production process.

The outlet of the reactor is cooled down and sent to a flash unit where part of the CO_2 and hydrogen mixed with CO are recovered and recycled to the process. Some of the gases are released to avoid the accumulation of mass within the process. The pressure of the liquid stream coming out from the flash unit is lowered and the stream is then sent to a second flash where most of the remaining CO_2 and hydrogen are separated from water and methanol. Finally, the liquid stream of the second flash is heated prior to the distillation column, where methanol is recovered with a mass purity of at least 99.9 wt. %. The production rate of methanol is fixed to 440 kton/y, as this is an average representative value used in conventional plants (Pérez-Fortes *et al.*, 2016). The gas emissions of both flashes can be released to the environment or used to generate steam at high pressure, which requires the addition of a furnace in the flowsheet. The wastewater is sent to treatment.

The decision variables to be optimised are shown in Table 5.2 including the values for the base case (BC), upper (UB), and lower bounds (LB). In the distillation column, the purity constraint was fixed in the simulation allowing the reflux ratio and methanol recovery to vary. This was aimed to avoid adding this additional constraint during the optimisation of the surrogate model.

Commodities	Cost (€/unit)	Production process taken from Ecoinvent database			
CO ₂ (kg)	From electricity compression	CO ₂ capture using MEA as solvent*.			
Hydrogen (kg)	3.09	Market for hydrogen.			
Steam (ton)	14.30	Steam production in the chemical industry			
Electricity (MW)	94.50	High voltage electricity mix			
Cooling water (m ³)	0.03	Tap water production, conventional treatment			
Catalyst (kg)	95.24	Not considered			
Steel (kg)	Capital costs	Steel production chromium steel 18/8			
Heat recovery (ton)	7.70	Steam production in chemical industry			
Wastewater treatment (m ³)	1.50	Treatment of wastewater			

 Table 5.3 Economic and environmental entries for the methanol production process.

* The impact embodied in the electricity consumed by the compressors is already accounted for in the value reported in the database.

Step 1a Sustainability assessment. The sustainability of the process is assessed from cradleto-gate defining 1 kg of methanol as functional unit. The indicators considered were the TAC and those included in the LCIA methodology CML 2001: acidification potential (AP), global warming potential (GWP), depletion of abiotic resources (DAR), fresh aquatic ecotoxicity (FAET), marine aquatic ecotoxicity (MAET), terrestrial ecotoxicity (TE), eutrophication potential (EP), human toxicity (HT), ozone layer depletion (OLD) and photochemical oxidation (PO). Therefore, a total of 11 indicators were included. For the economic evaluation, costs were taken from Pérez-Fortes (2016) when available. Equipment costs were calculated using correlations reported in the literature (Seider *et al.*, 2009; Towler and Sinnott, 2013). The environmental entries lying outside the boundaries of the plant were taken from the Ecoinvent database v3.2 (Wernet *et al.*, 2016) according to the processes described in Table 5.3. No allocation method is considered as methanol is the only product of the process.

The CO₂ captured being fed into the process is considered cost-free and has a pressure of 1 bar. As a result, the total cost of methanol production includes the compression of CO₂ from 1 to 78 bar. In the cost breakdown of the process, the cost of electricity consumption during CO₂ compression is embedded into the CO₂. However, during the environmental assessment, the CO₂ production process taken from the Ecoinvent database already accounts for this electricity, and therefore, it has been omitted during the calculations. In the GWP category, each kilogram of CO₂ in the feed stream was considered as a credit (-1 kg of CO₂-eq) and subtracted from the value reported in the database for the production of CO₂, resulting in a net value of -0.27 kg of CO₂-eq/ kg of CO₂ consumed.

Step 1.2 Process modelling. The detailed process was first modelled in Aspen-HYSYS and then used to build a surrogate model constructed using a two-layer feed-forward network with 10 sigmoid hidden neurons and linear output neurons. During the sampling and further optimisation, all the variables were allowed to vary according to the values in Table 5.2, and fixing the methanol purity to 99.9 wt. % in the simulation. The only additional constraint which was not imposed in the simulator was the methanol annual production rate of 440 kton/y.

The surrogate model was built using neural networks given their high degree of accuracy (Himmelblau, 2008). The surrogates were developed for the entire flowsheet rather than for its individual components separately. A summary of the surrogate building and calibration is provided in Figure 5.7, which shows how the convergence and feasibility of the sets improved

as the model was recalibrated and the boundaries of the variables tightened. A converged simulation is that in which the process simulator found a solution for the given set of variables. A feasible solution is that in which the methanol production achieved the desired rate of 440 kton/y, which is the only external constraint added to the model. The initial set of samples ($Z_1 = 1,000$) used to construct the surrogate was generated via the Latin hypercube design. From the 1,000 samples generated, 590 converged in the simulation, while 51% of these converged simulations achieved the annual methanol production rate (209 samples). To build the surrogate, 70% of the feasible samples were used to train the model, 15% to validate it and 15% to test it. In the validation stage, the parameters of the surrogate are still tuned after the training to avoid overfitting. During the test stage, the parameters of the surrogate are fixed and its results are compared against the data of the original model. After building and testing the surrogate, we evaluated the relative error for the entire set of feasible solutions for each metric m, defined as:

$$\operatorname{Error}_{m} = \frac{\sum_{1}^{Z} \left| 1 - \left(\operatorname{Value}_{\operatorname{surrogate}} / \operatorname{Value}_{\operatorname{simulation}} \right) \right|}{7}$$
(5.3)

Most of the categories resulted in average errors between 1 and 4%, having errors as low as 1% and as high as 8%. The exceptions were the categories of global warming potential and eutrophication potential, which had average relative errors of 7 and 8%, with errors as low as 2%, and as high as 24%, respectively. From the analysis of the main contributors to these indicators, it was not possible to identify a particular pattern for this increase in the error, as other categories behave similarly, yet presenting lower errors. However, a wider distribution of the data was observed for global warming potential (-0.1 to 0.2 kg CO₂-eq) and eutrophication potential ($2 \cdot 10^{-3}$ to 0.2 kg PO₄-eq), with multiple samples approaching zero. This could have resulted in the approximations made by the surrogate to be less accurate with respect to the

simulation, difference which is more significant in points close to zero, as the relative error is magnified in this region if the value of the simulation is very low.

The surrogate was next used in the objective reduction stage, which also involved a recalibration of the model in the optimal region. We note that the evaluation of the surrogate was significantly faster than running the Aspen-HYSYS model: the lowest time per evaluation in Aspen-HYSYS was 4s, which went up to 198s for non-converged designs. The average time per evaluation of the surrogate was below 0.005s.

As shown in Figure 5.2, the building of the surrogate involves an iterative procedure that ends when the desired error tolerance is achieved. In our case, the surrogate was recalibrated twice to improve the quality of the predictions made near the optimal region of the model. This recalibration was performed taking advantage of the optimisations required by the objectivereduction method applied. To do so, we generated a second set of samples (Z_2) optimising the surrogate separately for each objective using a single-objective genetic algorithm. The algorithm was set with an initial population of 120 individuals randomly generated, a limit of 1,000 generations and the boundaries described in table 5.2. The optimisation of each objective was performed 10 times to generate a total of 110 samples. Given the non-convexity of the model, as well as the stochastic nature of the genetic algorithm, it can be expected that the optimisation results in different combinations of variables that result in similar values of the corresponding objective function. As we populate the optimal region of each objective, we would expect the neural network to perform better in such areas since the training of the neural network implies the regression of the model according to the data used. The results of the optimisation were tested in the original model in Aspen-HYSYS and resulted in 91 converged simulations, out of which 85 were feasible. These 85 samples were then used to recalibrate the surrogate. As in the first iteration, 70% of the samples were used to train the model, 15% to validate it, and 15% to test it. The relative error for the entire set of feasible solutions (209+85

samples) was then calculated, resulting in average relative errors ranging from 1 to 6% in all the categories.

The final calibration of the surrogate was made using a third set of samples (Z_3) obtained by executing the MOGA five times using the surrogate model. After this procedure, we obtained a total of 91 solutions, out of which 83 converged and 79 were feasible after being evaluated in Aspen-HYSYS. This set of feasible solutions was added to the previous data and used to recalibrate the surrogate. The relative error for the entire set of feasible solutions (209+85+79 samples) was finally calculated, resulting in a maximum error of 3% for all the categories. In the final results retrieved from the MOGA, a total of 137 optimal points were generated. Among them, 126 converged and all of them satisfied the productivity constraint. The simulation in Aspen-HYSYS was evaluated a total of 1,338 times until we obtained the final Pareto frontier. To generate the surrogate, a total of 373 feasible samples were used (209 from Z_1 , 85 from Z_2 and 79 from Z_3).



FS = 209 FS = 209+85 FS = 294+79 evaluation Fig. 5.7 Summary of the surrogate evaluation in the production of methanol from CO₂ and hydrogen. The surrogate was first built and then recalibrated two times adding the feasible samples (FS) of each set. Initial iteration: 209 / 1,000 samples; recalibration 1: (209+85) / (1,000+110) samples; recalibration 2: (294+79) / (1,110+91) samples.

5.3.2 MOO Optimisation

Step 2.1 Objective reduction. The objective reduction step requires an initial approximation of the Pareto frontier. To build this approximation, we generated an initial set of points using a single-objective genetic algorithm coupled with the surrogate model and optimising the 11 objectives separately. In the genetic algorithm, the initial population 'evolves' according to the ranking of individuals at each generation and following mutation and crossover procedures, which leads to different solutions at different runs (Coello Coello *et al.*, 2007). To produce more consistent results, we ran the single-objective genetic algorithm 10 times for each objective. The set of decision variables obtained in the single-objective optimisations ($Z_2 = 110$) was tested in the original model and the best solutions for each objective were then used to build the initial Pareto frontier S_0 required for the objective reduction model. The solutions of the simulation in Aspen-HYSYS were used to make the first recalibration of the surrogate model (Figure 5.7). After normalising the Pareto frontier S_0 using Eq. B1, we carried out the objective reduction by performing an exhaustive exploration of the OR model in Eqs. B3-B10 for an approximation error $\overline{\delta} = 0$. The results of the MILP indicated that five objectives were required to ensure an approximation error of zero: TAC, GWP, EP, HT, and PO.

Step 2.2 Multi-objective optimisation and comparison between the full-space and reduced-space models. The MOO of the surrogate model was performed using the MOGA algorithm already implemented in the MATLAB optimisation toolbox (MATLAB, 2017). The methanol production rate, which was the only additional constraint omitted in the simulation model, was handled by defining a slack variable that measured the production of methanol in the model. This variable was affected by a penalty term and then added to the objective function. During the optimisation, we first ran the MOO algorithm in the reduced space to recalibrate the surrogate and then repeated the procedure to generate the final Pareto frontier. The MOGA was set with an initial population of 100 individuals and 1,000 generations as stopping criterion. We included as initial population the 85 feasible points obtained in the single-objective optimisations. The MOGA was executed five times and a total of 91 non-repeated solutions were obtained (Z_3). This set of solutions was evaluated in Aspen-HYSYS and resulted in 79 feasible samples, which were used to recalibrate the surrogate. After the fitting of the surrogate, we solved five more times the MOGA in the reduced space using the same initial population and stopping criterion, resulting in 137 non-repeated solutions. Among them, 126 points converged and all of them were feasible in the original model in Aspen-HYSYS. The summary of both evaluations is shown in Figure 5.7, and the boundaries of the final Pareto frontier presented in Table 5.4.

 Table 5.4 Lower and upper boundaries for the solutions contained in the final Pareto frontier. [Units per kg of methanol produced. LB: Lower bound; UB: Upper bound].

Reduce	ed space					
	TAC	GWP		EP	HT	РО
_	(€)	(kg CO ₂ -	eq) (kg	PO ₄ -eq)	(kg 1,4-DCB-eq)	(kg C ₂ H ₄ -eq·10 ⁻³)
LB	0.767	-0.029	C	.020	2.013	1.09
UP	0.847	0.142	C	.132	2.198	8.83
Remain	ning objectives					
	AP	DAR	FAET	MAE	T TE	OLD
	(kg SO ₂ -eq)	(kg Sb-eq)	(kg 1,4-DCB-	(kg 1,4-I	DCB- (kg 1,4-D	CB- (kg CFC-11-
	·10 ⁻³	·10 ⁻²	eq)	eq)	eq·10 ⁻³) $eq \cdot 10^{-7}$)
LB	4.42	1.18	0.42	1451	4.27	1.31
UB	5.23	1.33	0.49	1682	2 4.90	1.53

We now present in detail the total time spent to generate the final Pareto frontier. The sampling was the most time consuming part of the methodology, where a total of 15h were required to evaluate the 1,338 samples in Aspen-HYSYS (\approx 40s on average per evaluation). The building and recalibration of the surrogate required approximately 300s in total (\approx 100s per iteration). The single objective optimisations required a total of \approx 330s, while the MOGA used a total of \approx 185s for the five iterations previously described. The OR using the exhaustive exploration of model in Eqs. B1-B10 required 190s. The total time to generate the final Pareto

frontier required 15h for the evaluation of the original model plus \approx 1,000s in building the surrogate, reducing objectives and optimising the model. For comparison purposes, let us consider the same population size using the Aspen-HYSYS model coupled with the MOGA. If convergence was achieved in the same number of generations as in the surrogate (\approx 300 generations), approximately 30,000 simulations would have been required, resulting in 330h to obtain the Pareto solutions.

To further check if the use of fewer objectives in the MOO problem provided a real advantage, we compared the frontiers generated when optimising the surrogate model for five (S_r) and eleven (S_f) objectives, respectively. The comparison was made using the hypervolume indicator (Zitzler and Thiele, 1998), which measures the area dominated by the Pareto optimal solutions considering a reference point. The larger the value of the hypervolume, the better the quality of the Pareto frontier. Figure 5.8 shows the graphical representation of the hypervolume for two objectives.



Fig. 5.8 Graphical representation of the hypervolume indicator for two dimensions. The hypervolume corresponds to the area enclosed by the frontier and the reference point r.

In both, full and reduced spaces, the Pareto frontiers were generated using a MOGA having an initial random population of 100 individuals and 1,000 generations as stopping criteria. To calculate the hypervolume, we used the approximation developed by Everson *et al.* (2002), which is based on Monte Carlo sampling. The MOGA was run five times for each case, while the hypervolume was calculated after the five iterations. This approach was repeated ten times to ensure the consistency of the results.

MOGA	time* (s)	HVI avg.	1	2	3	4	5	6	7	8	9	10
Full domain S _f (11 objectives)	37.9	4.4	1.99	5.72	2.82	3.27	6.48	5.8	10.1	2.5	1.36	4.41
Reduced space S _r (5 objectives)	37.0	10.2	6.58	7.36	7.03	6.97	16.4	19.3	13.6	2.6	5.11	17.3

Table 5.5 Hypervolume indicator of the Pareto frontier for the original and reduced space.

*Time to run the MOGA having a population of 100 individuals and 1,000 generations as stopping criterion. Solution was reached before the stopping criterion of maximum number of generations in all the cases.

The results are shown in Table 5.5, where we present the hypervolume indicator for both frontiers, along with the average time spent by the MOGA to provide the Pareto frontier. According to Deb and Saxena (2006), the advantage of reducing objectives when using MOGA is twofold: the quality of the Pareto frontier improves while the time spent in the optimisation drops. While it is not possible to claim a significant time-reduction from the results presented in Table 5.5, we can certainly observe that the quality of the Pareto frontier in the reduced space S_r yields always a better non-dominated front compared to the original space S_f .

5.3.3 Multi-Criteria Decision Making

Step 3: Post-analysis of the Pareto frontier using DEA. The solutions obtained from the MOGA were ranked using the super-efficiency concept. To this end, we first normalised the 126 points assessed in the original model in Aspen-HYSYS, including the base case design (BC). The normalisation was performed using Eqs. B1-B2 and the DEA analysis was carried out in the reduced space modelling the five objectives as inputs, as we aimed to minimise them all. As output, we considered the production of 1 kg of methanol.

The values for the efficient solutions are shown in Figure 5.9. After solving model in Eqs. 5.10-5.14, only ten out of the 126 optimal points were found to be efficient, including the base case (s_{A1} to s_{A9} and BC). As we can see from these results, a significant number of solutions

were ruled out by applying the concept of efficiency in DEA. The reason is that the MOGA generated several points that approximated the final Pareto frontier but were finally discarded when DEA generated the convex envelop of the solutions. This also presents the opportunity to apply other multi-objective techniques, such as the epsilon-constraint, as this could represent a lower consumption of computational resources. However, the treatment of the constraints can impose additional challenges during the optimisation and non-convex points could still be generated. Design BC was also identified as efficient, the reason being that it showed the lowest impact value in the category of photochemical oxidation (PO) among the 127 designs. This behaviour is explained in the following sections.



Fig. 5.9 Values for the efficient units and case BC in the reduced space without constraints on the weights.

To rank the efficient solutions s_A and BC, we calculated the super-efficiency score by solving Eqs. 5.10, 5.13-14, and 5.16-17. The ranking of the efficient solutions is shown in Figure 5.10. In this case, the super-efficiency provided the best score for design s_{A1} , with a score of 1.26. This means that this process generates the same amount of output with a reduction of 26% of

its inputs (environmental impacts). We can also observe how the base case was ranked with the lowest super-efficiency score, indicating that designs with better performance were possible.

As explained in section 5.2.3, the super-efficiency concept allows ranking alternatives based on the shape of the Pareto front. This means that the final score of each solution is highly dependent on how the Pareto frontier was initially built. For instance, units in regions with a high density of points in the frontier are very likely to have low super-efficiency scores, while units in which points are located further away one from each other are very likely to increase their score. This is particularly relevant when a continuous Pareto front is assessed. If discrete points are used to perform the assessment, their close location would result in low scores of the super-efficiency, making the comparison either difficult or not meaningful at all.



In DEA, it is also possible to include additional constraints reflecting priorities in the indicators within the model presented in Eqs. 2.20-2.23. To exemplify this capability, we solved the DEA model again including the following constraint on the input multipliers v_1 :

$$v_{GWP} \ge v_{TAC} \ge v_{HT} \ge v_{EP} \ge v_{PO}$$
(5.4)

That is, we sorted the objectives from the most important (GWP) to the least one (PO). From the total of 127 designs used in the analysis, the solution of the primal model in Eqs. 2.20-2.23 including Eq. 5.4, indicated that only four designs were efficient in the reduced space.



Fig. 5.11 Values for the efficient units and BC in the reduced space using constraints on weights.

Figure 5.11 shows the values of the five objectives kept in the reduced space for the new efficient designs (i.e. those emerging as efficient when the constraints on weights are applied), and for the BC alternative. In this new analysis, BC became inefficient, displaying an efficiency score $\theta_{BC} = 0.53$. This is explained by the fact that in Eq. 5.4 the category PO, where BC performed extremely well, is given the lowest priority. As a result, the high impact value for the remaining categories prevented this design from becoming efficient when the new constraints on weights were added. The reduction in number of efficient solutions is typically the case when constraints of this type are introduced in the model, as the efficient frontier is restricted (Cook and Seiford, 2009).

