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**Conceptual Design of Chemical Plants  
by Multi-Objective Optimization of  
Economic and Environmental Criteria**

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*Not only strike while the iron is hot,  
but make it hot by striking.*

Oliver Cromwell  
English military and political leader



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# Abstract

This work presents a methodology that accounts for both environmental impact and price volatility to carry out improved feasibility studies of chemical plants. Recent global events brought to the realization that substantial changes in the design of products and processes are necessary for the sustainability of industrial systems. For instance, raw material and energy prices have been more volatile than ever in the last decade, and might face higher fluctuations in the future. Unfortunately, conventional feasibility studies assume that commodity and utility prices are constant throughout the operational life of the plant. This approach has huge limitations as financial markets are neither stationary nor systematic. For these reasons, this work proposes an innovative approach to conceptual design that considers the operative expenditures as a function of price fluctuations, and uses econometric models to devise a set of possible future scenarios of commodity and utility prices.

As far as the environmental performance of chemical processes is concerned, the Waste Reduction algorithm is a simple tool to be used by design engineers to determine the potential environmental impact (PEI) of a process. PEI is a relative measure of the potential for a chemical compound to have an effect on the environment, and is calculated by summing the PEI of individual chemicals over eight impact categories. Multi-objective optimization allows incorporating

the environmental concerns in the optimization of chemical processes, since it allows treating them as decision-making objectives. The applied case study, based on the cumene process, shows that economic and environmental objectives tend to be contradictory, thus tradeoffs are necessary to reach the preferred flowsheet configuration and its corresponding operating conditions. This work proves that whenever a modification is proposed to improve the environmental friendliness of a process, it is useful to question its economic viability under market uncertainty. Indeed, the cumene plant shows that the most environmentally friendly configurations are those most likely to be economically unfeasible under market uncertainty.

## **Keywords**

Conceptual design; chemical plant; sustainability; market uncertainty; price volatility; econometric model; waste reduction; environmental impact; multi-objective optimization; Pareto optimality; cumene process.

# Estratto

Il presente lavoro di tesi propone e descrive una procedura innovativa per la progettazione concettuale di impianti chimici sostenibili. Tale procedura si concentra sull'analisi della sostenibilità economica ed ambientale volta all'ottimizzazione di variabili progettuali ed operative. Al fine di prevedere la sostenibilità economica di impianto, viene illustrato un approccio sistematico allo studio delle incertezze di mercato. Questo approccio consiste nello sviluppo di opportuni modelli econometrici capaci di simulare l'andamento nel tempo dei prezzi e dei costi di materie prime, prodotti, coprodotti e utility. Così facendo, viene rimossa l'ipotesi di prezzi costanti per lunghi periodi di tempo, ammessa dagli studi di fattibilità convenzionali, e si elabora una stima probabilistica dei profitti attesi sulla base di un numero statisticamente significativo di possibili scenari economici futuri. Per quanto concerne l'analisi della sostenibilità ambientale, viene proposta l'implementazione del *Waste Reduction algorithm*, il cui scopo è determinare l'impatto ambientale potenziale (PEI) di un processo chimico e del relativo sistema di generazione di energia. Il PEI stima l'effetto che gli scarti di un impianto avrebbero se fossero rilasciati nell'ambiente e viene calcolato come somma dei PEI specifici di tutti i composti chimici di interesse, opportunamente pesati nei loro contributi alle diverse categorie di impatto ambientale. Il caso studio applicato, basato sul processo di sintesi del cumene, mette in evidenza le contrapposizioni tra gli

obiettivi economico ed ambientale, che conducono, anziché ad una singola configurazione ottimale di impianto, ad una serie di compromessi tra i rispettivi ottimi.

Questo elaborato dimostra che, ogni qualvolta ci si propone di apportare modifiche di impianto finalizzate al miglioramento della prestazione ambientale, è opportuno valutarne la fattibilità economica in condizioni di incertezza di mercato. Infatti, l'impianto del cumene mostra come le configurazioni più sostenibili dal punto di vista ambientale abbiano la maggiore probabilità di non esserlo dal punto di vista economico.

