Multi-objective optimization of sustainability criteria in the conceptual design of chemical plants

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“To raise new questions, new possibilities, to regard old problems from a new angle, requires creative imagination and marks real advance in science”

Albert Einstein
(1879-1955)

“We can only see a short distance ahead, but we can see plenty there that needs to be done”

Alan Turing
(1912-1954)

A special mention to J.M. Douglas, father of the Process System Engineering discipline, who passed away on February 2017
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Abstract

Sustainability is a primary issue in the design and retrofitting of chemical processes. The concept of sustainability embraces a broad spectrum of meanings and interdisciplinary topics, and is generally conjugated in three distinct dimensions: economic, environmental, and social. The economic dimension of sustainability denotes the capability of an industrial activity to sustain its capital and operative expenditures and generate profit, while the environmental and social dimensions deal with the possibility of harmonizing with the environment and society, respectively. The question that arises from this premise is: “How can sustainability factors be employed in the design and optimization of chemical processes?”. The present work aims at providing an insight on this still controversial question. When considering sustainability criteria, a Multi-Objective Optimization (MOO) problem needs to be stated (and solved), in which each of the three dimensions represents an objective function. As far as economic sustainability is concerned, an innovative approach to conceptual design is applied in order to account for price volatility and market uncertainty. Proper econometric models are employed to simulate future price trajectories of both commodities and utilities. The WAste Reduction (WAR) algorithm is then employed to assess the Potential Environmental Impact (PEI), a relative measure of the impact that the process produces on the environment, thus being an indicator of its environmental friendliness. Social sustainability, on the other hand, can be addressed in terms of well-being of plant operators and security of the neighboring population, i.e. health and safety issues. This approach covers the inherent safety aspect that aims to achieve safer processes at lower capital and operating costs. A proper methodology for hazard identification, assessment, and ranking is employed to assess the overall hazard potential of the plant, and therefore its level of inherent safety. Finally, the sustainability-based MOO problem is stated and a solution strategy is illustrated and discussed.

Keywords: Sustainability; Multi-Objective Optimization; Conceptual Design; Economic Assessment; Econometric model; Price volatility; Predictive Conceptual Design; WAste Reduction algorithm; Environmental Impact; Social Sustainability; Inherent Safety; Hazard Identification and Ranking; Cumene production; Pareto optimality; Pareto Front.
Estratto

La sostenibilità è un tema di primaria importanza nella progettazione e ammodernamento dei processi chimici. Il concetto di sostenibilità abbraccia un ampio spettro di significati ed è generalmente coniugato in tre diverse dimensioni: economica, ambientale e sociale. L’aspetto economico della sostenibilità è legato alla capacità di un’attività industriale di sostenere le proprie spese operative e di investimento e di generare profitti, mentre gli aspetti ambientali e sociali riguardano rispettivamente la possibilità di armonizzazione con l’ambiente e la società. La domanda che sorge da questa premessa è: “In che modo tali criteri di sostenibilità possono essere impiegati nella progettazione e ottimizzazione dei processi chimici?” Il presente lavoro vuole fornire una possibile risposta a questa domanda ancora controversa. Nel momento in cui si considerano diversi criteri di sostenibilità, risulta necessario formulare un problema di ottimizzazione multi-obbiettivo, in cui ciascuna delle tre dimensioni sopra citate rappresenta una funzione obiettivo. Per quanto riguarda la sostenibilità economica, un approccio innovativo è stato applicato all’analisi economica del processo al fine di tenere in conto la volatilità dei prezzi. Specifici modelli econometrici sono utilizzati per simulare le traiettorie future dei prezzi di commodity e utility. Il Waste Reduction Algorithm è invece impiegato per valutare l’impatto ambientale potenziale (PEI), una misura relativa dell’impatto dell’impianto sull’ambiente. Gli aspetti legati alla sostenibilità sociale sono affrontati in termini di salute e sicurezza degli operatori dell’impianto e della popolazione circostante. Questo approccio copre gli aspetti di sicurezza intrinseca necessari per ottenere processi più sicuri a costi operativi e di investimento più bassi. Una specifica metodologia di identificazione, valutazione e classificazione dei rischi è impiegata per valutare il potenziale di rischio dell’impianto, e di conseguenza il suo livello di sicurezza intrinseca. Infine, il problema di ottimizzazione multi-obbiettivo è definito e una strategia di soluzione illustrata e discussa.

Parole chiave: Sostenibilità; Ottimizzazione multi-obbiettivo; Progettazione concettuale; Analisi economica; Volatilità dei prezzi; Modelli econometrici; Predictive Conceptual Design; Waste Reduction algorithm; Impatto ambientale; Sostenibilità sociale; Sicurezza intrinseca; Identificazione dei rischi; Valutazione dei rischi; Produzione del cumene; Ottimo di Pareto; Fronte di Pareto.
## Acronyms

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>ADL</td>
<td>Autoregressive with Distributed Lag</td>
</tr>
<tr>
<td>AHI</td>
<td>Atmospheric Hazard Index</td>
</tr>
<tr>
<td>AP</td>
<td>Acidification Potential</td>
</tr>
<tr>
<td>AR</td>
<td>AutoRegressive</td>
</tr>
<tr>
<td>ARX</td>
<td>AutoRegressive with eXogenous input</td>
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<tr>
<td>ATP</td>
<td>Aquatic Toxicity Potential</td>
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<tr>
<td>CAPEX</td>
<td>CAPital EXpenditures</td>
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<td>CCGT</td>
<td>Combined Cycle Gas Turbine</td>
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<tr>
<td>CD</td>
<td>Conceptual Design</td>
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<td>CEI</td>
<td>Chemical Exposure Index</td>
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<tr>
<td>CFC</td>
<td>ChloroFluoroCarbons</td>
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<td>CO</td>
<td>Crude Oil</td>
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<td>DEP</td>
<td>Dynamic Economic Potential</td>
</tr>
<tr>
<td>DIPB</td>
<td>Di-IsoPropylBenzene</td>
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<tr>
<td>DoF</td>
<td>Degree of Freedom</td>
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<tr>
<td>EA</td>
<td>Economic Assessment</td>
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<td>EcSI</td>
<td>Economic Sustainability Index</td>
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<tr>
<td>EE</td>
<td>Electric Energy</td>
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<td>EHI</td>
<td>Environmental Hazard Index</td>
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<td>EHS</td>
<td>Environment Health Safety</td>
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<td>Acronym</td>
<td>Full Form</td>
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<tr>
<td>EnSI</td>
<td>Environmental Sustainability Index</td>
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<tr>
<td>EP</td>
<td>Economic Potential</td>
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<td>EWO</td>
<td>Enterprise Wide Optimization</td>
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<tr>
<td>F&amp;EI</td>
<td>Fire and Explosion Index</td>
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<td>FEDI</td>
<td>Fire and Explosion Damage</td>
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<tr>
<td>FEHE</td>
<td>Feed Effluent Heat Exchanger</td>
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<tr>
<td>FMEA</td>
<td>Failure Mode Effect Analysis</td>
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<td>FTA</td>
<td>Fault Tree Analysis</td>
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<tr>
<td>GDP</td>
<td>Gross Domestic Product</td>
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<td>GERA</td>
<td>Global Environmental Risk Assessment</td>
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<td>Global Warming Potential</td>
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<td>HydroDeAlkylation</td>
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<td>HEN</td>
<td>Heat Exchanger Network</td>
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<td>Health Hazard Score</td>
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<td>HIRA</td>
<td>Hazard Identification and Ranking Analysis</td>
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<tr>
<td>HP</td>
<td>Hazard Potential</td>
</tr>
<tr>
<td>HTPE</td>
<td>Human Toxicity Potential by inhalation or dermal Exposure</td>
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<tr>
<td>HTPI</td>
<td>Human Toxicity Potential by Ingestion</td>
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I2SI Integrated Inherent Safety Index
IDEF0 Integration Definition for Function Modeling
IEI Integrated Environmental Index
IETH Inherent Environmental Toxicity Hazard
ISD Inherently Safer Design
ISI Inherent Safety Index
ISIM Inherent Safety Index Module
ISO International Standard Organization
LCA Life Cycle Analysis
LD50 Lethal Dose for 50% of individuals
M&S Marshall & Swift index
MOO Multi-Objective Optimization
MSDS Material Safety Data Sheet
NFPA National Fire Protection Association
NG Natural Gas
NGO Non-Governmental Organization
NPS Normalized Process Sustainability
ODP Ozone Depletion Potential
OPEX OPerative EXpenditures
PAH Polycyclic Aromatic Hydrocarbon
PCD Predictive Conceptual Design
<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
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<td>PCOP</td>
<td>PhotoChemical Oxidation Potential</td>
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<tr>
<td>PEI</td>
<td>Potential Environmental Impact</td>
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<tr>
<td>PF</td>
<td>Pareto Front</td>
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<tr>
<td>PHA</td>
<td>Preliminary Hazard Analysis</td>
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<tr>
<td>PIPB</td>
<td>Poly-IsoPropylBenzene</td>
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<tr>
<td>PM</td>
<td>Particulate Matter</td>
</tr>
<tr>
<td>PSE</td>
<td>Process Systems Engineering</td>
</tr>
<tr>
<td>R&amp;D</td>
<td>Research and Development</td>
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<tr>
<td>REACH</td>
<td>Regulation, Evaluation, and Authorization/Restriction of Chemicals</td>
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<tr>
<td>RFM</td>
<td>Risk Factor Model</td>
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<tr>
<td>SC</td>
<td>Supply Chain</td>
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<tr>
<td>SCM</td>
<td>Supply Chain Management</td>
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<tr>
<td>SOO</td>
<td>Single-Objective Optimization</td>
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<td>SoSI</td>
<td>Social Sustainability Index</td>
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<td>SPA</td>
<td>Solid Phosphoric Acid</td>
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<td>TDI</td>
<td>Toxicity Damage Index</td>
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<tr>
<td>TLV</td>
<td>Threshold Limit Value</td>
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<tr>
<td>Toe</td>
<td>Ton of oil equivalent</td>
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<tr>
<td>TOPSIS</td>
<td>Technique for Order Preference by Similarity to Ideal Solution</td>
</tr>
<tr>
<td>TTP</td>
<td>Terrestrial Toxicity Potential</td>
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<tr>
<td>TWA</td>
<td>Time-Weighted Average</td>
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<tr>
<td>Abbreviation</td>
<td>Full Form</td>
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</tr>
<tr>
<td>UN</td>
<td>United Nations</td>
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<td>UNGC</td>
<td>United Nations Global Compact</td>
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<td>US Dollar</td>
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<td>UV</td>
<td>UltraViolet</td>
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<td>VCM</td>
<td>Vinyl Chloride Monomer</td>
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<tr>
<td>VOC</td>
<td>Volatile Organic Compound</td>
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<tr>
<td>WAR</td>
<td>WAste Reduction algorithm</td>
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<tr>
<td>WCED</td>
<td>World Commission on Environment and Development</td>
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<tr>
<td>WTI</td>
<td>West Texas Intermediate</td>
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1. Introduction

The concept of sustainability

The chemical industry plays a leading role in shaping our society and modelling our lifestyle. Nowadays, the quality of life in the industrialized countries is strongly influenced by the large availability of a wide range of chemical products. In the developing countries, the affordability of chemicals (fuel, pharma, plastics) represents one of the main drivers for economic development and the starting point for improving the quality of life for billions of people on the planet. From this perspective, the chemical industry is one of the main actors for the material progress of mankind.

On the other hand, human society has pursued and is still pursuing, quite often if not almost always, this objective in an unsustainable way and is going to face a set of dramatic challenges in the next future. A continuously increasing demand for energy, water and food; the increased rate of natural resources consumption and their future depletion; climate change and inequitable development are only some of the big concerns outlined by the Worldwatch Institute, an independent research institute devoted to global environmental concerns, in its annual report “State of the World” (Murphy, 2013).

Global consumption of energy has increased steadily in the last century, and energy production has occurred mainly from non-renewable fossil resources, like oil, coal, and natural gas. The overall energy demand increased from about 2500 Mtoe (millions of tons of oil equivalent) in 1960 up to 10,000 Mtoe in 2010 (Murphy, 2013). The depletion of non-renewables resources represents a relevant problem which can endanger the global economic system in the next decades. Periodic shortages or political and financial events have shown to be responsible for abrupt price fluctuations and persistent market uncertainty.

In 2013, the atmospheric concentration of carbon dioxide and other greenhouse gases has increased by 18% since 1960, and is nowadays about 400 ppm, one third higher than the pre-industrial value of 275 ppm in 1850 (Keeling et al., 2011; Neftel et al., 1982). CO₂
emissions are estimated to contribute for about 70% to the overall global warming. Severe weather events are considered as a natural consequence of the global warming of the planet: prolonged drought, torrential downpours, and other phenomena of unprecedented intensity, like cyclones and floods, are on the rise in the last decades. The depletion of the stratospheric ozone layer, which reached its peak in 2003, is another example of anthropogenic effects on the environment: ozone decomposition by CFC compounds resulted in increased surface levels of UV radiation, responsible for human skin danger and plant damage. Emission of atmospheric pollutants such as NO\textsubscript{x}, SO\textsubscript{x}, VOC, PAH, and PM from stationary and mobile sources contributes significantly to the global environmental impact, with a major role in smog formation, acid rain, human health problems, and destabilization of ecosystems (loss of biodiversity, species extinctions, migrations).

The expansionary model of development that characterized the global economy in the last sixty years has often shown to lack of ethical responsibility: unfair resource exploitation, inequitable distribution of wealth, and short-term vision clearly delineate a picture of unsustainable development.

The reason of this consolidated trend can be traced back to our “innate evolutionary compulsion to seek to exploit as much as we possibly can, in terms of wealth, material and energy” (Byrne and Fitzpatrick, 2009). From this “evolutionary” point of view, economy and human society are inherently expansionary; on the other hand, the environment – with its resources – is limited, as well as its capability to sustain and absorb the impact of human activities. The expansionary tendency has always been reinforced by a cultural model, according to which natural resources exist to be exploited by man for his exclusive interest, and which can be found in the Judaic-Christian tradition (“Be fruitful and multiply, teem over the earth and subdue it” (Genesis, 9:7)) as well as in the scientific thought (“It is possible to reach a kind of knowledge which will be of the utmost use to men and thereby make ourselves the lords and possessors of nature” (René Descartes, 1638). It was during the first scientific revolution, between the XVII and XVIII centuries, that the term “sustainability” appeared for the first time in 1713 in the work of the German scientist Hans Carl Carlowitz “Sylvicultura Oeconomica”, where he stated the necessity of preserving the capability of the forest to produce timber wood, largely used at that time in the mining industry, against its
wild consumption: “The heating, building, brewing, mining and smelting activities require the careful management of sustainable forestry resources” (Carlowitz, 1713).

In the present time, the call for sustainability emerges in 1987 with the publication of the document “Our Common Future” by the World Commission on Environment and Development (WCED), which stated the definition of sustainable development as “the development that meets the needs of the present without compromising the ability of future generations to meet their own needs” (WCED, 1987). This definition represented the starting point for a number of further steps, such as the Earth Summit in 1992 in Rio, which delivered the Agenda 21 document (UN, 1992), and the World Summit on Sustainable development in 2002, both promoted by the United Nations.

The WCED definition synthesizes in few words the concept of sustainability and delineates the main features of a new paradigm of development. It has the merit to have spread the studies on sustainability at an international level. On the other hand, it is quite general, qualitative, and not particularly helpful for engineering decision-making purposes (Bakshi and Fiksel, 2003). A more useful definition is the one proposed by Bakshi and Fiksel in 2003, according to which “a sustainable product or process is one that constrains resource consumption and waste generation to an acceptable level, makes a positive contribution to the satisfaction of human needs, and provides enduring economic value to the business enterprise”. This definition offers some interesting hints and outlines the fundamental characteristics of a sustainable system. First, the concept of “an acceptable level” as a threshold for sustainability introduces a technical matter: as already done in the field of occupational health for the Threshold Limit Value (TLV), a threshold value for each specific concern needs to be fixed. The general criterion for this purpose relies in the principle that “resources must not be consumed at a rate which is faster than the rate of replenishment, and that the waste generation must not exceed the carrying capacity of the surrounding ecosystem” (Robèrt, 2002). Secondly, this novel definition integrates the three dimensions (also referred to as “the Three Pillars”) of sustainability: the economic, the environmental, and the social one. Economic sustainability —defined as the capability to provide “enduring economic value to the business enterprise”- is the most studied and best established dimension of sustainability, and usually represents a mandatory condition of any economic
activity, related to its ability to sustain the capital and operative expenditures and to generate value. Environmental sustainability is addressed in the two faces of resource consumption and waste generation, while social sustainability can be defined as the ability “to make a positive contribution to the satisfaction of human needs” (Bakshi and Fiksel, 2003). In a nutshell, the environmental and social dimensions deal with the possibility of harmonizing human activities with the needs of both the environment and society, respectively. Figure 1 shows the triple dimension of sustainability.

![Figure 1: The three dimensions of sustainability (S.Mann, 2011)](image)

Each dimension of sustainability can be assessed with specific metrics, here briefly reported in Table 1. The third relevant aspect of Bakshi-Fiksel definition (Bakshi and Fiksel, 2003) is that it is specifically tied on products and processes: in this way, it fixes some kind of boundary conditions, thus restricting our analysis to a specific type of system. According to Sikdar (2009), four types of systems can be defined while considering sustainability matters:

- **Type I**: systems referring to global concerns such as ozone depletion, global warming, and poverty.
- **Type II**: systems that are defined by geographical boundaries, like regions, cities, or specific ecosystems.
• Type III: systems related to businesses and companies, which address sustainability issues by improving their industrial practices and by optimizing their operation.
• Type IV: technologies that are “sustainability-oriented”, which provide clean, efficient, and safe solution to the industrial activities.

As stated by the definition, process engineers should focus on type III and IV systems, i.e. on companies/businesses and technologies (Sikdar, 2009). A company or a technology cannot be sustainable if their products and processes are unsustainable: in other words, the performance of an industrial process and the feasibility of new sustainable technologies strictly depend on process and product design, which falls in the field of study of Process Engineering, and specifically, of Chemical Engineering.

From a practical point of view, Chemical Engineers must deal with a broad spectrum of company characteristics related to social and environmental responsibility, usually collected under the label of “Sustainability”. Corporations all over the world realized that such label can improve intangible assets as reputation, strategic relationships, and competitive advantage (Bakshi and Fiksel, 2003). Most of them publish their annual “Sustainability reports”, and consider sustainability as a “strategic target” for their business. The result is in many cases a cocktail made up of several ingredients, ranging from corporate ethics and accountability, transparency, responsibility, and environmental friendliness, sometimes (usefully) employed as marketing devices. The positive aspect of this generalized tendency is that in the last three decades the concept of Sustainability has shifted from “environmentalist-ecologist” to “economically attractive-competitive” and “socially responsible” (Schönsleben et al., 2010). The financial community has officially recognized the importance of sustainability in the economic system with the launch of the Dow Jones Sustainability Index in 1999 (Dow Jones et Sam Group, 2015). Nowadays, Sustainability is universally acknowledged as an economic driver; in other words, it is a good choice for businesses. The final goal of Chemical Engineers is to translate these ideas into industrial practices.
Table 1: A summary of metrics for sustainability

<table>
<thead>
<tr>
<th>Sustainability pillars</th>
<th>System</th>
<th>Metric</th>
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<tbody>
<tr>
<td></td>
<td><strong>Economic</strong></td>
<td>Capital and Operative costs</td>
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<td></td>
<td></td>
<td>Revenues, profit</td>
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<td></td>
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<td>Shareholder value</td>
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<td></td>
<td></td>
<td>Quality</td>
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<td></td>
<td></td>
<td>Investment (R&amp;D, safety, health)</td>
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<td></td>
<td><strong>External</strong></td>
<td>Cost of externalities</td>
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<tr>
<td></td>
<td></td>
<td>Benefits to local community</td>
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<td></td>
<td></td>
<td>Benefits to society</td>
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<tr>
<td></td>
<td><strong>Resource</strong></td>
<td>Renewable, Non-renewable</td>
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<tr>
<td></td>
<td></td>
<td>Material Intensity</td>
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<td></td>
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<td>Energy Intensity</td>
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<td></td>
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<td>Water usage</td>
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<td></td>
<td>Land usage</td>
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<td></td>
<td><strong>Emissions and Waste</strong></td>
<td>Products disposal</td>
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<tr>
<td></td>
<td></td>
<td>Manufacturing Operations</td>
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<td></td>
<td></td>
<td>Building, sites</td>
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<td></td>
<td></td>
<td>Effects on Ecosystem and Human Health</td>
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<td></td>
<td><strong>Social</strong></td>
<td>Occupational Health and Safety</td>
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<td></td>
<td></td>
<td>Noise, Odor</td>
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<td></td>
<td></td>
<td>Employee well-being</td>
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<td></td>
<td>Human Capital development</td>
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<td></td>
<td></td>
<td>Social Responsibility</td>
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<tr>
<td></td>
<td><strong>Community</strong></td>
<td>Stakeholder engagement</td>
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<tr>
<td></td>
<td></td>
<td>Nuisance (noise, odor, visual impact)</td>
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<tr>
<td></td>
<td></td>
<td>Human rights</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Social Responsibility</td>
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</table>
Sustainability in Process Systems Engineering

Process Systems Engineering (PSE) is a branch of Chemical Engineering which is concerned with the understanding and development of systematic procedures for the design and operation of chemical process systems, ranging from microsystems to industrial-scale continuous and batch processes (Grossmann and Westerberg, 2000). PSE represents nowadays a mature and well-established discipline that embraces the field of applied mathematics and computer science and aims at tying them to the traditional procedures of chemical engineering. From this perspective, PSE can be seen as a bridge between the “old” chemical engineering, based on unit operation analysis, and a “new” one, extensively computer-aided, multi-disciplinary, and deeply math-oriented.

A particular aspect of PSE is its involvement in the decision-making process during the lifecycle of the manufacturing process of chemical products, the so-called chemical supply chain, reported in Figure 2.

![Figure 2: The length scale of chemical supply chain (Grossmann and Westerberg, 2000)](image)

The chemical supply chain starts with the identification and analysis of the molecules involved in the chemical process, and proceeds by zooming out to clusters, particles and films; then it shifts from chemistry to engineering, and takes into account macroscopic multiphase systems and process unit operations, up to the whole plant. Finally, the single
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Plant is considered as a part of a larger production site, which in turn belongs to the commercial enterprise. Based on the concept of chemical supply chain, a broader definition of PSE has been proposed, according to which “Process Systems Engineering is concerned with the improvement of decision-making processes for the creation and operation of the chemical supply chain. It deals with the discovery, manufacture and distribution of chemical products in the context of many conflicting goals” (Grossmann and Westerberg, 2000). This definition has opened new intellectual and practical challenges in the field of PSE. It focuses on the development of systematic procedures and suitable tools to deal with the intrinsic complexity and multi-objective nature of the decision-making process along the entire supply chain. A possible criterion to lead the decision-making process is sustainability itself, conjugated in its economic, environmental, and social dimensions. From this perspective, it is clear than one of the most relevant challenges consists in the definition of a systematic framework for sustainable PSE (Bakshi and Fiksel, 2003), i.e. an holistic approach to introduce sustainability consideration in each stage of the chemical supply chain. This represents the last frontier, still largely unexplored, of PSE disciplines.

At present, several efforts have been devoted to the attempt of incorporating sustainability considerations into process design, or, in other words, to translate the theoretical principles of sustainability into design practices (Azapagic et al., 2006). Traditionally, process design was driven exclusively by micro-economic and technical considerations: the industrial process was—and still is, in most cases—designed in order to maximize the economic return and fit the minimum requirements imposed by legislation. Environmental and safety protection measures are considered as “add-ons” to be implemented once the economic aspects are fully optimized. The rising concern about sustainability has guided the process engineers to integrate the economic dimension with the environmental and social pillars of sustainability, and to include them in the early stages of process design.

Process Design consists of four stages which can be labelled as: Project Initiation, Preliminary Design, Detailed Design, and Final Design (Douglas, 1988).

During the Project Initiation stage, different processing routes are taken into account, together with alternative technologies, raw materials, and energy sources. Some sustainability criteria need to be identified and selected in order to help the decision-maker
– the process engineer – to discriminate among the different possibilities. Sustainability criteria can be based on micro and macro-economic issues, environmental concerns and social considerations: a processing route can be intrinsically more pollutant and hazardous than another one, and the starting material can have different costs or availability. In addition, at this stage, the location of the construction site should be identified: this choice must include some social considerations as the potential nuisances for the local community (noise, odor, visual impact), in order to obtain the so-called “social license to operate” (Azapagic & Perdan, 2000).