To calculate the improvement targets for the BC design, we solved Eqs. 2.24-2.28. To include Eq. 5.4 in the dual model, it is necessary to determine an Assurance Region (AR) (Cook and Seiford, 2009). The AR is defined as the feasible region in which the multipliers u_r and v_l will satisfy the new constraint. In our case, we applied the cone-ratio method (Thompson *et al.*,

1995), as described in section 2.7. In our case, matrix D, which transforms inputs and outputs to reflect the weights, was built using the optimal multipliers of the efficient units identified in the solution of the previous model (Cooper *et al.*, 2006):

$$D = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1.158 & 1.158 & 0.917 & 0.917 & 0.917 \\ 0 & 2.075 & 2.075 & 0.969 & 0.969 & 0.0 \\ 0 & 7.107 & 10.067 & 0.0 & 7.107 & 0.0 \\ 0 & 1.164 & 1.164 & 1.067 & 1.067 & 0.0 \end{pmatrix}$$
(5.5)

By substituting Eq. 5.5 in 2.31, the original inputs x_{1o} and outputs y_{ro} were transformed into \overline{X} and \overline{Y} , respectively. Eqs. 2.24-2.28 were then solved by replacing x_{1o} and y_{ro} by \overline{X} and \overline{Y} . The solution of the model for \overline{X} and \overline{Y} indicated that the inputs of design BC should be reduced to the level of solution s_{A1} ($y_{BC} = 1 \cdot y_{SA1}$). The reason why only one efficient unit was used to improve BC is that its projection onto the efficient frontier of the AR falls in the weakly efficient frontier (Figure 5.4). Therefore, the closest design in the efficient frontier was solution s_{A1} .

Typically, the improvement targets obtained from DEA in an input-oriented model will reduce the value of all the inputs (Cook and Seiford, 2009). However, this is not always the case when constraints on multipliers are included, as the efficient frontier is modified in order to fulfil such constraints. In our case study, the targets for the BC design entail a reduction in TAC by 1.84% (from 0.782 to 0.768 ϵ /kg_{MeOH}), GWP by 134% (from 0.07 to -0.03 kg CO₂ eq/kg_{MeOH}), and HT by 3.5% (from 2.10 to 2.03 kg 1,2-DCB eq/kg_{MeOH}). Conversely, the categories of EP and PO showed an increase by 10% (from 0.09 to 0.10 kg PO₄ eq/kg_{MeOH}) and 211% (from 0.001 to 0.003 kg C₂H₄ eq/kg_{MeOH}), respectively. Note that this does not imply that the BC design needs to deteriorate its performance in the latter categories (EP and PO), but rather that there is room for doing so while still being efficient. An analysis of the decision variables of the peers and how they impact the sustainability indicators provides further insight on how to achieve these targets. In this case, the decision variables of BC would have to move to those in design s_{A1}, as it was the unique peer identified.

Analysing the process performance of the best solutions calculated in the super-efficiency score, we found that hydrogen was the main contributor to the total value of the TAC (≈80 %), while CO_2 was the main contributor in HT (≈ 90 %). The reason for such a large contribution of CO_2 in the HT category is the use of solvents during the carbon capture process. In the case of GWP, hydrogen contributes with 0.42 kg CO₂-eq per kg of methanol, while in the case of CO₂, this value is -0.46 kg CO₂-eq per kg of methanol. The remaining impact is equally attributed to cooling water, heat recovery and emissions ($\approx 0.40 \text{ kg CO}_2$ -eq per kg of methanol in each case). The impacts in the categories of EP and PO were mainly caused by the emissions generated in the process (>90% and >70%, respectively). Note that, to reduce the impact, part of the purge shall be emitted to the atmosphere without any combustion. The reason for this is that when the purge is burned, the methanol contained in the stream is transformed into CO₂, thereby increasing the GWP indicator. On the other hand, if methanol is released in the purge stream, the PO indicator increases while GWP decreases. This also explains why design BC had the lowest value in the PO category, as it was the only option where all the purge was burned. We also identified the recycling ratio as one of the main decision variables of the process, given its effect on the flow rates of CO₂ and H₂ and the size of the equipment units. That is, when the recycling ratio was below 99.5%, the flow rate of raw materials increased while the size of the reactor and distillation column decreased. This was the case for designs s_{A1} , s_{A2} , s_{A3} , s_{A5} , s_{A6} , s_{A7}, and BC. For values above 99.5%, a lower flow rate of raw materials was required, but the reactor and distillation column increased their size to reach the production rate. Finally, the full methodology of SUSCAPE pointed designs s_{A1} and s_{A2} as the ones with the highest superefficiency score when no constraints were included on the indicators. This means that these designs attained the best performance (or savings) in comparison to the rest of points located in the efficient frontier, and could therefore be considered as the most sustainable options. The main difference between both designs was the higher consumption of H_2 in design s_{A2} (5,661

kg/h in s_{A2} versus 5,460 kg/h in s_{A1}). An additional difference between these designs was the inlet temperature of the distillation column, raising from 75 °C in s_{A1} to 86 °C in s_{A2} . Finally, the higher consumption of hydrogen in s_{A2} caused the TAC indicator to increase, making this design inefficient when constraints in the multipliers were included.

5.4 Conclusions

We introduced a framework for the optimal design of sustainable chemical processes that combines life cycle assessment principles, surrogate modelling, objective reduction techniques, multi-objective optimisation and multi-criteria decision analysis tools. What really makes our framework unique, besides the integration of the aforementioned tools, is the application of DEA to facilitate the post-optimal analysis of the Pareto points.

The framework presented was applied to the production of methanol from CO₂ and hydrogen, where the implementation of a surrogate model reduced the time and computational resources during the flowsheet optimisation. The sampling of the original model was the most time-consuming part of the methodology, as 15h were required to evaluate 1,338 samples in Aspen-HYSYS. Approximately 1,000s were required to build the surrogate, reduce objectives and optimise the model. These times represent a significant improvement to the option of directly optimising the original model in the genetic algorithm. If convergence was achieved in the same number of generations as in the surrogate (\approx 300 generations), approximately 30,000 simulations would have been required, resulting in 330h to obtain the Pareto solutions. An additional advantage of the framework is the objective-reduction, which proved increasing the Pareto front quality during the execution of the MOO algorithm. Finally, the application of DEA allowed us to narrow down the number of Pareto solutions from 126 to ten and to establish improvement targets for a base case design. Given the option to generate a surrogate model, the framework can be easily applied to more complex flowsheets, where the main limitations are

the actual capabilities of the process simulator as well as those of the mathematical model used to build the surrogate.

Future work should focus on incorporating the social dimension of sustainability together with the main uncertainties affecting the calculations. Similarly, the use and optimisation of more rigorous models should be incorporated in macro-scale analyses of the chemical industry. In these terms, our framework can also benefit from further developments in each of the areas and tools that it incorporates, including surrogate modelling, objective reduction and core methodologies for process design. Finally, contributions such as the one presented in this chapter will facilitate the development of a sustainable chemical industry by assessing new processes and technologies and also by identifying improvement targets for current suboptimal technologies.

Chapter 6 MULTI-SCALE SUSTAINABLE MODELLING: FROM PLANT TO PLANET

In this chapter we extend the framework introduced in Chapter 5 to a multi-scale assessment, in which we evaluate a process from catalyst development to planet implications. In this approach, we propose the use of an ideal catalytic model and compare its performance against a catalyst-based one. The primary objective of this comparison is to identify the potential role of catalysis and direct research efforts on the basis of an entire flowsheet performance and not only on the reactor. In addition, we also introduce the application of the concept of 'Planetary boundaries' in the assessment of chemical processes. The main contribution of this concept is to allow an absolute quantification of the environmental performance at a global scale while providing limits that should not be transgressed to preserve the Earth's natural behaviour. Overall, the work presented in this chapter allows an assessment from catalysis development to plant design to planet impact. The framework is presented in the same case study as Chapter 5, but addressing now the global environmental implications that the use of CO₂ and renewable hydrogen play to achieve sustainable development in the sector.

6.1 Background and problem statement

At present, a myriad of disruptive technologies are being investigated in academia and in the chemical industry and energy sector to meet the growing demand for products and energy more sustainably (Chin *et al.*, 2015; Rockström *et al.*, 2009; Steffen *et al.*, 2015; UNSD, 2017).

Innovative electrochemical routes to generate cleaner hydrogen and ammonia (Carmo et al., 2013; Martín et al., 2019; Shaner et al., 2016), and thermal and electrocatalytic strategies to utilise captured CO₂ as a feedstock for chemicals and fuels production represent prominent examples of this growing trend (Álvarez et al., 2017; Kondratenko et al., 2013; Martin et al., 2016; Otto et al., 2015; Prieto, 2017; Vogt et al., 2018; Wang et al., 2017). In relation to renewable H₂ production, alkaline electrolysis cells (AEC), proton-exchange electrolysis cells (PEMEC) and solid-oxide electrolysis cells (SOEC) stand as the most appealing technologies (Schmidt et al., 2017). In the area of CO₂ valorisation, methanol is receiving broad attention in view of its essential role as platform molecule and its potential as outstanding fuel (Behr, 2014). Similarly, it can be used as vector to synthetic fuels through established and upcoming methanol-to-olefins/hydrocarbons/kerosene technologies (Yarulina et al., 2018). At present, thermally-driven pathways are more developed than electrocatalytic routes and thus hold perspectives to reach commercialisation more rapidly (Behrens, 2016). The traditional Cu-ZnO/Al₂O₃ catalyst used for the current methanol production from syngas was initially investigated in the processing of CO₂-based streams, showing high activity, moderate selectivity, and a conditions-dependent stability. Among other systems investigated, In₂O₃/ZrO₂ and ZnO/ZrO₂ comprise exceptionally selective and robust catalytic systems, and the activity of the former could be effectively promoted by palladium (Frei et al., 2019; Martin et al., 2016; Wang et al., 2017). Further catalysts showing promising performance are K-CeO₂-MoP/SiO₂ and a CuZnGa material (Duyar *et al.*, 2018; Li *et al.*, 2018).

The widespread adoption of emerging processes designed to underpin sustainable development critically hinges on our ability to build strong cases, rooted on quantitative analyses, to replace (fossil-based) business-as-usual (BAU) practices. In this context, process modelling and techno-economic and environmental evaluation are pivotal to screen alternative solutions, identify technical barriers and, ultimately, enable the efficient allocation of resources

and a fast deployment of the most performing options. Despite their key role, current assessments focused at the plant (Luterbacher *et al.*, 2014; Pérez-Fortes *et al.*, 2016) or life-cycle (Cuéllar-Franca and Azapagic, 2015; Von Der Assen *et al.*, 2014, 2013) levels provide limited insight into the global influence of technologies on sustainable development and, consequently, cannot support research and policy making effectively. Indeed, conventional life cycle assessment (LCA) methods are useful to rank technologies, but cannot determine whether they are environmentally sustainable. Notably, investigations on CO₂-to-methanol *via* chemocatalytic routes have been accompanied by fragmented analyses that often overlooked impacts other than global warming and are quite hard to interpret from a world-wide sustainability viewpoint (Daggash *et al.*, 2018; Kim *et al.*, 2011; Luu *et al.*, 2015; Martín and Grossmann, 2012; Matzen and Demirel, 2016; Medrano *et al.*, 2017; Pérez-Fortes *et al.*, 2016; Pontzen *et al.*, 2011; Rihko-Struckmann *et al.*, 2010; Van-Dal and Bouallou, 2013).

In this chapter, we argue that full understanding on novel technologies considering sustainability from the molecular to the planet levels (Figure 6.1) is vital to address practical hurdles, set performance targets, and better inform policy, government and business bodies. Hence, this critical analysis integrates scientific disciplines across scales under the umbrella of absolute sustainability to study the potential role of green methanol in sustainable development and establish a hierarchy of priorities to guide future efforts. To this end, the concept of planetary boundaries (PBs) is for the first time coupled to process modelling and LCA to identify critical feedstock and reaction parameters and quantify the extent to which green methanol can contribute to operate safely within the Earth's capacity. More broadly, our PBs analysis aims to lie the foundations for a new generation of environmental assessment of fuels and chemicals, where absolute sustainability, often evaluated *ex post* through metrics that hardly access this information, should drive process development already from the early stages.

The work introduced in this chapter is organised as follows. Section 6.2 shows the plant-toplanet framework developed presented directly in the case study being analysed. This approach is undertaken aiming to point out the relevance of each step in the framework. Section 6.3 shows the results and their discussion. Section 6.4 presents the conclusions of the contribution.



Fig. 6.1 Representation of the scales considered in this analysis of technologies to valorise CO_2 into methanol, from the molecular to the planet level.

6.2 Methodology

The role of CO₂-based methanol synthesis in sustainable development was evaluated in this study taking five levels into account: (i) the catalyst level, providing the kinetics of the reaction;
chain level, covering the product's life cycle and (v) the planet level, pivoted on the concept of planetary boundaries. The methodology proposed uniquely combines several tools never integrated before into a single framework, *i.e.*, process modelling and optimisation, LCA, monetisation and PBs. A brief description of these stages is outlined here on, while their detailed treatment is provided in Appendix C.

6.2.1 Catalyst level: Kinetics of methanol synthesis

The catalyst level focuses on the chemical route and the solid mediating the reactions involved. Both the traditional and the emerging methanol synthesis processes are based on the same set of transformations (Eqs. 6.1-6.3). CO and CO₂ hydrogenation, i.e., Eqs. 6.1 and 6.3, are the main reactions when starting from syngas (CO-H₂) and from a CO₂-H₂ mixture, respectively, and are linked through the water gas-shift reaction, i.e., Eq. 6.2.

$$CO + 2H_2 \leftrightarrow CH_3OH$$
 (6.1)

$$CO + H_2O \leftrightarrow CO_2 + H_2 \tag{6.2}$$

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O \tag{6.3}$$

The commercial Cu-ZnO/Al₂O₃ catalyst was selected since it is the state-of-the-art material for conventional methanol synthesis from syngas. Novel solids offer higher methanol selectivities than this catalyst in the conversion of CO₂. However, Cu-ZnO/Al₂O₃ was also chosen as the heart of the emerging technology due to its appreciable activity and the availability of detailed reaction kinetic data, which are lacking for any other catalyst reported. CO₂-based methanol production over Cu-ZnO/Al₂O₃ likely mostly encompass the reverse water-gas shift reaction forming CO, which can be subsequently hydrogenated. On the basis of experiments at variable temperature and pressure in a bench-scale plug-flow reactor, Vanden Bussche and Froment (1996) built a Langmuir-Hinshelwood-type kinetic model for the reaction

system given above, which was implemented as such in the modelling of both the fossil- and CO₂-based processes.

6.2.2 Reactor level: Type and size of converter

Based on the literature (Luyben, 2010; Pérez-Fortes *et al.*, 2016), an ideal fixed-bed plugflow reactor (PFR) was selected for both process scenarios. For the fossil-based process, the volume and operating conditions were fixed to the values available in the original source (Luyben, 2010), comprising 100 m³ and a H₂/CO/CO₂ ratio of 9.8/3.3/1, a temperature of 267°C and a pressure of 110 bar. We underline that a small amount of CO₂ added to syngas exerts a promotional effect on Cu-ZnO/Al₂O₃, strategy that is also industrially exploited to boost methanol production. For CO₂-based methanol synthesis, the reactor volume and operating conditions were established by optimising the flowsheet.



Fig. 6.2 Flowsheets for a) the conventional methanol synthesis from fossil-based syngas and b) the emerging CO₂-based process consuming renewable hydrogen from various sources.

6.2.3 Plant level: Process modelling

At this stage, rigorous process flowsheets encompassing all of the tasks required to convert the reactants into methanol and accomplish its separation from by-products were developed. The flowsheets were based on the reaction system, catalyst and kinetic model described (Figure 6.2). Rather than performing a grass roots design following design principles, the traditional process was modelled according to Luyben (2010), while the green methanol flowsheet was based on the work by Pérez-Fortes *et al.* (2016). Essentially, in both cases methanol is produced in a PFR and purified to a 99.9% (molar basis) pure product using two flash separators and one distillation column. In the CO₂-based process scenario, the operating conditions of the Cu-ZnO-Al₂O₃ catalyst were optimised using a genetic algorithm coupled with the process simulation model, as presented in the previous chapter (Gonzalez-Garay and Guillen-Gosalbez, 2018). In this case, we minimised the total production cost as well as the monetary value of the environmental impact. For comparison purposes, an additional theoretical scenario was defined, in which an ideal catalyst permits to reach the thermodynamic limits for CO₂ conversion and full methanol selectivity. The latter is used to study the role of catalyst development in methanol production.

Previous studies on green methanol synthesis highlighted the need for cheaper, clean hydrogen to make this process economically competitive (Gonzalez-Garay and Guillen-Gosalbez, 2018; Pérez-Fortes *et al.*, 2016; Van-Dal and Bouallou, 2013). For this reason, our analysis covered four different non-fossil hydrogen sources, namely, biomass gasification (Susmozas *et al.*, 2015) and water electrolysis powered with nuclear (Utgikar and Thiesen, 2006), solar (Cetinkaya *et al.*, 2012), or wind (Spath and Mann, 2004) electricity. Furthermore, three CO₂ sources were considered, namely CO₂ captured from coal and natural gas (NG) power plants, as well as direct air capture (DAC). All details on the simulation models, optimisation

runs and cost parameters employed in the OPEX and CAPEX calculations can be found in Appendix C.

6.2.4 Supply chain level: Life-cycle assessment and monetisation

Here, life-cycle assessment (LCA) was applied to evaluate the environmental impact from cradle to gate. The LCA results for the BAU process, methanol from syngas derived from methane steam reforming, were directly taken from the Ecoinvent database v3.4 (Wernet *et al.*, 2016). This approach was followed as there was no inventory data for the syngas used as feed in the process, and the modelling of this additional process was outside the scope of this work. Therefore, the inventory flows obtained from the flowsheet in Figure 2 are used only during the economic assessment. In the case of the CO_2 -based methanol process, a full LCA was carried out considering the various hydrogen and CO_2 sources. The chemical plant was treated as the foreground system, over which we have a certain level of control, *e.g.*, by changing temperature, pressure, purge ratio, *etc.* The surrounding processes supplying raw materials and utilities constitute the background system which can be modified by varying the hydrogen and CO_2 sources.

With regards to the goal and scope definition, an attributional LCA was performed, where the functional unit corresponds to one kilogram of methanol product. Since methanol is the only relevant product of the process, no allocation method was needed. The purge gas of the process is burned to generate high-pressure steam, which was in first place used to satisfy the heating requirements of the plant, with any surplus being accounted as a positive credit. A cradle-to-gate scope was adopted that covers direct emissions and waste at the plant level, together with those burdens embodied in the inputs to the methanol process, *i.e.*, hydrogen, CO₂, electricity, heat and steel. Hence, the end-use phase and any alternative use of renewable energy and carbon capture were omitted.