## **Parole chiave**

Progettazione concettuale; impianto chimico; incertezza di mercato; volatilità dei prezzi; modello econometrico; riduzione dei rifiuti; impatto ambientale; ottimizzazione multi-obiettivo; ottimo paretiano; processo del cumene.

# Acronyms

ADL	Autoregressive Distributed Lag
AP	Acidification Potential
AR	AutoRegressive
ATP	Aquatic Toxicity Potential
B	Benzene
BPA	BisPhenol A
C	Cumene
CAPE	Computer-Aided Process Engineering
CAPEX	CAPital EXpenditures
CCGT	Combined Cycle Gas Turbine
CEPCI	Chemical Engineering Plant Cost Index
CIS	Commonwealth of Independent States
CME	Chicago Mercantile Exchange

CO	Crude Oil
COCO	CAPE-Open to CAPE-Open
COFE	CAPE-Open Flowsheeting Environment
CPU	Central Processing Unit
DEP	Dynamic Economic Potential
DIPB	DiIsoPropylBenzene
DOE	Department Of Energy
EE	Electric Energy
EIA	Energy Information Administration
EPA	Environmental Protection Agency
EWO	Enterprise-Wide Optimization
GDP	Gross Domestic Product
GME	Gestore Mercati Energetici
GWP	Global Warming Potential
HDA	HydroDeAlkylation
HTPE	Human Toxicity Potential by Exposure
HTPI	Human Toxicity Potential by Ingestion
IARC	International Agency for Research on Cancer

IChemE	Institution of Chemical Engineers
ICIS	Independent Chemical Information Services
IHS	Information Handling Services
KA	Ketone-Acetone
LCA	Life Cycle Assessment
M&S	Marshall and Swift
MOO	Multi-Objective Optimization
NG	Natural Gas
O&G	Oil and Gas
ODP	Ozone Depletion Potential
OPEC	Organization of the Petroleum Exporting Countries
OPEX	Operative EXpenditures
OSHA	Occupational Safety and Health Administration
P	Propylene
PCD	Predictive Conceptual Design
PCOP	PhotoChemical Oxidation Potential
PEI	Potential Environmental Impact
PEL	Permissible Exposure Limit

PF	Phenol-Formaldehyde
PSE	Process Systems Engineering
R&D	Research and Development
S	Steam
SCM	Supply Chain Management
SPA	Solid Phosphoric Acid
TTP	Terrestrial Toxicity Potential
UN	United Nations
UOP	Universal Oil Products
USA	United States of America
USD	United States Dollar
VAPCCI	Vatavuk Air Pollution Control Cost Indexes
WAR	Waste Reduction
WCED	World Commission on Environment and Development
WTI	West Texas Intermediate

# 1 Introduction

The chemical manufacturing industry is a multinational, varied scale sector that makes plenty of products available to promote social development and economic growth (Hall and Howe, 2010). Chemical industry is one of the four major energy-intensive industries, which also include iron and steel, cement, and pulp and paper (Schönsleben *et al.*, 2010). Recent global events brought to the realization that substantial changes in the design and operation of products and processes are necessary for the sustainability of industrial systems. For instance, the imperative of reducing carbon intensity represents a major engineering challenge (Clift, 2006). Indeed, Grossmann (2004) reports that the level of carbon dioxide (CO<sub>2</sub>) in the atmosphere has increased by a third since the beginning of the industrial age, and that it contributes more than 70% to global warming. In addition, raw material and energy pricing has been more volatile than ever in the last decade, and forced the chemical industry to discover energy efficient technologies to reduce energy intensity and manufacturing costs. For these reasons, process synthesis and planning play an important role in assessing and improving industrial sustainability. For instance, Marechal *et al.* (2005) include life cycle analysis, optimization, and other computer-aided systems among the recommended

research and development (R&D) priorities. In this respect, there has been a renewed interest in Process Systems Engineering (PSE), which has traditionally been concerned with the discovery, design, manufacture, and distribution of chemical products in the context of many conflicting goals (Grossmann and Westerberg, 2000). Given the complex, multiscale, and multidisciplinary nature of sustainability, PSE calls for expanding the scope of analysis beyond cost and performance issues to include environmental integrity and socio-economic wellbeing (Bakshi and Fiksel, 2003). Several frameworks of indicators have been developed to help classify the interacting elements of sustainability, and assist in setting strategies and monitoring progress towards sustainability goals (Batterham, 2006). In order to understand how to integrate these frameworks into process synthesis and planning, it is of primary importance to shed light on the meaning of sustainability for the chemical industry.