The preliminary design stage involves the construction of the basic flowsheet and the assessment of material and energy balances. Mass and energy balances, together with some knowledge about the equipment, provide the information to perform a preliminary sustainability analysis, from the economic, environmental, and safety point of view. The preliminary design stage is in fact the domain of Conceptual Design (Douglas, 1988), a hierarchical methodology which focuses on the basic design of a chemical process and its economic optimization. Conceptual Design – one of the keystones of PSE – represents the starting point to fully implement sustainability considerations in the preliminary design stage, as extensively discussed in Chapter 3. Further design steps involve: (i) the detailed engineering of the process, which involves energy integration, (ii) process control and instrumentation analysis, (iii) HAZOP analysis and safety measures, (iv) full economic and sustainability assessment; (v) civil and electrical work, and so on.

As shown in Figure 3, the conceptual phase, i.e. the early stage of Process Design, is the most suitable for making any decisions. Therefore, sustainability should be integrated in the design procedure as early as possible, during the Project Initiation and the Preliminary Design. This approach leads to the least implementation costs and to the highest influence on process performance.
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Scope and structure of the work

The final goal of the present thesis work is to carry out a Multi-Objective Optimization (MOO) of a chemical process based on sustainability considerations, and integrate the three pillars of Sustainability – Economic, Environmental, and Social – in the early phase of process design. This calls for the study of each dimension of Sustainability, its quantification, and implementation in an optimization problem. As each of them represents an objective function, the problem assumes a multi-objective nature and therefore is defined as a MOO problem.

As mentioned above, PSE involves the development and improvement of the decision-making process at different stages of the chemical supply chain, from the R&D phases up to the Supply Chain Management (SCM) and the Enterprise-Wide Optimization (EWO). In addition, the decision-making process should theoretically cover the whole lifecycle of the products, thus adopt a cradle-to-grave approach. Life Cycle Assessment (LCA), now an ISO-standardized method, represents a suitable tool for including upstream and downstream processes in the sustainability analysis, from the cradle of resource procurement to the grave of disposal or recycle (Heijungs et al., 2010). The main drawback of LCA is the need of a large amount of input data, usually difficult to obtain or unfit for the purposes of this work.
For process design purposes, it is straightforward to focus on the battery limits of the process, thus adopting a gate-to-gate approach, which shows a number of advantages when applied to chemical process design. First, the analysis focuses on the bottleneck of sustainability concern, i.e. the chemical manufacturing plant, which is considered a critical energy-intensive industry, together with the steel, cement, glass, and paper industries (Schönsleben et al., 2010). Secondly, the final aim of process design is to optimize the chemical process. Consequently, the optimization of a specific ring of the chain inevitably implies an improvement of the overall system, i.e. the chemical supply chain. Thirdly, the amount of information needed is much lower than that required by LCA. These data (prices, environmental impacts, and process technology) are largely available at on-line platforms, software, and in the scientific literature.

Chapter 2 presents the case study of the Cumene Production process: details are provided about the chemistry, market characteristics, and process technology. A specific attention is devoted to the description of the adopted methodology, in particular process simulation and optimization strategies.

Chapter 3 reviews the concept of Economic Sustainability. The Conceptual Design methodology (Douglas, 1988) is presented and its limitations are underlined. The Predictive Conceptual Design methodology (Manca et al., 2015) is then introduced, with the illustration of the econometric models as suitable tools to deal with market volatility and price fluctuation. Finally, the objective function for the Economic Sustainability is formulated and optimized: the results of the optimization problems are presented and discussed.

Chapter 4 analyzes the concept of Environmental Sustainability and discusses different techniques to deal with it. The WAste Reduction algorithm (Young et al., 2000) is then presented and the objective function formulated. Eventually, the results of the optimization are shown and discussed.

Chapter 5 discusses the concept of Social Sustainability and proposes different interpretations, with a specific focus on the concept of Inherent Safety. A proper methodology – the Hazard Identification and Ranking Analysis or HIRA (Khan and Abbasi, 1998) – is proposed to deal with health and safety issues in the preliminary design stage.
objective function is then formulated and optimized. The results of the optimization are shown and discussed.

Chapter 6 defines the Multi-Objective Optimization problem. The existing techniques to approach MOO problems and the strategies to deal with decision-making processes are reviewed. The 2D and 3D Pareto Fronts are illustrated and discussed. Consequently, a possible solution of the MOO problem is presented.

Chapter 7 draws some conclusions and opportunities for future research activities.
2. Case Study: Cumene production process

About Cumene

In this work, the manufacturing process for cumene (isopropyl benzene) is used as a case study to show a practical application of process/plant design in terms of multi-objective optimization for sustainability.

Cumene molecule (Figure 4) is made of an aromatic ring with an aliphatic substitution of an isopropyl group. Its manufacturing consumes a significant portion of the global benzene production, around 20%, and a small one of propylene (less than 5%).

Cumene is a key commodity of the petrochemical industry as an intermediate for many important products and as octane booster in gasoline blending. Phenol and acetone are its two most important derivatives obtained through the Hock process, representing 98% of the global cumene consumption. Polycarbonates and epoxy resins are the most significant products of phenol. The demand of those polymers is the main driving force of the cumene market, which is predicted to grow significantly in the future. In 2011, the global cumene demand was about 12.4 million tons and in 2022, as the market is growing in the developing countries, it is expected to reach 25 million tons, thus doubling in the following decade.
Multi-objective optimization of sustainability criteria in the conceptual design of chemical plants (Allied Market Research, 2017). The main chemical and physical properties of cumene are reported in Table 2 (Kim et al., 2016):

<table>
<thead>
<tr>
<th><strong>Table 2: Chemical and physical properties of pure cumene</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Name</strong></td>
</tr>
<tr>
<td><strong>Molecular formula</strong></td>
</tr>
<tr>
<td><strong>Molar weight</strong></td>
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<tr>
<td><strong>Boiling point</strong></td>
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<tr>
<td><strong>Melting point</strong></td>
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<tr>
<td><strong>Density</strong></td>
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<tr>
<td><strong>Volatile</strong></td>
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<tr>
<td><strong>Viscosity</strong></td>
</tr>
<tr>
<td><strong>Color</strong></td>
</tr>
<tr>
<td><strong>Odor</strong></td>
</tr>
<tr>
<td><strong>Solubility</strong></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td><strong>Flash point</strong></td>
</tr>
<tr>
<td><strong>Auto ignition</strong></td>
</tr>
</tbody>
</table>

**Process description**

The Friedel-Crafts catalytic alkylation of benzene with propylene is the current production route of cumene. Di-isopropylbenzene is the main byproduct, along with traces of higher hydrocarbons. Many researches focused on trying to improve this process in the past decades from the one discussed in Turton et al. (2008). Luyben (2010) introduced an improved version with an increased propylene conversion and the recovery of the heat of reaction for high pressure steam production by applying a proper optimization strategy (Douglas, 1988). Gera et al. (2011) suggested the addition of a purge column for inert propane instead of a simple flash drum, resulting in a significant decrease of benzene loss. Finally, (Pathak et al., 2011), replaced the conventional reactor and a significant separation section by adopting a reactive distillation column. All those works were focused on the
economic optimization of this process, while only few researches took into consideration the environmental impact (Flegiel et al., 2015). The aim of this work is to consider the economic as well as the environmental and social aspects of process sustainability.

For this purpose, two different process technologies have been selected: the conventional vapor phase process (Pathak et al., 2011) and the liquid phase process (Norouzi et al., 2014). Both processes are characterized by the same productivity and separation strategy, but they differ significantly for the reactor configuration and operating conditions.

**Reactions and kinetics**

In the cumene manufacturing process, the Friedel-Crafts alkylation of benzene with propylene to produce cumene is the main reaction:

\[ C_6H_6 + C_3H_6 \rightarrow C_9H_{12} \]

Unfortunately, di-isopropylbenze (DIPB) can be produced by further alkylation of cumene, representing the most important side reaction of this process:

\[ C_9H_{12} + C_3H_6 \rightarrow C_{12}H_{18} \]

Actually, even heavier poly-isopropylbenzenes (PIPBs) are formed in small amounts, but, for the sake of simplicity, these reactions are neglected. The DIPB was originally used as fuel (Turton et al., 2008), but recent process retrofitting included the possibility to recover this byproduct by converting it back to cumene by means of a transalkylation reaction with benzene:

\[ C_{12}H_{18} + C_6H_6 \leftrightarrow 2C_9H_{12} \]

Nowadays, the application of this technology is a common practice at the industrial scale of cumene production (Zhai et al., 2015), so it must be considered.

For both the liquid and the vapor configuration, the reactions are the same, but different kinetics schemes are proposed, as two different catalytic paths are involved.
Table 3: Reactions and kinetic formulas (Norouzi et al., 2014; Pathak et al., 2011). $C_b$: benzene concentration, $C_p$: propylene concentration, $C_c$: cumene concentration, $x_b$: benzene molar fraction, $x_d$: DIPB molar fraction, $x_c$: cumene molar fraction.

<table>
<thead>
<tr>
<th>Name</th>
<th>Reaction</th>
<th>Process</th>
<th>Reaction rates</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cumene reaction</td>
<td>$C_6H_6 + C_3H_6 \rightarrow C_9H_{12}$</td>
<td>vapor</td>
<td>$r_{c,v} = 2.8 \times 10^7 \exp\left(-\frac{104181}{RT}\right)C_bC_p$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>liquid</td>
<td>$r_{c,l} = 6510 \exp\left(-\frac{52564}{RT}\right)C_p$</td>
</tr>
<tr>
<td>DIPB reaction</td>
<td>$C_9H_{12} + C_3H_6 \rightarrow C_{12}H_{18}$</td>
<td>vapor</td>
<td>$r_{d,v} = 2.32 \times 10^9 \exp\left(-\frac{146774}{RT}\right)C_cC_p$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>liquid</td>
<td>$r_{d,l} = 450 \exp\left(-\frac{55000}{RT}\right)C_p$</td>
</tr>
<tr>
<td>Transalkylation reaction</td>
<td>$C_{12}H_{18} + C_6H_6 \leftrightarrow 2C_9H_{12}$</td>
<td>both</td>
<td>$r_{t,f} = 2.529 \times 10^8 \exp\left(-\frac{100000}{RT}\right)x_bx_d$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$r_{t,b} = 3.877 \times 10^9 \exp\left(-\frac{127240}{RT}\right)x_c$</td>
</tr>
</tbody>
</table>

Reaction rates reported in Table 3 are in kmol/(m$^3$s), concentration in kmol/m$^3$, $R$ is 8.316 kJ/(kmol K). Since the transalkylation reaction is reversible, both forward and backward rates are reported.

The commercial catalysts employed at the industrial scale include solid phosphoric acid (SPA), aluminum chloride (AlCl$_3$), and zeolites. SPA was originally used for converting light olefins into gasoline, then applied to cumene production for aviation fuels (Degnan et al., 2001). SPA does not catalyze the transalkylation reaction and the phosphoric acid that is liberated can lead to corrosion problem in downstream operations. The main alternative, licensed by Monsanto and Kellogg, is a mixture of AlCl$_3$ and hydrochloric acid (HCl), which does not remove the corrosion problems but allows converting the undesired DIPB back to cumene. Zeolite-based catalysts represent the most recent technology for the liquid phase-process: they carry out the transalkylation reaction and can be applied also to a reactive distillation column (Pathak et al., 2011).
Process flowsheet

Both processes are designed to achieve around 96,000 t/y (100 kmol/h) of cumene production. The flowsheets of the two process configurations are shown in Figure 5 and Figure 6. In the vapour phase process 105.26 kmol/h of refinery grade propylene containing 5% of propane impurity and 157.5 kmol/h of pure benzene are fed continuously to the plant. Fresh reactants are provided at 25 °C and 24.5 bar, mixed in the vaporizer (E1), heated up and vaporized by high-pressure steam. A feed-effluent heat exchanger (FEHE) allows recovering part of the released heat of reaction. Then, a furnace (E2) heats up the feed to the desired reactor inlet temperature. The reactor is a multitubular packed bed reactor with external cooling, in order to keep under control the exothermicity of the main reaction. The inlet stream to the reactor enters 1500 3-inch parallel tubes filled with SPA catalyst. A void fraction of 0.5 is assumed. The reactor is cooled by boiling water circulating in the shell side. The huge amount of heat released (around 2.7 MJ) produces high-pressure steam that can be used in other sections of the plant. After passing through the FEHE, the reactor outlet flow is cooled to 170 °C (E3) and laminated to 1.5 bar before entering the separation section. The first step of the separation consists in removing the unreacted propylene and inert propane in column 1 (C1), where they are purged. The second column (C2) recovers the unreacted benzene from the top which is partially recycled back to the vaporizer and partially fed to the transalkylation reactor. The bottom of C2 is rich in cumene, the desired product, but still contains DIPB to be removed. A further column (C3) is needed to recover cumene at the commercial purity (99.9%) from the top, while the DIPB leaving from the bottom is mixed with benzene to be converted back to cumene. Benzene/DIPB flow is heated to 240 °C in a proper heat exchanger (E4) by high-pressure steam before entering the transalkylator. The transalkylator is considerably smaller than the main reactor, indeed it comprises only 100 tubes, 1.6 m long and 3 in of diameter, filled with a zeolite-based catalyst. This reactor allows producing additional cumene and the outlet flow is recycled back to the C2 feed.
In the **liquid phase process** (Figure 6), the same amount of propylene is provided, while only 100 kmol/h of fresh benzene is required. Fresh reactants are provided at 25 °C and 24.5 bar. There is no vaporizer, since the reactor feed must be liquid. The reactor consists of a single tube filled with zeolites and it is run adiabatically. A void fraction of 0.5 is assumed. The separation section and the transalkylation reactor follow the same configuration of the vapor phase process. The last difference is the benzene recycle flowrate, which is around 58 kmol/h for the vapor phase process and around 400 kmol/h for the liquid phase process. This significant amount of benzene acts as thermal diluent and is required to run the reactor adiabatically.
Process simulation

In the early steps of process design procedure, the computation of material and energy balances is essential. At the very beginning of chemical engineering when computers were still and almost not available and numerical procedures were at their commencement, flowrates, temperature, pressures, phase conditions, and duties of each unit were estimated manually. Those procedures were extremely tedious and time-consuming, in particular for complex operations like recycle streams, reactors with multiple reaction or multi-stage separation units. In those conditions, with such low precision in the estimations, optimization procedures were not reliable and usually carried out only considering single units and very few degrees of freedom (DoF). From the early ’70s of last century, the availability of commercial software for steady-state simulations allowed chemical engineers to overcome the main obstacles of manual computation, and paved the way to the development of Computer Aided Process Engineering discipline (Kellner et al., 1999).
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Nowadays, computer simulation of chemical processes is a well-established methodology in chemical engineering design, in particular for optimization purposes. According to this philosophy, the present work employs UniSim Design R450 (Honeywell, 2016) as steady-state simulation software in order to carry out all the computations concerning material and energy balances.

Technical aspects of process simulation

Process simulation is a key step in process design in order to carry out the energy and material balances that are required for the optimization procedure, thus it deserves a specific attention.

![General optimization procedure scheme](image)

*Figure 7: General optimization procedure scheme*

First, a simulation routine needs to guarantee convergence, i.e. the solution of the material and energy balances of the whole flowsheet, conceivably for every combination of input variables. The optimization algorithm requires to change some input parameters and carry out a significant number of simulations; therefore, a reliable optimization procedure requires a good level of robustness at the simulation stage. For the sake of clarity, robustness is defined as "the degree to which a system or component can function correctly in the presence of invalid inputs or stressful environmental conditions" (IEEE, 1990). Moreover, a proper accuracy is needed, according to the process design assumptions and requirements. While a low precision can lead to clearly inconsistent results, on the other hand, there is no need to implement a highly-detailed description of each unit, as, at this
stage of process design, strong simplifying assumptions are still applied and a further exhaustive design of the single units will be object of analysis at later stages.

As far as this case study is concerned, a proper choice of the degrees of freedom of each unit is a crucial point to achieve the required robustness without penalizing excessively the accuracy of the computation. In the previous work about cumene, the process developed at the PSE-Lab of Politecnico di Milano (Sepiacci, 2016) running the simulations for the whole domain of the DoFs was extremely challenging and convergence could not be reached in a significant amount of points. This problem can be solved by changing one of the constraints of the process: instead of assigning a fixed value to the fresh benzene flowrate entering the plant (which is in excess with respect to propylene), the inlet benzene/propylene ratio is set to 1.55, which is the optimal value that guarantees enough benzene for the transalkylation reaction and limits the hot spot temperature in the main reactor (Pathak et al., 2011).
significantly improves the robustness of the solver and reduces the approximations introduced in the computation of the benzene recycle stream.

**Process optimization strategy**

As far as the optimization procedure is concerned, the first mandatory step is to define the objective function(s) to be maximized or minimized. As stated before, the purpose of this work is a multi-objective optimization based on sustainability criteria, so that a proper objective function must be developed for each of the three “pillars” of sustainability. The definition and discussion of the objective functions are reported in details in Chapters 3, 4 and 5.

The second step consists in the statement of the degrees of freedom of the problem. In such a complex system as a chemical process, there are plenty of design variables that should be considered. According to Douglas (1988), there are only few variables that are “dominant” and contribute significantly to the overall performance of the plant. Since this work adopts the cumene process as a case study to explain a methodology, the attention is focused only on the dominant variables, while for the remaining variables the values reported in the literature are assumed. Propylene conversion is commonly identified as the most important parameter of this process (Luyben, 2010). Therefore, the design variables that have a significant impact on it can be considered as dominant. Due to the introduction of the transalkylation technology, selectivity, which is usually a relevant constraint for the feasibility of the process, does not play a significant role in this plant. By simply analyzing the battery limits of the process, there is no DIPB stream leaving it, except for the impurities contained in the product (less than 0.1%). Therefore, one can assume the overall selectivity equal to 1. This means that the cumene production rate is governed by the conversion of the limiting reactant (propylene), and there are no selectivity issues, provided that the transalkylator is properly designed. To maximize the conversion per pass of the reactants, the length of the reactor tubes should be increased, which makes increasing the capital investment for the purchase and installation of that reactor. Actually, the reactor size versus the conversion extent is a typical trade-off of process design (Turton et al., 2008), so the tube length is the first degree of freedom of the problem. Moreover, the reaction
temperature is a controlling parameter for the reaction rate, thus it must be tuned as well. For the vapor phase process, the reactor outlet temperature is set at the highest possible value to use the boiling water as coolant. Therefore, it cannot be modified. The reactor inlet temperature, instead, can be adjusted in order to act on the propylene conversion. In the liquid phase the reactor is operated adiabatically, thus, by selecting the inlet temperature, the outlet one is determined, then it can be selected as a second degree of freedom. For both the degrees of freedom, a proper interval must be selected. Other design variables that have a relevant impact on process performances are the reactor pressure and the benzene recycle flowrate. Since the alkylation reaction occurs with a decrease in the number of moles, it is worth operating at the highest admissible pressure. For this reason, the reactor pressure is fixed at 25 bar, as reported in Pathak et al. (2011) and not optimized. The recycled benzene mainly acts as thermal diluent in the reactor and can affect the conversion of the process. As shown in Luyben, (2010), the recycle benzene flowrate has a much lower impact on the performances if compared to the reactor size. Therefore, this matter is not much relevant, as aim of the present work is to illustrate an application of a multi-objective optimization based on sustainability criteria, and not a detailed analysis of all the technical features of the cumene process.

As far as the reactor length is concerned, the minimum length is set at 4 m (Pathak et al., 2011), while the maximum one is limited to 12 m, since this is the maximum standard commercial length of steel pipes (USS, 2017). Regarding the reactor inlet temperature, the feasible range is mainly related to the catalyst activity, thus it is different for the two processes. In the vapor phase, to avoid catalyst deactivation due to coke deposition the hot-spot temperature should not exceed 400 °C, therefore, according to preliminary simulations, the inlet temperature upper bound is 350 °C. Below 300 °C for the inlet temperature, the reaction rate reduces significantly and leads to an inefficient use of the catalytic bed. In addition, the heat recovery in the FEHE is not fully exploited, so there are no reasons to operate under that limit. For the liquid phase process configuration, the inlet temperature bounds provided by Norouzi et al. (2014) are 150 °C and 200 °C.

The final step is the choice of the optimization algorithm. Due to the limited number of degrees of freedom, a Grid-Search approach is the most interesting solution. The principle
Multi-objective optimization of sustainability criteria in the conceptual design of chemical plants

behind it is rather simple: the value range of each DoF is discretized by dividing it into a proper number of finite intervals (defined by suitable support points), then all the possible combinations at the multidimensional support points are evaluated to identify the best one, according to the objective function. The main benefit of this kind of approach is its exhaustiveness: the whole admissible space of the optimization variables is evaluated, providing a complete picture of the behavior of each objective function. On the other hand, such method usually leads to a high computational time due to the large number of alternatives to be evaluated which grows exponentially with the number of DoFs. For example, by considering 7 DoFs, discretized into 10 points each, the total number of combination would be $10^7$, probably involving a prohibitive computational time for a typical process design evaluation. The Grid-Search algorithm is usually suitable in case of few degrees of freedom, as in the present case study. The variable space is discretized according to a grid-wise approach.

![Grid-Search optimization example](image)

*Figure 9: Grid-search optimization example: the color gradient is representative of the gradient of the objective function. Darker squares mean higher value of the objective function.*

In this case study, the discretization step is 5 °C for the inlet temperature and 0.5 m for the reactor tubes length. Thus, there are 11 alternative configurations for the reactor inlet temperature and 17 for the tubes length, leading to 187 different combinations. By focusing only on the two dominant variables, the aforementioned problems of the Grid-Search
algorithm are avoided. Moreover, this approach allows decoupling the simulations and the evaluation of the objective function: the values of each DoF are evaluated by the process simulations and, at a second stage, these values are provided to the optimization routine for the quantitative assessment of the objective functions. This feature is of great importance to reduce significantly the computational time in the Predictive Conceptual Design (see Chapter 3). When considering a high number of economic scenarios, a standard optimization routine (e.g. Sequential Quadratic Programming, Conjugate Gradients Methods etc.) should repeat the algorithm for each of them, which also involves solving the material and energy balances for every function call. The computational time, considering an average number of function call $N_{\text{function call}}$, can be evaluated as:

$$t_{\text{standard}} = N_{\text{function call}} * N_{\text{scenarios}} * (t_{\text{scenarios}} + t_{\text{simulation}})$$  \hspace{1cm} \text{Eq. (1)}$$

Where $N_{\text{scenarios}}$ is the number of economic scenarios, $t_{\text{scenarios}}$ is the time required to compute the value of the objective function of a single economic scenario and $t_{\text{simulation}}$ the time required by the process simulator to solve the balances.

By adopting a Grid-Search approach, the number of simulations is fixed and equal to the number of total combination of the DoFs ($N_{\text{combinations}}$) and, for each of them, all the scenarios must be evaluated. The resulting computational time is:

$$t_{\text{grid-search}} = N_{\text{combinations}} * (t_{\text{simulation}} + N_{\text{scenarios}} * t_{\text{scenarios}})$$  \hspace{1cm} \text{Eq. (2)}$$

In our case study, $t_{\text{scenarios}}$ is in the order of $10^{-2}$ s, $t_{\text{simulation}}$ is around 10 s, $N_{\text{combinations}}$ is 187, $N_{\text{scenarios}}$ is 3000. Supposing that a smart optimization routine can solve each scenario optimization with only 10 function calls, this would take $3*10^{5}$ s (about 83 hours). On the contrary, the Grid-Search routine can handle the same problem in $7.5*10^{3}$ s, which is slightly more than 2 hours. If the number of DoFs increases, the number of combinations rises much faster than the number of function call required and the Grid-Search will result slower than a standard optimization routine.

In order to run all the required simulations, a coupling between Matlab R2016b (The Mathworks Inc., 2016) and UniSim Design R450 (Honeywell, 2016) was implemented. As shown in Figure 10, a tailored script, the Simulator Controller, provides the input variables (i.e. the values of each DoF) to the process simulator (Unisim Design). Then, the process
simulator solves the material and energy balances for the whole flowsheet and returns the results to Matlab, which handles the organization and storage of the data in a suitable structure. Finally, each objective function is computed independently by reading the simulation results that were previously stored.

*Figure 10: Modified optimization procedure scheme*
3. Economic Sustainability

According to the Business Dictionary (2007), Economic Sustainability is defined as “the use of various strategies for employing existing resources optimally so that a responsible and beneficial balance can be achieved over the long term” (Webfinance Inc, 2007). This definition focuses on two fundamental aspects: first, the optimal employment of existing resources for the creation of economic value; second, the need to pursue a responsible and beneficial balance in the business context, thus connecting the economic and financial aspects to the environmental and social pillars of sustainability. From a practical point of view, to be economically sustainable – for an industrial activity – essentially means to be feasible on the economic and financial levels. The feasibility of an industrial process consists in its capability to sustain its own expenses and generate profit: in other words, to create new material wealth (Douglas, 1988).