In the inventory analysis, the life-cycle inventory (LCI) entries were quantified from the mass and energy flows retrieved from Aspen-HYSYS and data from Ecoinvent (Tables C2-C5). The LCI of hydrogen was determined by combining data from the literature (mass and energy flows in hydrogen production, Table C2) with data available in Ecoinvent accessed *via* SimaPro (PRé Consultants, 2019). In the damage assessment phase, the LCA was done implementing a monetisation method that expresses LCA impacts on a common monetary basis. This not only enables a more straightforward comparison of scenarios, but also allows a single-objective optimisation of the flowsheets. Following the approach reported by Weidema (2015), the endpoint categories of human health, ecosystems quality and resource scarcity in the ReCiPe 2016 (Huijbregts *et al.*, 2017) LCIA method, were monetised using specific economic penalties. Finally, in the interpretation phase, the various processes were compared in terms of total cost with externalities.

6.2.5 Planet level: Planetary boundaries

Standard LCAs are useful to compare and rank alternatives, but cannot determine whether they are truly sustainable because there are no reference values available to interpret the results. Therefore, they fail to evaluate the global implications of technologies on the environment. This limitation is particularly critical when assessing chemicals produced at very large volumes, as is the case of methanol. While facilitating the analysis, monetisation methods, often controversial, also fail to assess absolute sustainability precisely because they do not provide thresholds above which a product is deemed unsustainable. Furthermore, due to lack of consensus and some methodological issues, it is highly unlikely that such thresholds will ever become available.

To go beyond standard assessments, and in line with the Sustainable Development Goals (UNSD, 2017), the planetary boundaries (PBs) concept by Rockström *et al.* (2009) was applied here for the first time to evaluate a chemical process. The PBs framework provides the current

and background levels in nine Earth systems critical for the planet. These are key processes occurring on the Earth, for which thresholds were defined for ensuring safe worldwide operation, *i.e.*, planetary boundaries. They include climate change, ocean acidification, land use, biogeochemical flows of nitrogen and phosphorus, biodiversity loss, stratospheric ozone depletion, freshwater use, aerosol loading and chemical pollution. The PBs framework also offers limits that, if exceeded, could trigger abrupt environmental changes. These global limits can be downscaled at the country and sectoral levels by applying sharing principles. These establish shares of Earth systems that should be respected by a sector or an activity within the sector, such as methanol production, to remain within the safe operating space (Ryberg *et al.*, 2018a). Following this approach, the absolute sustainability level of methanol synthesis in terms of PBs was quantified based on the work by Ryberg *et al.* (2018a, 2018b) Accordingly, environmental flows referred to a functional unit (LCI) are translated into a set of control variables defined for the nine Earth systems.

Due to methodological limitations and data gaps in the PBs framework, the same selection criteria as in a previous study (Algunaibet *et al.*, 2019) were applied to focus on eight (out of fourteen) PBs linked to six (out of nine) Earth systems: (i) energy imbalance and (ii) atmospheric CO₂ concentration (climate change); (iii) global industrial and intentional biological fixation of nitrogen and (iv) global phosphorus flows from freshwater systems into the ocean (bio-/geochemical flows); (v) stratospheric ozone concentration (stratospheric ozone depletion); (vi) carbonate ion concentration, average global surface ocean saturation state with respect to aragonite (ocean acidification); (vii) area of forested land as percentage of original forest cover (land-system change) and (viii) maximum amount of consumptive blue water use (freshwater use). Following the work by Algunaibet *et al.* (2019), we accounted for the effect of dinitrogen oxides in stratospheric ozone depletion, which was omitted in the original method used to convert the LCI to PBs (Ryberg *et al.*, 2018a, 2018b). To establish the environmental

limits defined on PBs that should not be surpassed by methanol production, we applied the *status quo* sharing principle. This is a non-egalitarian principle in which the share of the safe operating space assigned to a process is proportional to its current contribution towards the total level of impact (Grasso, 2012). For instance, let us consider that the current atmospheric concentration of CO_2 caused by antropoghenic activities is equal to 121 ppm. If we assume that the global methanol production *via* the business as usual process contributes with 0.96 ppm, the *status quo* sharing principle would define a contribution from methanol production equal to 0.79%.

Based on the work by Ryberg *et al.* (2018a), the PBs calculations were carried out in two steps. Firstly, the percentwise share of the safe operating space assigned to methanol production was established, *i.e.*, the percentwise share of the maximum allowable impact that is allocated to methanol. According to the *status quo* principle, the percentage share of the safe operating space corresponding to methanol production was determined as follows:

$$PSHARE_{i} = \frac{IMPBAU_{i}}{IMPTOT_{i}} \quad \forall i$$
(6.4)

where PSHARE_i is the current percentage share of the safe operating space defined for a PB i that, according to the sharing principle, was assigned to methanol production; IMPBAU_i is the impact on a PB i exerted by the total production of methanol via the fossil-based BAU process based on syngas obtained from steam reforming of natural gas; and IMPTOT_i is the current total level of impact in the same PB subtracting the natural background level (Steffen *et al.*, 2015). The share of the safe operating space associated with methanol production (denoted by SHARE_i) was calculated based on the formula:

$$SHARE_i = PSHARE_i \cdot SOS_i \quad \forall i$$
 (6.5)

where SOS_i is the safe operating space in a PB i, corresponding to the difference between the bound value (BOUND_i), strict or relaxed, defining a given uncertainty region), and the natural background level (Steffen *et al.*, 2015) (NB_i), mathematically expressed as:

$$SOS_i = |BOUND_i - NB_i| \quad \forall i$$
 (6.6)

Finally, for a given technology, the level of transgression in a PB i (TT_i) was obtained by the quotient of its impact referred to the functional unit $(IMTP_i)$ over its share in the safe operating space:

$$TT_{i} = \frac{IMPT_{i}}{SHARE_{i}} \quad \forall i$$
(6.7)

When $TT_i < 1$, the technology operates within the safe space of PB i, while for values above unity the technology falls either within or beyond the zone of uncertainty, i.e., zones with increasing or high risk of deleterious or even catastrophic consequences, respectively.

To properly evaluate absolute sustainability, three pieces of information need to be assessed: (i) the value of the ratio IMPTOT_i/SOS_i, indicating whether a PB is currently being globally transgressed; (ii) the value of PSHARE_i, which quantifies the global role of a technology in meeting a given PB; and (iii) the value of TT_i, indicating whether the PB quota assigned to the technology is exceeded. Specifically, if $TT_i < 1$ for all PBs, a technology is deemed environmentally appealing, as it will ensure a safe operation provided that the same condition is met in all the remaining sectors of the global economy. Conversely, if $TT_i > 1$ for all PBs, the technology should be phased out, as it could potentially hamper our sustainable development if other sectors fail to offset its excess of PBs quota. When the technology shows values of TT_i above one in some PBs and below one in others, the analysis needs to consider also the IMPTOT_i/SOS_i ratio and the values of PSHARE_i to gain deeper insight into the implications. Accordingly, a technology will always be deemed environmentally appealing if $TT_i < 1$, particularly in PBs already transgressed and/or in PBs where its contribution towards the total impact level is large. A technology can still be appealing if $TT_i > 1$ in PBs within the safe operating space and/or in PBs where its contribution to the total impact is low. Performance is poor when $TT_i > 1$ in PBs already transgressed and having a large share in the total impact level. Our assessment, therefore, favours technologies with good performance in the most critical Earth systems and/or in those in which methanol plays a more significant role.

Overall, PBs provide a very powerful framework to evaluate processes and deal with the occurrence of burden shifting, i.e., one impact improves while worsening others, which is quite common in science and engineering (Algunaibet and Guillén-Gosálbez, 2019). We note that while the concept of PBs is not new, to our knowledge this is the first time they are applied to the assessment of chemical processes to quantify their absolute sustainability perfomance.

Due to its novelty, the PBs approach shows some limitations, mainly concerning the uncertainties involved in the quantification of global ecological limits and the performance of technologies in terms of these limits. These uncertainties stem from: (i) imprecise global ecological limits yet considered as rough estimates; (ii) the allocation method of choice to assign shares of the safe operating space; (iii) imprecise measurements of the elementary flows needed to compute the PBs, e.g., CO₂ emissions to air; and (iv) uncertainties in the impact model that converts these flows into PBs, e.g., impact on energy imbalance per unit of CO₂ emitted. Future work should, therefore, focus on reducing these uncertainties by defining more accurate ecological limits and fair and robust sharing principles, improving data collection on emissions and developing more accurate damage models to translate emissions into PBs. The definition of fair sharing principles collectively ensuring sustainable development will also require social and political efforts. It is also worth noting that we focused here only on those PBs for which characterisation factors are already available. Hence, as an example, biosphere integrity, regarded as a core planetary boundary, was omitted due to lack of robust methods to carry out the calculations.

6.3 Results and discussion

6.3.1 Green methanol as an alternative to fossil methanol based on traditional plant assessment

The first part of our investigation was centred on assessing the emerging methanol synthesis from CO₂ captured from a coal power plant and renewable hydrogen using established tools to compare it with methanol production from syngas derived from methane. The optimisation of the flowsheet for the CO₂-based process, which was run for every hydrogen source considering its corresponding cost and impact embodied, provided the best operating conditions for the Cu-ZnO/Al₂O₃ catalyst. The optimisation was performed using a single-objective genetic algorithm with an initial population of 40 individuals and a maximum of 1,000 generations. The objective function was defined by the TAC per kg of methanol plus the cost of the externalities embodied in each process. The results are presented in Table C6, and entail methanol yields higher than 91.5%, conversions per pass in the range of 12.4-15.8%, and methanol selectivities per pass above 99.0%. These values are quite close to those obtained with an ideal catalyst reaching the thermodynamic limit for the reaction system, which leads to methanol yields above 96.0%, conversions per pass between 20-35%, and methanol selectivities per pass of 100%. Furthermore, regardless of the provenance of renewable hydrogen, the optimal H₂/CO₂ ratio in the feed lies slightly below the stoichiometric value of three for both the real and ideal catalyst, which reduces the consumption of expensive hydrogen. Temperatures of 221-228°C were found optimal for green methanol synthesis at 50 bar (pressure consistent with the kinetic model) for any type of hydrogen feedstock (Table C2). These are sufficiently high for supplying heat via heat integration to other unit operations, mainly the reboiler of the distillation column, leading to a virtually zero energy demand. In the ideal case, optimal temperatures are in the range 101-131°C, which still enable heat integration, while optimal pressures fall in the interval of 24-32 bar. Optimisation does not decrease the pressure any further because there is a trade-off between lower compression duties (at lower pressures) and higher conversions due to equilibrium limitations of CO_2 hydrogenation to methanol (at higher pressures).



Fig. 6.3 Total cost, including externalities, of fossil-based methanol from syngas and CO₂-based methanol produced using renewable hydrogen from various sources, and an ideal catalyst reaching the thermodynamically allowed conversion and selectivity levels and the commercial Cu-ZnO/Al₂O₃ catalyst, together with the cost and externalities breakdowns.

Analysing the economic performance (Figure 6.3), fossil methanol has the lowest production cost (excluding externalities), with a value of 0.63 USD per kg of methanol. This process is followed by green methanol produced using hydrogen from biomass (0.81 USD / kg_{MeOH}), hydrogen from water electrolysis with nuclear (1.27 USD / kg_{MeOH}), wind (1.38 USD / kg_{MeOH}) and solar (2.09 USD / kg_{MeOH}) electricity, respectively. Even after accounting for externalities, fossil methanol remains the cheapest option with a value of 1.08 USD / kg_{MeOH}. It is followed by CO₂-based methanol relying on nuclear (1.38 USD / kg_{MeOH}), wind (1.51 USD / kg_{MeOH}), biomass (1.54 USD / kg_{MeOH}) and solar (2.43 USD / kg_{MeOH}) hydrogen sources. Methanol based on hydrogen from biomass leads to the largest externalities implying a cost of 0.74 USD / kg_{MeOH}, 41.5%), and green methanol based on solar (0.35 USD / kg_{MeOH}, 14.2%), wind (0.13 USD / kg_{MeOH}, 8.5%) and nuclear (0.11 USD / kg_{MeOH}, 8.1%) hydrogen.

The cost breakdown shows that hydrogen and, to a lesser extent, CO₂ are the main contributors towards the total methanol production cost for the CO₂-based process, with shares ranging between 51.6-89.4% for hydrogen (without externalities, and 26.9-78.6% with externalities), and between 3.2-26.7% for CO₂ (without externalities, and 2.8-4.7% with externalities). The performance attained by the Cu-ZnO/Al₂O₃ catalyst is already quite close to the best possible performance that could be achieved by an ideal catalyst. The latter would operate at the thermodynamic limit (highest possible yield), feature zero cost and reduce the compression needs to an optimal level according to the trade-off compression duties *vs*. conversion. Keeping the inputs sources constant, the implementation of an ideal catalyst would save 6.0-16.7% or 6.2-12.6% of the calculated costs with or without externalities, respectively, where these percentages represent the differences between the processes labelled with real and ideal in each scenario in Figure 6.3.

Consistent with other works, it is clear that producing cheap hydrogen as well as improving efficiency in CO₂ capture should become a priority for CO₂-based methanol to become economically appealing (Pérez-Fortes *et al.*, 2016). The contribution of catalyst and gaseous feedstock compression is of secondary importance at this stage, underlining the limited insights that could be gained by comparing the Cu-ZnO/Al₂O₃ with other emerging catalytic materials at present. To make green methanol more attractive, taxes on CO₂ emissions could be also envisaged, which are considered a crucial tool for economic analysis of climate policies (Pizer *et al.*, 2014). To compensate for the cost of hydrogen from the various sources, *i.e.*, nuclear, solar and wind electricity, minimum taxes of 430.5, 527.8 and 1,293.4 USD / t_{CO_2-eq} would be required, respectively. These values are substantially higher than the average estimated social cost of carbon of 62.35 USD / t_{CO_2-eq} (Wang *et al.*, 2019). The process based on biomass-derived hydrogen releases a larger amount of CO₂ than the BAU, ruling out the application of a carbon tax.

To understand prospects for CO₂-based methanol, we estimated future hydrogen costs for different electricity costs and electrolysis technologies, *i.e.*, AEC, PEMEC and SOEC. To do so, we used prospects on the technical specifications of electrolysis technologies, *i.e.*, CAPEX expenditures, efficiency and useful time, together with estimates of future electricity prices taken from the US Energy Information Administration (EIA, 2019). Full details are presented in Appendix C. According to our estimates, with the hydrogen prices determined, the cost of methanol, without and with externalities, could drop to 0.72/0.85 USD / kg_{MeOH} (wind), 0.74/1.09 USD / kg_{MeOH} (solar) and 0.76/0.87 USD / kg_{MeOH} (nuclear), respectively (Figure 6.4). Hence, methanol from hydrogen from electrolysis would outperform fossil methanol in the case of wind and nuclear electricity being applied, when considering externalities. Future trends will, therefore, make the role of the catalyst more predominant, increasing its share in the total cost up to 24.2%, which indicates the relevance of identifying

catalysts based on cheap metals operating efficiently at lower pressures. It is worth noting that these results omit future fluctuations in the natural gas price due to geopolitical factors and/or resources scarcity.



Fig. 6.4 Projected methanol price in 2030 depending on the electrolyser technology and the electricity cost associated with the energy source applied in water splitting. The contribution of externalities is included in a) and excluded in b).

Finally, new scenarios were defined to get insight into changes in CO₂ procurement, the second most important methanol cost contributor, considering CO₂ captured from NG power plants and Direct Air Capture (DAC) (Figure 6.3 and C3). The use of NG point sources slightly increases the methanol cost (differences across technologies below 1.35% and 5.2% with and without externalities, respectively). In contrast, DAC, regarded as an essential future carbon mitigation strategy (Smith *et al.*, 2019), worsens significantly the economic performance, *i.e.*, 7.87-20.99% without externalities and 12.27-21.82% with externalities. The reason is that DAC

consumes large amounts of electricity from the electricity mix, *i.e.*, 366 kWh / kg_{CO2}, which is yet to be decarbonised (current carbon intensity of 0.71 kg_{CO2-eq} / kWh).

A detailed analysis of the LCA indicators (Figures C1 and C2) evidences the occurrence of burden shifting across alternatives, *i.e.*, one impact becomes milder at the expense of worsening others. This happens at both the endpoint and midpoint levels. With regards to the breakdown of LCA impacts, hydrogen and CO₂ emerge as the main contributors towards the endpoint indicators, in line with the analysis of externalities. Notably, the large externalities of methanol using hydrogen from biomass are explained by the LCA results, which show how the global warming potential of hydrogen from biomass is significantly higher than that from water electrolysis (Figure C2b). The biomass results are further discussed in Appendix C, and should be taken with caution as they are highly dependent on the type of biomass and assumptions considered in the LCA analysis.

6.3.2 Green methanol as a potential sustainability enabler from a PBs perspective

Acknowledging the limitations of standard LCAs and monetisation tools to assess absolute sustainability accurately, we investigated methanol production in the frame of PBs (Figure 6.5). The base picture was produced analysing the present impact of global natural and anthropogenic activities on the Earth systems considered. In this regard, previous studies (Steffen *et al.*, 2015) showed that only three PBs (out of the eight considered here) are currently met, *i.e.*, stratospheric ozone depletion, ocean acidification and fresh water use. Three others lie in the zone of uncertainty, *i.e.*, atmospheric CO₂ concentration, phosphorus flow and land-system change, and two are transgressed, *i.e.*, energy imbalance and nitrogen flow. Focusing on the role of current methanol synthesis (Figure 6.6), it is manifest that its shares in the total impact vary substantially across PBs. Values as high as 0.53-0.79% are observed in PBs strongly linked to CO₂ emissions, namely, energy imbalance, atmospheric CO₂ concentration and ocean acidification, while values as low as $6.22 \times 10^{-6}-0.02\%$ are found in the others.



Fig. 6.5 Current impact of global natural and anthropogenic activities and of fossil-based methanol production over the commercial Cu-ZnO-Al2O3 catalyst on the PBs, along with the performance of methanol processes using CO_2 captured from coal power plants and renewable hydrogen. For methanol using H₂ from water electrolysis powered by wind, impacts are additionally presented that refer to the alternative use of CO_2 captured from NG power plants and through DAC. For each technology, TT_i values below zero are shown in violet, values between zero and one are depicted in green, and values above one are depicted either in yellow or red depending on whether the process lies in the zone of uncertainty or beyond. The normalisation scheme applied, explained in Appendix C, scales TT_i values above one considering the maximum level of transgression across technologies and Earth systems. The outer rings of the radar plots represent individual contributions of feedstocks and energy forms to the TT_i values in each PB.