## 1.1 Definition of sustainability

The idea of sustainability took root in the international scientific community after the publication of the book *Our Common Future* by the World Commission on Environment and Development (WCED) in 1987. WCED focused on the issues of environmental degradation and social inequity that result from the wasteful consumption of natural resources, and recognized that sustainable development “*meets the needs of the present without compromising the ability of future generations to meet their own needs*”. WCED paved the way for many UN-sponsored events and initiatives, such as the Rio Summit in 1992, and the Kyoto Protocol in 1997, which set a number of targets to be met in the following years.

The definition of sustainable development provided by WCED (1987) left space for various interpretations. To understand the implications of sustainability

for chemical engineering, Sikdar (2003) identified four types of sustainable systems:

- I. systems referred to global concerns or problems, such as global warming and ozone depletion;
- II. systems characterized by geographical boundaries (*e.g.*, cities, villages, defined ecosystems);
- III. businesses, either localized or distributed, which strive to be sustainable by practicing cleaner technologies, eliminating waste products, reducing the emissions of greenhouse gases, and reducing the energy intensity of processes;
- IV. any particular technology that is designed to provide economic value through clean chemistries.

The sequence of sustainable systems proposed by Sikdar (2003) is hierarchical, and reduces the region of influence by moving from the first to the last item. Systems III and IV are more suitable for chemical engineers, because their performance depends on process and product design, and manufacturing methods.

For any of the abovementioned systems, sustainability can be illustrated as three intersecting circles: each circle represents one of the three pillars of sustainability, *i.e.* economy, environment, and society (Figure 1). Consequently, a certain engineering solution must agree with social requirements, and has to be economically feasible and environmentally friendly (García-Serna *et al.*, 2007). In particular, a sustainable product or process can be defined as *“the one that constraints 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”* (Bakshi and Fiksel, 2003).

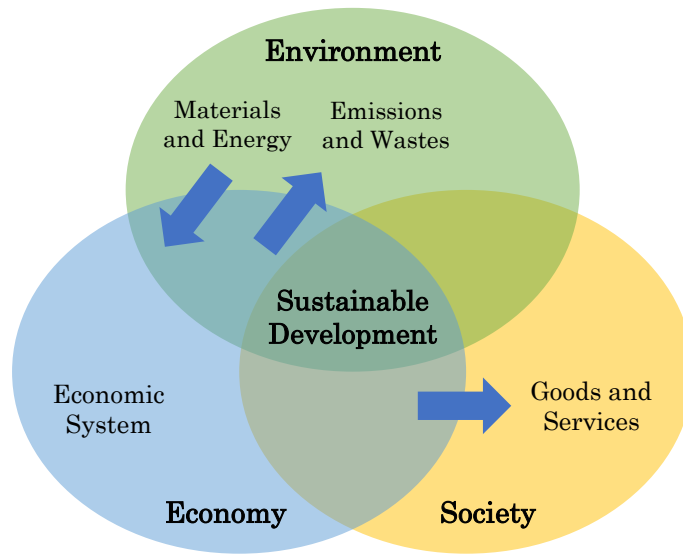


Figure 1: A model of sustainable development (adapted from Azapagic and Perdan, 2000).

The step that follows the definition of sustainability is the identification of proper indicators that can be used to measure the sustainability performance of products and processes.

## 1.2 Sustainability indicators

For the sake of clarity, an indicator is *“a parameter, or a value derived from parameters, which points to, provides information about, or describes the state of a phenomenon”* (Sala *et al.*, 2012). The parameter can be quantitative, semi-quantitative, or qualitative, and derived from a model, often through software, applications, and databases. Several indicators have been proposed in the literature to assist in measuring sustainability. For instance, Saisana and Tarantola (2012) listed twenty-four indicators in the economic, environmental, social, and R&D areas that can be applied to an entire country. However, these indicators do not offer precise information relevant to chemical engineering problems. In this respect, a significant effort was made by Azapagic and Perdan (2000), who developed a framework of sustainability indicators for industry: they provided thirty-one indicators categorized over the three pillars

of sustainability (Table 1). In relation to the type and purpose of the analysis, three types of assessment are distinguished: product-, process-, and company-oriented.