A growing concern about market uncertainty and price volatility has emerged in the last few decades. Sustainability considerations should account for this aspect, as price fluctuations and abrupt changes of the economic scenarios – due to financial and political contingencies, but also to technological developments and natural events – can endanger the economic feasibility of industrial activities. In the design of a chemical process, whose profits largely depend on the price of sharply-fluctuating commodities like crude oil and utilities like electric energy, price volatility must be taken into account during the economic assessment and optimization (Manca and Grana, 2010).

In the first section of this chapter, Conceptual Design (CD) is first presented as standard methodology for the economic assessment of a chemical process, and its main features are illustrated. In the second section, a methodology to consider price volatility and market uncertainty in the CD – the so-called Predictive Conceptual Design (PCD) - is proposed. The third section carries out the optimization of the economic objective functions (the Economic Potential for CD and the Dynamic Economic Potential for PCD) and discusses the advantages of the dynamic/predictive approach.
Conceptual Design

Economic sustainability represents a mandatory condition for the survival and growth of every economic activity. Consequently, it has been the first pillar of sustainability to be extensively studied and assessed. To achieve this purpose, several economic assessment (EA) techniques have been developed through the years and a number of metrics have been proposed. In his work “Conceptual Design of Chemical Processes” (1998), J.M. Douglas proposed a systematic methodology to assess the economic feasibility of a chemical process in the preliminary design stage. This methodology represents nowadays a standard way to address economic sustainability in the PSE field. Although there are several restrictions, Conceptual Design has been successfully applied to the design of complete process flowsheets, as well as to specific sub-problems including heat integration, heat-integrated distillation trains, multiple-effect distillation, and the separation of azeotropic systems (Luyben et al., 1997).

Conceptual Design indicates that stage of design which deals with the basic elements of a process: the structure of the flowsheet, material and energy balances, equipment specifications, utility consumption, and economic profitability (Dimian et al., 2014). It follows a hierarchical approach, according to which the design problem is decomposed into five decision-levels of increasing complexity. Such hierarchical structure allows the decision-maker analyzing sequentially the process at different levels of detail, discarding the unfeasible configurations, and singling out a range of optimal process layouts. At each level, the flowsheet is progressively enriched in details and an economic assessment is carried out by computing the Economic Potential (EP), to discriminate the most promising alternatives. In the present work, the EP is evaluated in USD/y. The five levels involve the following decisions:

1. Batch vs Continuous;
2. Input-Output structure of the flowsheet;
3. Recycle structure of the flowsheet;
4. General structure of the separation systems;
The first level is relatively simple and involves the choice to adopt a batch or a continuous configuration. The Economic Potential of level 1, namely EP1, does not assume any numerical value and can be assimilated to a logical variable of Boolean type (ON/OFF, 0/1, yes/no). The discriminant parameter is usually the capacity of the process: a capacity greater than 5000 ton/y, usually requires a continuous plant; a capacity lower than 500 ton/y can be achieved by adopting a batch configuration, which shows a number of advantages in terms of flexibility.

The second level involves a set of relevant decisions related to the general structure of the process flowsheet. At this stage, all the streams entering and exiting the battery limits of the plant need to be fully assessed in terms of their phase, composition, and operating conditions. The streams are classified in different categories and are listed in ascending order of boiling point. We usually have purge streams, recycles, reactants, products, by-products and waste. The Economic Potential of level 2 (EP2) is associated to the simple Input-Output structure of the flowsheet and is calculated as:

$$EP2 = (Product(s) \text{ price} + Byproduct(s) \text{ Value}) - Raw Material(s) \text{ Cost} \quad \text{Eq. (3)}$$

This formula represents a simple economic balance between the revenues obtained by selling the products and/or using the by-products (e.g., as fuel inside the plant) and the costs of buying the raw materials (reactants). It is evident that – in order to be economically feasible – the EP2 must be definitely positive. The same applies for the EP3 and EP4. If this condition is met, the design procedure goes on to the next level.

The third level focuses on the structure of the recycle streams. The Economic Potential of level 3 (EP3) quantifies the economic load that the reaction section and its recycle configuration have on the overall process. The separation train is still considered as a black box. Decisions must be taken according to the performance of the reaction (conversion, selectivity, heat generation) and to the type of products (phase, composition). The EP3 takes into account the capital and operative expenses (CAPEX and OPEX) for the reactor(s) and compressor(s) if a gaseous recycle stream is present.

$$EP3 = EP2 - Reactors and Compressors (CAPEX + OPEX) \quad \text{Eq. (4)}$$
The fourth level considers the structure of the separation systems and generally requires a detailed analysis of the downstream operations (e.g., the design of the distillation columns). The EP4 takes into account the costs (both CAPEX and OPEX) related to the separation section:

\[
EP4 = EP3 - \text{Separation costs} \ (CAPEX + OPEX)
\]  
Eq. (5)

The fifth level involves the economic assessment of the Heat Exchanger Network (HEN) and calls for the thermal integration of the process, i.e. the optimization of the HEN, by means of different techniques (e.g., pinch technology) which may lead to an improvement of the Economic Potential of level 5.

\[
EP5 = EP4 \pm \text{Heat Exchanger Network} \ (CAPEX + OPEX)
\]  
Eq. (6)

The thermal integration of the HEN is out of scope of the present work; therefore, the conceptual design is stopped at level 4.

The CAPEX terms, i.e. the capital costs to purchase and install the equipment, can be estimated by means of specific cost correlations and employing a suitable cost index (Peters and Timmerhaus, 1991). A cost index allows updating the value of a piece of equipment if the cost of the same unit, referred to a past period, is known, as illustrated in Eq. (7):

\[
\text{Present Cost} = \text{Original Cost} \times \frac{\text{Present Cost Index}}{\text{Original Cost Index}}
\]  
Eq. (7)

The most commonly used cost indexes in the process industry are: Marshall & Swift, suitable for the process industry; Nelson-Farrar for refinery construction index, the Chemical Engineering Plant Cost Index (CEPCI), and the Vatavuk Air Pollution Control Cost Index (VAPCCI). A cost correlation is a formula that relates the cost of purchase and installation of a piece of equipment to its geometric dimensions, material of construction, and operating pressure. In the present work, the Guthrie’s formulas (Guthrie, 1969) are adopted as standard cost correlations.

The OPEX terms, i.e. the expenditures to be sustained during the operational life of the plant, strictly depend on the prices/costs of raw material, products, and utilities. According
to Douglas’ approach, these prices/costs are assumed constant throughout the operating period of the plant (Douglas, 1988), as expressed in Eq. (8):

\[ OPEX(t) = OPEX(t_0) \quad \forall \ t \in T \]  
Eq. (8)

Where \( t \) is the generic time over the lifetime of the plant; \( t_0 \) is an arbitrary time at which the price set is selected; \( T \) is the time length of the economic assessment.

The hypothesis of fixed prices/costs represents a strong simplification, as in reality the price of chemicals and utilities is constantly fluctuating. The phenomenon of price volatility and its effect on the feasibility of a chemical process can be observed in the conceptual design of the hydrodealkylation (HDA) process, already studied by Douglas in 1998, which converts toluene to benzene on an equimolar basis. The following graph shows the trend of price of toluene and benzene from 2004 to 2015.

![Graph showing the Price trends of Toluene and Benzene (Sepiacci, 2016)](image)

\( Figure\ 11:\ Price\ trends\ of\ Toluene\ and\ Benzene\ (Sepiacci,\ 2016)\)

Beyond the strong variability that affects the price evolution (e.g., the abrupt price fall in the second semester of 2008, due to the outbreak of the economic crisis), it is possible to observe a continuous crossing between the trajectories of toluene and benzene prices. Consequently, the EP2 of the process continuously oscillates above and below the zero value, which represents the extreme condition of economic unfeasibility.
It is now evident that considering price volatility during Conceptual Design is mandatory if a reliable economic assessment and a consistent solution of the optimization problem are desired.

**Predictive Conceptual Design**

As briefly shown in the previous section, the Economic Sustainability of a chemical process depends significantly on the volatility of demand, supply, and prices of raw materials, final products, and utilities (Manca, 2015). This section proposes and analyses a dynamic approach to the economic assessment of chemical plants based on the development and employment of econometric models (EM) to simulate the future trajectories of prices and costs. This innovative methodology, named Predictive Conceptual Design (PCD) (Barzaghi et al., 2016) represents an evolution of the conventional Conceptual Design, based on a steady-state approach (Eq. (8)). PCD accounts for the intrinsic variability of the OPEX terms, thus introducing a direct time dependence in the expression of Douglas’ Economic Potentials, which are labelled as Dynamic Economic Potentials (DEPs). Econometric models are used to generate a set of possible future trajectories of commodity and utility prices, i.e. a set of *economic scenarios*. For each economic scenario, PCD identifies an optimal process configuration. As a large number of stochastic economic scenarios can be generated, PCD comes up with a set of optimal solutions and with a distribution of Dynamic Economic Potentials. From this perspective, this methodology allows to move from a deterministic approach, characterized by fixed prices/costs of commodities and utilities, to a probabilistic approach, based on the stochastic fluctuation of the OPEX terms (Manca et al., 2015).

The procedure for the development of econometric models goes along the following sequence:

1. Identification of a reference component;
2. Identification of the discretization time and time horizon for the economic assessment;
3. Identification of an econometric model for the reference component;
4. Identification of econometric models for raw material(s) and product(s)
5. Identification of econometric models for utilities

Each step is briefly analyzed in the following subsections.

**Identification of a reference component**

The identification of a reference component is highly recommended, as it allows linking the price variability of commodities and utilities to the price fluctuations of that component. As extensively discussed in Manca (2013), the reference component must be selected according to the market field of the chemical plant and it needs to be a key component for either the process or the sector where the plant operates. In addition, its cost should be well-known, largely available and frequently updated. For the petrochemical industry and generally for the Oil&Gas sector a good candidate to be selected as reference component is crude oil (CO). Crude oil represents the precursor of a number of chemical products, in particular for the petrochemical industry, and plays a major role with respect to many industrial utilities (electricity, steam, fuel). Once identified the potential future price trajectories of crude oil, it is then possible to estimate the possible trends of both commodities and utilities, and therefore of the OPEX terms.

**Identification of the discretization time and time horizon**

Price volatility can cover short-, medium-, or long-term periods. In fact, price fluctuations can be observed on an hourly basis, as in the case of electric energy, whose quotations are updated every hour; on a daily basis, as in the case of crude oil or other fundamental commodities; up to monthly and seasonal basis for other raw materials or assets. The time granularity (i.e. the discretization time) of volatility also depends on the time horizon that is investigated. For instance, as we consider the volatility of electric energy, it is possible to observe a daily trend as well as a seasonal trend, depending on the time horizon under consideration. Therefore, the choice of a suitable discretization time is based on the following considerations:

1. The availability of real prices/quotations, which can be sampled daily, weekly, monthly, quarterly or yearly;
2. The number of steps that the model can forecast consistently;
3. The time horizon that is investigated.

As far as the time horizon for the economic assessment is concerned, it can cover (i) few days or weeks when facing problems of tactical resource allocations and supply chain management, (ii) up to months or years in the case of complex projects (Manca and Grana, 2010). In case of economic sustainability of an industrial plant, the time horizon for the economic assessment should cover the lifetime of the plant or a significant fraction of it, i.e. 10-15 years. Consequently, in case of PCD, a suitable discretization time (i.e. sampling time) is one month (Sepiacci and Manca, 2015).

Identification of an econometric model for the reference component

This section reports a concise description of the methodology to develop econometric models. For further details, please refer to: Dées et al., (2007); Kilian and Park, (2009); Barzaghi et al., (2016); Klein (1947); Manca et al., (2015); Manca and Grana (2010); Sepiacci and Manca (2015).

An econometric model is a model that specifies the statistical relationship which is assumed to hold between various economic quantities (e.g., prices, incomes, interest rates) pertaining to an economic phenomenon under study (Sims, 1980). Econometric models are tools that economists use for the purpose of testing hypotheses, forecast future trends and validate economic models (Klein, 1947). For the sake of clarity, economic models account for economic real variables (e.g. demand, inventories, production, GDP) and simulate market fluctuations according to the supply and demand law. On the contrary, econometric models simulate price variability and possible future trends based on the statistical analysis of past price series and shocks.

The formulation of an econometric model for crude oil involves the acquisition of the historical price series and the statistical analysis of these data. By looking at a generic historical price series $X(t)$, it is possible to recognize three different behaviors: a trend $T(t)$, i.e. a long-term systematic increase or decrease; a periodical pattern, usually seasonal $S(t)$; and an irregular-stochastic behaviour $I(t)$.
\[
X(t) = T(t) + S(t) + I(t) \quad \text{Eq. (9)}
\]
As suggested by Barzaghi et al., (2016), the trend \(T(t)\) of the price series can be captured by using moving-averaged values of prices with four-month time spans. The moving average operator allows filtering the high-frequency fluctuations and confers a smoother trend to the time series:

\[
X_{\text{averaged}} = \frac{1}{n} \sum_{i=0}^{n-1} X(t - i) \quad \text{Eq. (10)}
\]

As shown in Figure 12, moving-averaged data are affected by a time-delay with respect to the historical price series. The extent of the delay depends on the \(n\) terms of the moving average: in case of \(n = 4\), the time delay is approximately 2 months, fully acceptable for the PCD purposes (Manca et al., 2015).

\[
\text{Figure 12: Comparison between the historical and moving-averaged data (Sepiaci, 2016)}
\]

The next step in the formulation of the econometric model consists in identifying the time-correlation between price shocks, i.e. to verify if price fluctuations depend in some way on previous historical values or are purely stochastic. The price shock at time \(t\) is defined as follows (Barzaghi et al., 2016):
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\[ Shock(t) = \frac{P(t) - P(t - 1)}{P(t - 1)} \quad \text{Eq. (11)} \]

Where \( P(t) \) and \( P(t-1) \) are the prices at time \( t \) and \( t-1 \) respectively.

The correlation index is used to quantify the correlation between present and past price shocks. It is a measure of the correlation between two generic sets of values \( X \) and \( Y \):

\[ Corr(X,Y) = \frac{cov(X,Y)}{\sqrt{var(X)var(Y)}} \quad \text{Eq. (12)} \]

It can assume a value in the range \([-1,1]\). If the two sets are perfectly correlated (e.g., are the same set), the correlation index is 1. On the contrary, if they are anti-correlated (e.g., the two sets have opposite trends), it is -1.

In case of crude oil price shocks, the two sets are represented by the same series of price shocks, but shifted by a certain time lag. Therefore, the correlation index of the reference component quantifies the autocorrelation of crude oil price shock series. The autocorrelation of a series \( X \) with time lag \( j \) is (Stock and Watson, 2003):

\[ Corr(X_t, X_{t-j}) = \frac{cov(X_t, X_{t-j})}{\sqrt{var(X)var(X_{t-j})}} \quad \text{Eq. (13)} \]

Correlograms are diagrams that report the correlation index of two series \( X \) and \( Y \) as a function of the time lag introduced between them. The correlogram, which reports the autocorrelation of a series is called autocorrelogram, and shows how the shocks depend on previous values. The autocorrelogram of WTI crude oil shocks is shown in Figure 13. It is easy to observe that the correlation is high for time lags of 1 and 2 months, where the correlation index assumes values of 0.8 and 0.6 respectively. Once assessed the time dependence of the shock price series, it is possible to define the econometric model to be employed.
A suitable type – linear, rather simple and flexible – is the autoregressive model, also known as ARX model, from AutoRegressive with eXogenous input (Ljung, 1987), characterized by the structure shown in Eq. (14):

\[ X(t) = a_0 + a_1 X(t - 1) + a_2 X(t - 2) + \ldots + a_q X(t - q) \]  

Eq. (14)

As outlined by the WTI autocorrelogram in Figure 13, the autoregressive model of crude oil price is formulated as follows:

\[ P_{CO_t} = a_0 + a_1 P_{CO_{t-1}} + a_2 P_{CO_{t-2}} \]  

Eq. (15)

Where \( P_{CO_{t-1}} \) and \( P_{CO_{t-2}} \) represents the value of crude oil price at time \( t-1 \) and \( t-2 \) respectively, and \( a_0, a_1, a_2 \) are linear regression coefficients, which can be simply computed with a linear regression procedure based on the minimization of the sum of the squared errors between the real quotations and the values estimated by the model.

\[
\min_{a_0, a_1, a_2} \sum_{t=1}^{n} \left[ P_{CO_t}^{REAL} - P_{CO_t}^{MODEL} \right]^2
\]

Eq. (16)

Figure 14 shows how the econometric model is able to fit the real trend of crude oil price with a good accuracy. The goodness of the model is measured by the coefficient of determination \( R^2 \) reported in Table 4, together with the values of the adaptive parameters, the standard deviation, and the average of the price shocks.
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![Real trend and model forecast of crude oil market](Sepiacci, 2016)

**Figure 14: Real trend and model forecast of crude oil market** (Sepiacci, 2016)

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_0$ [USD/bbl]</td>
<td>3.3207</td>
</tr>
<tr>
<td>$a_1$</td>
<td>1.8286</td>
</tr>
<tr>
<td>$a_2$</td>
<td>-0.8711</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.9813</td>
</tr>
<tr>
<td>$\sigma_{CO}$</td>
<td>0.0313</td>
</tr>
<tr>
<td>$X_{CO,AVE}$</td>
<td>-0.0028</td>
</tr>
</tbody>
</table>

It is also necessary to introduce a stochastic contribution in the expression of the autoregressive model, in order to take into account the intrinsic volatility of crude oil price. Stochasticity is modelled by means of a random function that generates a number between -1 and 1. By doing so, random fluctuations of oil price can be simulated and possible price trajectories forecasted. The econometric model assumes the following expression:
\[ P_{CO_t} = (a_0 + a_1 P_{CO_{t-1}} + a_2 P_{CO_{t-2}})(1 + RAND \times \sigma_{CO} + X_{COave}) \]  

Eq. (17)

Barzaghi et al. (2016) have shown that the seasonal component of crude oil price can be neglected. For PCD purposes, Eq. (17) allows evaluating a large number of price trajectories, thus moving from a deterministic economic assessment, based only on one single economic scenario, to a probabilistic approach, more robust and reliable, based on a distribution of thousands of viable future economic scenarios. Figure 15 shows the simulation of 10 price trajectories:

![Crude Oil](image)

**Figure 15: Crude Oil economic scenarios**

**Identification of econometric models for raw materials and products**

As previously stated, the majority of chemicals employed and produced by the petrochemical industry are strictly related to crude oil, and their quotations depend significantly on its price. Sepiacchi et al. (2017) showed how the prices of benzene, propylene, and cumene, the main chemicals involved in the cumene production process, follow the trend of WTI quotations (Figure 16).
For each chemical, an autoregressive model can be formulated as previously done for crude oil. The formulation of an AR model implies the availability of the price series of that specific chemical and involves the same statistical analysis followed for crude oil: construction of the correlogram, identification of the relevant time lags, formulation of the model, and linear regression to find the values of the adaptive parameters. In addition, it is possible to correlate the price of the chemical to the price of crude oil. Consequently, the econometric model assumes the structure of Eq. (18):

\[ Y(t) = a_0 + a_1 X_{t-1} + a_2 X_{t-2} + \ldots + a_q X_{t-q} + b_1 Y_{t-1} + b_2 Y_{t-2} + \ldots + b_p Y_{t-p} \]  

Eq. (18)

Where \( X \) and \( Y \) are the independent variable (i.e. the price of crude oil) and the dependent variable (i.e. the price of the specific chemical) at time \( t \), respectively; \( q \) and \( p \) are the number of time lags for \( X \) and \( Y \), respectively. Generally speaking, an autoregressive model with \( p \) time lags for the independent variable and \( q \) time lags for the dependent variables is indicated as \( \text{ADL}(p,q) \), which stands for Autoregressive with Distributed Lag (Stock and Watson, 2003). The ADL model represents a good candidate for several chemical products over different time intervals (Manca, 2015).

The econometric models of benzene, propylene and cumene, to be employed in the Predictive Conceptual Design of the cumene production process, were formulated by
Sepiacci et al. (2017). Their market quotations are available from online databases (ICIS, 2015; IHS, 2015). As reported in Table 5, the highest correlation was observed for crude oil quotations at the same month (no time lag) and for their own quotations with unitary time lag (i.e. one month):

Table 5: Econometric models for benzene, propylene, and cumene

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Econometric Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>( P_{B_t} = (a_0 + a_1P_{CO_t} + b_1P_{B_{t-1}})(1 + RAND * \sigma_B) )</td>
</tr>
<tr>
<td>Propylene</td>
<td>( P_{P_t} = (a_0 + a_1P_{CO_t} + b_1P_{P_{t-1}})(1 + RAND * \sigma_P) )</td>
</tr>
<tr>
<td>Cumene</td>
<td>( P_{C_t} = (a_0 + a_1P_{CO_t} + b_1P_{C_{t-1}})(1 + RAND * \sigma_C) )</td>
</tr>
</tbody>
</table>

Table 6 reports the values of the adaptive parameters obtained by a linear regression of the econometric models:

Table 6: Coefficients of commodities econometric models

<table>
<thead>
<tr>
<th>Commodity</th>
<th>( a_0 ) [USD/kmol]</th>
<th>( a_1 ) [USD/bbl]</th>
<th>( b_1 ) [-]</th>
<th>( R^2 ) [-]</th>
<th>( \sigma ) [-]</th>
<th>( X_{AVE} ) [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>2.6984</td>
<td>0.0754</td>
<td>0.9012</td>
<td>0.9407</td>
<td>0.0843</td>
<td>-0.0098</td>
</tr>
<tr>
<td>Propylene</td>
<td>1.3533</td>
<td>0.1124</td>
<td>0.7792</td>
<td>0.9201</td>
<td>0.0885</td>
<td>-0.0113</td>
</tr>
<tr>
<td>Cumene</td>
<td>6.7938</td>
<td>0.1924</td>
<td>0.8447</td>
<td>0.9138</td>
<td>0.0880</td>
<td>-0.0068</td>
</tr>
</tbody>
</table>

The coefficient of determination \( R^2 \) shows that a good agreement between real and model prices exists. It is worth observing that an additional stochastic factor is incorporated in the formulation of the ADL models to account for the random variability of the commodity itself. The econometric models of benzene, propylene, and cumene are used to generate a set of possible economic scenarios, as shown in Figure 17, Figure 18, and Figure 19 where 10 price trajectories are reported.
Figure 17: Benzene economic scenarios

Figure 18: Propylene economic scenarios
In order to perform a reliable economic assessment, a few thousands of economic scenarios should be simulated. In our case, 3000 different economic scenarios are considered.

Identification of econometric models for utilities

In a chemical plant, several utilities are usually employed, such as electric energy, steam, fuel gas or oil, cooling water, diathermic and cryogenic fluids. In most cases, the only ones that can have a relevant impact on the economic balance of the process are electric energy, steam and fuel gas or oil, and their econometric model are briefly illustrated in this section.

The development of a detailed econometric model of electric energy price is reported by Manca, (2013b). It was observed that the price of electric energy oscillates periodically with different time granularity, fluctuating hourly as well as seasonally, and with different intensity. It was also remarked that it shows a time delay of approximately 3 months, i.e. a quarter, with respect to crude oil quotation. Because of these observations, Eq. (19) was proposed to forecast the price of electric energy as a function of crude oil quotations:

![Cumene economic scenarios](image-url)
Multi-objective optimization of sustainability criteria in the conceptual design of chemical plants

\[ P_{EE_{i,j}} = a_j + b_j P_{CO_{t-t_d}} + c_j \sin \left( \frac{2\pi}{T_j} + \varphi_j \right) \]  \hspace{1cm} \text{Eq. (19)}

Where:

- \( P_{EE_{i,j}} \) is the price of electric energy at the \( i \)-th discrete time period (e.g. week) for the \( j \)-th interval of the day (e.g. morning, afternoon, evening, night);
- \( a \) and \( b \) are adaptive coefficients that model the long-term correlation of electric energy from crude oil price;
- \( c \) is the proportionality constant of the seasonal term based on the \( T \) period and \( \varphi \) phase;
- \( t_d \) is the time delay between electric energy price and crude oil quotation \( P_{CO} \);

Concerning the natural gas, there is no significant correlation with the WTI, according to Sepiacci (2016). Thus, an autoregressive model should be developed, adopting the same structure as \textit{Eq. (18)}. Since it is common practice to use natural gas as fuel to produce steam in chemical plants, their costs are strictly related. The fuel expenses are dominant in steam production. Considering an average efficiency of a boiler equal to 85\%, Idris et al. (2016), estimated the cost of steam as reported in \textit{Eq. (20)}:

\[ P_s = 0.003 \frac{MBtu}{kg} P_{NG} \]  \hspace{1cm} \text{Eq. (20)}

For the sake of simplicity, also for the electric energy, an ADL model can be adopted to forecast monthly quotations. Since in the USA, natural gas covers about 33\% of the national electric energy production (EIA, 2016), a good correlation between them is expected. Table 7 and Table 8 summarize the model developed by Sepiacci (2016) and provides the required parameters. Like for the commodities, 10 simulated price trajectories for the utilities are reported in Figure 20, Figure 21, and Figure 22:
### Table 7: Econometric models for utilities

<table>
<thead>
<tr>
<th>Utility</th>
<th>Econometric Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural Gas</td>
<td>( P_{NG_t} = (a_0 + a_1 P_{NG_{t-1}} + b_1 P_{NG_{t-2}})(1 + RAND \times \sigma_{NG}) )</td>
</tr>
<tr>
<td>Electric Energy</td>
<td>( P_{EE_t} = (a_0 + a_1 P_{NG_{t}} + b_1 P_{EE_{t-1}})(1 + RAND \times \sigma_{EE}) )</td>
</tr>
<tr>
<td>Steam</td>
<td>( P_s = a_0 P_{NG_t} )</td>
</tr>
</tbody>
</table>

### Table 8: Coefficients of utilities econometric models

<table>
<thead>
<tr>
<th>Utility</th>
<th>( a_0 )</th>
<th>( a_1 )</th>
<th>( b_1 )</th>
<th>( R^2 )</th>
<th>( \sigma )</th>
<th>( X_{AVE} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural Gas</td>
<td>0.2106 USD/MBtu</td>
<td>1.7442</td>
<td>-</td>
<td>0.9619</td>
<td>0.0436</td>
<td>-0.0087</td>
</tr>
<tr>
<td>Electric</td>
<td>4.7255 USD/MWh</td>
<td>2.0285 MBtu/MWh</td>
<td>0.7209</td>
<td>0.9560</td>
<td>0.0680</td>
<td>0.0002</td>
</tr>
<tr>
<td>Steam</td>
<td>0.003 MBtu/kg</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

![Figure 20: Natural gas economic scenarios](image-url)
Definitions of the Dynamic Economic Potential(s)

The same hierarchical approach to Conceptual Design, proposed by Douglas in 1988, can be applied to the dynamic assessment of the Economic Potentials. In Predictive Conceptual
Design, a time dependence in the expression of Douglas’ Economic Potentials is introduced, thus resulting in the so-called Dynamic Economic Potentials (DEPs) (Manca, 2015; Manca and Grana, 2010).