The level of transgression values TT_i calculated for fossil-based methanol synthesis reveal that its global sustainability level mimics that of the planet, with only three PBs met, *i.e.*, ocean acidification, stratospheric ozone depletion and freshwater use. This performance, explained by the status quo sharing principle applied, clearly highlights the need for a more sustainable methanol production. CO₂-based methanol technologies consuming hydrogen from water electrolysis increase the number of PBs met from three to five (Figure 6.5), *i.e.*, energy imbalance, CO₂ concentration, ocean acidification, land-system change and stratospheric ozone depletion. In contrast, methanol attained using hydrogen from biomass only meets two PBs, *i.e.*, stratospheric ozone depletion and land-system change. Still, due to burden shifting there is some collateral damage when moving from fossil to green methanol. Indeed, CO₂-based processes using hydrogen from water electrolysis improve energy imbalance, CO₂ concentration, land-system change and ocean acidification, the former three now lying beyond the safe zone. Still, this is accomplished at the expense of worsening the global nitrogen flow, already at high risk, fresh water use, in the safe zone, phosphorus flow in the risk zone, and stratospheric ozone concentration in the safe zone (except in the case of methanol from hydrogen generated using wind, for which it improves).

It could be argued that worsening water consumption and stratospheric ozone concentration, both in the safe space, should be of less concern. In contrast, negative side effects in the nitrogen flow and, to a lesser degree, the phosphorus flow might deserve further attention. However, the marginal role of methanol synthesis in the four Earth systems that can worsen upon implementing CO₂-based technologies, *i.e.*, 6.22 x 10^{-6} -1.48 x 10^{-20} %, suggests that the collateral damage of CO₂-based methanol might be negligible in all four cases. Certainly, other sectors with larger shares of the safe operating space in those PBs could counterbalance the poor performance of green methanol, mitigating its unwanted side effects. Particularly, agricultural regions strongly utilising nitrogen- and phosphorus-based compounds could trade

quotas on these Earth systems in exchange for quotas on energy imbalance, CO₂ concentration, and ocean acidification. Given that agricultural regions are the main contributors towards the total anthropogenic impact in the global nitrogen and phosphorus flows (Steffen *et al.*, 2015), this would allow the agriculture industry to operate under less stringent CO₂ limits. As a result, the sector would benefit from cost savings that would act as a strong incentive to spur cross-sectoral cooperation.



Fig. 6.6 Share of the safe operating space allocated to methanol production in the different Earth-system processes.

The PBs breakdown (outer rings of the radar plots in Figure 6.5) reveals that CO_2 and hydrogen are the main contributors towards the total impact in all Earth-system processes (56.0-99.3%). Particularly, CO_2 mostly affects climate change (18.0-76.1% in energy imbalance and 18.1-76.5% in CO_2 concentration) and ocean acidification (18.1-76.6%), both PBs being strongly connected to CO_2 emissions. The largest share of hydrogen generation is found in freshwater use (38.8-97.9%), linked mostly to biomass growth in biomass-based hydrogen, and to the use of water in both the operation of the electrolysis technologies and the construction and operation of power generation systems for renewable energy.

The PBs performance varies very little when considering CO_2 from natural gas, but it worsens substantially when using DAC. Again, this is due to the high electricity demand of DAC, which is powered with the current electricity mix, yet to be decarbonised.

Overall, quantifying absolute sustainability through PBs uncovers the potential environmental benefits of CO₂-based methanol. This approach goes beyond conventional LCA, mainly used for comparison purposes, by establishing unambiguously whether a technology is environmentally sustainable or not.

6.4 Conclusions

This chapter introduced a critical analysis of green methanol synthesis intertwining state-ofthe-art methods and the first-time application of planetary boundaries to assess a chemical process, identifying and categorising the main technical barriers toward its wide implementation and discussing future plausible scenarios.

Based on the conventional evaluation and omitting future prospects favouring CO₂-based methanol, green methanol is economically unappealing due to the high price of renewable hydrogen. This holds even when externalities, *i.e.*, indirect environmental costs, are considered. At present, green methanol could become economically competitive with respect to its fossil analogue by imposing a tax on CO₂ of at least 430.50 USD / t_{CO_2-eq} , *ca*. 5-fold higher than the average social cost of carbon.

Hence, future efforts should consider a hierarchy of priorities, where the most pressing target is rendering hydrogen production economically and environmentally more efficient *via* improvements in renewable energy generation and electrolysis technologies, calling for better catalysts for H_2O splitting. A second need is the development of better processes, solvents and adsorbents to lower the cost of CO_2 capture. Identifying catalytic technologies for methanol synthesis closer to the thermodynamic limit, although relevant, could be considered comparatively less urgent in the nearest term.

Future costs of hydrogen from water electrolysis will reduce the gap with fossil methanol, making CO₂-based methanol economically appealing when externalities are considered. In contrast, replacing CO₂ captured from coal or natural gas power plants, which lead to similar

performances, by CO₂ from DAC will worsen the economic and environmental footprint of methanol substantially. This scenario could be reverted if DAC is powered by electricity with low-carbon intensity. Furthermore, the use of waste biomass for hydrogen production could also help making green methanol appealing, especially coupling gasification technologies with carbon capture and storage, which could render hydrogen from this source close to carbon neutral. Limited biomass availability, however, will result in a hard competition with electricity generation, particularly in view of the future role of biomass energy with carbon capture and storage (BECCS) in combatting climate change.

Extending the assessment from the plant to the planet level provided insight out of the reach of conventional tools. LCA failed to determine whether methanol is environmentally sustainable, while monetisation wrongly showed that fossil-based methanol is superior even when considering monetised impacts. PBs, on the contrary, led to a radically different picture by uncovering the potential role of CO₂-based methanol in avoiding the transgression of climate change. This core planetary boundary, currently surpassed by the fossil-based methanol, could by itself lead to a new state of the Earth system. Due to inherent trade-offs between Earth systems, replacing traditional methanol by the green alternative based on water electrolysis would mostly negatively influence the global nitrogen and phosphorus flows, and freshwater use. This collateral damage is negligible at the current state considering the more pronounced positive effects on energy imbalance, atmospheric CO₂ concentration and ocean acidification.

In view of our results, cross-sectoral cooperation emerges as a necessary strategy to counterbalance side detrimental impacts. This could help to more effectively handle multiple ecological limits simultaneously by exploiting the asymmetric shares of technologies in Earth systems. The type and extent of the optimal cross-sectoral cooperation needed will depend upon how economic sectors, including the chemical industry, will transition toward a more sustainable economy. Green methanol, in particular, will very likely become an essential

chemical, and might be ultimately fully produced from CO₂ obtained *via* direct air capture (once the mix is decarbonised) or biogenic point sources to close the carbon loop. In this context, the temporal evolution of electricity mixes, CO₂ sources available, and natural gas and hydrogen prices will dictate the best plan forward considering global ecological limits and economic and social criteria.

Overall, the work presented in this chapter highlights the need to improve current environmental assessments to embrace absolute sustainability criteria, and drive decisions in technology development across scales and more effectively. By enhanced systems evaluation with the concept of PBs, the potential role of emerging technologies can be appreciated in its full world-wide scope. Furthermore, technical barriers and improvement opportunities can be identified more easily, minimising the risk of overshadowing local scenarios. To this end, it is also highly recommended to include technical and environmental uncertainties in the assessment. This will ultimately guide future research and policy making in a much more sensible manner than possible at the present stage.

Chapter 7 CONCLUSIONS AND FUTURE WORK

7.1 Conclusions

This work has aimed to advance in the sustainable development of the chemical industry *via* process systems engineering and life cycle thinking. We have developed a systematic approach which incorporates process modelling and optimisation with LCA methods to address sustainability in the sector from catalyst development to plant implementation to planet implications. The methods developed entailed the integration of simulation-based optimisation, surrogate modelling, and multi-criteria decision analysis tools. Additionally, we proposed the modelling of ideal processes along catalyst-based models to identify performance improvements and guide research efforts in the catalysis field. In combination with absolute environmental metrics through the concept of 'Planetary boundaries', this systematic approach is expected to open up a new generation of sustainability assessments in the sector.

The capabilities of the methods presented have been tested in relevant applications that can certainly improve the sustainable performance of the industry and address present and future challenges in the sector. We presented how concepts like circular economy, waste valorisation, and renewable raw materials bring benefits to the industry compared to their fossil-based alternatives. However, we also showed that the development of new processes and technologies is very likely to shift environmental impacts from one category to another, concluding that inter-

sectoral cooperation will become essential to meet the SDGs. The key conclusions of this work are summarised according to the general objectives of this thesis (section 1.4): process design and life cycle modelling, process optimisation, multi-scale assessment, and applications.

In terms of process modelling, we presented how energy integration techniques, such as heat waste recovery and heat integration, proved to significantly reduce the energy requirements of a process. This resulted not only in energy savings but also a lower environmental impact as we reduce the consumption of resources. In chapter 4, we showed the variability in the sustainable performance of chemical processes through the incorporation of technical and environmental uncertainties *via* Monte Carlo sampling. We remarked the importance of this analysis, as they present a more robust picture of the processes under consideration.

The optimisation of chemical processes was addressed in chapter 5, where we introduced a general framework (SUSCAPE) that incorporates surrogate models, objective-reduction techniques, multi-objective optimisation, and multi-criteria decision analysis tools. The framework was successfully applied to perform a simulation-based optimisation using a genetic algorithm incorporating integer variables and process constraints. The results demonstrated that surrogate models are an appealing technique to alleviate the computational effort during the optimisation stage. Similarly, objective-reduction techniques proved to generate Pareto front with higher quality when coupled with Multi-Objective Genetic Algorithms (MOGA). Finally, the application of Data Envelopment Analysis (DEA) as multi-criteria decision analysis tool enhanced the analysis by filtering optimal solutions, ranking them, and determining improvement targets for suboptimal alternatives. This was attained while avoiding the subjectivity attached to weights-based methods.

Aiming to provide clearer guidance to researchers and policy-making through a plant-toplanet analysis, in chapter 6 we presented an extension of the framework included in chapter 5. In this work, we proposed the evaluation and comparison of an ideal process against its catalystbased counterpart to help to identify catalysis targets and define potential research priorities in the implementation of sustainable processes. In terms of sustainability assessment, we proposed the incorporation of 'Planetary boundaries' (PBs), an absolute LCIA method, determined the global environmental impact of a process at a global scale. This chapter presents a direct comparison between monetary LCA values, a standard LCIA endpoint methodology and the framework of PBs. We concluded that while monetary values facilitate the analysis, they fail to provide thresholds above which a product is deemed unsustainable. Similarly, standard LCIAs are useful to compare and rank alternatives, but cannot determine whether they are truly sustainable because there are no reference values available to interpret the results. PBs, on the contrary, led to a radically different picture by uncovering the potential role of the process under study in avoiding the transgression of different earth systems.

To develop a sustainable industry, it is required to consider and ensure the exploitation of all byproducts and waste streams in across processes. In this work, we presented different relevant applications that proved the application of concepts such as circular economy, waste valorisation, carbon capture and renewable raw materials. In chapter 3, circular economy certainly showed waste PE pyrolysis as an appealing route to close the loop in the ethylene production process and enhance the development of a sustainable industry. The results also encourage research in the field to generate kinetic data to properly identify, model, and optimise the distribution of the products and pre-treatment processes for waste PE. The cost and environmental impact of this process were benefited from the byproducts generated. However, these byproducts can become an additional problem if their allocation in the market is not guaranteed. This is the case of waste glycerol, a byproduct in diesel production, which has become an abundant feedstock and whose production can become difficult to allocate in the near future. In chapter 4, we presented the valorisation of this raw material into propylene glycol, which presented an appealing pathway to promote sustainable practices. An innovative

route with a gradient temperature reactor showed how basic principles can certainly improve process performance. Yet, not all the routes seem promising and careful examination of glycerol purification and kinetic data are further required. Finally, as the industry develops, it is essential that new processes and technologies are developed under the umbrella of renewable resources. This concept was presented in chapters 5 and 6, where the production of methanol from carbon captured and hydrogen from renewable sources was assessed. The results presented in chapter 6 showed methanol production from carbon captured and hydrogen from water electrolysis as economically unappealing due to the high price of renewable hydrogen. As a result, future efforts should consider a hierarchy of priorities, where the most pressing target is rendering hydrogen production economically and environmentally more efficient. The PBs framework presented in this chapter also uncovered the potential role of CO₂-based methanol in avoiding the transgression of climate change. This core planetary boundary, currently surpassed by the fossil-based methanol, could by itself lead to a new state of the Earth system.

An adequate use of renewable raw materials is the way forward to achieve sustainable development in the long term. However, burden shifting seems inevitable and cross-sectorial cooperation appears as the only way to achieve the SDGs.

7.2 Future work

In terms of process modelling, process integration could potentially improve process performance. The generation of standard software packages to use integrated units coupled with process simulators or algebraic modelling could bring great benefits to the community. Similarly, the exploration of additional energy, mass, or property integration techniques could result in substantial improvements.

The optimisation of sustainable processes is certainly one of the most challenging areas. In the generation of surrogates, the use of adaptive sampling techniques can reduce the effort spent in the evaluation of the original model, which is the most time-consuming stage. Additionally, models able to capture the uncertainty of the model can provide more robust insights. The use of objective reduction techniques showed benefits during the multi-objective optimisation. Here, new approaches could be less computationally demanding and avoid the need for individual optimisations. As for the optimisation, derivative-based methods could improve the quality of the Pareto frontier generated. Finally, during the post analysis of the frontier, techniques could be incorporated not only to determine improvement targets using DEA, but actually modify the process variables aiming to achieve the best performance of suboptimal processes. The incorporation of these tools within a unified software would greatly help practitioners.

Within the framework of 'Planetary boundaries', impact levels are still without definition for some Earth systems, and others still carry some degree of uncertainty. A deeper analysis to accurately define the safe operating space and uncertainty region is crucial for this approach to succeed in the future.

The isolated assessment of chemical processes certainly benefits the industry. However, the current status of the Earth calls for powerful and decisive directions to achieve the SDGs. For this, is necessary to escalate sustainability assessments at the sectorial level. This will not only identify the routes that help to reduce the impact of the industry but also will reduce philosophical questions related to the boundaries of a system during the LCA application. In this context, the extension of these type of models to cover multiple sectors could guide research efforts and policy making.

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APPENDIX A

Table A1 Prices considered for raw ma	terials, products, consuma	bles, waste treatment and utilities.
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Commodity	Price (USD)				
Glycerol 90 wt. % ¹	0.25 \$/kg				
Hydrogen ²	2.68 \$/kg				
Water ³	0.50 \$/ton				
Raney nickel catalyst ⁴	25.00 \$/kg				
Cooper catalyst ⁴	120.00 \$/kg				
Wastewater treatment ³	1.50 \$/ton				
Natural Gas ⁵	3.79·10 ⁻⁶ \$/kJ				
Electricity ³	0.07 \$/kWh				
Steam (high pressure) ³	14.29 \$/1000 kg				
Propylene oxide ⁴	1.70 \$/kg				
Propylene glycol ⁶	2.65 \$/kg				
Dipropylene glycol ⁶	2.10 \$/kg				
Tripropylene glycol ⁶	1.05 \$/kg				
Ethylene glycol ⁶	4.15 \$/kg				
Methanol ⁷	0.27 \$/kg				
Ethanol ⁸	0.48 \$/kg				
Propanol ⁶	1.00 \$/kg				
Ethylene glycol ⁶	4.15 \$/kg				

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Table A2 Decinivent data for the compounds outside the boundaries of the plant. System model Anocation cut-on by classification											
Component [base unit]	Technology	Acidification Potential [kg SO2-eq]	Climate change [kg CO2-eq]	Depletion of abiotic resources [kg Sb-eq]	Freshwater aquatic ecotoxicity [kg 1,4- DCB-eq]	Marine aquatic ecotoxicity [kg 1,4- DCB-eq]	Terrestrial ecotoxicity [kg 1,4- DCB-eq]	Eutrophicati on [kg PO4-eq]	Human toxicity [kg 1,4- DCB-eq]	Ozone layer depletion [kg CFC-11- eq]	Photochemic al oxidation [kg C2H4-eq]
Hydrogen [kg]	hydrogen cracking, APME	3.54.10-3	1.70	3.31.10-2	2.34.10-2	1.06.102	8.89.10-5	3.20.10-4	3.90.10-2	3.77.10-10	2.77.10-4
Glycerol [kg]	Esterification of soybean oil	4.73·10 ⁻³	1.09	5.90.10-3	2.29.10-1	7.29.102	1.90.10-3	1.92.10-3	4.56·10 ⁻¹	1.13.10-7	6.56.10-4
Water [kg]	Market for tap water	8.42.10-7	1.62.104	1.08.10-6	4.58.104	3.16.10-1	3.52.10-6	2.59.10-7	1.81.10-4	1.58.10-11	7.12.10-8
Propylene oxide [kg]	Propylene oxide production, liquid	2.26.10-2	4.93	4.84.10-2	1.97	6.42·10 ³	2.14.10-2	1.11.10-2	2.98	1.96.10-6	2.74.10-3
Methanol [kg]	Market for methanol	6.02.10-3	0.73	1.75.10-2	1.83.10-1	5.31·10 ²	8.54E-04	6.37.10-4	3.85.10-1	1.71.10-7	4.21.10.4
Caustic soda [kg]	Sodium hydroxide for neutralizing agent	6.67.10-3	1.25	8.33·10 ⁻³	6.42·10 ⁻¹	2.07·10 ³	8.29.10-3	2.82.10-3	9.44·10 ⁻¹	7.46.10-7	2.79.10-4
HCl [kg]	Hydrochloric acid, without water, in 30% solution	8.27·10 ⁻³	1.54	1.09.10-2	8.44.10-1	2.70·10 ³	7.73·10 ⁻³	3.41.10-3	1.37	7.01.10-7	3.48.10.4
Steam HP [MJ]	Heat production, natural gas	1.80.104	6.72·10 ⁻²	5.52.10-4	2.91.10-3	$1.07 \cdot 10^{1}$	2.14.10-5	9.67.10-6	1.43.10-2	5.26.10-9	1.11.10-8
Electricity [kWh]	Electricity, high voltage, production mix	2.26.10-3	6.29·10 ⁻¹	4.64.10-3	3.88.10-1	1.21.103	9.28.10-4	2.25.10-3	3.57.10-1	5.23.10-8	1.04.10-4
Steel [kg]	Market for steel, low- alloyed	8.44.10-3	1.74	1.15.10-2	2.65	4.88·10 ³	3.67.10-2	5.74.10-3	8.13	9.81.10-8	9.57.104
Wastewater [m ³]	Market for wastewater from vegetable oil refinery	4.52.10-3	1.01	5.29.10-3	6.12.10-1	1.23.103	4.27.10-3	1.20.10-2	8.66·10 ⁻¹	4.01.10-8	2.43.10.4

Table A2 Ecoinvent data for the compounds outside the boundaries of the plant. System model 'Allocation cut-off by classification'

Glycerol impact values: Modelling of the transesterification process.