Table 1: Sustainability indicators for industry proposed by Azapagic and Perdan (2000).

Environmental indicators	Economic indicators	Social indicators
<ul style="list-style-type: none"> <li>• Environmental impacts               <ul style="list-style-type: none"> <li>- Resource use</li> <li>- Global warming</li> <li>- Ozone depletion</li> <li>- Acidification</li> <li>- Eutrophication</li> <li>- Photochemical smog</li> <li>- Human toxicity</li> <li>- Ecotoxicity</li> <li>- Solid waste</li> </ul> </li> <li>• Environmental efficiency               <ul style="list-style-type: none"> <li>- Material and energy intensity</li> <li>- Material recyclability</li> <li>- Product durability</li> <li>- Service intensity</li> </ul> </li> <li>• Voluntary actions               <ul style="list-style-type: none"> <li>- Environmental management systems</li> <li>- Environmental improvements above the compliance levels</li> <li>- Assessment of suppliers</li> </ul> </li> </ul>	<ul style="list-style-type: none"> <li>• Financial indicators               <ul style="list-style-type: none"> <li>- Value added</li> <li>- Contribution to GDP</li> <li>- Expenditure on environmental protection</li> <li>- Environmental liabilities</li> <li>- Ethical investments</li> </ul> </li> <li>• Human-capital indicators               <ul style="list-style-type: none"> <li>- Employment contribution</li> <li>- Staff turnover</li> <li>- Expenditure on health and safety</li> <li>- Investment on staff development</li> </ul> </li> </ul>	<ul style="list-style-type: none"> <li>• Ethics indicators               <ul style="list-style-type: none"> <li>- Preservation of cultural values</li> <li>- International standards of conduct</li> <li>- Intergenerational equity</li> </ul> </li> <li>• Welfare indicators               <ul style="list-style-type: none"> <li>- Income distribution</li> <li>- Work satisfaction</li> <li>- Satisfaction of social needs</li> </ul> </li> </ul>

Another contribution was made by IChemE (2002), which presented the indicators in the three domains of economy, environment, and society. As economic indicators, IChemE specified a number of value-added quantities and the R&D costs. At the environmental level, IChemE classified energy, material, water, and land uses. Eventually, the proposed social indicators were

based on employee benefits, safety, and how workers are treated by the company.

As reported above, it is common to categorize sustainability indicators over the three pillars of economy, environment, and society. However, Sikdar (2003) suggested a new approach to the classification of sustainability indicators, and developed a hierarchical system based on three groups:

1. 1-D indicators (economic, ecological, and sociological);
2. 2-D indicators (socio-economic, eco-efficiency, and socio-ecological);
3. 3-D indicators (sustainability indicators).

According to this framework, every indicator should be analyzed in depth to find its possible membership to more than one pillar of sustainability. In particular, 3-D indicators can be obtained from the intersection of all the three attributes (that is why they can be called true sustainability indicators). For instance, Sikdar (2003) classified energy, material use, and pollutant dispersion as 3-D indicators, as they can have direct environmental impact, economic cost, and effect on the health of people.

The frameworks reported above provide useful indicators that can be applied at different process or business scales. In fact, sustainability assessments can embrace a process plant, a group of plants, part of a supply chain, or a whole supply chain depending on the purpose. Besides, it is possible to perform sustainability assessments based on mono-, bi-, and three-directional searches as a function of the number of dimensions taken into account. Indeed, the three pillars of sustainability allow moving on a single axis (1-D) at a time, onto a plane (2-D), or inside the whole region (3-D) contained by those attributes (Manca, 2015).