The Economic Potential of level 1 remains the same also in PCD as it only discriminates between continuous and batch processes.

\[ DEP_1 = EP_1 \]  
Eq. (21)

The dynamic (i.e. time-dependent) feature is introduced at level 2, where the prices/costs of raw materials, final products, and by-products are generated by the econometric models. A new DEP2 is introduced as:

\[ DEP_{2k}[USD/y] = \frac{\sum_{t=1}^{n_{Months}} (Revenues_{2t,k} * nHpM)}{n_{Months}/12} \]  
Eq. (22)

\[ k = 1, ..., n_{Scenarios} \]

Where:

\[ Revenues_{2t,k}[USD/h] = \max\left[0, \left( \sum_{prod} F_{prod} C_{prod_{t,k}} - \sum_{raw} F_{raw} C_{raw_{t,k}} \right) \right] \]  
Eq. (23)

For example, for the cumene production process the Revenues of level 2 are:

\[ Revenues_{2t,k}[USD/h] = \max\left[0, \left( P_{C_{t,k}} F_C - P_{B_{t,k}} F_B - P_{P_{t,k}} F_P \right) \right] \]  
Eq. (24)

\( P_{C_{t,k}} \) is the price/cost of component (e.g., cumene) at time t in the economic scenario k; \( F \) is the flowrate of component entering or exiting the plant (e.g. cumene productivity); \( nHpM \) is the number of hour in one month of operation; \( n_{Months} \) is the number of months over the time-horizon of the economic assessment. The \( \max \) function allows neglecting negative revenues: when the costs to buy the raw materials are higher than the profit from selling the products, the plant is shut down and the revenues are zeroed.

As levels 3 and 4 are considered, the economic assessment incorporates the CAPEX terms of the reaction, recycle, and separation systems, as outlined in the following:
Multi-objective optimization of sustainability criteria in the conceptual design of chemical plants

\[
DEP3_k[\text{USD/y}] = \frac{\sum_{t=1}^{n\text{Months}} (\text{Revenues3}_{t,k} \cdot nHpM)}{n\text{Months}/12} - \frac{\text{CAPEX}_{\text{reactor+compressor}}}{n\text{Months}/12} \quad \text{Eq. (25)}
\]

\[
\text{Revenues3}_{t,k}[\text{USD/h}] = \max\left(0, \left(\sum_{\text{prod}} F_{\text{prod}}G_{\text{prod},t,k} - \sum_{\text{raw}} F_{\text{raw}}G_{\text{raw},t,k} - W_C C_{EE,t,k}\right)\right) \quad \text{Eq. (26)}
\]

And finally, for level 4:

\[
DEP4_k[\text{USD/y}] = \frac{\sum_{t=1}^{n\text{Months}} (\text{Revenues4}_{t,k} \cdot nHpM)}{n\text{Months}/12} - \frac{\sum_{e=1}^{n\text{Equip}} \text{CAPEX}_e}{n\text{Months}/12} \quad \text{Eq. (27)}
\]

\[
\text{Revenues4}_{t,k}[\text{USD/h}] = \max\left(0, \left(\sum_{\text{prod}} F_{\text{prod}}G_{\text{prod},t,k} - \sum_{\text{raw}} F_{\text{raw}}G_{\text{raw},t,k} - \sum_{\text{utility}} W_u C_{u,t,k}\right)\right) \quad \text{Eq. (28)}
\]

Where \(n\text{Equip}\) is the number of equipment pieces; \(W_C\) is the energy duty of the compressor; \(C_{EE,t,k}\) is the cost of electric energy at time \(t\) in the economic scenario \(k\); \(W_u\) the generic duty of utility \(u\); \(C_{u,t,k}\) is the cost of utility \(u\) at time \(t\) in the economic scenario \(k\). The computation of the overall CAPEX involves the purchase and installation costs of the whole equipment of the plant. The Revenues of level 3 include the operative expenses for running the compressor, needed in presence of a recycle stream in the gas phase, while the Revenues of level 4 involve the economic impact of the utilities employed in the plant.

It is worth remarking that the DEP4 is not a single value, but a distribution of values, one for each economic scenario. The \(\max\) function suggests running the plant only when the revenues are positive. One weakness of DEP4 formulation is that it does not take into account the feasibility, impact, and cost of periodically running and stopping the production (i.e. startups and shutdowns), both in terms of economic allocation of resources and physical stress and impact on the plant equipment (Manca, 2015). For this reason, the present work neglects the \(\max\) function and accounts for possible negative DEP4 values.
Economic Optimization of the cumene production process

Definition of the objective function

According to the original Conceptual Design methodology, the objective function to be maximized is represented by the cumulated EP4, i.e. the Economic Potential of 4\textsuperscript{th} level cumulated over the time-horizon of the economic assessment. It is calculated as the product between the EP4, expressed in USD/y, and the number of years \(nY\):

\[
EP4\text{cumulated} = EP4 \ast nY
\]

Eq. (29)

The EP4 accounts for both operative and capital expenses (OPEX and CAPEX) of the plant. The OPEX terms are calculated under the hypothesis of fixed prices. For the cumene process, the EP4 is expressed as:

\[
EP4 \ [\text{USD/y}] = \frac{(Revenues4 \ast nHpM) \ast nMonths}{nY} - \sum_{e=1}^{nEq} \frac{CAPEX_e}{nY}
\]

Eq. (30)

\[
Revenues4 \ [\text{USD/h}] = P_C F_C - P_B F_B - P_P F_P - P_S F_S - P_w F_w - P_{EE} W_{EE}
\]

Eq. (31)

Where \(P_C\), \(P_B\), \(P_P\) are the prices of cumene, benzene and propylene respectively, in USD/kmol; \(P_S\), \(P_W\), \(P_{EE}\) are the costs of steam (in USD/MBtu), cooling water (equal to 0.16 USD/GJ) and electric energy (in USD/MWh) respectively. \(F\) is the flow rate of the component entering or exiting the plant (e.g. \(F_C\) is the cumene productivity); \(W_{EE}\) is the required power of electric energy (in W). \(nHpM\) is the number of operating hours in one month; \(nMonths\) is the number of months over the time-horizon of the economic assessment. The number of years \(nY\) is assumed to be equal to 10 years. The number of working hours per year is assumed 8000 h/y.

According to PCD, the objective function is the cumulated DEP4, i.e. the Dynamic Economic Potential of 4\textsuperscript{th} level over the 10 years’ period, expressed as:

\[
DEP4\text{cumulated}_k [\text{USD}] = DEP4_k \ast nY
\]

Eq. (32)

As stated before, the DEP4 accounts for the price volatility of raw materials, final products, and utilities. Therefore, the hypothesis of fixed prices is no longer valid and the prices/costs
are updated every month by the econometric models. The general expression of the DEP4 is reported in Eq. (27). For the cumene process, the expression of the Revenues of 4th level is the following:

\[
Revenues_{4,t,k} \left( \frac{USD}{h} \right) = P_{C,t,k}F_C - P_{B,t,k}F_B - P_{P,t,k}F_P - P_{S,t,k}F_S - P_{W}F_W - P_{EE,t,k}W_{EE}
\]  

Eq. (33)

\( P_{C,t,k} \) is the price/cost of component or utility at time \( t \) in the economic scenario \( k \).

**Computation of (Dynamic) Economic Potential**

The algorithm for the (D)EP4 computation is here briefly illustrated. As far as capital costs estimation is concerned, the Guthrie’s formulas reported in Table 9 were adopted. Guthrie’s formulas allow the designer to estimate the purchase and installation cost of several pieces of equipment as a function of some parameters as the geometric size, the material of construction, the power duty to be provided (e.g. for pumps and compressor), and other specific features. The Marshall & Swift index (M&S) is assumed equal to 1457 (Barzaghi et al., 2016). With reference to Table 9, \( D, L \) and \( A \) are the unit diameter, length, and area respectively, in inches and squared inches. \( H \) is the tray stack height of the distillation column. \( F_p \) and \( F_m \) depend on the operating pressure and construction material, respectively. \( F_d \) depends on the type of heat exchanger, while \( F_t \) and \( F_s \) depend on the tray typology and spacing, respectively. Further details can be found in Guthrie (1969) and (Turton et al., 2008). For the pump’s correlation, \( P \) and \( Q \) are the pump outlet pressure and duty, respectively. The geometric dimensions of the process units are provided by the simulation or can be calculated from the simulation results. For instance, the areas of the heat exchangers are calculated according to the duty to be provided or removed.

The OPEX terms are estimated as a function of the specific prices/costs provided by the econometric models and of the inlet/outlet flowrates and the utility consumption given by the steady-state mass and energy balances. The main utilities employed in the cumene process are high-pressure steam, cooling water, and electric energy.
Table 9: Guthrie’s cost correlations for the units of the cumene process (Turton et al., 2008)

<table>
<thead>
<tr>
<th>Process Unit</th>
<th>Costs Estimation Correlation</th>
</tr>
</thead>
</table>
| Reactor (Multitubular) | \[
\frac{M&S}{280} \ast 101.3 \ast A^{0.65} (2.29 + F_c) \\
F_c = (F_d + F_p) \ast F_m
\] |
| Reactor (Tubular)     | \[
\frac{M&S}{280} \ast 101.9 \ast D^{1.066}L^{0.802} (2.18 + F_c) \\
F_c = F_p \ast F_m
\] |
| Heat Exchanger        | \[
\frac{M&S}{280} \ast 101.3 \ast A^{0.65} (2.29 + F_c) \\
F_c = (F_d + F_p) \ast F_m
\] |
| Distillation Column   | \[
CAPEX_{vessel} = \frac{M&S}{280} \ast 101.9 \ast D^{1.066}L^{0.802} (2.18 + F_c) \\
CAPEX_{trays} = \frac{M&S}{280} \ast 4.7 \ast D^{1.55}H \ast F_c \\
F_c = F_t + F_s + F_m
\] |
| Pump                 | \[
CAPEX_{pump} = C_p \ast (1.8 + 3.624 \ast F_p) \\
\log(C_p) = 3.5793 + 0.3208 \ast \log(P) + 0.0285 \ast \log(P^2) \\
F_p = 0.1682 + 0.3466 \ast \log(Q) + 0.48411 \ast \log(Q^2)
\] |

Economic optimization results

Figure 23 and Figure 26 show a schematic representation of the optimization strategies for the Conceptual Design and the Predictive Conceptual Design, respectively. As far as the conventional CD methodology is concerned, based on the hypothesis of fixed prices, the Grid-Search optimization algorithm receives as input data the simulation results, the set of fixed prices, and the algorithm for the EP4 computation, and returns a single optimal solution. The set of prices/costs is taken from the quotations of cumene, benzene,
propylene, electric energy, and steam of a specific month, e.g. of January 2016, and is kept constant over the whole time-horizon.

The question that arises is the following: what happens to the optimal solution when a different set of prices/costs (e.g. the quotations of March 2008 instead of January 2016) is provided to the Grid-Search algorithm? Does the optimizer come up with a different optimal solution? This section wants to investigate the influence of the choice of the prices/costs set on the optimal process configuration. To do so, the optimization has been performed for 118 different prices/costs sets, corresponding to the market quotations from January 2004 to October 2013. Each prices/costs set can be considered as a different (constant) economic scenario. Figure 24 shows on the x-axis the months at which the market quotations are taken and on the y-axis the index of plant configuration. It is possible to observe that 7 different optimal solutions (i.e. 7 different plant configurations) for the vapor phase process are identified depending on the prices/costs data.
Table 10 reports an overview of the seven optimal solutions. As regards the inlet temperature, all the solutions converge to the maximum allowable temperature (350 °C); on the other hand, the optimal reactor length ranges from 4 to 11 meters. The probability of optimality is also reported: it is possible to observe that configurations #121 and #143 are the most probable winners, with 33 and 32% of probability of being optimal, respectively.

Table 10: Summary of the optimal configuration for the Conceptual Design methodology (vapor phase)

<table>
<thead>
<tr>
<th># Configuration</th>
<th>Inlet Temperature [°C]</th>
<th>Reactor Length [m]</th>
<th>Probability of optimality</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>350</td>
<td>4</td>
<td>&lt; 1 %</td>
</tr>
<tr>
<td>33</td>
<td>350</td>
<td>5</td>
<td>2 %</td>
</tr>
<tr>
<td>66</td>
<td>350</td>
<td>6.5</td>
<td>4 %</td>
</tr>
<tr>
<td>88</td>
<td>350</td>
<td>7.5</td>
<td>5 %</td>
</tr>
<tr>
<td>121</td>
<td>350</td>
<td>9</td>
<td>33 %</td>
</tr>
<tr>
<td>143</td>
<td>350</td>
<td>10</td>
<td>32 %</td>
</tr>
<tr>
<td>165</td>
<td>350</td>
<td>11</td>
<td>23 %</td>
</tr>
</tbody>
</table>

However, it is possible to conclude that a univocal and clear solution of the optimization problem is not provided, and the designer should decide among multiple optimal
configurations. In addition, more than 10% of the available market quotations give place to solutions that are clearly inconsistent and non-optimal over the long-term horizon (configurations #11, #33, #66, #88). The dispersion of the optimal solutions in a spectrum of different process configurations is a direct consequence of the price volatility of raw materials (benzene, propylene) and final products (cumene). The bar graph reported in Figure 25 shows on the x-axis the time series of market quotations and on the y-axis the value of the cumulated EP4: each bar represents the value of the EP4 calculated by considering the market quotations of the corresponding month based on the specific plant configuration that maximizes the EP4 value. It is possible to observe a continuous fluctuation of the EP4 on a monthly basis, which leads also to negative values.

![Economic Potential fluctuation](image)

*Figure 25: Fluctuation of the EP4 according to the market quotations*

A more reliable tool for dealing with market uncertainty and price volatility is represented by the Predictive Conceptual Design methodology. The following paragraph assesses the performance of PCD and outlines its advantages over the CD approach. Figure 26 illustrates the optimization strategy followed by PCD. The Grid-Search algorithm receives as input parameters no longer the current market quotations, but the economic scenarios (i.e. the prices/costs sets) generated by the econometric models. The number of stochastic economic scenarios to be generated is arbitrary, and can be very high (several thousands). The
optimization algorithm does not return a univocal solution, but a range of optimal points associated with their probability of optimality.

Figure 26: Dynamic Conceptual Design optimization strategy

For the PCD methodology, 3000 economic scenarios have been generated. However, in order to compare PCD and CD methodologies, the same number of economic scenarios, equal to 118 and corresponding to the number of available monthly quotations (from March 2008 to January 2016), are reported for the vapor phase process. Figure 27, fully analogous to Figure 24, shows that 3 different solutions are found. Therefore, the dispersion of the optimal solutions is reduced from 7 alternatives of the Conceptual Design to 3 optimal process configurations. In addition, the “background noise” that in the CD was constituted by the low-probability solutions (configurations #11, #33, #66, #88) disappears completely when the PCD approach is adopted. This aspect represents a good advantage, as it reduces the risk of identifying an inconsistent solution whenever an “unlucky” market scenario is considered at the beginning of the CD methodology. Finally, as it is possible to observe in Table 11 and in the pie charts of Figure 28, the PCD identifies a clear winner: in fact, configuration #143 results to be optimal in the 76% of the economic scenarios, with an average cumulated DEP4 of about USD 68.61 million over a 10-year time span.
Multi-objective optimization of sustainability criteria in the conceptual design of chemical plants

Figure 27: Optimal configuration for the Predictive Conceptual Design methodology (vapor phase)

Table 11: Summary of the optimal configuration for the Predictive Conceptual Design methodology (vapor phase)

<table>
<thead>
<tr>
<th># Configuration</th>
<th>Inlet Temperature [°C]</th>
<th>Reactor Length [m]</th>
<th>Probability of optimality</th>
<th>Average DEP4 cumulated [MUSD]</th>
</tr>
</thead>
<tbody>
<tr>
<td>121</td>
<td>350</td>
<td>9</td>
<td>21 %</td>
<td>68.57</td>
</tr>
<tr>
<td>143</td>
<td>350</td>
<td>10</td>
<td>76 %</td>
<td>68.61</td>
</tr>
<tr>
<td>165</td>
<td>350</td>
<td>11</td>
<td>3 %</td>
<td>68.51</td>
</tr>
</tbody>
</table>

The pie charts reported in Figure 28 compare the performance of CD and PCD methodologies in terms of probability of optimality of the different optimal process configurations. It is possible to observe how the red portion, corresponding to configuration #143 expands from 32% to 76% and results to be the clear winner of the first pillar of process sustainability, which is the economic optimization. The 3D plot reported in Figure 29 shows the trend of the cumulated DEP4 for the vapor phase process as a function of the two degrees of freedom, i.e. the reactor length and the reactor inlet temperature. As previously stated in Definitions of the Dynamic Economic Potential(s), the DEP4 is not represented by a single value, but by a distribution of values, one for each economic scenario. Consequently, each process configuration is characterized by a distribution of DEP4. In order to have a
single value of the economic objective function for each configuration, the average value of the cumulated DEP4 has been considered. The red dot shows the maximum value of the DEP4, corresponding to a reactor length of 10 m and an inlet temperature of 350 °C.

![Probability of Optimality for CD and PCD](image)

*Figure 28: Comparison between probability of optimality of CD and PCD (vapor phase)*

![Average DEP4 Cumulated](image)

*Figure 29: 3D plot of the Economic Sustainability objective function (vapor phase)*
As far as the liquid phase process is concerned, the Conceptual Design methodology identifies a spectrum of four optimal solutions, with a clear winner that reaches 80% of probability of optimality. Equally, shifting to the PCD approach, a single optimum is obtained in 100% of the economic scenarios. As reported in Table 12 and in the pie charts of Figure 30, configuration #32, corresponding to a reactor length of 5 m and an inlet temperature of 195 °C is the univocal winner of the economic optimization.

Table 12: Summary of the optimal configuration for the Predictive Conceptual Design methodology (liquid phase)

<table>
<thead>
<tr>
<th># Configuration</th>
<th>Inlet Temperature [°C]</th>
<th>Reactor Length [m]</th>
<th>Probability of optimality</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>195</td>
<td>4</td>
<td>3 %</td>
</tr>
<tr>
<td>21</td>
<td>195</td>
<td>4.5</td>
<td>8 %</td>
</tr>
<tr>
<td>32</td>
<td>195</td>
<td>5</td>
<td>80 %</td>
</tr>
<tr>
<td>43</td>
<td>195</td>
<td>5.5</td>
<td>9 %</td>
</tr>
</tbody>
</table>

The 3D plot reported in Figure 31 shows the trend of the cumulated DEP4 for the liquid phase process, averaged on the 118 economic scenarios, as a function of the two degrees of freedom. The red dot shows the maximum value of the economic objective function, corresponding to USD 66.97 million over a 10-year time horizon. It is possible to observe how the DEP4 slightly decreases for reactors longer than 5 m, as an effect of the increased
capital cost of the reactor. A maximum behavior is observed also for the reactor inlet
temperature at low values of the reactor length, which is mainly due to DIPB formation and
increased separation costs.

As a conclusion of the comparison between the conventional CD and PCD methodologies, it
is reasonable to state that PCD represents a more robust and reliable tool for the economic
assessment and optimization of chemical processes. The main advantages of PCD over CD
for the cumene process are:

1. Lower dispersion of the optimal solutions (from 7 to 3 configurations in the vapor
phase process; from 3 to 1 in the liquid phase process);
2. Lower “background noise”, i.e. elimination of the low-probability solutions;
3. Identification of a clear optimum (configuration #143, for the vapor phase process,
raises from 32% to 76% of optimal probability; configuration #32, for the liquid phase
process, moves from 80% to 100%).

Figure 31: 3D plot of the Economic Sustainability objective function (liquid phase)
4. Environmental Sustainability

The concept of Environmental Sustainability

Traditionally, technical and economic criteria were predominant in the design of chemical processes. Process design was mostly focused on the economic feasibility of industrial plants. Recently, more stringent regulations, such as the EU-REACH legislation (ECHA, 2015), have pushed the chemical industry to include environmental criteria in the design phase (García-Serna et al., 2007). During the last twenty years, efforts have been spent to decrease the environmental impact of chemical manufacturing through the improvement of energy efficiency and the development of new “green” technologies (Abbaszadeh and Hassim, 2014). This trend was also fueled by the growing concern on sustainability. In most cases, the application of technological solutions and environmental strategies has led to reduced costs and increased profits and made these solutions economically appealing.

Since economic feasibility is usually considered as a mandatory pre-condition to develop any industrial activity, environmental sustainability represents nowadays the major target of chemical companies and – more generally – of industrialized countries. In fact, when talking about sustainability, one immediately thinks to ecological and environmental issues. The final goal of environmental sustainability is to harmonize the human activity – in this context the industrial activities – with the surrounding environment, both at the local and global scale, in order to preserve essential ecological equilibria and prevent harm to the environment and human health. A set of four conditions, which state the basic principles of environmental sustainability, were formulated by The Natural Steps, an international organization founded in Sweden in 1989 with the aim of promoting the concept of sustainability in the academic, industrial, and financial world (Robèrt, 2002):

I. Substances from the Earth crust, such as fossil CO$_2$ and heavy metals, must not systematically increase in concentration in the ecosphere, i.e. the global sum of all the ecosystems;
II. Substances produced by society must not systematically increase in concentration in the ecosphere;

III. The physical basis for the productivity and diversity of nature must not be systematically deteriorated;

IV. There must be an efficient use of resources with respect to meeting the basic human needs.

To achieve this purpose, several philosophies have emerged in the scientific community, which introduced fresh ideas and innovative theories in the debate about sustainability. Theories and disciplines like Biomimicry (Benyus, 1997), Cradle-to-Cradle (McDonough and Braungart, 2002), Getting to Zero Waste (Palmer, 2003) and Resilience Engineering (Hollnagel, 2014) have had a major role in inspiring the academic and industrial world towards the development of environmentally-oriented disciplines like Green Chemistry and Green Engineering.

Green Engineering can be seen as the natural continuation of Chemical Engineering, extended to "the design, commercialization and use of processes and products that are feasible and economical while minimizing pollution at the source and risk to human health and the environment" (Allen and Shonnard, 2001). The aim of Green Engineering is to employ the principles and practices of Chemical Engineering "to eliminate the waste or scrap generated as a result of design and manufacturing if possible, otherwise reduce it to the best possible limits" (Singh and Falkenburg, 1993). Green Engineering relies on 12 principles that provide a general framework for scientists and engineers for applications across different disciplines and scales of design (Anastas and Zimmerman, 2007). The principles of Green Engineering focus on some fundamental concepts of environmental sustainability, such as pollution prevention, process intensification, employment of inherently safe and non-hazardous materials, heat integration, and improvement of purification efficiency. Efforts have been made to incorporate these principles in a hierarchical methodology (Chen and Shonnard, 2004; Diwekar, 2003; Lapkin et al., 2004). As already discussed for Douglas’ Conceptual Design, a hierarchical method involves a sequence of decisional levels. As proposed by Diwekar (2003), five levels of implementation are considered, starting from the
steady-state process simulation and ending with the numerical solution of multi-objective optimization problems, involving both economic and environmental criteria.