Since different allocation methods or assumptions can be made in the LCA of a specific product, we validated the environmental impact loads attached to glycerol taken from Ecoinvent database. First, we modelled the LCA of the transesterification process considering the 5 different biomass sources shown in table A4. Inventory data for the transesterification process were taken from Haas et al.(2006) and are presented in table A3. In all of the cases, the values obtained from the model were consistent with the Ecoinvent database, having relative errors below 20% as presented in Table A5.

oils taken from Haas et al.(2006)								
Component	Net value used for the production of 4230 kg/h of biodiesel.							
Vegetable oil	4255.7 kg							
Methanol	460.1 kg							
Tap water	186.2 kg							
Sodium hydroxide	1.8 kg							
Hydrochloric acid	10.6 kg							
Heat production	713.0 MJ							
Electricity	98.0 kWh							

Table A3 Inventory data for the transesterification of vegetable

Table A4 Vegetable oil sources considered in the production of biodiesel.

ID	Raw material	Process	Location
1	Crude soybean oil	Soybean meal and crude oil production, market	Market
2	Crude soybean oil	Soybean meal and crude oil production, chemical route	United States
3	Crude soybean oil	Soybean meal and crude oil production, chemical route	Brazil
4	Palm oil	Palm oil mill operation	Global
5	Rape oil	Rape oil mill operation	Global

Table A5 Relative error obtained in the LCIA values for the transesterification of vegetable oil between Ecoinvent database and the simulation model developed by Haas *et al.* (2006).

Raw material	Location	Acidification Potential [kg SO2-eq]	Climate change [kg CO2-eq]	Depletion of abiotic resources [kg Sb-eq]	Freshwater aquatic ecotoxicity [kg 1,4- DCB-eq]	Marine aquatic ecotoxicity [kg 1,4- DCB-eq]	Terrestrial ecotoxicity [kg 1,4- DCB-eq]	Eutrophicati on [kg PO4-eq]	Human toxicity [kg 1,4- DCB-eq]	Ozone layer depletion [kg CFC-11- eq]	Photochemic al oxidation [kg C2H4-eq]
soybean crude oil	Global	8.8%	0.8%	9.1%	6.4%	17.4%	0.2%	1.9%	0.3%	16.9%	1.8%
soybean crude oil	United States	8.4%	7.7%	11.2%	19.9%	19.4%	22.3%	8.0%	15.0%	30.9%	0.3%
soybean crude oil	Brazil	27.3%	5.9%	21.9%	33.0%	28.5%	9.2%	8.6%	10.0%	21.2%	3.8%
palm oil mill operation	Global	6.0%	2.5%	17.0%	1.7%	19.8%	0.4%	2.3%	2.0%	10.8%	1.5%
rape oil mill operation	Global	1.5%	3.9%	6.8%	1.1%	6.7%	0.1%	0.5%	3.7%	2.2%	4.0%

Production of propylene glycol using different biomass sources.

Table A6 LCIA values for the production of propylene glycol from biodiesel glycerol under different sources of biomass. Values compared against the business as usual alternative.

Case	Biomass / Raw material	Acidificatio n Potential [kg SO2- eq]	Climate change [kg CO ₂ - eq]	Depletion of abiotic resources [kg Sb-eq]	Freshwater aquatic ecotoxicity [kg 1,4- DCB-eq]	Marine aquatic ecotoxicity [kg 1,4- DCB-eq]	Terrestrial ecotoxicity [kg 1,4- DCB-eq]	Eutrophica tion [kg PO4- eq]	Human toxicity [kg 1,4- DCB-eq]	Ozone layer depletion [kg CFC- 11-eq]	Photochem ical oxidation [kg C2H4- eq]
BAU	Propylene oxide	2.04*10-2	4.75	4.54*10-2	1.66	5.41*10 ³	1.7710-2	9.29*10 ⁻³	2.60	1.66*10-6	2.35*10-3
GB-1	soybean crude oil Global	9.83*10 ⁻³	3.99	1.24*10 ⁻²	0.62	1.12*10 ³	2.04*10-2	1.19*10 ⁻²	2.60	1.73*10 ⁻⁷	2.28*10-3
GB-1	soybean crude oil United States	7.57*10-3	1.90	1.19*10-2	0.35	1.10*10 ³	2.77*10-3	2.79*10 ⁻³	0.71	1.83*10-7	9.72*10-4
GB-1	soybean crude oil Brazil	1.09*10-2	4.84	1.32*10-2	0.61	1.58*10 ³	1.65*10-2	1.47*10-2	3.50	1.81*10-7	3.86*10-3
GB-1	palm oil mill operation Global	1.09*10-2	5.65	9.00*10-3	3.05	6.66*10 ²	1.26	7.58*10 ⁻³	3.50	8.79*10-8	2.71*10-3
GB-1	rape oil mill operation Global	3.84*10 ⁻²	3.29	1.68*10 ⁻²	3.77	1.78*10 ³	1.47	3.02*10-2	1.60	3.10*10-7	7.97*10 ⁻⁴

Uncertainty analysis

To evaluate the uncertainty attached to the model, we first performed a sensitivity analysis over some of the technical parameters of the processes, such as flowrates, product yields, prices of products and raw materials and operating conditions of different equipment. Afterwards, we identified the most critical parameters and developed a normal distribution of 300 samples for each one of them. The use of 300 samples ensure that the mean of the model has a relative error below 5% for a confidence level of 95% for all the parameters evaluated. Finally, the model was assessed for the samples generated and the uncertainty was evaluated. The parameters considered for the sensitivity analysis and their impact to the economic and environmental indicators are presented in tables A7 and A8.

To generate the samples related to the environmental uncertainties, we apply the Pedigree matrix with the data entries shown in Table A9 and the basic uncertainty factor (U_b) values of the main emissions for each impact, which are given in Table A10. With the distribution parameters obtained from the Pedigree matrix, we generated 10 additional scenarios for each sample generated in the model uncertainty.

A total of 3,000 samples were used to evaluate the uncertainty of the LCA models, ensuring that the mean of the model has a relative error below 5% for a confidence level of 95% for all the environmental impact categories in all the alternatives according to the approach presented by Law (2015). In this approach, to obtain an estimate of the mean μ with a relative error of γ (0< γ < 1) and a confidence interval of 100(1- α) percent, an initial number of replications n_0 is chosen and the usual confidence interval half-length calculated as:

$$\delta(\mathbf{n}, \alpha) = t_{i-1, 1-\alpha/2} \sqrt{S^2(n)/n} \tag{A1}$$

Where n is the number of samples, $t_{i-1,1-\alpha/2}$ is the upper 1- $\alpha/2$ critical point for a standard normal random variable, and $S^2(n)$ the sample variance. The number of samples is satisfactory when $\delta(n, \alpha)/|\bar{X}(n)| \leq \gamma'$, where γ' is given by:

$$\gamma' = \frac{\gamma}{1+\gamma} \tag{A2}$$

And

$$\gamma = \frac{|\bar{X} - \mu|}{|\mu|} \tag{A3}$$

Table A7 Sets of conversions evaluated for the different routes proposed.

Case	Conversions					
BAU (McKetta and Cunningham, 1993)	$x_1 = 93.1 \pm 1.5\%$; $x_2 = 7.1 \pm 21.6\%$; $x_3 = 5.0 \pm 38.36\%$					
GB-1 (Pudi et al., 2015; Wołosiak-Hnat et al., 2013)	$x_4 = 88.7 \pm 1.4\%$; $x_5 = 94.3 \pm 1.5\%$; $x_6 = 2.2 \pm 6.8\%$					
GB-2 (Akiyama et al., 2009)	$x_4 = 100 - 1.5\%$; $x_5 = 96.1 \pm 1.5\%$; $x_6 = 2.2 \pm 16\%$					
GB-3 (Maglinao and He, 2012, 2011)	$x_7 = 93.1 \pm 0.38\%$; $x_8 = 49.6 \pm 7.7\%$; $x_9 = 38.9 \pm 15\%$; $x_{10} = 91.5 \pm 0.1\%$; $x_{11} = 2.1 \pm 44\%$; $x_{12} = 20.2 \pm 2.2\%$					

x_i: molar conversion. Indexes refer to the equations presented in the process description. Lower and upper bounds retrieved from literature sources.

Alternative	Technical parameter	Base case value and variation data	TCOP per kg of PG	EP per kg of PG	Economic allocation	Life cycle impact assessment variation (%)
BAU	Conversion	Table S7	0.72%	3.23%	0.89%	1.49%
	Flash pressure (kPa)	100±20%	0.36%	1.89%	0.01%	1.12%
	DC1 pressure (kPa)	10±5 kPa	0.88%	2.59%	0.45%	0.94%
	DC2 pressure (kPa)	10±5 kPa	0.10%	0.14%	0.04%	0.02%
	DC3 pressure (kPa)	10±5 kPa	0.70%	1.39%	0.01%	0.88%
	PG composition	0.996±0.20%	0.14%	0.01%	0.09%	0.04%
	PO flowrate (kg/h)	75±10%	1.25%	0.62%	0.33%	0.73%
	PO price (\$/kg)	1.70±15%	12.98%	19.29%	0.00%	0.00%
	PG price (\$/kg)	2.65±15%	0.00%	34.02%	1.53%	1.53%
	DPG price (\$/kg)	2.10±15%	0.00%	3.75%	1.49%	1.49%
	TPG price (\$/kg)	1.00±15%	0.00%	2.11%	0.85%	0.85%
GB-1	Conversion	Table S7	0.71%	0.52%	0.23%	0.95%
	Flash temperature (°C)	30±25%	0.10%	0.03%	0.00%	0.08%
	DC1 pressure (kPa)	10±5 kPa	0.23%	0.11%	0.00%	0.02%
	DC3 pressure (kPa)	10±5 kPa	0.12%	0.07%	0.00%	0.32%
	Gas purge ratio (% open)	0.57±20%	0.64%	0.24%	0.02%	0.32%
	Water purge ratio (% open)	0.027±20%	1.10%	0.40%	0.00%	0.16%

Table A8 Technical para	ameters considered in	the sensitivity anal	vsis of the PG processes.
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Alternative	Technical parameter	Base case value and variation data	TCOP per kg of PG	EP per kg of PG	Economic allocation	Life cycle impact assessment variation (%)
	Glycerol flowrate (kg/h)	118±10%	2.58%	1.03%	0.01%	0.26%
	PG composition	0.996±0.20%	0.58%	0.04%	0.16%	0.39%
	Hydrogen price (\$/kg)	2.68±15%	1.74%	0.60%	0.00%	0.00%
	Glycerol price (\$/kg)	0.25±15%	7.80%	2.67%	0.00%	0.00%
	PG price (\$/kg)	2.65±15%	0.00%	19.94%	0.40%	0.40%
	EG price (\$/kg)	4.15±15%	0.00%	0.51%	0.37%	0.38%
	MeOH price (\$/kg)	0.27±15%	0.00%	0.02%	0.02%	0.02%
GB-2	Conversion	Table S7	3.13%	2.47%	0.51%	0.51%
	Flash temperature (°C)	30±25%	0.02%	0.02%	0.05%	0.05%
	DC1 pressure (kPa)	100±20%	0.04%	0.02%	0.00%	0.00%
	DC2 pressure (kPa)	100±20%	0.36%	0.22%	0.11%	0.11%
	DC3 pressure (kPa)	100±20%	0.05%	0.03%	0.05%	0.05%
	DC4 pressure (kPa)	100±20%	0.34%	0.11%	0.44%	0.44%
	Gas purge ratio (% open)	0.95±15%	3.73%	1.23%	0.37%	0.37%
	Glycerol flowrate (kg/h)	118±10%	1.04%	0.60%	0.11%	0.11%
	PG composition	0.996±0.20%	0.14%	0.15%	0.06%	0.06%
	Hydrogen price (\$/kg)	2.68±15%	2.00%	0.62%	0.00%	0.00%
	Glycerol price (\$/kg)	0.25±15%	8.08%	2.53%	0.00%	0.00%
	PG price (\$/kg)	2.65±15%	0.00%	19.35%	0.41%	0.41%
	EG price (\$/kg)	4.15±15%	0.00%	0.58%	0.39%	0.39%
	MeOH price (\$/kg)	0.27±15%	0.00%	0.24%	0.01%	0.01%
GB-3	Conversion	Table S7	7.93%	54.62%	0.01%	12.19%
	Flash temperature (°C)	30±25%	0.44%	2.19%	0.00%	0.21%
	Flash pressure (kPa)	100±20%	0.05%	0.30%	0.00%	0.01%
	DC1 pressure (kPa)	100±20%	0.04%	0.26%	0.00%	0.00%
	DC2 pressure (kPa)	10±5 kPa	0.09%	0.68%	0.00%	0.15%
	DC3 pressure (kPa)	10±5 kPa	0.27%	1.54%	0.00%	0.07%
	DC4 pressure (kPa)	100±20%	0.29%	1.47%	0.00%	1.84%
	Glycerol flowrate (kg/h)	118±10%	3.37%	17.01%	0.19%	1.18%
	PG composition	0.996±0.20%	0.50%	1.65%	0.03%	0.49%
	Glycerol price (\$/kg)	0.25±15%	6.89%	37.12%	0.00%	0.00%
	PG price (\$/kg)	2.65±15%	0.00%	105.43%	0.49%	0.50%
	MeOH price (\$/kg)	0.27±15%	0.00%	0.33%	0.05%	0.05%
	EtOH price (\$/kg)	0.48±15%	0.00%	2.02%	0.34%	0.34%
	PrOH price (\$/kg)	1.00±15%	0.00%	0.70%	0.10%	0.10%

Table A8 Technical parameters considered in the sensitivity analysis of the PG processes.

*Highlighted parameters were considered for the uncertainty analysis.

Tables A9 presents the scores considered in the evaluation of the Pedigree matrix. Uncertainty basic factors (U_b) of the main emissions within each impact category are presented in Table A10.

Component [base unit]	Technology	Reliability U1	Completene ss U ₂	Temporal correlation U ₃	Geographic al correlation U ₄	Further technologica l correlation U ₅
Hydrogen [kg]	hydrogen cracking, APME	2	3	1	2	1
Glycerol [kg]	Esterification of soybean oil	1	3	1	1	1
Water [kg]	Market for tap water	5	5	1	3	4
Propylene oxide [kg]	Propylene oxide production, liquid	2	5	1	2	1
Steam HP [MJ]	Heat production, natural gas	2	4	1	3	1
Electricity [kWh]	Electricity, high voltage, production mix	5	5	1	1	1
Steel [kg]	Market for steel, low- alloyed	3	5	1	2	5
Wastewater [m ³]	Market for wastewater from vegetable oil refinery	3	5	1	3	5

 Table A9 Scores applied in the evaluation of the Pedigree matrix.

Table A10 Basic uncertainty factor (U_b) of the main emission per impact category.

Impact category	Main emission	Basic uncertainty factor (U _b)
Acidification Potential	Pollutants emitted to air: NOx	1.50
Climate change	Pollutants emitted to air: CO2	1.05
Depletion of abiotic resources	Resources: primary energy carriers	1.05
Freshwater aquatic ecotoxicity	Pollutants emitted to water: individual hydrocarbons	3.00
Marine aquatic ecotoxicity	Pollutants emitted to water: COD	1.50
Terrestrial ecotoxicity	Pollutants emitted to soil: metals	1.50
Eutrophication	Pollutants emitted to water: PO4	1.50
Human toxicity	Polycyclic aromatic hydrocarbons	3.00
Ozone layer depletion	Halogenated non-aromatic	1.50
Photochemical oxidation	Individual hydrocarbons	2.00

Table A11 Overall mass and energy balances for pa	propylene glycol production per kg of PG generated.
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Concept	BAU	GB-1	GB-2	GB-3

Raw materials

Concept	BAU	GB-1	GB-2	GB-3
Propylene oxide (kg/kg of PG)	0.900±0.156	-	-	-
Glycerol solution 90 wt. % (kg/kg of PG)	-	1.422±0.263	1.390±0.240	3.689±0.709
Hydrogen (kg/kg of PG)	-	0.0311±0.006	0.041 ± 0.014	-
Water (kg/ kg of PG)	0.211±0.024	0.009 ± 0.000	-	0.559±0.112
Total (kg/kg of PG)	1.111 ± 0.180	1.462±0.269	1.431±0.253	4.248±0.821
Waste streams				
Gas Purge (kg/kg of PG)	-	0.005 ± 0.000	0.007 ± 0.000	2.648±0.516
Wastewater (kg/kg of PG)	-	0.438±0.031	0.374 ± 0.007	0.398±0.285
Products				
Byproducts (kg/kg of PG)	Dipropylene glycol:	Methanol: 0.0104±0.001	Methanol: 0.013±0.010	Methanol: 0.032±0.010
	0.082±0.045 Tripropylene	Ethylene glycol: 0 0165+0 001	Ethylene glycol: 0.026+0.021	Ethanol: 0 149+0 030
	glycol 0.0735±0.051	0.0103-0.001	0.020-0.021	Propanol: 0.020±0.017
Propylene glycol production (kg)	1±0.014	1±0.073	1±0.026	1±0.124
Energy consumption				
Electricity (kW/ kg of PG)	0.123±0.001	$0.058 {\pm} 0.001$	$0.058 {\pm} 0.001$	0.120±0.012
Net heating demand (MJ/ kg of PG)	11.973±0.037	4.956±0.245	4.980±0.296	20.041±2.926
Net cooling demand (MJ/ kg of PG)	13.380±0.036	6.296±0.340	6.264±0.266	15.664±1.699

 Table A11 Overall mass and energy balances for propylene glycol production per kg of PG generated.

Table A12 Raw materials annualised costs under uncertainty.