Several approaches to sustainability can be differentiated based on both the width of the assessment horizon and the number of objectives that are taken into account. For instance, Life Cycle Assessment (LCA) is supposed to

evaluate the environmental performance of a product system from the *cradle* of primary resources to the *grave* of recycle or safe disposal (Azapagic, 1999; Clift, 2006). The main drawback of LCA is the large amount of information required over the entire life cycle, and the lack of public data due to legal or intellectual property concerns (Jiménez-González *et al.*, 2000; Tugnoli *et al.*, 2011). In this respect, some authors prefer to adopt the so-called *cradle-to-gate* approach that covers the production stages that go only from manufacturing to the factory gate, *i.e.* before products are delivered to the customer (Guillén-Gosálbez *et al.*, 2008; Othman *et al.*, 2010; Ouattara *et al.*, 2012; Ruiz-Mercado *et al.*, 2012; Yue and You, 2013). This spatially reduced approach is more suitable to design problems, which are often under-defined due to either lack of data or insufficient time and resources (Dimian *et al.*, 2014). The focal point of a design problem is the conceptual phase (Figure 2), whose goal is to find the best process flowsheet (*i.e.* to select the process units and the interconnections among these units) and estimate the optimal design conditions (Douglas, 1988).

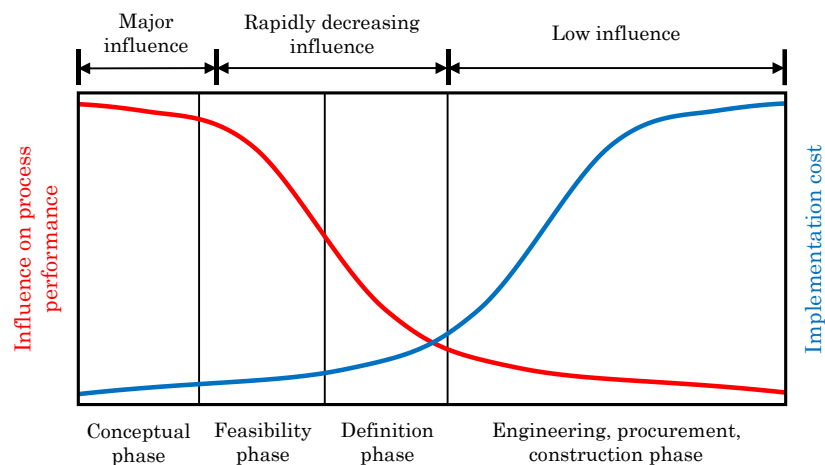


Figure 2: The early stages of process design are the most effective to make decisions having the minimum implementation cost and the highest potential to influence the behavior of the process during its operation (adapted from Ruiz-Mercado *et al.*, 2011).

Putting the concept of sustainability into operation requires practical ways to assess performance and measure progress. Sustainability indicators should be easy to calculate, useful for decision-making, and scientifically rigorous (Schwarz *et al.*, 2002). Unfortunately, some indicators are just qualitative or semi-quantitative, and have little significance at the process design level. For instance, the social attribute of sustainability is the most difficult to quantify and the most lacking in an underlying theoretical framework (Ruiz-Mercado *et al.*, 2011). The growing importance of corporate ethics and accountability has made some companies deeply committed to their social responsibilities (Manca, 2015), but the linkages between PSE and social performance remain elusive (Bakshi and Fiksel, 2003). In fact, economic and environmental aspects can be assessed by quantitative indicators relevant to the design and operational level, while the social aspects require the analysis of the complex interactions among the stakeholders, *i.e.* local community, suppliers, business partners, customers, investors, employees, and managers (Simões *et al.*, 2014). For these reasons, PSE applications to sustainability problems have so far focused on economic and environmental aspects, with social criteria being considered only very recently (Azapagic *et al.*, 2016).

These considerations pave the way to the presentation of the scope and structure of this work.

### **1.3 Scope and structure of the work**

As mentioned above, the inclusion of sustainability issues in PSE applications can be made at different decision-making levels. Figure 3 illustrates the taxonomy of hierarchical levels considered in PSE applications together with their spatial and temporal scale. The bottom of the pyramid corresponds to the optimization of single equipment units, production lines, and entire chemical plants, whereas the top corresponds to multi-site problems, *i.e.* supply chain

management (SCM) and enterprise-wide optimization (EWO). As far as single-site problems are concerned, the area of process synthesis is particularly relevant to sustainability, as it allows to include environmental issues at the early stages of process design. For the sake of clarity, process synthesis (Douglas, 1985) can be referred to as conceptual design (Douglas, 1988).