A growing interest is taking place in the scientific community to include Environmental Sustainability in process design. The role of process simulation and optimization software is of paramount importance for this purpose. In addition, environmental issues are not treated anymore as constraints in the economic optimization, but are expressed as objective functions. In this chapter, a review of different approaches for assessing environmental sustainability is presented and a suitable methodology, the WAste Reduction algorithm, is illustrated in details. Then, an application of that methodology to the cumene production process is reported.

**The WAste Reduction algorithm**

As previously hinted, the aim of Green Engineering is to achieve a condition of inherent environmental friendliness of chemical processes. In most cases, the chemical industry faces environmental problems by adopting the so-called “end-of-pipe” measures, aiming at controlling the emissions by add-on processes (e.g., exhaust after-treatment, incineration, landfilling). Such a strategy, however, does not eliminate the intrinsic hazard of the process, which is related to the amount and toxicity of the wastes that are generated. In addition, it represents a costly solution that needs to be continuously updated to cope with the evolving regulations. An inherently environmental-friendly process can be achieved only through the prevention or elimination of the intrinsic hazard coming from the process (Abbaszadeh and Hassim, 2014). For this reason, environmental sustainability is deeply linked with pollution prevention, i.e. the reduction of the waste generated by the process, or simply waste reduction. Waste reduction cannot be decoupled from the technical and economic aspects of the process, and should be implemented as soon as possible in the design procedure, i.e. in the preliminary design stage. To achieve this purpose, it is mandatory to have a reliable tool for assessing quantitatively the environmental impact of the process.

Among the various techniques to assess the Environmental Sustainability of products and processes, Life Cycle Assessment (LCA) received a great attention and finally became an ISO-
codified methodology. LCA is defined as “an objective process to evaluate the environmental burdens associated with a product, process or activity by identifying and quantifying energy and materials used and wastes released to the environment; to assess the impact of those energy and material releases to the environment; and to evaluate and implement opportunities to effect environmental improvements” (Consoli et al., 1993). According to ISO 14040, LCA is a technique that consists in “compiling an inventory of relevant inputs and outputs of a product system; evaluating the potential environmental impacts associated with those inputs and outputs; and interpreting the results of the inventory and impact phases in relation to the objectives of the study” (ISO, 2006). LCA follows the life cycle of a product, process or activity from the cradle to the grave, i.e. from the extraction of raw materials to final disposal or recycling, and represents a promising tool in the evaluation of environmental performances. On the other hand, its applicability is not straightforward, as it requires a large amount of information that is usually not available when designing or retrofitting a chemical process. More specifically, LCA is usually not helpful for process optimization purposes.

If the analysis is restricted to the conceptual design phase, a number of different techniques for assessing the environmental impact and hazards are available in the literature. They can be divided in two different classes based on two corresponding criteria (Abbaszadeh and Hassim, 2014). The first criterion is the object of the assessment and discriminates between:

1. Substance-based methods, which are focused on the impact of specific substances on the environmental media and human health. Among them, the most widespread are: the Atmospheric Hazard Index (AHI) (Gunasekera and Edwards, 2003), the Inherent Environmental Toxicity Hazard (IETH) (Gunasekera and Edwards, 2006), the Global Environmental Risk Assessment (GERA) (Achour et al., 2005), the Technique for Order Preference by Similarity to Ideal Solution (TOPSIS) (Li et al., 2009).

2. Process-based methods, which take into account the whole process, its operating conditions, and technical features. Examples of process-based methods are the WAste Reduction algorithm (WAR) (Cabezas et al., 1999), the Environmental Hazard Index (EHI) (Cave and Edwards, 1997), the Integrated Environmental Index (IEI), the IDEF0/EHS model (Hirao et al., 2008).
The second criterion is the target design stage for which the methodology is developed, that can be:

1. The route-selection stage, i.e. the screening of the process alternatives during the R&D phase and the selection of the most appropriate synthesis route, representing the very first step of Conceptual Design. The AHI, EHI, IETH, TOPSIS and IDEFO/EHS belong to this first category.

2. The preliminary design stage, i.e. the construction of the process flowsheet, the analysis of mass and energy balances and of the main unit operations. Among them, there are WAR, GERA and IEI.

This twofold classification is visualized in Figure 32:

![Figure 32: Classification of methods for assessing environmental sustainability of chemical processes](image)

Since WAR (the WAste Reduction algorithm) is classified as a process-based method and is targeted towards the preliminary design stage, it is a suitable methodology for the aim of this chapter, i.e. the assessment of environmental sustainability for optimization purposes. It also shows a number of additional advantages:
1. It takes into account the environmental impact of the process during normal operations and neglects accidental releases and their consequence on the environment;
2. It is a computer-aided method that can be implemented in a simulation software; therefore, it is a suitable tool in either the design of new processes or the retrofitting of current processes (Young et al., 2000);
3. It considers only the manufacturing step of the entire life cycle of a product, as shown in Figure 33. In case of chemicals, the manufacturing step is the chemical process itself.

![Figure 33: Product life cycle (Young and Cabezas, 1999)](image)

The WAR algorithm was first developed by Hilaly and Sikdar (1994), who introduced the concept of pollution balance; then Cabezas et al. (1999) proposed the generalized WAR algorithm based on the Potential Environmental Impact (PEI) balance; finally, Young and Cabezas (1999) extended the PEI balance to the energy consumption of chemical processes.

The PEI of a given quantity of material or energy is defined as the potential effect that this material or energy would have on the environment if emitted (Young and Cabezas, 1999). It is a conceptual quantity that cannot be measured directly, but only estimated on the basis of
mass and energy emissions. The system boundaries of the PEI balance are drawn around the manufacturing process and the energy generation facilities (boilers, gas turbines, burners, etc.) as shown in Figure 34.

![Figure 34: PEI balance boundaries (Young et al., 2000)](image)

The PEI balance equation assumes the following expression:

$$\frac{dI_{tot}}{dt} = j_{in}^{cp} + j_{in}^{ep} - j_{out}^{cp} - j_{out}^{ep} - j_{we}^{ep} - j_{we}^{cp} + t_{gen}$$  \hspace{1cm} \text{Eq. (34)}$$

Where $I_{tot}$ is the total amount of potential environmental impact inside the system, measured in PEI units; $I$ is the rate of PEI, expressed in PEI/h, which can be associated to: input or output streams ($I_{in}$, $I_{out}$), waste energy ($I_{we}$), and generation ($I_{gen}$); in each case, PEI can be related to material streams, pertaining to the chemical process ($cp$), or to energy streams, coming from the energy generation ($ep$) processes.

The general PEI balance can be simplified by considering: (1) steady-state operations, thus putting the accumulation term (i.e. the derivative one) equal to zero; (2) negligible waste energy dissipations, since they will have minor impacts when compared to the amount of
energy and materials that are consumed or produced (Young et al., 2000); (3) negligible impact associated to energy input streams, much lower than the impacts associated to energy output, which involves exhaust gas emissions. The simplified balance is here reported:

$$I_{gen}^{tot} = I_{out}^{cp} + I_{out}^{ep} - I_{in}^{cp} \quad \text{Eq. (35)}$$

According to Eq. (35), the environmental efficiency of a chemical process can be measured by the rate of PEI generation. In order to make use of it, it is necessary to relate the PEI to measurable quantities. A generalized theory has been formulated by Cabezas et al. (1999) which relates PEI to stream flow rates, compositions, and specific environmental impacts $\psi_k$. The following expressions for PEI rates associated to the chemical process are here proposed:

$$I_{in}^{cp} = \sum_{j=1}^{NS} M_{in}^j \sum_{k=1}^{NC} x_{jk} \psi_k \quad \text{Eq. (36)}$$

$$I_{out}^{cp} = \sum_{j=1}^{NS} M_{out}^j \sum_{k=1}^{NC} x_{jk} \psi_k \quad \text{Eq. (37)}$$

Where NS is the number of material streams entering and exiting the battery limits of the process; $M_j$ is the flowrate of stream j; NC is the number of chemical species in stream j; $x_{jk}$ is the molar fraction of species k in stream j; $\psi_k$ is the overall specific PEI of chemical k, which can be expressed as a weighted sum of specific PEI of chemical k associated to category $l\psi_{kl}$, as expressed in Eq. (38):

$$\psi_k = \sum_{l=1}^{NK} \alpha_l \psi_{kl} \quad \text{Eq. (38)}$$

Where NK is the number of environmental impact categories and $\alpha_l$ is the weighting factor for category $l$. The weighting factors are used to express the relative importance of the impact categories; their value can be assigned arbitrarily by the expert user in order to emphasize or de-emphasize specific concerns of the chemical plant under study.

The expression for the output PEI associated to the energy generation system is:
\[ I_{\text{out}}^{\text{ep}} = \sum_{j=1}^{\text{NE}} M_{j}^{\text{out}} \sum_{k=1}^{\text{NC}} x_{jk} \psi_{k} \]  \hspace{1cm} \text{Eq. (39)}

Where \( \text{NE} \) is the number of emitted material streams from the energy generation system, which are usually divided into gaseous and solid streams. The gaseous streams mainly consist of air pollutants, e.g. \( \text{NO}_x \), \( \text{SO}_x \), PAH, greenhouse gases as \( \text{CO}_2 \), and other harmful compounds. The solid streams can consist of coal slag, i.e. non-combustible ashes and residue, heavy metals, and other impurities. \( M_j \) is the flowrate of the \( j \)-th gaseous or solid emission due to energy generation. They can be quantified by multiplying the energy demand by proper emission factors. Generally, electric energy is provided by a combined cycle gas turbine (CCGT) and steam is produced in a large wall-fired boiler. A CCGT is essentially an electric power plant in which a gas turbine and a steam turbine are used in combination to achieve higher efficiency. A large wall-fired boiler is characterized by a series of burners located on a single-wall of the furnace that provide heat to a tube bundle for vaporizing water. Natural gas is commonly used as fuel in both CCGT and wall-fired boiler. The energy demand of the process is calculated by summing all the energy duties of the process: the compressors, pumps, and refrigeration systems usually require electric energy, while reboilers of distillation columns and heat exchangers require high pressure or medium pressure steam. Once assessed the amount of electric energy and steam to be provided to the plant, it is possible to find the needed amount of natural gas through the efficiency of the unit and natural gas heat content. Finally, the flowrates of single pollutants are calculated through the emission factors, as reported in Table 13.

**Table 13: Emission due to utilities production** (US Environmental Protection Agency, 2016)

<table>
<thead>
<tr>
<th>Chemical</th>
<th>CCGT Emission factor [kg/MBtu]</th>
<th>Large wall-fired boiler Emission factor [kg/m³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{NO}_2 )</td>
<td>1.45E-01</td>
<td>3.04E-03</td>
</tr>
<tr>
<td>( \text{CO} )</td>
<td>3.72E-02</td>
<td>1.34E-03</td>
</tr>
<tr>
<td>( \text{CO}_2 )</td>
<td>4.99E+01</td>
<td>1.92</td>
</tr>
<tr>
<td>( \text{SO}_2 )</td>
<td>1.54E-03</td>
<td>9.60E-06</td>
</tr>
<tr>
<td>( \text{CH}_4 )</td>
<td>3.90E-03</td>
<td>3.68E-05</td>
</tr>
</tbody>
</table>
Eight impact categories are proposed to quantify the overall PEI of a specific chemical component (Heijungs et al., 1997). Four of them address global atmospheric concerns, namely the global warming potential (GWP), the ozone depletion potential (ODP), the acidification or acid-rain potential (AP), and the photochemical oxidation or smog formation potential (PCOP). The remaining four refer to local toxicological problems, i.e. the human toxicity potential by ingestion (HTPI), the human toxicity potential by inhalation or dermal exposure (HTPE), the aquatic toxicity potential (ATP) also named eutrophication potential, and the terrestrial toxicity potential (TTP).

![General scheme of PEI computation and impact categories](image)

The specific PEI of chemical \( k \) for category \( l \) \( \psi_{kl} \) quantifies the impact of the chemical on that specific category and must be normalized in order to allow their combination in the weighted sum. The general structure of \( \psi_{kl} \) is the following:

\[
\psi_{kl} = \frac{(Score)_{kl}}{<Score>_{kl}}
\]

Eq. (40)

Where \((Score)_{kl}\) represents the value of chemical \( k \) on some arbitrary scale for category \( l \) and \(<Score>_{kl}\) represents the average value of all chemicals in category \( l \) (Young et al., 2000). In this way, the score is normalized: a value of \( \psi_{kl} \) higher than 1 means that the chemical is more harmful than the average with respect to the specific category of impact. In other cases, this formula is inverted. For example, in case of HTPI, the score is LD50, i.e. the lethal dose for 50% of individuals (e.g., rats, mice, rabbits) subjected to that chemical by oral...
ingestion, expressed in mg/kg_{body} for rats, mice or rabbits. It is evident that the lower the value of the LD50, the higher the concern associated to that chemical. Therefore, the expression is reversed. By considering an average LD50 equal to 1, the expression of \( \psi_{k,HTPI} \) becomes the following:

\[
\psi_{k,HTPI} = \frac{1}{(LD50)_k}
\]

Eq. (41)

Table 14 gives an overview of the impact categories, their physical meaning, and the expressions to calculate their specific PEI.

The PEI balance equation shows three different terms: a term associated to PEI generation \( \dot{i}_{gen}^{tot} \), one associated to PEI output \( \dot{i}_{out}^{tot} \), and one to PEI input \( \dot{i}_{in}^{cp} \). Two different classes of environmental impact indexes can be defined: those associated with PEI output and those with PEI generation (Cabezas et al., 1999). In fact, it is possible to observe that the PEI input represents an environmental impact that enters the battery limits of the plant, and therefore does not actually affect the environment. From a formal point of view, it is possible to subtract it to the PEI generation term, thus obtaining an expression of the net generated PEI:

\[
\dot{i}_{gen}^{NET} = \dot{i}_{gen}^{tot} - \dot{i}_{in}^{cp}
\]

Eq. (42)

Replacing it in the PEI balance, the net generated PEI results to be equal to the total output PEI, which accounts for the products stream, the emissions, and the waste production occurring in the manufacturing and energy generation process:

\[
\dot{i}_{gen}^{NET} = \dot{i}_{out}^{cp} + \dot{i}_{out}^{ep}
\]

Eq. (43)

Since the products stream do not have a direct environmental impact (they are not dispersed in the environment, but stored and commercialized), their PEI is neglected.

Therefore, the computation of the overall output PEI is restricted to the non-product streams:
## Table 14: Impact categories for PEI evaluation, definitions and computation (Li et al., 2009)

<table>
<thead>
<tr>
<th>Category</th>
<th>Definition</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>GWP</strong></td>
<td>Potential contribution to global warming (in terms of infrared radiation absorption) from a given quantity of gas compared to the contribution from an equivalent quantity of CO₂</td>
<td>[ \psi_{k,GWP} = \frac{GWP_k}{GWP_{CO_2}} ]</td>
</tr>
<tr>
<td><strong>ODP</strong></td>
<td>Potential contribution to ozone depletion (in terms of rate of reaction) from a given quantity of gas compared to the contribution from an equivalent quantity of CFC-11 (CFC₃₁₁)</td>
<td>[ \psi_{k,ODP} = \frac{ODP_k}{ODP_{CFC-11}} ]</td>
</tr>
<tr>
<td><strong>AP</strong></td>
<td>Potential contribution to acid rain formation (in terms of release of H⁺ in the atmosphere) from a given quantity of gas compared to the contribution from an equivalent quantity of SO₂</td>
<td>[ \psi_{k,AP} = \frac{AP_k}{AP_{SO_2}} ]</td>
</tr>
<tr>
<td><strong>PCOP</strong></td>
<td>Potential contribution to smog formation (in terms of rate of reaction with hydroxyl radicals) from a given quantity of gas compared to the contribution from an equivalent quantity of ethylene (C₂H₄)</td>
<td>[ \psi_{k,PCOP} = \frac{PCOP_k}{PCOP_{C_2H_4}} ]</td>
</tr>
<tr>
<td><strong>HTPI</strong></td>
<td>Potential contribution to human health harm for ingestion in terms of rat-oral LD50 compared to an LD50 equal to 1 mg/kg rat.</td>
<td>[ \psi_{k,HTPI} = \frac{1}{LD50_k} ]</td>
</tr>
<tr>
<td><strong>HTPE</strong></td>
<td>Potential contribution to human health harm for inhalation or dermal contact in terms of TLV-TWA compared to a TLV-TWA equal to 1</td>
<td>[ \psi_{k,HTPE} = \frac{1}{TLV - TW A_k} ]</td>
</tr>
<tr>
<td><strong>ATP</strong></td>
<td>Potential contribution to aquatic ecosystem harm in terms of LC50 for Pimephales Promelas (common fish also named fathead minnow) compared to an LC50 equal to 1</td>
<td>[ \psi_{k,ATP} = \frac{1}{LC50_k} ]</td>
</tr>
<tr>
<td><strong>TTP</strong></td>
<td>Potential contribution to terrestrial ecosystem harm in terms of LD50 for Mus Musculus Lynnaeus (the common rat) compared to an LD50 equal to 1</td>
<td>[ \psi_{k,TTP} = \frac{1}{LD50_k} ]</td>
</tr>
</tbody>
</table>
\[ i_{out}^{tot} = \sum_{j=1}^{N_{sp}+N_{E}} \dot{M}_j^{out} \sum_{k=1}^{NC} x_{jk} \sum_{l=1}^{8} \alpha_l \psi_{kl} \]  
Eq. (44)

Where \( N_{sp} \) is the number of non-product streams. Finally, the fugitive emissions, accounting for the possible material releases during storage and transportation operations, are estimated as one thousandth of the streams entering and exiting the battery limits of the plant (Smith et al., 2004). The final expression of the overall output PEI is the following:

\[ i_{out}^{tot} = \sum_{j=1}^{N_{sp}+N_{E}} \dot{M}_j^{out} \sum_{k=1}^{NC} x_{jk} \sum_{l=1}^{8} \alpha_l \psi_{kl} + 0.001 * \left( \sum_{j=1}^{N_{in/out}+N_{E}} \dot{M}_j^{out} \sum_{k=1}^{NC} x_{jk} \sum_{l=1}^{8} \alpha_l \psi_{kl} \right) \]  
Eq. (45)

Where \( N_{in/out} \) is the number of streams entering and exiting the plant, considering both reactants and products streams. This last equation takes into account all the material streams related to emissions and waste generation.

### Environmental Optimization

The objective function to be optimized is the normalized overall output Potential Environmental Impact, i.e. the PEI for unit of mass of product. In the proposed case study, it is represented by the overall PEI per kilogram of cumene \( i_{out}^{tot} \).

\[ F_{cumene}^{out} = \frac{i_{out}^{tot}}{F_{cumene}^{out}} \]  
Eq. (46)

Where \( F_{cumene}^{out} \) is the cumene productivity in \( kg_{cumene}/h \).

Table 15 reports the \( \psi_{kl} \) values expressed in PEI/kg of all the chemicals involved in the cumene production and energy generation. The \( \psi_{kl} \) values are normalized within each impact category, in order to ensure that the values of different categories have, on average, comparable scores. The ODP category is omitted as none of the chemicals contributes to it.

Table 15 is graphically represented by the bar chart of Figure 36: each bar is composed of portions with different colors, representing the seven impact categories. It clearly shows that DIPB, the main by-product, is the most environmentally critical compound, as it is characterized by a relevant value (6.50) of ATP, i.e. aquatic toxicity potential or eutrophication potential. A relevant environmental impact is also related to the high value of...
PCOP, i.e. photochemical oxidation potential, of propylene and NO$_2$, equal to 3.83 and 1.57 respectively.

Table 15: Normalized impact scores of the chemicals involved in both cumene production and energy generation processes as provided by WAR algorithm add-in included in the COCO/COFE simulator (Barrett et al., 2011).

<table>
<thead>
<tr>
<th>Chemical</th>
<th>HTPI</th>
<th>HTPE</th>
<th>TTP</th>
<th>ATP</th>
<th>GWP</th>
<th>PCOP</th>
<th>AP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>1.38E-01</td>
<td>2.26E-01</td>
<td>1.38E-01</td>
<td>1.06E-01</td>
<td>-</td>
<td>2.29E-01</td>
<td>-</td>
</tr>
<tr>
<td>Propylene</td>
<td>-</td>
<td>8.42E-03</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>3.83</td>
<td>-</td>
</tr>
<tr>
<td>Propane</td>
<td>-</td>
<td>4.02E-03</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.51E-01</td>
<td>-</td>
</tr>
<tr>
<td>Cumene</td>
<td>1.57E-01</td>
<td>2.96E-02</td>
<td>1.57E-01</td>
<td>4.11E-02</td>
<td>-</td>
<td>8.11E-01</td>
<td>-</td>
</tr>
<tr>
<td>DIPB</td>
<td>1.34E-01</td>
<td>-</td>
<td>1.34E-01</td>
<td>6.50</td>
<td>-</td>
<td>1.13</td>
<td>-</td>
</tr>
<tr>
<td>NO$_2$</td>
<td>-</td>
<td>8.05E-01</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.57</td>
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<tr>
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<td>1.73E-01</td>
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<td>2.44E-04</td>
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<tr>
<td>CH$_4$</td>
<td>-</td>
<td>1.10E-02</td>
<td>-</td>
<td>-</td>
<td>5.61E-03</td>
<td>4.55E-01</td>
<td>-</td>
</tr>
</tbody>
</table>

Figure 36: Graphical representation of Table 15, showing the bar graph of specific PEI of the chemicals involved in both cumene production and energy generation processes.
Eutrophication consists in the enrichment of a water body with an excess amount of nutrients that induces growth of plants and algae and consequent oxygen depletion. Eutrophication has several impacts on the environment, such as the uncontrolled growth of toxic phytoplankton species and loss of biodiversity (Richardson and Jørgensen, 1996). For this reason, the production of DIPB as by-product of cumene represents a relevant ecological hazard. However, under normal operating conditions, DIPB is completely recycled inside the plant and consumed in the transalkylator. Therefore, transalkylation technology represents a valid solution not only from the economic but also from the environmental point of view, as it extinguishes the hazard related to DIPB formation.

After DIPB, propylene results to be the most environmentally-unfriendly chemical involved in cumene production. Its PEI is mostly due to the high value of photochemical oxidation potential (PCOP). Photochemical oxidation reactions are initiated by sunlight and occur with highly reactive chemicals such as NO$_x$ and VOC (volatile organic compounds): they entail the formation of radical oxidant species such as hydroxyl or singlet oxygen radicals, which in turn generate ozone, particulate matter and other pollutants (aldehydes, ketones) that constitute the so-called photochemical smog (Sillman, 2013). Smog is associated to severe health effects in particular for older people and children, more subjected to heart and lung problems. Propylene is shown to be a significant contributor to smog formation. In the cumene production process, propylene is employed as a reactant in the benzene alkylation and purged from the top of the first distillation column (C1) together with inert propane. The amount of purged propylene is considered as a waste, as it is not possible to separate it from propane and reuse it. Relevant losses of propylene from C1 occur when a significant amount of unreacted propylene leaves the reaction section, i.e. at low conversion conditions. On the contrary, at high conversion conditions, propylene – which is in defect with respect to benzene – is consumed almost completely and only few traces are measured in the C1 condenser. Figure 37 shows the trend of the normalized PEI of the process as a function of the two design variables. As expected, the environmental impact is minimized at high values of both reactor length and reactor inlet temperature, corresponding to high propylene conversion. The red dot points to the optimum, i.e. the minimum value of the objective function, corresponding to configuration #187 (350 °C and 12 m).
The objective function is reduced by one order of magnitude, from about 0.1 PEI/kg\textsubscript{cumene} for configuration #1 down to 0.01 PEI/kg\textsubscript{cumene} for configuration #187. A reference state can be found by considering a highly polluting process, such as VCM (vinyl chloride monomer) or acrylic acid production processes. The normalized PEI of VCM is about 0.3 PEI/kg\textsubscript{VCM} (Young and Cabezas, 1999), and about 0.4 PEI/kg\textsubscript{acrylic acid} (Young et al., 2000). Generally speaking, a normalized PEI higher than 0.15 should be considered critical.

Figure 38 shows the bar graph of the normalized PEI of each chemical involved in the cumene production and energy generation processes for three different process configurations. It is possible to observe that propylene represents the dominant species, in particular at low conversion (300 °C, 4 m), where a large amount of unconverted propylene escapes from C1 and is wasted.

As far as the liquid phase process is concerned, the trend of the normalized PEI of the process is shown in the 3D plot of Figure 39. The plot is cut in the low-conversion region to better visualize the transition from low to high environmental impacts. The maximum value of PEI reported in the graph is 0.15 PEI/kg\textsubscript{cumene}, but it grows up to 4 PEI/kg\textsubscript{cumene} for configuration #1 because of a very low value of conversion. The red dot shows the optimum
Environmental Sustainability point, corresponding to configuration #153 (190 °C, 12 m). Figure 40 shows that propylene and NO₂ are the main responsible of the environmental impact of the process.