Raw material	Business as usual case (BAU)	Glycerol-based case 1 (GB-1)	Glycerol-based case 2 (GB-2)	Glycerol-based case 3 (GB-3)
Glycerol (\$)	-	1.45±0.13·10 ⁷	$1.52 \pm 0.13 \cdot 10^7$	$1.45 \pm 0.13 \cdot 10^7$
Hydrogen (\$)	-	$3.38 \pm 0.25 \cdot 10^{6}$	$4.76 \pm 0.80 \cdot 10^{6}$	0.00
Water (\$)	$4.13 \pm 0.46 \cdot 10^3$	198±3	-	4356±352
Propylene Oxide (\$)	$5.86 \pm 1.02 \cdot 10^7$	-	-	-
Catalyst (\$)	-	6.19·10 ⁵	$1.95 \cdot 10^{6}$	$2.38 \cdot 10^4$
Total	$5.86 \pm 1.02 \cdot 10^7$	$1.79 \pm 0.15 \cdot 10^7$	$2.19 \pm 0.21 \cdot 10^7$	$1.45 \pm 0.13 \cdot 10^7$

Altownotivo	Equipment	Characteristics	Total Cost (USD)
Alternative	Equipment	Value 20 m3	
BAU	Flash	Diameter: 1.68 m	$2.58 \cdot 10^{5}$ 3.61 \cdot 10^{5}
	Pidsii	Height: 5.87 m	5.01 10
	Vacuum column 1	8 stages	1.19.106
		Diameter: 3.1 m	
	Vacuum column 2	Height: 9.6 m	4.62,105
	vacuum corumn 2	Diameter: 1.83 m	7.02 10
		Height: 9 m	
	Vacuum column 3	15 stages	$1.77 \cdot 10^5$
		Height: 4.8 m	
	Pumps	6 pumps	$2.19 \cdot 10^{5}$
	1 unipo	17.4 kWh	
	Heat Exchanger Network	Cooling tower: 760 l/s	$4.52 \cdot 10^{6}$
CD 1	Deceter	9heat exchangers (395m ²)	1 22 106
GB-I	Flash	Diameter: 0.7 m	$1.22 \cdot 10^{5}$ 1 18 \cdot 10^{5}
	Plash	Height: 3.4 m	1.10 10
	Vacuum column 1	9 stages	$4.52 \cdot 10^5$
		Diameter: 1.981 m	
	Vacuum column 2	Height: 7.20 m	2 67.106
	vacuum corumn 2	Diameter: 3.658 m	2.07 10
		Height: 13.00 m	
	Vacuum column 3	58 stages	$1.91 \cdot 10^{6}$
		Diameter: 0.457 m	
	Distillation column 1	Area Area Area Area Area Area Area Area	$1.90 \cdot 10^{5}$
	Distillation column 1	Diameter: 0.457 m	1.90 10
		Height: 1.82 m	
	Pumps	5 pumps	$1.77 \cdot 10^5$
	Compressors	KWN 1 compressor	$1.68 \cdot 10^{6}$
	Compressors	5.28 kWh	1.00 10
	Heat Exchanger Network	Cooling tower: 409 1/s	3.50.106
CD A	D. (14 heat exchangers (609 m ²)	1.65.106
GB-2	Flach	Volume: 17.7 m ²	1.65.10°
	r lasii	Height: 5.86 m	5.10 10
	Distillation Tower 1	17 stages	$3.27 \cdot 10^{5}$
		Diameter: 1.2 m	
	Distillation Trans 2	Height: 9.30 m	1.52.106
	Distillation Tower 2	Diameter: 2.7 m	1.55*10*
		Height: 18.9 m	
	Distillation Tower 3	14 stages	1.43.105
		Diameter: 0.6 m	
	Distillation Towar 4	Height: 5./ m	5 90.105
	Distillation Tower 4	Diameter: 1.4 m	5.90 10
		Height: 20.1 m	
	Heat Exchanger Network	Cooling tower: 448 l/s	3.63.106
CD 2	Deaster	Total volume: 311 m ³	1 399-107
GD-J	Reactor	(4 reactors)	1.577 10
	Flash 1	Diameter: 0.8 m	1.38·10 ⁵
		Height: 4.2 m	
	Flash 2	Diameter: 0.8 m	1.38.105
	Distillation Tower 1	30 stages	$2.24 \cdot 10^{5}$
	Distillation 10wei 1	Diameter: 0.86 m	2.27 10
		Height: 13.8 m	
	Distillation Tower 2	32 stages	$2.13 \cdot 10^5$
		Diameter: 0.7 m Height: 13.5 m	
	Distillation Tower 3	71 stages	2 89.105
	Distinution Tower 3	Diameter: 0.5 m	2.07 10
		Height: 30.7 m	
	Distillation Tower 4	90 stages	$4.00 \cdot 10^5$
		Diameter: 0.9 m	

Alternative	Equipment	Characteristics	Total Cost (USD)						
		Height: 25.2 m							
	Vacuum column 1	10 stages	3.58·10 ⁵						
		Diameter: 1.7 m							
		Height: 12.0 m							
	Vacuum column 2	4 stages	1.35.105						
		Diameter: 0.8 m							
		Height: 3.8 m							
	Extractive column 1	20 stages	1.52.105						
		Diameter: 0.5 m							
		Height: 9.2 m							
	Pumps	4 pumps	1.43.105						
		10.83 kWh							
	Heat Exchanger Network	Cooling tower: 409 1/s	7.31.106						
	8	20 heat exchangers (4,179 m ²)							

Table A13. Capital Costs Summary

Table A14 Costs summar	u for the	proposed alternative	s under uncertainty
Table A14. Costs summar	y for the	proposed alternative	s under uncertainty.

Indicator	BAU	GB-1	GB-2	GB-3
Raw materials (\$.10 ⁷ /y)	5.86±1.02·10 ⁷	1.79±0.15·10 ⁷	2.19±0.21·10 ⁷	1.45±0.13·10 ⁷
Utilities ($(10^{6}/y)$	4.087±0.010	1.818±0.045	1.956±0.114	3.559±2.313
Fixed Capital Costs (\$.107)	1.478±0.023	1.682±0.053	1.326±0.063	3.673±0.693
Variable costs of production (VCOP) (\$·10 ⁷ /y)	6.274±1.017	2.184±0.275	2.371±0.311	1.810±0.364
Fixed costs of production (FCOP) ($\$ \cdot 10^{6}$ /y)	2.985±0.024	3.090±0.027	2.908±0.032	4.111±0.355
Revenue ($(.10^8/y)$	1.108±0.178	1.106±0.198	1.207±0.201	0.432±0.009
Total Annualised Cost (TAC) $(\$ \cdot 10^{7}/y)$	6.868±1.017	2.829±0.140	2.927±0.311	2.956±0.484
TAC (\$) per kilogram of Propylene Glycol	1.792±0.133	0.695±0.064	0.669±0.075	1.887±0.385
Economic potential (EP) $(\$ \cdot 10^{7}/y)$	2.637±1.352	5.230±1.264	5.849±1.312	0.627±0.709
EP per kilogram of Propylene Glycol (\$·10 ⁷ /y)	0.689±0.352	1.285±0.298	1.336±0.303	0.393±0.420

 Table S15. Percentage contributions to the economic allocation evaluated under uncertainty

Case	Contribution to total revenue.	
BAU	PG: 85.5±13.8 %	
GB-1	PG: 97.37±0.45 %	
GB-2	PG: 95.97±3.38 %	
GB-3	PG: 96.35±1.02 %	

Heat integration – Nominal case

Table S16 presents a summary of the results obtained after the solution of the MINLP for heat integration of the nominal cases.

BAU										
Cooling duty (kJ/h)	Heating duty (kJ/h)	Capital	cost (\$)							
2,006,406	11,412,614	327	,735							
Hot streams	1	2	3	4						
T in (K)	375	398	435	464						
T out (K)	303	303	303	303						
FCp (kJ / (h*K))	32,362	4,074	298	182						
Cold streams	1									
T in (K)	303									
T out (K)	463									
FCp (kJ / (h*K))	33,533									
Exchangers					Heaters			Coolers		
hot stream	cold stream	stage	area (m2)	duty (kJ/h)	stream	area (m2)	duty (kJ/h)	stream	area (m2)	duty (kJ/h)
1	1	3	221.0	1,863,784	1	33.1	3,170,171	1	20.2	454,533
2	1	2	13.5	94,037				2	6.7	68,424
2	1	3	43.2	223,390				3	0.9	21,326
3	1	2	1.3	18,019				4	1.2	13,052
4	1	2	1.8	16,200						

Table S16. Heat integration results for the nominal cases using MINLP.

			Table S16. Heat	integration result	ts for the nom	inal cases usin	g MINLP.			
GB-1										
Cooling duty (kJ/h)	Heating duty (kJ/h)	Capital	cost (\$)							
43,659,379	36,529,673	634	,711							
Hot streams	1	2	3	4	5	6	7	8	9	10
T in (K)	478	398	373	406	478	335	320	383	398	337
T out (K)	298	303	303	303	303	303	310	373	388	327
FCP (kJ / (h*K))	17,546	4,573	4,739	73	5,451	58	535,553	164,736	319,872	22,785
Cold streams	1	2	3	4	5	6				
T in (K)	307	299	398	462	406	373				
T out (K)	478	478	408	472	416	383				
FCP (kJ / (h*K))	9,063	2,578	594,843	160,139	327,479	50,096				
Exchangers					Heaters			Coolers		
hot stream	cold stream	stage	area (m2)	duty (kJ/h)	stream	area (m2)	duty (kJ/h)	stream	area (m2)	duty (kJ/h)
1	1	2	21.0	823,636	1	4.3	724,164	1	24.6	1,108,040
1	3	1	31.9	1,226,550	2	26.2	205,990	2	15.0	434,489
5	2	2	100.4	256,545	3	24.2	4,340,806	3	5.7	330,874
5	3	1	20.5	381,072	4	25.6	1,601,386	4	0.2	7,517
9	6	1	46.1	500,962	5	26.3	3,274,786	5	14.3	316,344
					6	0.0	0	6	0.1	1,845
								7	148.4	5,355,530
								8	20.7	1,647,361
								9	29.2	2,697,759
								10	6.0	227,847

Table S1C Heat into quetio MINI D · 1

Table S16. Heat integration results for the nominal cases using MINLP.										
GB-2										
Cooling duty (kJ/h)	Heating duty (kJ/h)	Capital	cost (\$)							
26,713,680	26,686,923	626,309								
Hot streams	1	2	3	4	5	6	7	8	9	
T in (K)	378	373	460	373	470	330	460	338	373	
T out (K)	298	328	303	303	303	303	450	328	363	
FCP (kJ / (h*K))	21,065	35,345	4,847	2,423	81	49	502,273	38,892	403,724	
Cold streams	1	2	3	4	5	6				
T in (K)	293	296	379	460	470	373				
T out (K)	473	473	395	470	480	383				
FCP (kJ / (h*K))	8,305	2,798	249,972	210,770	502,288	50,493				
Exchangers					heaters			coolers		
hot stream	cold stream	stage	area (m2)	duty (kJ/h)	stream	area (m2)	duty (kJ/h)	stream	area (m2)	duty (kJ/h)
1	1	3	17.4	616,785	1	1.4	189,235	1	24.4	867,744
1	2	3	91.6	200,655	2	14.2	93,222	2	23.6	1,593,030
3	1	2	11.5	398,340	4	23.8	2,107,700	3	6.0	363,555
5	1	3	0.5	6,053	5	92.7	5,022,878	4	3.8	168,656
5	2	1	4.3	7,417				6	0.1	1,325
7	1	1	13.8	284,398				8	18.5	388,922
7	2	1	43.8	193,110				9	44.9	4,037,235
7	3	2	91.4	4,040,294						
7	6	2	10.1	504,930						

			Table S16. Heat	integration result	s for the nor	linal cases usin	Ig MIINLP.				
GB-3											
Cooling duty (kJ/h)	Heating duty (kJ/h)	Capital	cost (\$)								
17,004,672	1,446,315	1,037,259									
Hot streams	1	2	3	4	5	6	7	8	9	10	11
T in (K)	513	369	350	337	454	352	398	351	355	373	319
T out (K)	298	346	320	218	348	293	303	303	303	303	303
FCP (kJ / (h*K))	23426	103228	26509	2900	218	423	1694	309	54	1283	0
Cold streams	1	2	3								
T in (K)	307	406	363								
T out (K)	513	454	401								
FCP (kJ / (h*K))	18323	9814	8072								
Exchangers					heaters			coolers			
hot stream	cold stream	stage	area (m2)	duty (kJ/h)	stream	area (m2)	duty (kJ/h)	stream	area (m2)	duty (kJ/h)	
1	1	1	1058.6	1556339	1	9.3	401754	1	519.7	1558701	
1	1	2	774.1	1208776				2	30.7	2378270	
1	2	1	181.1	467087				3	8.9	185285	
1	3	1	35.8	245686				4	6.6	345193	
3	1	3	66.8	614530				5	0.1	5506	
5	3	2	0.8	17584				6	1.8	24752	
7	3	2	3.7	42041				7	3.4	118974	
								8	0.7	14744	
								9	0.1	2781	
								10	1.5	89314	



Uncertainty results

Figure A1 Environmental life cycle assessment results under uncertainty for the proposed alternatives. Impacts expressed per kg of PG.

APPENDIX B

Objective reduction (OR)

In OR approaches, redundant objectives are identified by quantifying a minimum approximation error using an initial approximation of the whole Pareto frontier. This initial frontier can be typically constructed in several ways. One possible manner to generate this approximation to the frontier is to run single-objective optimisations for each metric separately and then use the extreme points obtained in doing so for OR. Another possible way is to generate points in the space of every combination of two objectives. After the approximation of the Pareto frontier is obtained and prior to the application of the OR model, a normalisation step is carried out to improve the numerical performance of the OR algorithm according to the following expressions:

$$f_{ni} = (f_i - f_{imin}) / (f_{imax} - f_{imin})$$
(B1)

$$f_{ni} = (f_{imax} - f_i) / (f_{imax} - f_{imin})$$
(B2)

Where f_{ni} represents a normalised value in objective i, and f_{imax} and f_{imin} represent the maximum and minimum values of objective i, respectively. Equation B1 is used for those objectives to be minimized, while equation B2 is employed for objectives to be maximized.

The OR method seeks to identify a subset of objectives k from the full space K ($k \subseteq K$) such that the dominance structure of the Pareto front is preserved within a minimum allowable error. We next provide an overview of the MILP, while further details can be found in Guillen-Gosalbez (2011).

The MILP carries out a dimensionality reduction analysis considering an initial set of Pareto points p belonging to the set P and considering |K| objectives, some of which will be omitted based on an error metric. To evaluate the approximation error incurred when removing objectives, that is, when producing the Pareto front of dimension k instead of the original one containing |K| criteria (k < K), we define the binary parameter YP_{p,p',i} and the binary variables ZO_i and ZD_{p,p'}. YP_{p,p',i} models the dominance relationship between solutions p and p' in objective i, and takes the value of one if solution p is better than solution p' in objective i and zero otherwise. ZO_i models the decision of eliminating objectives from the original space, and is one if objective i is removed and zero if it remains in the set. ZD_{p,p'} models the dominance relationship between solution p' dominates p in the reduced Pareto space (after removing objectives) and zero otherwise.



Figure A1. Illustration of variables used in objective reduction model.

This notation is clarified in Figure B1, where three optimal solutions are considered for a problem with four objectives. In this example, objective two is removed from the original space, resulting in $ZO_2 = 1$. Figure B1 also shows how solution p_2 dominates solution p_3 in the reduced space, which results in $ZD_{3,2} = 1$. This does not happen in the original space, where p3 is Pareto optimal due to its good performance in objective 2. Furthermore, the values of the binary parameter $YP_{p,p',i}$ are presented in the table attached to the figure.

In essence, the MILP seeks to minimise the approximation error of removing objectives from the original space. This error is expressed by the variable $\delta_{p,p',i}$, which quantifies the maximum difference in the removed objective i between solutions p' (e.g., p2) and p (e.g., p3), where the former dominates the latter in the reduced domain, such that p' would also dominate p in the original space. To clarify this, let us consider the example in Figure B1. As previously described, solution p_2 dominates solution p_3 in the reduced space; however, this is not true when objective 2 is removed. For solution p_2 to dominate solution p_3 in the full space, the value of solution p_2 in objective 2 should be at least equal to the one in solution p_3 . This difference between solutions p_2 and p_3 in objective 2 is employed to quantify the approximation error $\delta_{3,2,2}$. This error is calculated as follows:

$$\delta_{\mathbf{p},\mathbf{p},\mathbf{i}} = \left(\mathbf{f}_{\mathbf{p}',\mathbf{i}} - \mathbf{f}_{\mathbf{p},\mathbf{i}}\right) \text{ZOD}_{\mathbf{p},\mathbf{p}',\mathbf{i}} \quad \forall \mathbf{p} \neq \mathbf{p}'$$
(B3)

Where $ZOD_{p,p',i}$ is defined by the following constraints:

$$ZOD_{p,p',i} \le ZO_i \quad \forall \ p \neq p' \tag{B4}$$

$$ZOD_{p,p',i} \le ZD_{p,p'} \quad \forall \ p \neq p' \tag{B5}$$

$$ZOD_{p,p',i} \ge ZO_i + ZD_{p,p'} - 1 \quad \forall \ p \neq p'$$
(B6)

Using Eq. B3, the value of $\delta_{p,p',i}$ is determined only for those solutions p dominated by at least another solution p' in the reduced space ($ZD_{p,p'} = 1$) and only when objective i is omitted ($ZO_i = 1$). In contrast, if solution s is not dominated in the reduced space ($ZD_{p,p'} = 0$) or objective i is not omitted ($ZO_i = 0$), then $\delta_{p,p',i}$ will take a zero value.

The definition of $ZD_{p,p}$, is enforced by the following constraints:

$$\left(K - \sum ZO_{i}\right) - K\left(1 - ZD_{p,p'}\right) \leq \sum_{i} YP_{p',p,i}(1 - ZO_{i}) \leq \left(K - \sum ZO_{i}\right) + K\left(1 - ZD_{p,p'}\right) \quad \forall p \neq p' \quad (B7)$$

$$\sum_{i} YP_{p',p,i}(1 - ZO_i) \le \left(K - \sum_{i} ZO_i\right) - 1 + KZD_{p,p'} \quad \forall p \neq p'$$
(B8)

From Eq. B7, if solution p is dominated by solution p' in the reduced space, the variable $YP_{p',p,i}$ will be equal to one for all the objectives kept in the reduced space ($ZO_i = 0$). In that case, the sum of $YP_{p',p,i}$ will be equal to the reduced number of objectives for which $ZD_{p,p'}$ equals one. If solution p is not dominated by solution p', the sum of $YP_{p',p,i}(1 - ZO_i)$ will be lower than the number of objectives kept and Eq. B8 will force $ZD_{p,p'}$ to be equal to zero.

Considering that our goal is to identify the minimum number of objectives for a given error $\overline{\delta}$, we can impose an upper bound on $\delta_{p,p',i}$ as follows:

$$\delta_{\mathbf{p},\mathbf{p}',\mathbf{i}} \le \bar{\delta} \tag{B9}$$

Finally, the MILP formulation can be expressed in compact form as follows:

$$\max\sum_{i} ZO_{i}$$
(B10)

s.t. constraints B3-B9.

The solution of this MILP provides the minimum combination of objectives for which $\delta_{p,p',i} \leq \overline{\delta}$. Note that additional constraints can be added to avoid calculating errors between two solutions

that are not Pareto optimal in the reduced space (see original paper for details (Guillén-Gosálbez, 2011)).

Note that it may happen that the exhaustive exploration of all combinations of objectives may be faster than solving the MILP, particularly in cases where many objectives can be eliminated without increasing the approximation error.

APPENDIX C

Process modelling of methanol production

The traditional syngas-based process was modelled according to Luyben (2010). Here, a stream containing 11,450 kmol h^{-1} of syngas at 50°C and 51 bar is compressed to 75 bar, cooled to 38°C, and pressurised again to 110 bar, which corresponds to the operating pressure in the reactor. The syngas, generated by steam reforming of natural gas (NG), has a mole composition of 67.47% H₂, 22.97% CO, 6.86% CO₂, 0.23% H₂O, 2.17% CH₄, and 0.3% N₂. The pressurised stream of syngas is mixed with three recycled streams, and then heated to 150°C before being fed to the reactor. The latter is a plug-flow reactor (PFR) holding a packed catalyst bed with a volume of 100 m³. The Cu-ZnO-Al₂O₃ catalyst follows the kinetics already reported by Vanden Bussche and Froment (1996).