Figure 38: Normalized PEI of each chemical, given by the product between the specific PEI and the flowrate for three different process configurations (vapor phase)

Figure 39: 3D plot of the Environmental Sustainability objective function (liquid phase)
Figure 40: Normalized PEI of each chemicals, given by the product between the specific PEI and the flowrate for three different process configurations (liquid-phase)

As a conclusion, it is possible to state that the WASTE Reduction algorithm allows identifying the most critical sources of environmental impact in terms of chemical species and unit operations. It provides to the designer an important tool for stating a priority of interventions for optimization or retrofitting purposes. In addition, it allows assessing environmental improvements on a quantitative basis, and selecting the most appropriate measures to enhance the environmental sustainability of the chemical process.
5. Social Sustainability

The concept of Social Sustainability

Social sustainability represents the least defined and least understood dimension of sustainability. A univocal definition of social sustainability is still lacking in the dedicated literature. It embraces several different topics such as social responsibility, equity, security, and quality of life. An attempt to collect these aspects in a simple definition was made by the United Nations Global Compact, a UN initiative to encourage worldwide businesses to adopt sustainable and socially responsible policies. According to UNGC, “Social Sustainability is about identifying and managing business impacts, both positive and negative, on people” (UN Global Compact, 2000). Given this concise assertion, it is evident that the quality of company relationships and engagement with its stakeholders is critical. Directly or indirectly, companies affect what happens to employees, workers in the value chain, customers, and local communities. The so-called “social license to operate”, i.e. the approval within the local community and – generally – a broad public acceptance, represents an intangible asset that is of vital importance for a company and depends significantly on its social sustainability efforts (Hall and Jeanneret, 2015). Equally, a lack of social concern can hinder business operations and growth. In addition, socially-committed policies may unlock new markets, help retain and attract business partners, or be the driving force for innovation of new products and services.

It is rather manifest that the promotion of social sustainability within an industrial activity is nowadays economically appealing. In the era of social media and in a strictly interconnected world, the echo of negative issues within a company can rapidly deteriorate its image and endanger its businesses. The Starbucks dossier shows the importance of social issues on company reputation and business. Starbucks is a US-based multinational company and coffeehouse chain. It is the world’s top coffee retailer with revenues averaging USD 19 billion and 238,000 employees in 2016. It is worth mentioning that coffee represents the most traded commodity after crude oil, with a market value of about USD 100 billion in 2013 (Business Insider, 2014). Coffee is traded more than natural gas, gold, corn, and wheat. In
2000 Starbucks faced the censure of Global Exchange, an international NGO, leader of the “corporate accountability” movement. Global Exchange criticized publicly the coffee giant for profiting at the farmer’s expenses instead of adopting fair trade coffee beans (Argenti, 2004). Fair Trade coffee is certified as having been produced to fair trade standards, i.e. based on better trading conditions for farmers, transparency, and respect. The business risk for Starbucks was twofold, both direct and indirect: the direct risks involved the protests of the activists at stores and their presence at shareholders meeting. The indirect risk was to lose its partners’ trust, thus compromising the integrity of the corporate supply chain. Starbucks decided to overcome that potential crisis by serving Fair Trade coffee in its stores. Eventually, this strategy was found to be not effective to meet coffee farmers’ interests, and Starbucks decided to focus on other initiatives to develop high-quality Fair Trade beans – in collaboration with Oxfam and the Ford Foundation – and arrange prices independently from market quotations. Such policy resulted successful on the long-term horizon, preserved the company brand, and fueled its core business at the international level.

The central role of social sustainability in the Supply Chain Management (SCM) clearly emerges from Starbucks case study. A socially-oriented SCM is the one that takes into account the issues which are relevant to the suppliers, workers, population, distributors, and customers of the company by means of a cradle-to-grave approach (Manca, 2015). It grants better working conditions and transparent information to the surrounding population about critical concerns such as safety exposure and hazards. A systematic methodology for assessing social sustainability in supply chains was proposed by Popovic et al. (2016), which considers 16 impact categories according to the different social mid-points of the supply chain, which are: 1) Employment benefits and characteristics; 2) Employment practices and relations; 3) Health and Safety (H&S) practices and incidents; 4) Training, education and personal skills; 5) Diversity and equal opportunities; 6) Employee welfare; 7) Innovation and competitiveness; 8) Human rights implementation and integration; 9) Basic human rights and practices; 10) Community funding and support; 11) Community involvement; 12) Corruption in business; 13) Fair business operations; 14) Stakeholder participation; 15) Consumer health and safety; 16) Product management and consumer satisfaction. Each of these categories belongs to one or more stages of the corporate supply chain. For example, the importance of human rights respect must be present at all levels of the chain, while
others are mostly referred to a specific stage: innovation is mainly related to the R&D phases and to the company’s commercial strategies, while corruption issues are associated to the corporate management and its relationships with the public authorities.

The present work focuses the attention only on the manufacturing stage, which is usually the most exposed to incidents and hazards, and not on the whole supply chain. At the manufacturing level, Health and Safety (H&S) aspects play a paramount role and are in most cases delineated and compelled by law constraints. In few words, an industrial activity cannot be socially sustainable without being safe for the workers and the surrounding population. Social sustainability criteria take into account the interests of employees and of the neighboring communities by addressing health and safety issues associated with the construction, operation, and decommissioning of the manufacturing plant (Azapagic et al., 2006). In addition, they also consider the potential nuisance that can be caused to the surrounding population through odor, noise, and visual impact (Azapagic and Perdan, 2000). For this purpose, the attention is focused on the battery limits of the manufacturing plant, thus adopting a gate-to-gate approach that starts from raw materials input and stops to final products output, and neglecting the rest of the supply chain. Various quantitative methods for their assessment have been developed and are mainly based on the evaluation of health hazard from raw materials used in the process or on the evaluation of a potential safety risk from fire, explosion, chemical release, and other undesired events. The assessment of social sustainability also allows identifying the ‘hot spots’ of the system, i.e. the operations which contribute most to the social impact and should be targeted for maximum improvements (Azapagic and Perdan, 2005). As far as the chemical industry is concerned, a promising approach for addressing health and safety issues in the preliminary design stage is that based on the concept of Inherent Safety, named as ‘Inherently Safer Design’ (ISD), that will be the object of the following section.

The concept of Inherent Safety

In the ‘70s of the last century, after the disasters of Flixborough (1974) and Seveso (1976), the concern about industrial safety in the chemical industry quickly increased and the need for a better way to deal with hazards and manage risks emerged. Since then, academia and
industry have increased their effort into the development of alternative synthesis route that are inherently safer and result in reduced health and safety hazards (Shah et al., 2003).

The idea of Inherent Safety was first suggested in the paper “What you Don’t Have Can’t Leak”, published on the review Chemistry & Industry in 1978 by Trevor Kletz, a prolific author on chemical engineering safety, who proposed that the chemical industry should re-direct its efforts towards the elimination of hazards – where possible – instead of devoting extensive resources in safety systems and procedures to manage risks (Kletz, 2013). The design philosophy inaugurated by Kletz was called “Inherently Safer Design” (ISD), and is nowadays of great interest for the design of sustainable chemical processes. In the last two decades, many researchers have devoted their studies to investigate and develop the concept of Inherent Safety in the chemical industry.

An inherently safer design is defined as the one that avoids hazards instead of controlling them, in particular by removing, reducing, or substituting the amount of hazardous material in the plant or the number of hazardous operations. It is based on a set of basic design principles, illustrated and discussed in several papers (Heikkilä, 1999; Kletz, 1999; Kletz, 2003). The most important ones are the following, considered as the fundamental design principles for achieving the state of Inherent Safety in chemical processes:

1. Intensification: the use of minimal amounts of hazardous materials in order to reduce the consequences of accidents arising from the release of materials; this implies the need for smaller inventories and plant scale-out (e.g. micro-reactors), as well as more efficient technology in terms of energy and material intensity (e.g. reactive distillation).

2. Substitution: the use of less hazardous materials (less flammable, toxic, volatile) instead of the standard ones.

3. Attenuation: the use of hazardous materials, when they cannot be substituted, under less hazardous conditions or, possibly, in the least hazardous form.

4. Limitation of effects: the change of the design or operating conditions to limit the consequences of failure rather than the use of protective equipment that may fail or be neglected.
5. Simplification: the elimination of unnecessary complexity, thus reducing the opportunities for error, information overload, redundancy, and failure.

In the early stage of process design these five principles help choosing the safest materials, process conditions, and process technology (Heikkilä, 1999). The remaining principles are meant to make the chemical plant more user-friendly – and therefore safer – and include the necessity of avoiding knock-on effects, making incorrect assembly impossible, tolerating errors and deviations and so on (Maher et al., 2012).

It is nowadays accepted that achieving a good level of inherent safety in the initial stages of chemical process design not only leads to safer and environmentally-friendly plants, but also results in reduced overall costs (Shah et al., 2003). The possibility for affecting the inherent safety of a process decreases as the design proceeds and more and more engineering and financial decisions are made (Heikkilä, 1999). It is much easier to affect the process configuration and inherent safety in the conceptual design phase than in the later phases of process design, as shown in Figure 41 (Kletz, 1991).

![Figure 41: Opportunities to implement inherent safety features in different process design stages (adapted from Kletz, 1999b)](image)

The big concern on Inherent Safety assessment in preliminary process design is the lack of information. During the conceptual design stage, a detailed scheme of the plant, including
the P&I diagram, is still not available. Therefore, it is important to exploit all the available details that may affect the inherent safety of the process: the chemical and physical properties of all the substances, the operating conditions, the equipment characteristics, and the interconnection between different pieces of plant equipment.

As previously mentioned, the conceptual design phase contains the most valuable opportunities for adopting inherently safer technologies, as the changes for safety will be most profitable and no expensive modifications are needed. These opportunities can be identified by performing an hazard identification study using the process flow diagrams (Suokas and Kakko, 1989). As shown in Figure 42, a Preliminary Hazard Analysis (PHA) can be carried out during the conceptual design phase.

![Risk analysis procedures applicability in different stages of chemical process life (adapted from Kletz, 1999b)](image)

A Preliminary Hazard Analysis allows the designer to detect the intrinsic hazards of the process and quantify, on the basis of the plant characteristics, the level of hazard of that process, usually referred as Hazard Potential (Koller et al., 2001). The Hazard Potential (HP) can be seen as a measure of the inherent safety of the process: the lower HP, the higher the level of Inherent Safety. The next section presents a review of different methodologies for
assessing HP of a chemical process and illustrates the Hazard Identification and Ranking (HIRA) methodology.

**Hazard Identification and Assessment**

Identification and assessment of hazards is an important task during the different design phases, and in particular for the conceptual design stage where the modifications are the most cost-effective. At the detailed design and procurement stages, the opportunity for implementing changes decreases significantly due to associated costs and other impediments (Maher et al., 2012).

A wide range of methods is proposed in the literature to identify and assess the HP of chemical processes at different levels of the design procedure. For the sake of clarity, few definitions are reported to delineate the object of the present analysis. A *hazard* is any agent that can cause harm or damage to life, health, property, or the environment. Hazards can be dormant or potential, with a certain probability of taking place. An *incident* is an event that is caused by the interaction with a hazard. A *risk* is a function of the likely severity of the incident associated with an hazard and of the probability of its occurrence (Sperber, 2001).

Identification of hazards represents the first step in performing a risk assessment. The *Hazard Potential* emerges from the quantitative assessment of the different hazards that characterize a chemical plant, and can be considered as a measure of the likely severity of a potential incident (e.g., a fire or a toxic release), and in some cases a measure of the associated risk. For the purpose of the present work, the Hazard Potential is simply a dimensionless indicator of the safety level of the plant. It should be considered as early as possible in the design procedure in order to avoid negative consequences as higher costs, longer development times, and higher risks. However, detailed procedures for hazard evaluation like the Hazard and Operability (HAZOP) Analysis, the Fault Tree Analysis (FTA), and the Failure Mode Effect Analysis (FMEA) are not applicable in the early stages of process design as they need a large amount of information about technical measures that are usually still not available (Koller et al., 2001). When dealing with the conceptual design stage, a number of simplified methods can be applied for hazard evaluation. Several index-based methods have been developed in order to capture some Inherent Safety aspects of the
Multi-objective optimization of sustainability criteria in the conceptual design of chemical plants

process: the most cited are the Inherent Safety Index (ISI) (Heikkilä, 1999), the Integrated Inherent Safety Index (I2SI) (Khan and Amyotte, 2004), the Inherent Safety Index Module (ISIM) (Leong and Shariff, 2008), the Environment, Health and Safety Index (EHS) (Koller et al., 2000), the Health Hazard Score (HHS) (Sheng and Hertwich, 1998). Other tools have been developed to assess the Hazard Potential of existing chemical plants and require a varying amount of information. They are usually employed for hazard investigation and safety optimization. Among them, there are the Dow Fire and Explosion Index (Dow F&EI) (Gupta et al., 2003), the Dow Chemical Exposure Index (Dow CEI) (Marshall and Mundt, 1995), the Hazard Identification and Ranking (HIRA) (Khan and Abbasi, 1998), the Risk Factor Model (RFM), and the Concept for Solvent Selection (Shering) (Koller et al., 2001).

These methodologies can be classified according to two criteria (Koller et al., 2001). The first criterion is related to the object of the methodology and discriminates between:

1. Substance-based methods, which are focused on the hazards that are intrinsically related to the substances employed in the process, without taking into account the hazards coming from the process itself and its operation. Among them, there are the RFM and the HHS methods, as well as the Schering methodology.

2. Process-based methods, which take into account also the hazards that arise from process operations and are influenced by the operating conditions. Among them, there are the Dow CEI, Dow F&EI, the HIRA methodology, the ISI, I2SI, ISIM, and EHS methods.

The second criterion is related to the final goal of the methodology and distinguishes between:

1. Ranking methods, which are employed to rank different process routes and the consequent selection of the best alternatives. Among them, there are the ISI, IS2I, ISIM, EHS, and Dow CEI methods.

2. Assessment methods, which evaluate the hazard of a substance or a process in a quantitative or semi-quantitative way. Among them, there are the Dow F&EI, the HIRA methodology, the RFM, and HHS methods.

The twofold classification is visualized in Figure 43:
5. Social Sustainability

Figure 43: Classification of the methodologies for inherent safety assessment

As it is classified as a process-based method and is formulated for the quantitative assessment of HP of a chemical plant, the HIRA methodology represents a suitable tool for the aim of the present work, i.e. the assessment of the Hazard Potential of the plant and therefore, indirectly, of the Inherent Safety and Social Sustainability of the chemical process.

The HIRA methodology

The HIRA methodology represents a systematic, comprehensive, and easy to implement system for hazard identification, ranking, and assessment. It was first reported in the paper “Multivariate Hazard Identification and Ranking System” (Khan and Abbasi, 1998) and later integrated by safety considerations (Khan et al., 2001), and inherent safety concerns (Khan and Amyotte, 2004). It leads to the computation of two indexes:

1. The Fire and Explosion Damage Index (FEDI)
2. The Toxicity Damage Index (TDI)

A brief description of the methodology is here reported. It can be easily visualized by considering Figure 44, which reports the general algorithm of HIRA. The first step consists in subdividing the plant into manageable units (1). Then, each unit is classified in one of the
five categories (2) according to the type of operation that is involved, as discussed later on. The type of hazard inherent to the specific unit is then identified (3), e.g., a fire and explosion hazard, a toxic hazard, or both. Databases are available online (PubChem, 2016; US National Library of Medicine, 2005) to assess the intrinsic hazards of the chemicals used in the process, in terms of their chemical-physical and toxicological properties under normal conditions. At this point, the damage potentials for Fire and Explosion hazard and/or for Toxic Release hazard can be calculated: for FEDI assessment, the first step involves the computation of the energy factors (4a) based on fluid-dynamic models; then, some penalties are calculated (5a) and incorporated with the energy factors to give the Damage Potential (6a). Finally, the Damage Potential is converted to the corresponding value of FEDI (7a). As concerns TDI, the procedure is quite similar and consists in the calculation of a core factor G (4b), followed by the estimation of specific penalties (5b); then, the Damage Potential is calculated (6b) and finally converted to the corresponding value of TDI (7b). The Hazard Potential of the single unit is calculated as the maximum between the FEDI and the TDI. On the basis of this value, a rank of hazard is assigned to each unit (8). Once all the units are ranked, the procedure stops. The overall Hazard Potential is calculated as the sum of all the HPs of the single units. The sequential and detailed procedures for calculating FEDI and TDI, the two contributes of the HP, are reported in the following sections.
Figure 44: HP computation flowchart
Computation of the Fire and Explosion Damage Index (FEDI)

For the purpose of computing the Fire and Explosion Damage Index (FEDI), the various units of the process are classified as follows:

1. Storage units;
2. Units involving physical operations such as heat transfer, phase change (e.g. flash, distillation columns), pumping, compression;
3. Units involving chemical reactions;
4. Transportation units;
5. Other hazardous units such as furnaces, boilers, flares, direct-fired heat exchangers.

The second step involves the evaluation of the energy factors $F_1$, $F_2$, $F_3$, $F_4$, based on the physical and chemical properties of the compounds under consideration, the physical state of the chemical, and the operating conditions. $F_1$ takes into account the chemical energy of the stream, and is a function of the combustion enthalpy of its various compounds: it is a measure of the energy that can be released by the combustion of a certain amount of a specific chemical. $F_2$ and $F_3$ account for the physical energy, and their expression is derived from the thermodynamic equations for isentropic expansion of pressurized gases and liquids, respectively. Eventually, $F_4$ is associated to the units involving chemical reactions, i.e. the chemical reactors, and takes into account the energy released due to the chemical reactions. The expressions of the four energy factors are reported below:

$$F_1 = 0.1 \cdot M \cdot \frac{\Delta H_{comb}}{K} \quad \text{Eq. (47)}$$

$$F_2 = 1.304 \cdot 10^{-3} \cdot P_p \cdot V \quad \text{Eq. (48)}$$

$$F_3 = \frac{1.0 \cdot 10^{-3}}{T + 273} \cdot (P_p - V_p)^2 \cdot V \quad \text{Eq. (49)}$$

$$F_4 = M \cdot \frac{\Delta H_{rxn}}{K} \quad \text{Eq. (50)}$$
Where:

- $M$ [kg/s], mass flow rate of chemical for continuous process; in case of batch process or storage units, $M$ is the mass hold-up in [kg]
- $\Delta H_{\text{comb}}$ [J/mol], heat of combustion of the chemical
- $K$ constant, equal to 3.148 [-]
- $P_p$ [kPa], processing pressure
- $V_p$ [kPa], vapour pressure of the chemical at standard conditions
- $V$ [$m^3/h$], volumetric flow rate of chemical for continuous processes; in the case of batch processes or storage units, $V$ is the volume of the unit in [$m^3$]
- $\Delta H_{\text{rxn}}$ [kJ/kg], heat of reaction

Once the energy factors are evaluated, some penalties are assigned to account for the impact of various parameters on the total damage potential. The impact of temperature is measured in terms of penalty $p_{n1}$ by considering the flash, fire, and auto-ignition points of the chemical, and the operating temperature of the unit. The impact of pressure is quantified in terms of the two energy factors $F_2$ and $F_3$, but also by one additional penalty $p_{n2}$, which is a function of the operating pressure, the vapor pressure and the atmospheric pressure. The other penalties take into account the capacity of the unit ($p_{n3}$), the characteristics of flammability and reactivity of the chemical ($p_{n4}$), the distance from the nearest hazardous unit ($p_{n5}$), the density of process units in the plant ($p_{n6}$). For units involving chemical reactions, two additional penalties are assigned, concerning the type of the reactions ($p_{n7}$) and the possibility of side reactions or runaway reactions ($p_{n8}$). Storage, transportation, and hazardous ancillary units are assessed with adequate and specific penalties which are not reported in the present work. For the sake of simplicity, the systematic procedure for only physical and chemical operations is here reported.

**Penalty 1, effect of the operating temperature**

The effect of the temperature is accounted by comparing the operating temperature with other parameters that involve flammability hazards, such as the flash point, fire point, and auto-ignition point (Figure 45). If flash or auto-ignition point of a chemical is unavailable, $p_{n1}$ assumes value 1.
Penalty 2, effect of the operating pressure

Penalty 2 is evaluated by following the procedure described in Figure 46, thus considering the operating pressure ($P_p$), the atmospheric pressure ($A_p$), and the vapor pressure ($V_p$) at standard conditions.

If the process works under vacuum conditions, $pn_2$ is assigned with a value ranging from 1.2 to 1.65 depending on the extent of vacuum (1 atm to 0.001 atm).
Penalty 3, quantity of chemical handled in the process unit (capacity)

Penalty 3 is evaluated by using Figure 47, as a function of the quantity of chemical and the NFPA ranking for flammability (NF) and reactivity (NR). Empirical equations obtained from the graph are reported in Appendix A.

The NFPA ranking for every chemical compound is available on the aforementioned database and on the usual MSDS (Material Safety Data Sheet) in the NFPA diamond of Figure 48 (National Fire Protection Association, 1968).
Penalty 4: flammability and reactivity characteristics of the chemical
Penalty 4 accounts for flammability and instability as intrinsic characteristics of each chemical species. It is calculated as:

\[ p_{n4} = 1 + 0.25 \times (N_F + N_R) \]

Where NF and NR are the NFPA ranks for flammability and reactivity.

Penalty 5: distance from the nearest hazardous unit
Penalty 5 accounts for the distance of the unit under consideration from the nearest hazardous unit, according to Figure 49. It is possible to observe that when this distance is very high (above 255 meters) the penalty assumes unitary value.

\[ p_{n5} = 1.955 \quad p_{n5} = 2.55/d^{0.165} \quad p_{n5} = 2.0867/d^{0.11} \quad p_{n5} = 1 \]

Penalty 6: density of process units
Penalty 6 accounts for the density of process units inside the plant:

\[ p_{n6} = 1 + \frac{\% \text{ space occupied by the unit in an area of 30 m radius}}{100} \]

Penalty 7: type of the chemical reactions
Penalty 7 accounts for the type of chemical reaction that takes place in the process unit (see Table 16). Sixteen typologies of chemical reactions are considered. In the case of the cumene production process, an alkylation reaction is taking place.

Penalty 8: possibility of side or runaway reactions
Penalty 8 accounts for the nature of the side reaction(s) and the possibility of runaway reaction(s) (e.g., autocatalytic side reactions), as reported in Table 17.
### Table 16: Penalty 7 values for different class of reactions

<table>
<thead>
<tr>
<th>Reaction Type</th>
<th>pn7</th>
<th>Reaction Type</th>
<th>pn7</th>
<th>Reaction Type</th>
<th>pn7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxidation</td>
<td>1.60</td>
<td>Reduction</td>
<td>1.10</td>
<td>Hydrogenation</td>
<td>1.35</td>
</tr>
<tr>
<td>Electrolysis</td>
<td>1.20</td>
<td>Aminolysis</td>
<td>1.40</td>
<td>Alkylation</td>
<td>1.25</td>
</tr>
<tr>
<td>Nitration</td>
<td>1.95</td>
<td>Halogenation</td>
<td>1.45</td>
<td>Polymerization</td>
<td>1.50</td>
</tr>
<tr>
<td>Esterification</td>
<td>1.25</td>
<td>Sulphonation</td>
<td>1.30</td>
<td>Pyrolysis</td>
<td>1.45</td>
</tr>
</tbody>
</table>

### Table 17: Penalty 8 values for side or runaway reactions

<table>
<thead>
<tr>
<th>Nature of the side reaction</th>
<th>pn8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Autocatalytic side reaction</td>
<td>1.65</td>
</tr>
<tr>
<td>Non-auto-catalytic side reaction, probable to occur at above normal reaction conditions</td>
<td>1.45</td>
</tr>
<tr>
<td>Non-auto-catalytic side reaction, probable to occur at below normal reaction conditions</td>
<td>1.20</td>
</tr>
</tbody>
</table>

Appendix A reports the detailed algorithms for computing penalties 1, 2, 3, and 5 for FEDI assessment.