The heat released upon reaction is used to generate high-pressure steam at 254°C and 42 bar. The effluent of the reactor exiting the unit at 266°C is cooled down to 38°C, and then sent to the first flash separator. Part of the gas stream in this unit is pressurised to 110 bar and recycled back to the process, while the rest is released to the environment through a purge, which contains 49.7% H₂, 32.6% CH₄, 8.6% CO₂, 4.5% N₂, 4.1% CO, and 0.5% methanol. The liquid stream is depressurised to 2 bar and fed into a second flash separator. The gas stream from the second flash is again pressurised to 110 bar and recycled to the process, while the liquid stream is sent to a distillation column. The column implements a partial condenser, where the gases collected are pressurised and recycled back to the process. The liquid stream at the bottom of the column mostly comprises water, which is recovered and sent to a wastewater treatment unit.

increased to match the reactor conditions, *i.e.*, 50 bar. Hydrogen is available at 30 bar and needs to be compressed to reach the same pressure. The two gases are mixed with a recycled stream and heated between 180-280°C to carry out the reaction at 50 bar. As in the previous case, the outlet stream is cooled down and sent to a flash unit, where part of the vapour stream containing CO_2 , hydrogen and CO is recovered and recycled back to the reactor, while a certain amount is purged to avoid the build-up of species within the system. This purge contains unreacted H₂ (\approx 80%), CO₂ ($\approx 10\%$), CO ($\approx 4\%$), methanol ($\approx 6\%$), and water (<1%). The liquid stream leaving the flash unit is depressurised to 2 bar, and then sent to a second flash unit, where most of the remaining gases are separated from water and methanol. The liquid stream from the second flash separator is heated to 80°C and then fed to a distillation column, where methanol is recovered with a molar purity of 99.9 %. The gaseous emissions from the first flash unit are used to generate steam at high pressure, in a furnace added to the conventional flowsheet. Two different reactor models were implemented in the CO₂-based flowsheet. The first was an equilibrium reactor providing the best possible performance based on the thermodynamic limit of the reaction system. In essence, this model implements an ideal catalyst attaining the equilibrium in the main reaction, *i.e.*, CO₂ hydrogenation, while fully inhibiting the unwanted parallel reverse water-gas shift (RWGS) reaction. The second was a plug-flow reactor loaded with the Cu-ZnO-Al₂O₃ catalyst following the same kinetic model previously mentioned. In both cases, the fresh CO_2 feed was fixed to 2,000 kmol h^{-1} to ensure a minimum annual production of 440 kton y⁻¹, a value often found for conventional plants.(Pérez-Fortes et al., 2016)

Overall, three rigorous models were developed in Aspen-HYSYS v9: (i) the business-as-usual process producing methanol from syngas from natural gas, the operating conditions of which were

not optimised in this work but rather fixed to the values reported by Luyben; (ii) CO₂ hydrogenation over an ideal catalyst reaching the thermodynamic limit; and (iii) the same CO₂-based process implementing the copper-based catalyst. The optimisation of the two CO₂-based flowsheets was performed using a genetic algorithm coupled with the simulation model in Aspen-HYSYS, where the decision variables optimised correspond to temperature and pressure in the reactor, and hydrogen fresh feed and purge ratio for the ideal flowsheet, and volume and temperature of the reactor, and hydrogen fresh feed and purge ratio for the one based on the Cu-ZnO-Al₂O₃ catalyst. Given that equilibrium reactors produce the same results regardless of the reactor volume, *i.e.*, equilibrium is assumed to be attained instantly, the volume was set at a standard value of 63 m^3 in the ideal CO₂-based scenario (Gonzalez-Garay and Guillen-Gosalbez, 2018). An additional compressor was included when the hydrogen feed pressure in the optimisation raised above 30 bar (hydrogen feed pressure). In the copper catalyst-based process, the pressure was fixed to 50 bar, as reported in the original source of the kinetic data for the Cu-ZnO-Al₂O₃ catalyst (Vanden Bussche and Froment, 1996). The ordinary differential equations system that models the kinetics was solved with Aspen-HYSYS by defining the corresponding kinetic expression in the reactor model. During the optimisation of the flowsheets, heat integration was performed using the targets obtained with the composite curve. Once the optimum value was found, a detailed heat exchanger network design was carried out applying the MINLP approach of Yee and Grossmann (1990).

The OPEX of the various flowsheets were estimated using the cost parameters listed in Table A1, while the CAPEX were calculated using the correlations and standard economic parameters given by Towler and Sinnot (2013), considering the installation factors reported therein for each equipment unit, and estimating the annualised capital cost. All the cost values were expressed in

2015USD. CAPEX from year 2010 where projected to year 2015 using the CEPCI index, with a value of 570.5.

Table C1 Cost parameters used in the OPEX calculations.						
Flow	Cost (USD unit ⁻¹)					
CO2 coal-based power plant(Rubin et al., 2015) (kg)	0.047					
CO2 natural gas-based power plant(Rubin et al., 2015) (kg)	0.075					
CO2 direct air capture(Keith et al., 2018) (kg)	0.16					
H ₂ biomass (Parkinson et al., 2019) (kg)	2.24					
H2 nuclear (Parkinson et al., 2019) (kg)	4.63					
H ₂ wind (Parkinson et al., 2019) (kg)	5.24					
H ₂ solar (Parkinson et al., 2019) (kg)	8.87					
Steam (Seider et al., 2009) (ton)	14.30					
Electricity(Pérez-Fortes et al., 2016) (MWh)	104.61					
Cooling water(Pérez-Fortes et al., 2016) (m ³)	3.30.10 ⁻²					
Catalyst (kg)	125.00					
Heat recovery (Martín and Grossmann, 2012) (ton of steam)	7.70					
Wastewater to be treated (Gonzalez-Garay and Guillen-Gosalbez, 2018) (m^3)	1.50					
Hydrogen from water electrolysis in 2030	Cost (USD unit ⁻¹)					
Alkaline electrolyser + nuclear electricity (kg)	2.27-3.92					
PEM electrolyser + wind electricity (kg)	2.03-5.39					
SOEC electrolyser + solar electricity (kg)	2.12-7.26					
Alkaline electrolyser + nuclear electricity (kg)	2.25-3.78					
PEM electrolyser + wind electricity (kg)	2.06-5.26					
SOEC electrolyser + solar electricity (kg)	2.15-7.16					
Alkaline electrolyser + nuclear electricity (kg)	2.39-3.70					
PEM electrolyser + wind electricity (kg)	2.18-5.17					
SOEC electrolyser + solar electricity (kg)	2.26-7.10					

LCA of methanol production and its limitations

The LCA results for the BAU process were directly taken from the Ecoinvent database version 3.4,(Wernet et al., 2016) while a full LCA encompassing the four LCA phases was applied to assess the methanol production process from CO₂ and hydrogen procured from various sources, using Recipe 2016 to quantify the environmental impacts on human health, ecosystem quality and resource scarcity. A cradle-to-gate scope was adopted that covers direct emissions and waste at the plant level together with those burdens embodied in the methanol process inputs, *i.e.*, H₂, CO₂, electricity, heat and steel. Hence, the end-use phase and any alternative use of renewable energy and carbon capture were omitted in our analysis. The motivation for this was twofold. Firstly, the use phase of methanol, either as platform chemical or fuel, is the same across technologies and, therefore, its inclusion would add no discriminatory power to the analysis. Secondly, evaluating alternative uses of renewable energy and carbon capture and storage, *i.e.*, methanol production *vs*. decarbonisation of the electricity mix, would require the detailed consideration of capacity and reliability constraints of a specific national mix, which is out of the scope of this work.

The LCI entries for methanol production were obtained from the mass and energy flows embodied in its inputs, *i.e.*, H₂, CO₂, electricity, heat and steel, plus the direct emissions and waste generated in the main process flowsheet. The inventory flows embodied in H₂ and CO₂ are given in Tables C2 and C3, respectively. The LCI entries embodied in electricity, heat and steel were retrieved from Ecoinvent v3.4, as described in Table C4, which also displays the inventory flows used in the quantification of the impact embodied in hydrogen and CO₂. Finally, Table C5 shows the inputs and outputs for each flowsheet, namely the amount of H₂, CO₂, electricity, heat and steel consumed as well as the direct emissions and waste of the main methanol process for each hydrogen source and considering that the CO₂ is captured from coal plants.
A monetisation method was then applied to express LCA impacts on a common monetary basis that enables a more straightforward comparison of scenarios. The approach reported by Weidema (2015) was followed. The monetary factors applied were $7.4 \cdot 10^3$ EUR2003 per 1 DALY in the human health category and $9.5 \cdot 10^6$ EUR2003 per 1 lost species in the ecosystem quality indicator. The resources depletion indicator is already expressed in monetary values (USD2003). ReCiPe 2016 was applied in all of the LCA calculations, updating the monetary factors of the human health and ecosystems category to USD2015 by applying a factor of 1.41. The category of resources depletion was updated to USD2015 using a factor of 1.25.

The main limitations of the LCA study are summarised next:

- Consistent with the literature, we consider that the impact embodied in the electrolyser is negligible compared to the total impact of hydrogen production via water electrolysis. This is because the impact embodied in the electricity powering the electrolyser has been shown to be the main contributor towards the total hydrogen impact.
- Similarly, following the literature sources used to model the CO₂ capture technologies, we neglected the impact embodied in the CO₂ capture facilities. The reason for this is, again, that the impact embodied in the amount of energy required to desorb the CO₂ from the absorbent is the main contributor towards the total impact.
- Fugitive emissions from equipment units were neglected, while the impact embodied in the catalyst was also omitted. This is a common practice in many LCA studies of chemical processes, where the main contributors to the total impact are raw materials and energy consumption.
- We consider that the impact of the construction phase can be approximated by the impact embodied in the equivalent amount of stainless steel contained in the equipment units. This

impact of construction is often either neglected or approximated with the same simplification we adopt here.

Furthermore, the PBs method show also some limitations, mainly concerning the uncertainties involved in the quantification of global ecological limits and the performance of technologies in terms of these limits. These uncertainties stem from: (i) imprecise global ecological limits yet considered as rough estimates; (ii) the allocation method of choice to assign shares of the safe operating space; (iii) imprecise measurements of the elementary flows needed to compute the PBs, e.g., CO₂ emissions to air; and (iv) uncertainties in the impact model that converts these flows into PBs, e.g., impact on energy imbalance per unit of CO₂ emitted. Future work should, therefore, focus on reducing these uncertainties by defining more accurate ecological limits and fair and robust sharing principles, improving data collection on emissions and developing more accurate damage models to translate emissions into PBs. The definition of fair sharing principles collectively ensuring sustainable development will also require social and political efforts.

It is also worth noting that we focused here only on those PBs for which characterisation factors are already available. Hence, as an example, biosphere integrity, regarded as a core planetary boundary, was omitted due to lack of robust methods to carry out the calculations.

Technology	Biomass gasification for oil poplar-wood chips	Nuclear-powered water electrolysis	Solar-powered water electrolysis	Wind-powered water electrolysis
By-products	0.85 kg hard coal	n.a.	n.a.	n.a.
Materials (inputs)				
Tap water (kg)	20.59	18.04	18.04	18.04
Electricity (kWh)	3.76	52.26	52.26	52.26
Wood chips	18.15	-	-	-
Natural gas (m ³)	$1.88 \cdot 10^{-3}$	-	-	-
Transport (tkm)	1.19	-	-	-
Waste (undesired o	outputs)			

Table C2 li	nventory flows of the	e foreground system p	er kilogram of hydroger	n at 30 bar.
Waste wood, sanitary landfill (kg)	1.81.10 ⁻⁴	-	-	-
Wastewater treatment plant residuals, to unsanitary landfill (kg)	10.97	-	-	-
Direct emissions (undesire	ed outputs)			
CO ₂ (kg)	21.43	-	-	-
SO ₂ (kg)	$2.69 \cdot 10^{-3}$	-	-	-
NO ₂ (kg)	$4.03 \cdot 10^{-3}$	-	-	-
HCl (kg)	$6.98 \cdot 10^{-4}$	-	-	-
Particulates, unspecified (kg)	$1.97 \cdot 10^{-4}$	-	-	-

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Table C3 Inventory flows of the foreground system per kilogram	ı of CC	b captured at 1 bar.
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Technology	Capture from coal power plant using chemical absorption with monoethanolamine	Capture from natural gas power plant using chemical absorption with monoethanolamine	Capture from direct air capture using an aqueous KOH sorbent coupled to a calcium caustic recovery loop				
By-products	Electricity: 0.775 kWh	Electricity: 3.23 kWh	-				
Materials (inputs)							
Air (kg)	-	20.19	-				
Water (kg)	-	1.45165161	3.105				
Water decarbonised (kg)	-	1.0645	-				
Natural gas (m3)	0.00078	0.8636	0.1895				
Catalyst (mg)	-	2.97	-				
Electricity (kWh)	-	-	0.366				
Calcium carbonate (kg)	-	-	0.02				
Limestone (kg)	0.04263	-	-				
Light fuel oil (kg)	0.00620	-	-				
Hard coal (kg)	0.52093	-	-				
Monoethanolamine (kg)	0.00155	0.0088	-				
NaOH (kg)	0.00012	-	-				
NH3 (kg)	0.00115	-	-				
Waste (undesired outputs)							
Municipal solid waste, to sanitary landfill	0.00406	-	-				
Wastewater (kg)	-	1.6452	-				
Catalyst disposal (mg)	-	2.97	-				
Direct emissions to air (unde	esired outputs)						

CO2 (kg)	0.05240	0.3286	-
SO2 (kg)	0.00007	-	-
NO (kg)	0.00106	0.0016	-
Particulates, unspecified (kg)	0.00011	-	-
NH3 (kg)	0.00027	-	-
Monoethanolamine (kg)	0.00009	0.0035	-

Appendix C

Flow	Technology involved	Description in Ecoinvent
NH3	CO ₂ coal	Ammonia at plant as 100% NH3
Electricity from nuclear consumed by water electrolysis	H ₂ nuclear	Electricity, high voltage electricity production, nuclear, pressure water reactor
Electricity from solar consumed by water electrolysis	H ₂ solar	Electricity production, photovoltaic, 570 kWp open ground installation, multi-Si
Electricity from wind consumed by water electrolysis	H ₂ wind	Electricity, high voltage electricity production, wind, <1MW turbine, onshore (86.1%); electricity, high voltage [RoW] electricity production, wind, 1-3MW turbine, offshore (13.9%)
Electricity high voltage	All	Electricity, high voltage, production mix
Hard coal	CO ₂ coal	Market for hard coal
Heat	Methanol	Market for heat, from steam, in chemical industry
Light fuel oil	CO_2 coal	Light fuel oil, petroleum refinery operation
Limestone	CO ₂ coal	Limestone from nature
Monoethanolamine	CO ₂ coal and NG	Market for monoethanolamine
Municipal solid waste, to sanitary landfill	CO ₂ coal	Disposal municipal solid waste, 22.9% water to sanitary landfill
Natural gas	Methanol / CO ₂ NG and DAC	Natural gas production
NaOH	CO ₂ coal	Production mix sodium hydroxide (50% NaOH)
Water	H ₂ biomass / CO ₂ NG and DAC	Market for tap water
Calcium carbonate	CO ₂ DAC	Market for calcium carbonate, precipitated
Steel production	Methanol	Steel production, converter, chromium steel 18/8
Catalyst	CO ₂ NG	Market for spent automobile catalyst
Tap water	H_2	Tap water production, conventional treatment
Transport	H ₂ biomass	Transport: transport, freight, lorry 16-32 metric ton, EURO4
Waste wood sanitary landfills	H ₂ biomass	Waste wood sanitary landfill: treatment of waste wood, untreated, sanitary landfill
Wastewater treatment plant residuals, to unsanitary landfill	H ₂ biomass	Wastewater treatment plant residuals, to unsanitary landfill: treatment of residue from cooling tower, sanitary landfill
Wastewater	CO ₂ NG	Market for wastewater, average
Catalyst disposal	CO ₂ NG	Treatment of spent catalyst base from ethyleneoxide production, residual material landfill
Wood chips	H ₂ biomass	Wood chips, wet, measured as dry mass

 Table C4 Inventory flows of the foreground system retrieved from Ecoinvent v3.4.

Table C5 Inputs/ou	Inputs/outputs of the main nowsheet per knogram of methanol produced.										
Inputs/outputs	H ₂ biomass	H ₂ nuclear	H ₂ solar	H ₂ wind							
Raw materials											
CO ₂ (kg)	1.50	1.47	1.45	1.45							
Hydrogen (kg)	0.20	0.19	0.19	0.19							
Utilities											
Cooling water (MJ)	4.96	4.97	4.97	4.95							
Heating (MJ)	0	0	0	0							
Electricity (kW)	0.30	0.30	0.30	0.30							
Heat recovered (MJ)	0.44	0.48	0.42	0.39							
Emission and waste											
CO ₂ (kg)	0.110831	0.093737	0.075773	0.077025							
Methanol (kg)	0.010091	0.010091	0.010091	0.010091							
NO ₂ (kg)	0.000181	0.000194	0.000170	0.000178							
Wastewater, average (m ³)	5.75.10-4	5.70.10-4	5.72.10-4	$5.71 \cdot 10^{-4}$							

Process modelling results

Table C6 Optimisation results for the fossil- and CO2-based methanol synthesis process scenarios. Decision variables optimised are shown in italics.

Ν	Model Reactor		H ₂ feed	Purge	Y _{MeOH}	X _{COx}	S _{MeOH}		
		V (m ³)	P (bar)	T (°C)	(kmol h ⁻¹)	released (%)	(%)	(%)	(%)
BAU		100	110	250	11,450 (syngas)	2.2	96.6	33.4	100
H ₂ biomass	ideal	63	29	108	5,872	0.22	96.4	24.2	99.97
	Cu-ZnO-Al2O3	50	50	221	5,894	0.25	91.5	12.4	99.30
H ₂ nuclear	ideal	63	24	107	5,926	0.16	97.2	24.6	99.98
	Cu-ZnO-Al ₂ O ₃	50	50	230	5,776	0.25	93.4	13.6	99.8
H_2 solar	ideal	63	31	131	5,828	0.11	96.0	20.0	99.99
	Cu-ZnO-Al ₂ O ₃	50	50	228	5,842	0.21	93.6	15.7	99.52
H ₂ wind	ideal	63	32	101	5,911	0.56	98.5	35.0	99.97
	Cu-ZnO-Al ₂ O ₃	51	50	228	5,842	0.23	93.8	15.8	99.55

 Y_{MeOH} = overall process yield, *i.e.*, moles of methanol obtained as final product per mole of CO and or CO₂ in the feed of the flowsheet.

 X_{COx} = conversion of CO or CO₂ per pass, *i.e.*, moles of CO or CO₂ converted in the reactor per mole of CO or CO₂ fed to the reactor.

S_{MeOH} = methanol selectivity per pass, *i.e.*, moles of CO or CO₂ converted into methanol in the reactor per mole of CO or CO₂ reacted in the reactor.