The Damage Potential associated with fire and explosion hazards is then calculated as follows:

1. For process units involving physical operations:

\[
Damage\ Potential = (F1 * pn1 + F * pn2) * pn3 * pn4 * pn5 * pn6
\]  \hspace{1cm} \text{Eq. (53)}

2. For units involving chemical operations:

\[
Damage\ Pot. = (F1 * pn1 + F * pn2 + F4 * pn7 * pn8) * pn3 * pn4 * pn5 * pn6
\]  \hspace{1cm} \text{Eq. (54)}

Finally, FEDI is computed with the following equation:

\[
FEDI = 4.76 \times (Damage\ Potential)^{\frac{1}{3}}
\]  \hspace{1cm} \text{Eq. (55)}
Computation of the Toxic Damage Index (TDI)

Toxic Damage Index (TDI) represents the lethal toxic load over a certain area. It is measured in terms of radius of the area (in meters) which is affected by a 50% probability of fatality. Its computation is based on transport phenomena and empirical models based on the quantity of chemicals involved in the unit, their physical state, their toxicity, the operating conditions and the site characteristics (Khan and Abbasi, 1998). The dispersion is assumed to occur under “slightly stable atmospheric conditions”, a stability class that represents a median condition between high stability and high instability (Pasquill, 1961). The procedure to calculate TDI is similar to that of FEDI: the first step consists in the evaluation of a core factor G that accounts for the release rate and the release conditions. Then, few penalties are calculated to incorporate the effects of temperature (pn1), pressure (pn2), vapor density (pn3), toxicity (pn4), and site characteristics (pn5). The core factor G is calculated as:

\[
G = A \times m
\]  
Eq. (56)

Where \(A\) accounts for the release conditions, and \(m\) is the release rate in kg/s. Parameter \(A\) takes into account the different phenomena related to the release of a chemical, according to its physical conditions and toxicity NFPA ranking (NH). For instance, in case of release of super-heated liquid (liquid processed under pressure and above its normal boiling point), a fraction of the liquid flashes to vapors and a fraction forms a liquid pool that starts evaporating. On the other hand, liquefied gases would have two-phase releases with subsequent dispersion and build-up of toxic loads. For this reason, parameter \(A\) would assume a higher value in case of release of liquefied gases. The values of \(A\) are reported in the Table 18:

<table>
<thead>
<tr>
<th>NFPA ranking</th>
<th>Liquid</th>
<th>Liquefied gas</th>
<th>Gas</th>
<th>Solid</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>4.0</td>
<td>8.0</td>
<td>13.4</td>
<td>0.13</td>
</tr>
<tr>
<td>3</td>
<td>0.4</td>
<td>0.8</td>
<td>1.34</td>
<td>0.013</td>
</tr>
<tr>
<td>2</td>
<td>0.2</td>
<td>0.4</td>
<td>0.67</td>
<td>0.006</td>
</tr>
<tr>
<td>1</td>
<td>0.07</td>
<td>0.1</td>
<td>0.25</td>
<td>0.0025</td>
</tr>
</tbody>
</table>
**Penalty 1, effect of the operating temperature**

As for physical operation, penalty 1 accounts for the effect of temperature by comparing the operating temperature with other threshold values, in this case assumed equal to two times and four times the value at ambient temperature. If the chemical NH is at least 1, the value of the pn1 is provided by Figure 50. It is possible to observe that the minimum value of penalty 1 is 1.1, thus accounting for the toxicity of the chemical even at low temperature (NH>1).

![Figure 50: Penalty 1 assessment (TDI), adapted from Sharma et al., (2013)](image)

**Penalty 2, effect of the operating pressure**

Penalty 2 is assigned as a function of the operating pressure ($P_p$), the atmospheric pressure ($A_p$), and the vapor pressure ($V_p$) at standard conditions, according to Figure 51:

![Figure 51: Penalty 2 assessment (TDI), adapted from Sharma et al., (2013)](image)
Penalty 3: Vapor density
Vapors having density higher than air take more time to disperse and their plumes are closer to the ground. Therefore, these gases are responsible for build-up of toxic loads for longer time. Vapor density is evaluated at process conditions, while air density at ambient conditions. Penalty 3 is calculated as follows:

\[ p_{n3} = 1.2 \times \frac{\text{vapor density}}{\text{air density}} \quad \text{for vapor or gas release} \]  
\[ p_{n3} = 1 \quad \text{for liquid release} \]  

Eq. (57)

Eq. (58)

Penalty 4: Toxicity of chemical
Penalty 4 accounts for the intrinsic toxicity of the chemical, and is assessed by using the NFPA health factor NH.

\[ p_{n4} = \max(1, 0.6 \times NH) \]  

Eq. (59)

Penalty 5: Site characteristics
The effect of site characteristics takes into account the population density in the surrounding of the plant site. It is computed as follows:

\[ p_{n5} = \max(1, 0.1538 \times \text{population density}) \]  

Eq. (60)

Where population density is expressed in thousands of people per km\(^2\).

Appendix B reports the detailed algorithm for computing penalties 1 and 2 for TDI assessment.

Finally, TDI is calculated as follows:

\[ TDI = a \times (G \times p_{n1} \times p_{n2} \times p_{n3} \times p_{n4} \times p_{n5})^b \]  

Eq. (61)

Where \(a\) and \(b\) are constant and estimated by studying release and dispersion of a range of chemicals in different phases (super-heated liquids, liquefied gases, gases, etc.). The most appropriate values are estimated as \(a = 25.35\) and \(b = 0.425\) (Khan and Abbasi, 1998).
Hazard Ranking

Table 19 summarizes the hazard ranking according to FEDI and TDI values:

<table>
<thead>
<tr>
<th>FEDI</th>
<th>TDI</th>
<th>Ranking</th>
</tr>
</thead>
<tbody>
<tr>
<td>FEDI&gt;500</td>
<td>TDI&gt;700</td>
<td>Extremely hazardous</td>
</tr>
<tr>
<td>500&gt;FEDI&gt;400</td>
<td>700&gt;TDI&gt;500</td>
<td>Highly hazardous</td>
</tr>
<tr>
<td>400&gt;FEDI&gt;200</td>
<td>500&gt;TDI&gt;200</td>
<td>Hazardous</td>
</tr>
<tr>
<td>200&gt;FEDI&gt;100</td>
<td>200&gt;TDI&gt;50</td>
<td>Moderately hazardous</td>
</tr>
<tr>
<td>100&gt;FEDI&gt;20</td>
<td>50&gt;TDI&gt;5</td>
<td>Slightly hazardous</td>
</tr>
</tbody>
</table>

The Hazard Potential (HP) is finally calculated as the maximum between FEDI and TDI.

\[
\text{Hazard Potential} = \max(FEDI, TDI)
\] \hspace{1cm} Eq. (62)

Hazard Potential optimization

The Overall Hazard Potential is taken as objective function of the conceptual design optimization problem as far as the social sustainability is concerned.

\[
\text{Overall Hazard Potential} = \sum_{j=1}^{N \text{ units}} HP_j
\] \hspace{1cm} Eq. (63)

As concerns the vapor phase process for cumene production, Figure 52 reports the trend of the Overall Hazard Potential as a function of the two design variables. The red dot shows the optimum, i.e. the configuration that is characterized by the minimum value of HP. The optimal point corresponds to configuration #136 (335 °C, 4.5 m). It is possible to observe that the Overall HP increases by increasing the reactor length, as a consequence of the increased capacity. Similarly, a higher value of the reactor inlet temperature has a detrimental effect on the safety level of the plant, thus resulting in a higher value of the HP.
Figure 52: 3D plot of the Social Sustainability objective function (vapor phase)

The bar graph in Figure 53 shows that the reactor HP decreases significantly when passing from configuration #187 (red bar: 350 °C, 12 m) to configuration #1 (blue bar: 300 °C, 4 m), as both reactor length and inlet temperature assume lower values. Indeed, HP decreases from 600, corresponding to a hazard level labelled as extremely hazardous down to 430 (highly hazardous). It is worth observing that propylene, a highly flammable and reactive compound, plays a key role in the HP computation. Figure 53 illustrates how the more hazardous units, characterized by a value of HP higher than 200, are those in which a significant amount of propylene is circulating (Reactor, C1, E1, E3, FEHE, RebC1). For this reason, conversion extent has a relevant impact on the Overall HP of the process. The effect of conversion can be observed in the trend of the HP for distillation column C1, where an increased conversion results in a lower amount of propylene in the first column, with a consequent decrease of its HP. A similar trend can be observed for other units such as the feed-effluent heat exchanger (FEHE), the condenser of C1 and the heat exchanger E3. Consequently, the optimal configuration represents a trade-off solution among these conflicting phenomena, i.e. the detrimental effect of temperature/capacity and the positive
effect of conversion. Configuration #136 (335 °C, 4.5 m) is in fact characterized by a medium value of conversion.

Figure 53: Bar graph showing the Hazard Potential of each unit in the vapor phase process for 3 different configurations at low, medium and high conversions.

Figure 54 shows the trend of the Overall HP for the liquid phase process for cumene production. In the liquid phase process, the temperature range is shifted to lower temperatures (150-200 °C) and propylene is highly diluted in a large excess of benzene (Benzene/Propylene = 4:1). In addition, the reactor consists of a single tube filled with zeolites catalyst and is operated adiabatically. Given these operating conditions, the Overall HP of the process is less affected by temperature and/or capacity increases. On the other hand, it is strongly influenced by propylene conversion. At low values of conversion (i.e. low temperature and short reactor length) the HP reaches its maximum value. The optimal point, i.e. the minimum of the Overall HP, identified with the red dot, corresponds to the maximum value of conversion (configuration #187: 200 °C, 12 m).
Figure 54: 3D plot of the Social Sustainability objective function (liquid phase)

Figure 55 shows that the reactor is no more the most hazardous unit, whose HP is 250-300, in a range that is ranked as *hazardous*. On the contrary, the first distillation column is the actual *hot-spot* of the process, with HP ranging from 400 to 500. This is due to the increased dimension of C1 with respect to that employed in the vapor phase process, as a much higher flow rate is circulating through it. It is possible to see how the HP of C1 decreases from 500 (*extremely hazardous*) for a low-conversion configuration (identified by the blue bar) to 400 (*hazardous*) as the conversion is increased (green and red bar). The same trend can be observed for all the units where propylene is present in significant amounts, i.e. the reactor, C1, E3, FEHE, and C1 condenser. This effect is due to the build-up of propylene in downstream units (mainly column C1 and heat exchangers E3 and FEHE) in case of low propylene conversion.
Eventually, by comparing vapor phase and liquid phase process configurations, it is easy to observe that the vapor phase process is characterized by a lower average value of Overall HP, in the range of 3100-3200, against a window of 3100-3350 for the liquid phase process. On the other hand, the optimal points of the two configurations are comparable (around 3100). The actual difference between them consists in the distribution of the Overall HP among the various process units: in particular, the hot-spot is shown to be the reactor for the vapor phase process, while in the other case the first distillation column (C1) is the most critical unit. From this perspective, this type of hazard analysis allows the designer to identify the weakest link(s) of the chain, i.e. the units that need to be targeted for maximum improvement in the preliminary design stage, and/or state a proper priority of interventions in case of process retrofitting.
6. Multi-objective optimization

Definitions and problem statement

The search for the optimal solution of a problem is a common issue in every industrial sector. Actually, many real-life optimizations involve multiple conflicting criteria rather than a single one. This type of mathematical problems, involving more than one objective function, is called Multi-Objective Optimization (MOO), multi-criteria optimization, or multi-performance optimization, and is defined as the “process of optimizing systematically and simultaneously a collection of objective functions” (Marler and Arora, 2004). While in Single-Objective Optimization (SOO) the optimal solution is usually unique, this is no longer true in a MOO problem, which is characterized by a trade-off among conflicting objective functions. Hence, the term ‘optimize’ means finding the set of values of the objective functions which are all acceptable to the decision maker (Osyczka, 1978). Solving a MOO problem requires de facto some human decision-making, which can be supported by dedicated tools and strategies.

From a mathematical point of view, a generic MOO problem can be formulated as:

\[
\begin{align*}
\min_{\mathbf{x}} \mathbf{F}(\mathbf{x}) &= \{ f_1(\mathbf{x}), f_2(\mathbf{x}), \ldots, f_{NF}(\mathbf{x}) \} \\
h_j(\mathbf{x}) &= 0 \\
g_k(\mathbf{x}) &\leq 0
\end{align*}
\]

Eq. (64)

Where \( \mathbf{F}(\mathbf{x}) \) is the vector of objective functions, \( NF \) is the number of objective functions, \( \mathbf{x} \) is the vector of the decision variables, subject to the equality constraints \( h_j(\mathbf{x}) \) and inequality constraints \( g_k(\mathbf{x}) \).

The set of compromise solutions is characterized by a trade-off among different conflicting criteria, and is defined as the “Pareto optimal set”. This concept, introduced by the Italian economist Vilfredo Pareto (Pareto, 1897), defines as “Pareto optimal solutions” (also known as “dominant” or “non-dominated” solutions) those points within the decision space, whose corresponding objective functions cannot be all simultaneously improved (Chiandussi et al.,
From a mathematical point of view, Pareto Optimality or Dominance is defined as follows:

\[
\text{given } \Omega = \{x \in \mathbb{R}^n\} \text{ as the decision variable space}
\]

\[
x \in \Omega \text{ is Pareto Optimal w.r.t. } \Omega \text{ iff } \nexists x' \in \Omega \text{ s.t. } F(x') \text{ dominates } u = F(x)
\]

Where vector \( v \), containing the values of the objective functions corresponding to the set of decision variables \( x' \) is said to dominate the vector \( u = F(x) \), (denoted as \( v \preceq u \) in a minimization problem), i.e.:

\[
v \preceq u \text{ iff } v_i \leq u_i \forall i \in \{1, \ldots, k\} \land \exists i \in \{1, \ldots, k\} : v_i < u_i
\]

The set of decision variables that are Pareto Optimal or Dominant is called Pareto Optimal set \( \mathcal{P}^* \) and is defined as follows:

\[
\mathcal{P}^* = \{x \in \Omega | \nexists x' \in \Omega \text{ s.t. } F(x') \preceq F(x)\}
\]

When plotted in the objective function space, the dominant solutions vectors are known as Pareto Front \( \mathcal{PF} \), mathematically defined as follows:

\[
\mathcal{PF} = \{u = F(x) | x \in \mathcal{P}^*\}
\]

Many MOO solution techniques are available in the dedicated literature. Generally speaking, they are classified according to the way in which they handle the search and decision-making processes (Cohon and Marks, 1975):

1. “a priori” methods establish the decision criteria before the searching phase, and assume that a certain desired goal or hierarchy of importance of the objective functions can be stated a priori, i.e. previously;
2. “a posteriori” methods postpone the decision process after the searching phase, therefore no a priori information about any preference criteria needs to be provided;
3. “Progressive Preference” methods integrate the decision-making with the searching phase, usually based on a two-step procedure: first, a dominant solution is found, then the decision maker expresses its preference and/or modifies it progressively according to the results, then the procedure is repeated until the decision maker is satisfied or no further improvement is achievable.
A straightforward “a posteriori” method is the simple visualization of the Pareto Front, which is presented to the decision maker who analyzes it and identifies the preferred point(s). In case of a bi-objective optimization problem, the Pareto Front is a 2D curve, also called trade-off curve, which gives full information on objective values and trade-offs. It represents a powerful tool for the decision-making process: it informs on how improving one objective function leads to deteriorate the other one while moving along it. In case of MOO problems with three objective functions, the Pareto Front can be a surface or a bunch of points in the space, and usually it does not give a clear picture of the trade-off between the three criteria. In this case, it is typically easier to look for a possible solution by analyzing the three 2D Pareto Fronts obtained by each pairing.

Concerning “a priori” methods, an interesting technique for solving MOO problem is scalarization. This methodology aims at aggregating the objective functions into a single one by a suitable scalarization function. In this way, a MOO problem can be converted to a SOO problem. The choice of the scalarization function is the crucial point of this method. The simplest possibility is the linear combination (or weighted sum) of the objective functions, but more complex functions are provided in the literature (Miettinen and Mäkelä, 2002). The relative importance among the objective functions is set by selecting suitable weighted factors. In this case, the selection of weight values represents the core of the decision-making process. *Eq. (65)* shows the general formulation of the MOO linear scalarization, where \( G(x) \) is the new single objective function, \( NF \) is the number of objective functions of the MOO problem, \( w_i \) are the weights, and \( h_j \) and \( g_k \) the equality and inequality constraints of the problem.

\[
\begin{align*}
\min_x G(x) &= \sum_{i=1}^{NF} w_i f_i(x) \\
h_j(x) &= 0 \\
g_k(x) &\leq 0
\end{align*}
\]

*Eq. (65)*

The scalarization technique is employed in the present work in order to solve the optimization of sustainability for the cumene production process, which is the subject of the following section.
Multi-objective optimization of sustainability criteria in the conceptual design of chemical plants

Sustainability Optimization

Optimization is a key activity in every engineering sector, where the search of the best solution to a problem is of primary importance. Optimizing the nominal and operative conditions of a chemical plant is one of the main challenges that chemical engineers have to face to enhance efficiency, performance, and reduce costs of industrial processes. The advance of numerical calculus and the growing interest in improving existing chemical processes and developing new ones represent the main driving forces of Process Systems Engineering.

Sustainability-based optimization is intrinsically a MOO problem, as sustainability consists of three dimensions (aka pillars) that can conflict with each other. In the present work, a proper objective function has been presented for each pillar of sustainability: cumulated DEP4 for the economic, normalized PEI for the environmental, and overall HP for the social ones. Since the cumulated DEP4 accounts for the expected profits, it must be maximized. On the contrary, PEI and HP quantify the potential impact on environment and people, respectively; therefore, they must be minimized. The MOO problem is formulated as a minimization problem and consequently the sign of the economic objective function must be changed. The MOO problem is stated as follows:

$$\min_{T,L} F(T, L) = \{-\text{cumulated DEP4, PEI, HP}\}$$  \hspace{1cm} \text{Eq. (66)}

Where $T$ is the reactor inlet temperature and $L$ the reactor tube length. Material and energy balances represent the set of equality constraints of the minimization problem.

Pareto Fronts analysis: vapor phase process

A solution strategy is here proposed for the sustainability-based MOO of the cumene production process. The first step consists in analyzing the trade-offs between each couple of objective functions. By doing so, the original MOO problem is decomposed into three bi-objective optimization problems and the most relevant trade-offs are individuated. When two objective functions are considered, the problem can be dealt with by visualizing its Pareto Front, which provides full information about objectives trade-off. Starting from the whole set of possible combinations (named as Pareto Curve), the Pareto optimal solutions
can be found numerically by means of some specific algorithm. In the present work, the algorithm reported in Mishra and Harit (2010) has been employed. The Pareto Fronts for the cumene production process are here presented and discussed. For both vapor phase and liquid phase configurations, three different Pareto Fronts are reported, accounting each for a pairing of the three objective functions (i.e. DEP4/PEI, DEP4/HP, PEI/HP).

For the sake of clarity, the difference between the so-called Pareto Curve and the Pareto Front can be outlined by comparing Figure 56 and Figure 57. Figure 56 illustrates the Pareto Curve for the vapor phase process of the economic and environmental objective functions, i.e. cumulated DEP4 and PEI. The blue points represent the dominated solutions, while the red ones are the dominant or Pareto optimal solutions. It is possible to observe that there is no actual conflict between the economic and environmental criteria, as the PEI decreases for increasing DEP4. In fact, both PEI and DEP4 strictly depend on propylene conversion, which increases the productivity and decreases the emissions. The dominant solutions are concentrated in the bottom right corner of the graph, corresponding to high values of DEP4 and low values of PEI.

![Pareto Curve](image)

*Figure 56: Non-Pareto (blue dots) and Pareto optimal solutions (red dots) of the MOO problem involving economic and environmental criteria. Each solution corresponds to a process configuration.*

By zooming on the bottom right corner of Figure 57, the Pareto optimal solutions can be identified and analyzed. Figure 57 shows that only 4 out of 187 possible process
configurations are dominant and eligible as optimal solutions of the MOO problem. The Pareto Front identifies a trade-off between the objective functions. Even if in a small range, it is worth observing that an increase of the DEP4 corresponds to an increase of PEI, thus resulting in a trade-off situation between environmental and economic criteria.

![Pareto Front](image)

*Figure 57: Pareto Front of the bi-objective problem involving PEI and cumulated DEP4 for the vapor phase process. The red dots represent the Pareto optimal solutions.*

Table 20 reports all the data required to identify and characterize two Pareto optimal solutions, such as the configuration index, the values of reactor length and inlet temperature, and the values of the three objective functions.

*Table 20: Pareto Optimal configurations with respect to economic and environmental criteria for the vapor phase process, corresponding to the top right and bottom left corner points of Figure 57, respectively.*

<table>
<thead>
<tr>
<th># Configuration</th>
<th>Reactor Length [m]</th>
<th>Reactor Inlet Temperature [°C]</th>
<th>Cumulated DEP4 [MUSD]</th>
<th>Normalized PEI [PEI/kg-cumene]</th>
<th>HP</th>
</tr>
</thead>
<tbody>
<tr>
<td>#143</td>
<td>10</td>
<td>350</td>
<td>68.611</td>
<td>0.0133</td>
<td>3158</td>
</tr>
<tr>
<td>#187</td>
<td>12</td>
<td>350</td>
<td>68.203</td>
<td>0.0107</td>
<td>3169</td>
</tr>
</tbody>
</table>
Configuration #143 corresponds to maximum DEP4 solution, i.e. the best configuration from the economic point of view. On the other hand, configuration #187 corresponds to minimum PEI, and is the optimal trade-off solution on the environmental level.

The Pareto Front for the MOO problem involving economic and social criteria is shown in Figure 58. It highlights an evident trade-off between the economic and social objective functions, as an increase in DEP4 corresponds to an increase of the Hazard Potential of the process, thus resulting in a detrimental effect for process safety. This is because both DEP4 and HP, in the vapor phase process, are maximized at maximum conversion. Consequently, they conflict with each other. Among 187 process configurations, 25 have shown to be Pareto optimal.

As reported in Table 21, the DEP4 ranges from about USD 58 million up to USD 68 million, corresponding to value of HP equal to 3132 and 3158 respectively. Configuration #143 corresponds to the top left point of the graph, characterized by maximum DEP4. Configuration #19, on the contrary, minimizes the HP.

![Figure 58: Pareto Front of the bi-objective problem involving HP and cumulated DEP4 for the vapor phase process.](image)

As reported in Table 21, the DEP4 ranges from about USD 58 million up to USD 68 million, corresponding to value of HP equal to 3132 and 3158 respectively. Configuration #143 corresponds to the top left point of the graph, characterized by maximum DEP4. Configuration #19, on the contrary, minimizes the HP.
Table 21: Pareto Optimal configurations with respect to economic and social criteria for the vapor phase process, corresponding to the top right and bottom left corner points of Figure 58, respectively

<table>
<thead>
<tr>
<th># Configuration</th>
<th>Reactor Length [m]</th>
<th>Reactor Inlet Temperature [°C]</th>
<th>Cumulated DEP4 [MUSD]</th>
<th>Normalized PEI [PEI/kgcumene]</th>
<th>HP [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>#143</td>
<td>10</td>
<td>350</td>
<td>68.611</td>
<td>0.0133</td>
<td>3158</td>
</tr>
<tr>
<td>#19</td>
<td>4.5</td>
<td>335</td>
<td>58.762</td>
<td>0.0643</td>
<td>3132</td>
</tr>
</tbody>
</table>

Figure 59 illustrates the last Pareto Front for the vapor phase process, i.e. for the MOO problem involving environmental and social criteria. It clearly shows that the objective functions for environmental and social sustainability conflict with each other. Indeed, this aspect can sound paradoxical, as the common sense would suggest that an environmentally-friendly process should be also socially compatible and sustainable. Anyway, the sustainability study that was carried out in the previous chapters leads to the opposite conclusion. At high conversions, the PEI of the process decreases because of propylene consumption; on the other hand, the HP increases because of higher operating temperature and increased reactor capacity.

![Pareto Front](image)

*Figure 59: Pareto Front of the bi-objective problem involving HP and PEI for the vapor phase process.*
Among the 187 configurations, 31 result to be Pareto optimal. Table 22 reports the two dominant configurations that minimize PEI and HP respectively.

Table 22: Pareto Optimal configurations with respect to social and environmental criteria for the vapor phase process, corresponding to the top left and bottom right corner points of Figure 59, respectively

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Reactor Length [m]</th>
<th>Reactor Inlet Temperature [°C]</th>
<th>Cumulated DEP4 [MUSD]</th>
<th>Normalized PEI [PEI/kg\text{cumene}]</th>
<th>HP</th>
</tr>
</thead>
<tbody>
<tr>
<td>#187</td>
<td>12</td>
<td>350</td>
<td>68.203</td>
<td>0.0107</td>
<td>3169</td>
</tr>
<tr>
<td>#19</td>
<td>4.5</td>
<td>335</td>
<td>58.762</td>
<td>0.0643</td>
<td>3132</td>
</tr>
</tbody>
</table>

Pareto Fronts analysis: liquid phase process

As far as the liquid phase process is concerned, different trade-offs are outlined. Figure 60 shows the Pareto Curve for the MOO problem involving economic and environmental criteria. According to the Pareto Curve, the two objective functions do not conflict with each other. It is worth observing that few blue points – which correspond to dominated solutions – are characterized by negative DEP4. The Pareto optimal solutions, identified by the red dots, are concentrated in the bottom right corner of the graph.