LCA results

Figure C1 and C2 depict the endpoint and disaggregated midpoint indicators for the BAU methanol process and the alternative processes based on CO₂ captured from coal power plants, from NG power plants and through DAC, and renewable hydrogen from distinct sources. Figure C3 provides the cost of methanol, including externalities, for all of the process scenarios considered.

Note that, methanol from CO₂, regardless of its source, and biomass-based hydrogen performs significantly worse than fossil methanol due to the large impact embodied in hydrogen procurement. The biomass type considered in the analysis is wood chips in hardwood, for which Ecoinvent provides values of CO₂ captured from air (CO₂ fixation) of 0.477 kg_{CO2-eq} kg_{biomass}⁻¹. This value is way below to the 1.01 kg_{CO2-eq} kg_{biomass}⁻¹ reported in the original source(Susmozas et al., 2015), which includes not only the CO₂ fixation from air, but also the emissions coming from land transformation which are omitted in our analysis given the uncertainty associated with the quantification method. The amount of CO₂ captured by the biomass in our model cannot offset the emissions of the gasification process, ultimately leading to a carbon-positive methanol. This and other choices made in the last version of Ecoinvent, which was used for consistency across technologies, lead to discrepancies with the LCA values for biomass-based hydrogen reported in the original source, *i.e.*, 3.79 vs. 16.4 kg_{CO2-eq} kg_{H2}⁻¹. In any case, we found a large variability in the environmental impact of biomass, particularly in the CO₂ fixated per kg of biomass across biomass types in Ecoinvent, e.g., 0.477-1.63 kg_{CO2-eq} kg_{biomass}⁻¹. The recommendation is, therefore, to take the LCA and PB results for the biomass-related scenario with caution, as they are highly dependent on the biomass source, which shows a strong regional dependency.



Figure C1 ReCiPe 2016 LCI analysis at the endpoint level of all methanol process scenarios analysed.



Figure C2a. ReCiPe 2016 LCI analysis at the midpoint level of all methanol process scenarios analysed, contributions to human health.



Figure C2a continued ReCiPe 2016 LCI analysis at the midpoint level of all methanol process scenarios analysed, contributions to human health.



Figure S2a continued ReCiPe 2016 LCI analysis at the midpoint level of all methanol process scenarios analysed, contributions to human health.



Figure S2b ReCiPe 2016 LCI analysis at the midpoint level of all methanol process scenarios analysed, contributions to ecosystems quality.



Figure S2b continued ReCiPe 2016 LCI analysis at the midpoint level of all methanol process scenarios analysed, contributions to ecosystems quality.



Figure S2b continued ReCiPe 2016 LCI analysis at the midpoint level of all methanol process scenarios analysed, contributions to ecosystems quality.



Figure S2b continued ReCiPe 2016 LCI analysis at the midpoint level of all methanol process scenarios analysed, contributions to ecosystems quality.



Figure S2c ReCiPe 2016 LCI analysis at the midpoint level of all methanol process scenarios analysed, contributions to resource scarcity.



Figure C3. Total cost, including externalities, of methanol from all of the process scenarios analysed.

Future costs of hydrogen from water electrolysis

Future hydrogen costs were estimated from prospects on the technical specifications of electrolysis technologies, *i.e.*, CAPEX expenditures, efficiency and useful time, together with estimates of future electricity prices taken from the US Energy Information Administration (EIA, 2019). The capital cost of the electrolysers, efficiency and stack lifetime reported in Tables C7-C9 were retrieved from Schmidt *et al.* (2017) The CAPEX expenditures were annualised applying the annual capital charge factor proposed by Towler and Sinnott (2013) considering an interest rate of 15%, and a useful time computed from the stack lifetime of the electrolyser available in Schmidt *et al.* (2017) The OPEX expenditures were approximated from the amount of electricity consumed per kg of hydrogen generated and the corresponding electricity cost. The electricity consumption per kg of hydrogen was obtained from the electrolyser efficiency and heat content of hydrogen. Lower and upper bounds on the methanol cost from water electrolysis are provided, which correspond to the best and worst future scenarios. The former assumes the lowest values for the CAPEX of the electrolyser and the electricity costs, and the maximum values for the electrolyser efficiency and useful life time, while the upper bound assumes the highest CAPEX and electricity costs and the lowest efficiencies and useful life times.

As the basis for the calculations, we assumed an enthalpy for water electrolysis of 65.83 kWh $\text{kmol}_{H_2}\text{o}^{-1}$, corresponding to 32.92 kWh $\text{kg}_{H_2}^{-1}$. The real energy of water electrolysis referred to 1 kg of H₂ was calculated adjusting this value by the electrolyser efficiency:

Real energy =
$$\frac{\text{Enthalpy of water electrolysis}}{\text{Electrolyser efficiency}} \left[\frac{\text{kWh}}{\text{kg}_{\text{H}_2}}\right]$$

The total amount of H₂ produced per year was calculated assuming 4,500 operating hours, which result in 4,500 kWh per year, given the intermittency of the operation in the electrolyser:

$$Hydrogen \ production = \frac{Annual \ electricity \ consumption}{Real \ energy} \left[\frac{kg_{H_2}}{yr}\right]$$

The operating costs per kg of H₂ were then calculated as follows:

$$OPEX = \frac{Annual electricity consumption \times Electricity cost in 2030}{Hydrogen production} \left[\frac{EUR}{kg_{H_2}}\right]$$

The CAPEX per kg of H_2 were calculated by multiplying the total capital cost of the electrolyser by its corresponding annual capital charge (ACC):

$$CAPEX = \frac{Electrolyser capital cost \times ACC}{Hydrogen production} \left[\frac{EUR}{kg_{H_2}}\right]$$

Externalities for H₂ were calculated following the approach reported in Section 2.

The total cost was finally calculated as the sum of OPEX, CAPEX and H_2 externalities in the corresponding cases. The calculations were performed using EUR and converting the final results into USD using a factor of 1.1. The methanol costs for the various projected costs of H_2 are compiled in Table C10.

		Wind	electricit	y + extern	nalities		Wind electricity					
Electrolyser	A	EC	PEN	ЛЕС	so	EC	AI	EC	PEMEC		SOEC	
Bound	min	max	min	max	min	max	min	max	min	max	min	max
Electrolysis												
Enthalpy of water electrolysis referred to $H_2(kWh kg_{H_2}^{-1})$	32.9	32.9	32.9	32.9	32.9	32.9	32.9	32.9	32.9	32.9	32.9	32.9
Real energy of water electrolysis referred to $H_2(kWh kg_{H_2}^{-1})$	47.7	52.2	42.2	52.2	40.1	40.1	47.7	52.2	42.2	52.2	40.1	40.1
H ₂ production (kg yr ⁻¹)	94.3	86.1	106.6	86.1	112.1	112.1	94.3	86.1	106.6	86.1	112.1	112.1
Operating costs												
Electricity cost (EUR kWh ⁻¹) 2030	0.034	0.055	0.034	0.055	0.034	0.055	0.034	0.055	0.034	0.055	0.034	0.055
OPEX future (EUR $kg_{H_2}^{-1}$)	1.623	2.883	1.436	2.883	1.366	2.215	1.623	2.883	1.436	2.883	1.366	2.215
Capital costs												
Capital cost (EUR kW ⁻¹)	350	550	400	1320	550	2500	350	550	400	1320	550	2500
Electrolyser efficiency (%LHV based)	0.69	0.63	0.78	0.63	0.82	0.82	0.69	0.63	0.78	0.63	0.82	0.82
Stack lifetime (h)	82500	82500	90000	80000	115000	35000	82500	82500	90000	80000	115000	35000
Electricity consumption (kWh yr ⁻¹)	4500	4500	4500	4500	4500	4500	4500	4500	4500	4500	4500	4500
Stack lifetime (yr)	18	18	20	18	26	8	18	18	20	18	26	8
Annual capital charge (ACC)	0.163	0.163	0.160	0.164	0.154	0.226	0.163	0.163	0.160	0.164	0.154	0.226
Annualised capital cost (EUR kW ⁻¹ yr ⁻¹)	56.89	89.39	63.90	216.00	84.89	565.79	56.89	89.39	63.90	216.00	84.89	565.79
Capital cost per kg H ₂ (EUR kg ⁻¹)	0.603	1.038	0.599	2.508	0.757	5.047	0.603	1.038	0.599	2.508	0.757	5.047
Externalities												
Externalities (EUR $kg_{H_2}^{-1}$)	0.102	0.102	0.102	0.102	0.102	0.102	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Total												
Projected cost of $H_2 2030$ (EUR $kg_{H_2}^{-1}$)	2.328	4.022	2.137	5.492	2.224	7.363	2.226	3.921	2.035	5.391	2.123	7.262
Projected cost of H ₂ 2030 (USD $kg_{H_2}^{-1}$)	2.560	4.424	2.350	6.041	2.447	8.100	2.449	4.313	2.238	5.930	2.335	7.988

Table C7 Hydrogen cost projections for water electrolysis powered by wind electrolysis.

		Nucle	ear electric	ity + exter	nalities		Nuclear electricity						
Electrolyser	A	EC	PEN	4EC	SO	EC	A	EC	PEMEC		SO	EC	
Bound	min	max	min	max	min	max	min	max	min	max	min	max	
Electrolysis													
Enthalpy of water electrolysis referred to $H_2(kWh kg_{H_2}^{-1})$	32.9	32.9	32.9	32.9	32.9	32.9	32.9	32.9	32.9	32.9	32.9	32.9	
Real energy of water electrolysis referred to $H_2(kWh kg_{H_2}^{-1})$	47.7	52.2	42.2	52.2	40.1	40.1	47.7	52.2	42.2	52.2	40.1	40.1	
H ₂ production (kg yr ⁻¹)	94.3	86.1	106.6	86.1	112.1	112.1	94.3	86.1	106.6	86.1	112.1	112.1	
Operating costs													
Electricity cost (EUR kWh ⁻¹) 2030	0.037	0.051	0.037	0.051	0.037	0.051	0.037	0.051	0.037	0.051	0.037	0.051	
OPEX future (EUR $kg_{H_2}^{-1}$)	1.782	2.666	1.576	2.666	1.499	2.048	1.782	2.666	1.576	2.666	1.499	2.048	
Capital costs													
Capital cost (EUR kW ⁻¹)	350	550	400	1320	550	2500	350	550	400	1320	550	2500	
Electrolyser efficiency (%LHV based)	0.69	0.63	0.78	0.63	0.82	0.82	0.69	0.63	0.78	0.63	0.82	0.82	
Stack lifetime (h)	82500	82500	90000	80000	115000	35000	82500	82500	90000	80000	115000	35000	
Electricity consumption (kWh yr ⁻¹)	4500	4500	4500	4500	4500	4500	4500	4500	4500	4500	4500	4500	
Stack lifetime (yr)	18	18	20	18	26	8	18	18	20	18	26	8	
Annual capital charge (ACC)	0.163	0.163	0.160	0.164	0.154	0.226	0.163	0.163	0.160	0.164	0.154	0.226	
Annualised capital cost (EUR kW ⁻¹ yr ⁻¹)	56.89	89.39	63.90	216.00	84.89	565.79	56.89	89.39	63.90	216.00	84.89	565.79	
Capital cost per kg H ₂ (EUR kg ⁻¹)	0.603	1.038	0.599	2.508	0.757	5.047	0.603	1.038	0.599	2.508	0.757	5.047	
Externalities													
Externalities (EUR $kg_{H_2}^{-1}$)	0.085	0.085	0.085	0.085	0.085	0.085	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	
Total													
Projected cost of $H_2 2030$ (EUR $kg_{H_2}^{-1}$)	2.470	3.789	2.261	5.259	2.342	7.181	2.385	3.704	2.175	5.174	2.257	7.096	
Projected cost of H ₂ 2030 (USD $kg_{H_2}^{-1}$)	2.717	4.168	2.487	5.785	2.576	7.899	2.623	4.075	2.393	5.692	2.482	7.805	

Table C8. Hydrogen cost projections for water electrolysis powered by nuclear electrolysis.

		Solar e	electricity	+ extern	alities		Solar electricity					
Electrolyser	AI	EC	PEN	MEC	so	EC	A	EC PE		EMEC		EC
Bound	min	max	min	max	min	max	min	max	min	max	min	max
Electrolysis												
Enthalpy of water electrolysis referred to H_2 (kWh kgH $_2^{-1}$)	32.9	32.9	32.9	32.9	32.9	32.9	32.9	32.9	32.9	32.9	32.9	32.9
Real energy of water electrolysis referred to H_2 (kWh kg H_2^{-1})	47.7	52.2	42.2	52.2	40.1	40.1	47.7	52.2	42.2	52.2	40.1	40.1
H ₂ production (kg yr ⁻¹)	94.3	86.1	106.6	86.1	112.1	112.1	94.3	86.1	106.6	86.1	112.1	112.1
Operating costs												
Electricity cost (EUR kWh ⁻¹) 2030	0.035	0.053	0.035	0.053	0.035	0.053	0.035	0.053	0.035	0.053	0.035	0.053
OPEX future (EUR $kg_{H_2}^{-1}$)	1.649	2.751	1.458	2.751	1.387	2.113	1.649	2.751	1.458	2.751	1.387	2.113
Capital costs												
Capital cost (EUR kW ⁻¹)	350	550	400	1320	550	2500	350	550	400	1320	550	2500
Electrolyser efficiency (%LHV based)	0.69	0.63	0.78	0.63	0.82	0.82	0.69	0.63	0.78	0.63	0.82	0.82
Stack lifetime (h)	82500	82500	90000	80000	115000	35000	82500	82500	90000	80000	115000	35000
Electricity consumption (kWh yr ⁻¹)	4500	4500	4500	4500	4500	4500	4500	4500	4500	4500	4500	4500
Stack lifetime (yr)	18	18	20	18	26	8	18	18	20	18	26	8
Annual capital charge (ACC)	0.163	0.163	0.160	0.164	0.154	0.226	0.163	0.163	0.160	0.164	0.154	0.226
Annualised capital cost (EUR kW ⁻¹ yr ⁻¹)	56.89	89.39	63.90	216.00	84.89	565.79	56.89	89.39	63.90	216.00	84.89	565.79
Capital cost per kg H_2 (EUR kg ⁻¹)	0.603	1.038	0.599	2.508	0.757	5.047	0.603	1.038	0.599	2.508	0.757	5.047
Externalities												
Externalities (EUR $kg_{H_2}^{-1}$)	0.303	0.303	0.303	0.303	0.303	0.303	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Total												
Projected cost of $H_2 2030$ (EUR $kg_{H_2}^{-1}$)	2.555	4.092	2.361	5.562	2.447	7.463	2.252	3.789	2.058	5.259	2.145	7.161
Projected cost of $H_2 2030 (USD kg_{H_2}^{-1})$	2.810	4.501	2.597	6.118	2.692	8.210	2.477	4.168	2.264	5.785	2.359	7.877

Table C9. Hydrogen cost projections for water electrolysis powered by solar electrolysis.

Electrolyser	AEC		1 2030. PEMEC		SOEC	
Bound	min	max	min	max	min	max
$CO_2 \text{ coal} + H_2 \text{ wind}$	0.785	1.154	0.743	1.473	0.762	1.881
$CO_2 \text{ coal} + H_2 \text{ nuclear}$	0.812	1.095	0.768	1.409	0.785	1.819
$CO_2 \text{ coal} + H_2 \text{ solar}$	0.789	1.124	0.747	1.444	0.766	1.857
$CO_2 NG + H_2$ wind	0.826	1.194	0.784	1.514	0.803	1.921
$CO_2 NG + H_2$ nuclear	0.854	1.136	0.809	1.450	0.826	1.861
$CO_2 NG + H_2 solar$	0.830	1.164	0.788	1.484	0.807	1.898
$CO_2 DAC + H_2$ wind	0.949	1.318	0.908	1.638	0.927	2.045
$CO_2 DAC + H_2$ nuclear	0.979	1.261	0.934	1.575	0.951	1.986
$CO_2 DAC + H_2 solar$	0.953	1.288	0.911	1.608	0.930	2.021
$CO_2 \text{ coal} + H_2 \text{ wind} + \text{externalities}$	0.913	1.282	0.872	1.602	0.891	2.009
CO ₂ coal + H ₂ nuclear + externalities	0.924	1.206	0.879	1.520	0.896	1.931
$CO_2 \text{ coal} + H_2 \text{ solar} + \text{externalities}$	1.135	1.470	1.093	1.790	1.112	2.203
CO ₂ NG + H ₂ wind + externalities	0.932	1.300	0.890	1.620	0.909	2.027
$CO_2 NG + H_2$ nuclear + externalities	0.942	1.224	0.898	1.539	0.915	1.949
CO ₂ NG + H ₂ solar + externalities	1.154	1.488	1.112	1.808	1.130	2.222
CO ₂ DAC + H ₂ wind + externalities	1.233	1.601	1.191	1.921	1.210	2.328
$CO_2 DAC + H_2$ nuclear + externalities	1.247	1.529	1.202	1.843	1.219	2.254
$CO_2 DAC + H_2 $ solar + externalities	1.454	1.789	1.412	2.108	1.431	2.522

Kinetic model

The kinetic model used for the simulation is described by the following equations. The production of methanol is given by:

$$r_{MeOH} = \frac{k_1 p_{CO2} p_{H2} \left[1 - k_6 \left(\frac{p_{H2O} p_{CH3OH}}{p_{H2}^3 p_{CO2}} \right) \right]}{\left(1 + k_2 \left(\frac{p_{H2O}}{p_{H2}} \right) + k_3 p_{H2}^{0.5} + k_4 p_{H2O} \right)^3} \left[\frac{mol}{kg_{cat}s} \right]$$

While the water-gas shift reaction is given by:

$$r_{\text{RWGS}} = \frac{k_5 p_{\text{CO2}} \left[1 - k_7 \left(\frac{p_{\text{H2O}} p_{\text{CO2}}}{p_{\text{CO2}} p_{\text{H2}}} \right) \right]}{\left(1 + k_2 \left(\frac{p_{\text{H2O}}}{p_{\text{H2}}} \right) + k_3 p_{\text{H2}}^{0.5} + k_4 p_{\text{H2O}} \right)} \left[\frac{\text{mol}}{\text{kg}_{\text{cat}} s} \right]$$

Kinetic constants follow the Arrhenius expression:

$$k = A * \exp(-E/RT)$$

Pressures are in bar and temperature in K. Details of the catalyst are given in Table C11 and values of the kinetic parameters are presented in Table C12.

Table C11 Catalyst properties.				
Density	1,775 kg/m ³			
Fixed bed porosity	0.5			
Mass	34.8 g			
Pellet diameter	0.0005 m			

Table C12 Parameters of the kinetic model.				
k1	A1	1.07		
	E1	36,696		
k2	A ₂	3,453.4		
	E ₂	0.00		
k3	A ₃	0.499		
	E3	17,197		
k4	A4	6.62.10-11		
	E4	124,119		
k5	A5	$1.22 \cdot 10^{10}$		
	E ₅	94,765		
k6	A_6	$4.19 \cdot 10^{10}$		
	E ₆	18,707		
k7	A ₇	$1.14 \cdot 10^8$		
	E7	58,392		