![Pareto Curve](image.png)

*Figure 60: Pareto Curve of DEP4/PEI MOO problem. The blue and red dots represent the dominated and dominant solutions respectively. Each dot corresponds to a process configuration.*
By zooming on them, the Pareto Front can be visualized and is reported in Figure 61. The Pareto optimal solutions outline a trade-off condition between environmental and economic criteria. The range of DEP4 variation is quite large, and goes from about USD 53 million to USD 64 million. On the other hand, the PEI lays in a very narrow range, about 0.0025 PEI/kg$_{\text{cumene}}$. For this reason, it does not make sense to select a low PEI configuration (e.g., #185, as reported in Table 23), as the gain on the environmental level is negligible and not sufficient to justify such a relevant loss (about USD 11 million) from the economic point of view.

![Figure 61: Pareto Front of the MOO problem involving environmental and economic criteria for the liquid phase process.](image)

Table 23: Pareto Optimal configurations with respect to economic and environmental criteria for the liquid phase process, corresponding to the top right and bottom left corner points of Figure 61, respectively

<table>
<thead>
<tr>
<th># Configuration</th>
<th>Reactor Length [m]</th>
<th>Reactor Inlet Temperature [°C]</th>
<th>Cumulated DEP4 [MUSD]</th>
<th>Normalized PEI [PEI/kg$_{\text{cumene}}$]</th>
<th>HP</th>
</tr>
</thead>
<tbody>
<tr>
<td>#32</td>
<td>5</td>
<td>195</td>
<td>64.640</td>
<td>0.0254</td>
<td>3181</td>
</tr>
<tr>
<td>#185</td>
<td>12</td>
<td>190</td>
<td>53.271</td>
<td>0.0223</td>
<td>3128</td>
</tr>
</tbody>
</table>
The Pareto Front of Figure 62 shows the trade-off between the economic and social objective functions. The trend is in line with that observed for the vapor phase process, according to which an increase of conversion (and therefore of DEP4) has a detrimental effect on the safety level of the process. The ranges of variation of DEP4 and HP are both significant. DEP4 moves from USD 53 million for configuration #32 up to USD 64 million for configuration #187; similarly, HP goes from 3085 to 3181, as reported in Table 24. The value of PEI is quite constant and low, about 0.02 PEI/kg\text{cumene} for all the optimal solutions.

![Pareto Front](image)

*Figure 62: Pareto Front of the bi-objective problem involving HP and DEP4 for the liquid phase process.*

<table>
<thead>
<tr>
<th># Configuration</th>
<th>Reactor Length [m]</th>
<th>Reactor Inlet Temperature [°C]</th>
<th>Cumulated DEP4 [MUSD]</th>
<th>Normalized PEI [PEI/kg\text{cumene}]</th>
<th>HP</th>
</tr>
</thead>
<tbody>
<tr>
<td>#32</td>
<td>5</td>
<td>195</td>
<td>64.640</td>
<td>0.0254</td>
<td>3181</td>
</tr>
<tr>
<td>#187</td>
<td>12</td>
<td>200</td>
<td>53.358</td>
<td>0.0223</td>
<td>3085</td>
</tr>
</tbody>
</table>

*Table 24: Pareto Optimal configurations with respect to economic and social criteria for the liquid phase process, corresponding to the top right and bottom left corner points of Figure 62, respectively*

Figure 63 illustrates the Pareto Front for the social and environmental objective functions, and shows that only 5 configurations result to be Pareto optimal. It is easy to see that the
range of PEI variation is almost negligible. Consequently, the configuration that is eligible as optimal solution is the one characterized by the lowest value of HP, i.e. configuration #187 (Table 25).

![Pareto Front](image.png)

*Figure 63: Pareto Front of the bi-objective problem involving HP and PEI for the liquid phase process.*

<table>
<thead>
<tr>
<th>#</th>
<th>Configuration</th>
<th>Reactor Length [m]</th>
<th>Reactor Inlet Temperature [°C]</th>
<th>Cumulated DEP4 [MUSD]</th>
<th>Normalized PEI [PEI/kg&lt;sub&gt;cumene&lt;/sub&gt;]</th>
<th>HP</th>
</tr>
</thead>
<tbody>
<tr>
<td>#185</td>
<td>12</td>
<td>190</td>
<td>53.271</td>
<td>0.0223</td>
<td>3128</td>
<td></td>
</tr>
<tr>
<td>#187</td>
<td>12</td>
<td>200</td>
<td>53.358</td>
<td>0.0223</td>
<td>3085</td>
<td></td>
</tr>
</tbody>
</table>

**Table 25: Pareto Optimal configurations with respect to social and environmental criteria for the liquid phase process, corresponding to the top left and bottom right corner points of Figure 63, respectively**

**Scalarization method**

As already outlined, Pareto Fronts provide the final decision maker with some useful bits of information about the main trade-offs among the objective functions and identify a set of potential solutions of the overall MOO problem. However, when dealing with more than three objective functions, this approach can be confusing and sometimes misleading.
An interesting and rather simple technique that can be applied for solving the Sustainability MOO problem is scalarization. As explained in the previous section, scalarization consists in transforming a MOO problem into a SOO (Single-Objective Optimization) problem, by collecting all the conflicting criteria in a single objective function. In this work a general methodology for condensing the economic, environmental and social pillars of sustainability is proposed and discussed.

Scalarizing an objective function essentially means normalizing it in order to make it comparable with other scalarized objective functions. Different scalarization methods can be adopted and the choice is usually arbitrary. In the present case, i.e. the MOO of sustainability criteria, each objective function is normalized in order to assume a value of 1 for the “most sustainable” solution and of 0 for the unsustainable one(s). As far as the economic sustainability of the process is concerned, a value of 1 is assigned to maximum DEP4, and a value of 0 to DEP4 equal to zero. This index, ranging from 0 to 1, is christened Economic Sustainability Index (EcSI), and is expressed as:

$$EcSI_i = \begin{cases} \frac{DEP4_i}{\max(DEP4)} & \text{if } DEP4_i > 0 \\ 0 & \text{if } DEP4_i \leq 0 \end{cases}$$

Eq. (67)

Where $DEP4_i$ is the value of DEP4 for configuration $i$, and $i = 1, \ldots, NC$ with NC as the number of process configurations (equal to 187). EcSI assumes value 0 when the process becomes unsustainable, i.e. when the DEP4 is zero or negative. The same reasoning is followed for the expression of the Environmental Sustainability Index (EnSI), which assumes a value of 1 when PEI is minimum and value 0 when PEI is greater than 0.15 PEI/kg cumene. As stated in Chapter 4, this value can be considered as a threshold value above which the process becomes unsustainable from the environmental point of view. EnSI is formulated as:
As far as the social sustainability is concerned, no threshold values are provided for the overall Hazard Potential in order to discriminate between sustainable and unsustainable processes. A possible way to normalize HP is to assign 1 to the lowest value, and 0 to the highest value. The Social Sustainability Index (SoSI) of the process is expressed as:

\[
SoSI_i = \begin{cases} 
\frac{(\max(HP) - HP_i)}{\max(HP) - \min(HP)} & \text{if } HP_i \leq 0.15 \\
0 & \text{if } HP_i > 0.15 
\end{cases}
\]

Eq. (69)

Finally, the objective function of the scalarized MOO problem is simply the linear combination of the Economic, Environmental, and Social Sustainability Indexes. Each of them is properly weighted, according to the relative importance of the three pillars of Sustainability. Several decision-making techniques can be employed to establish a hierarchy of importance among different criteria (Triantaphyllou and Shu, 1998). In the present work, it simply consists in assigning a value to the weighting factor for each index, and the choice is left to the final user. The hierarchy of importance that is here proposed considers the economic aspect of sustainability as predominant, followed by environmental sustainability, and finally by social sustainability. Therefore, a value of 0.5 is assigned to the economic pillar, and values of 0.3 and 0.2 to the environmental and social ones, respectively. The scalarized objective function is named as Normalized Process Sustainability (NPS), and the scalarized MOO problem is stated as follows:

\[
\max_{T,L} \ NPS(T,L) = \{w_{Ec} \cdot EcSI + w_{En} \cdot EnSI + w_{So} \cdot SoSI\}
\]

Eq. (70)

Where \(T\) is the reactor inlet temperature and \(L\) the reactor tube length. \(w_{Ec}, w_{En},\) and \(w_{So}\) are the weighting factors for the economic, environmental, and social sustainability indexes, respectively. Material and energy balances represent the set of equality constraints of the optimization problem. In addition, the value of NPS is set to 0 whenever one of the three
indexes assumes value 0 or negative. This means that when a configuration is unsustainable for at least one of the three dimensions, it should be considered globally unsustainable. For example, if a process configuration results to be optimal from the environmental and social point of view but leads to negative value of DEP4 (i.e., it does not generate profit, thus being unsustainable from the economic point of view), its value of NPS is set to 0.

NPS optimization: vapor phase process

Figure 64 shows the trend of the Normalized Process Sustainability as a function of the two degrees of freedom for the vapor phase process. It is possible to observe that the maximum, identified by the red dot, lies in a medium-conversion region. As far as economic and environmental criteria are concerned, the Pareto optimal solutions lie in the high-conversion region, characterized by high values of both inlet temperature and reactor length. On the other hand, the social criteria, i.e. the Hazard Potential, is optimal at very low conversions. Therefore, the high-conversion solutions are penalized and the optimum moves towards the medium-conversion region. This optimal point represents a good trade-off among the three sustainability objective functions. The optimal solution corresponds to configuration #125 (315 °C, 9 m) (Table 26) with a value of NPS equal to 0.938.

![Normalized Process Sustainability](image)

*Figure 64: 3D plot of the Normalized Process Sustainability for the vapor phase process.*
The big advantage of the scalarization method is that identifies a single solution of the MOO problem. By optimizing a single objective function - which results from the weighted sum of the three sustainability indexes - this global approach allows individuating a univocal trade-off configuration. On the other hand, the previous method based on the pairing of the objective functions and the analysis of their 2D Pareto Fronts provides the decision maker with a range of possible optimal solutions, thus leaving space to subjective opinion and preference criteria in the selection of the MOO solution.

Table 26: Optimal “trade-off” configuration for the vapor phase process, individuated by MOO scalarization method

<table>
<thead>
<tr>
<th>#</th>
<th>Configuration</th>
<th>Reactor Length [m]</th>
<th>Reactor Inlet Temperature [°C]</th>
<th>Cumulated DEP4 [MUSD]</th>
<th>Normalized PEI [PEI/kg cumene]</th>
<th>HP</th>
</tr>
</thead>
<tbody>
<tr>
<td>#125</td>
<td></td>
<td>9</td>
<td>315</td>
<td>67.58</td>
<td>0.0188</td>
<td>3139</td>
</tr>
</tbody>
</table>

NPS optimization: liquid phase process

Figure 65 illustrates the trend of the NPS for the liquid phase process as a function of the two degrees of freedom. As already observed for the vapor phase process, the scalarization method identifies a trade-off solution among the three objective functions. As far as the environmental and social criteria are concerned, the optimal points lie in the neighborhood of configuration #187 (200 °C, 12 m), corresponding to maximum conversion. On the other hand, the economic optimum lies in a different point of the grid, corresponding to configuration #32 (195 °C, 5 m). Therefore, the optimum of the scalarized MOO problem, identified by the red dot, lies more or less halfway between these optimal solutions, and corresponds to configuration #99 (200 °C, 8 m) (Table 27), with a value of NPS equal to 0.944. At low temperature and short reactors, propylene conversion is very low, thus leading to negative values DEP4 and high values PEI. Process configurations that are characterized by negative DEP4 or PEI higher than 0.15 PEI/kg are considered unsustainable. Therefore, the corresponding values of NPS are set to 0. This explains the flat portion of Figure 65 in the low conversion region.
Figure 65: 3D plot of the Normalized Process Sustainability for the liquid phase process.

### Table 27: Optimal “trade-off” configuration for the liquid phase process, individuated by MOO scalarization method

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Reactor Length [m]</th>
<th>Reactor Inlet Temperature [°C]</th>
<th>Cumulated DEP4 [MUSD]</th>
<th>Normalized PEI [PEI/kg cumene]</th>
<th>HP</th>
</tr>
</thead>
<tbody>
<tr>
<td>#99</td>
<td>8</td>
<td>200</td>
<td>61.43</td>
<td>0.0228</td>
<td>3127</td>
</tr>
</tbody>
</table>

Once the solution of the scalarized MOO problem is found, it must be analyzed and the compatibility with each criteria should be checked. An analysis of the optimal solutions obtained for the vapor and liquid phase processes is reported in Table 28, and shows that DEP4 is kept high and close to the maximum in both cases, with value of the Economic Sustainability Index equal to 0.985 and 0.950 respectively. It is worth recalling that a value of 1 corresponds to maximum DEP4. Similarly, the normalized PEI is kept sufficiently lower than the threshold value of 0.15, and close to the minimum in both cases, with Environmental Sustainability Index equal to 0.942 for the vapor phase and 0.997 for the liquid phase. The HP for the vapor phase process is equal to 3139, a value that can be considered sufficiently low if compared to the minimum and maximum values of HP, which are about 3085 and
3200 respectively. In the same way, the HP for the liquid phase process, equal to 3127, is close to the minimum value of HP (3100) and significantly lower than the maximum (3350). The value of NPS is calculated as weighted sum of the three normalized indexes, and is shown to be quite high (above 0.9) in both cases.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Vapor phase</td>
<td>#125</td>
<td>0.985</td>
<td>67.58</td>
<td>0.942</td>
<td>0.0188</td>
<td>0.813</td>
<td>3139</td>
<td>0.938</td>
</tr>
<tr>
<td>Liquid phase</td>
<td>#99</td>
<td>0.950</td>
<td>61.43</td>
<td>0.997</td>
<td>0.0228</td>
<td>0.850</td>
<td>3127</td>
<td>0.944</td>
</tr>
</tbody>
</table>

It is worth underlying that these indexes are not fit for comparing and ranking different processes. This is due to the fact that they are normalized over the optimal value of their objective function. For example, by looking at the value of PEI and EnSI, it is easy to observe that the liquid phase configuration is characterized by a higher value of PEI with respect to the vapor phase configuration, and therefore should be less sustainable from the environmental point of view. However, because of normalization, its value of EnSI results to be higher with respect to the vapor phase process. Therefore, it is not possible to state that a process is more sustainable than another one on the basis of its value of NPS, as it is developed exclusively for optimization purposes. The ranking between different processes can be carried out by analyzing one by one the values of DEP4, PEI and HP.

It is possible to conclude that the scalarization method showed to be a reliable tool for approaching MOO problem and finding nice trade-off solutions. In addition, it represents a simple and user-friendly technique that can be easily applied to process optimization both at the industrial and academic-didactic levels.
7. Conclusions and future developments

This work presented a methodology to assess the sustainability in the conceptual design of chemical processes, both for optimization and retrofitting purposes. Indeed, a global concern about sustainability and sustainable development has emerged in the last decades. This interest in sustainability issues, born in the academic context, gradually spread across the industrial and financial worlds. Nowadays, almost every relevant company considers sustainability as a strategic target for its business. As the chemical industry showed to play a leading role in the global economic development, the need to make its manufacturing processes sustainable has become mandatory. Sustainability can be faced on three different levels: the economic, the environmental, and the social ones, which represent the so-called “three Pillars of Sustainability”. In this work, each of them has been defined, assessed, and employed as a criterion to carry out a Multi-Objective Optimization (MOO) of a chemical process. The cumene production process was adopted as a case study to show an application of such methodology. First, the cumene production process was simulated by means of a dedicated simulation software (Honeywell, 2016). Two design variables that play a relevant impact on the process performances were selected as degrees of freedom of the optimization problem, i.e. the reactor inlet temperature and reactor tube length. In addition, two different process configurations were considered, i.e. the vapor phase and the liquid phase, which can account as a third “Boolean” degree of freedom. The Grid-Search algorithm was selected as optimization strategy because of its exhaustiveness and robustness. Then, a proper objective function was formulated for each pillar of sustainability.

The Conceptual Design methodology was adopted to assess the economic sustainability of the process. It leads to the computation of the Economic Potential of 4th level (EP4), which accounts for both OPEX and CAPEX terms of a chemical plant. However, it considers constant OPEX terms over the time-horizon of the economic assessment. This means that prices/costs of commodities and utilities are assumed constant over long periods. Clearly, this represents...
a significant limitation, as the financial market is not stationary but highly fluctuating and uncertain. Indeed, the prices of raw materials, products, and utilities oscillate in time. To account for price volatility, an innovative approach to Conceptual Design, named Predictive Conceptual Design, has been adopted to devise a set of possible economic scenarios (i.e. possible future prices/costs of commodities and utilities) by means of specific econometric models. As far as the petrochemical industry is concerned, it is possible to identify a functional dependence of commodity and utility prices on the quotations of crude oil. Once identified the possible price trajectories of crude oil, it is possible to assess the corresponding price trajectories of raw materials, products, and utilities, and therefore of the OPEX of the plant. The Dynamic Economic Potential was taken as the objective function for the assessment of the economic sustainability of the process. Both CD and PCD were applied to the economic optimization of the cumene plant, and the advantages of PCD were analyzed and discussed. In particular, PCD showed a clear and univocal optimum and eliminated the non-consistent solutions that were found under the hypothesis of fixed prices.

The WAste Reduction algorithm was adopted to assess the environmental sustainability of the process. WAR allows estimating the Potential Environmental Impact (PEI) of a chemical process by analyzing the amount of waste and emissions generated by the plant. PEI is a conceptual quantity of the environmental impact that a chemical compound may have on the environment if released or emitted. It accounts for both the quantity of chemical generated or emitted and its specific environmental impact, which is a function of several ecological and toxicological concerns (e.g., global warming potential, eutrophication potential, human toxicity etc.). The overall PEI was normalized respect to the productivity of the plant. The normalized PEI was taken as the objective function for environmental sustainability. The environmental optimization highlighted the main compound in charge for the environmental hazard in terms of chemical species and unit operations and identified the operating conditions that lead to minimum PEI. For the cumene production process, propylene resulted the main cause of environmental impact, because of its significant emissions from the purge column and its high potential for smog formation. The lowest PEI was achieved for the highest conversion, as more propylene is consumed in the reaction section. WAR represents a useful tool for both optimization and retrofitting purposes.
7. Conclusions and future developments

The general concept of social sustainability was finally discussed and the main links with Supply Chain Management underlined. As far as the manufacturing process is concerned, social sustainability should be addressed in terms of the well-being of plant operators and the security of neighboring population, i.e. health and safety issues. The concept of Inherent Safety was introduced and a review of methods for identifying and assessing hazards in chemical plant was presented. The Hazard Identification and Ranking Analysis (HIRA) was then illustrated. The overall Hazard Potential of the plant was taken as the objective function for the plant Inherent Safety and Social Sustainability. For the vapor phase process, the Hazard Potential (HP) was dominated by the severity of the operating conditions. Therefore, the optimal solution lies at low temperature and low reactor capacity. On the other hand, the conversion for the liquid phase process showed to be the dominant parameter, as the main hazards are due to the presence of unconverted propylene, which is highly flammable and reactive, at the outlet of the reactor and in the first distillation column. The HIRA methodology allowed identifying the best operating conditions to ensure high safety levels, and identify the “hot spots” that need to be targeted for maximum improvements.

Finally, the MOO problem involving the three sustainability criteria was defined, discussed, and solved in two different ways. The first involved the visualization of the 2D Pareto Fronts for each pairing of the objective function (DEP4-PEI, DEP4-HP, PEI-HP). The Pareto Fronts allowed individuating the main trade-offs between sustainability criteria and the set of Pareto optimal points, which are eligible as the solution of the MOO problem. The second approach was the scalarization method, which allows passing from multi-objective to single-objective optimization. Each objective function was normalized in order to obtain an index ranging from 0 to 1. Then the objective function of the scalarized MOO problem was defined as the weighted sum of these three indexes, named as Normalized Process Sustainability (NPS). The values of the weighting factors were assigned to highlight a hierarchy among the three criteria. The result of the optimization represented a good trade-off solution for both the vapor and liquid phase processes.

Several future developments of the present work can be accomplished. First, it will be worth increasing the level of detail of the economic assessment, by adopting more reliable and accurate formulas for CAPEX estimation, and including financial aspects such as depreciation.
and cash-flow analysis. In addition, further studies can be carried out to improve the reliability and robustness of econometric models. Since natural gas is gaining ground not only as fuel for power and heat generation but also as feedstock for the organic synthesis, a deeper analysis can be dedicated to its dependence from the price of crude oil and to the formulation of an accurate econometric model. In many processes, it could be chosen as reference component.

As far as the environmental dimension of sustainability is concerned, a further development could be expanding the boundaries of the study to upstream and downstream processes, thus considering the life cycle of the product from the cradle of primary resources to the grave of final disposal. In addition, the speculation about social sustainability in the design of chemical processes is at an embryonal stage and a systematic procedure to evaluate it is still lacking. Further studies should be dedicated to further investigate inherent safety issues and their inclusion in a hierarchical procedure for the preliminary design stage.

Eventually, the proposed MOO of sustainability criteria should be applied to new processes involving a larger number of design variables, to make the optimization procedure more compliant with real plants. The comparison of different process technologies and alternative routes deserves a particular attention and may be of great interest for both design and retrofitting purposes. An example can be the analysis of the two different routes for maleic anhydride production, starting from either benzene or butane. The choice between these alternatives could be easily taken according to economic, environmental, and social criteria. Sustainability assessment can play the role of discerning methodology among different process alternatives and technologies, and ultimately, the driving force for the development of a new paradigm for advanced chemical industries.
Appendix A: FEDI penalty functions

Penalty 1, effect of the operating temperature

\[ pn_1 = f (\text{flash } T, \text{fire } T, \text{autoignition } T, \text{operating } T) \]

if (operating \( T < \) flash \( T \))

\[ pn_1 = 1.1 \]

else if (flash \( T < \) operating \( T < \) fire \( T \))

\[ pn_1 = 1.45 \]

else if (fire \( T < \) operating \( T < 0.75 \) autoignition \( T \))

\[ pn_1 = 1.75 \]

else

\[ pn_1 = 1.95 \]

Penalty 2, effect of the operating pressure

if \( (V_p > A_p \text{ and } P_p > V_p) \)

\[ pn_2 = f_{p1} (P_p, A_p, V_p) \]

\[ F = F_2 + F_3 \]

else

\[ pn_2 = f_{p2} (P_p, A_p, V_p) \]

\[ F = F_2 \]

if \( (A_p > V_p \text{ and } P_p > A_p) \)

\[ pn_2 = f_{p3} (P_p, A_p, V_p) \]

\[ F = F_3 \]
else

\[ pn2 = 1.1 \]

\[ F = F3 \]

Where:

\[ fp1 = 1 + \left( \frac{P_p - V_p}{P_p} \right) \times 0.6 \]

\[ fp2 = 1 + \left( \frac{P_p - V_p}{P_p} \right) \times 0.4 \]

\[ fp3 = 1 + \left( \frac{P_p - V_p}{P_p} \right) \times 0.2 \]

If the process works under vacuum conditions \( pn2 \) is assigned with a value ranging from 1.2 to 1.65 depending on the extent of vacuum (1 atm to 0.001 atm).

**Penalty 3, quantity of chemical handled in the unit (capacity).**

if \( \max(NF, NR) = 4 \)

\[ pn3 = 0.0102 \times \text{Capacity[ton]} + 0.9936 \]

else if \( \max(NF, NR) = 3 \)

\[ pn3 = 0.0076 \times \text{Capacity[ton]} + 0.9956 \]

else if \( \max(NF, NR) = 2 \)

\[ pn3 = 0.0051 \times \text{Capacity[ton]} + 0.9935 \]

else if \( \max(NF, NR) = 1 \)

\[ pn3 = 0.0026 \times \text{Capacity[ton]} + 0.992 \]

else

\[ pn3 = 1 \]
Penalty 5: distance from the nearest hazardous unit

if distance < 5 m

\[ pn5 = 1.955 \]

else if 5 m < distance < 75

\[ pn5 = \frac{2.55}{\text{distance}^{0.165}} \]

else if 75 m < distance < 255 m

\[ pn5 = \frac{2.0867}{\text{distance}^{0.11}} \]
Appendix B: TDI penalty functions

Penalty 1, effect of the operating temperature

if (chemical is toxic or corrosive: \(NH > 1\))

  if (operating \(T > 4 \times \text{Ambient} T\))
      \(pn1 = 1.55\)
  else if (operating \(T > 2 \times \text{Ambient} T\))
      \(pn1 = 1.35\)
  else
      \(pn1 = 1.1\)
else

  \(pn1 = 1\)

Penalty 2, effect of the operating pressure

if (\(V_p > A_p\))

  if (\(P_p > 3.0 \times A_p\))
      \(pn2 = 0.0009 + 0.4341 \times \log(P_p)\)
  else
      \(pn2 = 1.3\)
else if (\(P_p < V_p\) and \(P_p < 3.0 A_p\))

      \(pn2 = 2.9952 - 6.556 \times P_p + 65.238 \times P_p^2 - 111.11 \times P_p^3\)
  else

      \(pn2 = 1.2\)
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Nicola
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Federico