Accounting for environmental issues at the early stages of design problems increases the complexity of the design task, which is further complicated by several sources of uncertainty (Grossmann and Guillén-Gosálbez, 2009). For instance, raw material and energy prices have been more volatile than ever in the last decade, and might face higher fluctuations in the future (Harjunkoski *et al.*, 2014). Unfortunately, conventional feasibility studies base the forecast for incomes and outcomes on the discounted-back approach. This means that prices/costs of commodities and utilities are assumed constant for long periods with the reference point being usually the date when the economic assessment is performed.

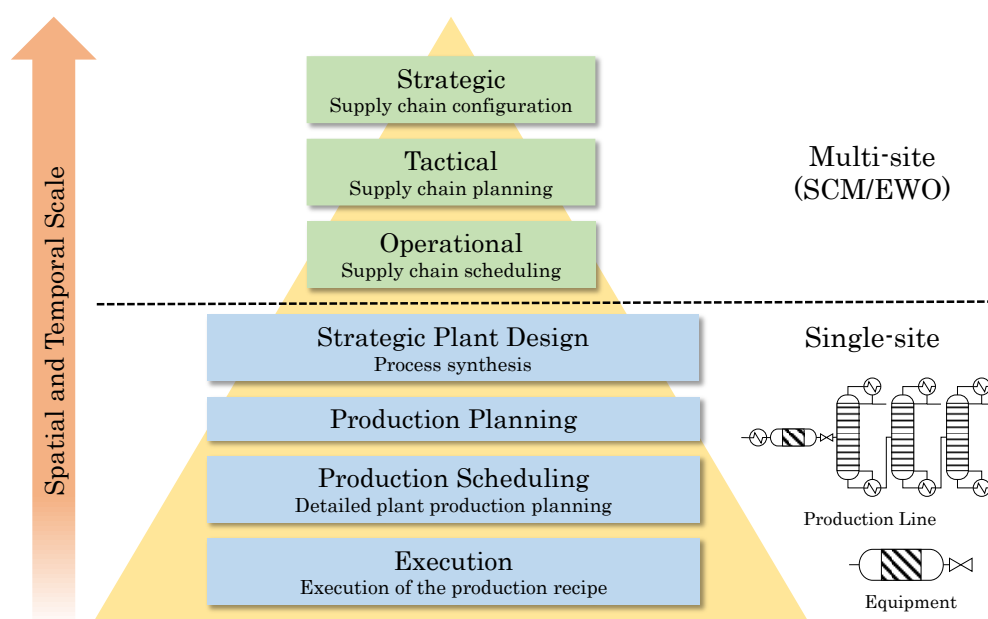


Figure 3: Decision-making levels in PSE (adapted from Grossmann and Guillén-Gosálbez, 2009). The bottom of the pyramid corresponds to activities where the temporal and spatial scales are of small/medium size, whereas the top corresponds to multi-site problems involving a wider temporal and spatial scope.

Clearly, this approach has significant limitations as it neither accounts for prices/costs volatility nor contemplates features such as market oscillations and fluctuations (Manca, 2012).

In light of the above, this work presents a methodology that accounts for both the environmental impact and price/cost volatility to carry out improved feasibility studies of chemical plants (Figure 4). The work is organized as follows. Chapter 2 illustrates the role played by market uncertainty on the optimal design of chemical plants, and shows how the conventional approach to conceptual design, which is based on the hypothesis of fixed prices/costs of commodities and utilities, is intrinsically unreliable. Chapter 3 introduces the applied case study, based on the cumene manufacturing process, and identifies the possibilities for improving the performance of the plant under market volatility. Chapter 4 proposes and discusses a dynamic approach to the economic assessment of chemical plants that is primarily based on econometric models and dynamic trajectories of prices/costs. Chapter 5 evaluates the environmental friendliness of the cumene plant, including the predominant emissions from the energy generation process. Chapter 6 shows how multi-objective optimization (MOO) is well suited to incorporate environmental concerns in the optimization of chemical processes, and uses the models derived in Chapters 4 and 5 to identify a set of optimal plant configurations, *i.e.* the best tradeoffs between economic and environmental performance. Finally, some conclusions about this work are drawn in Chapter 7.

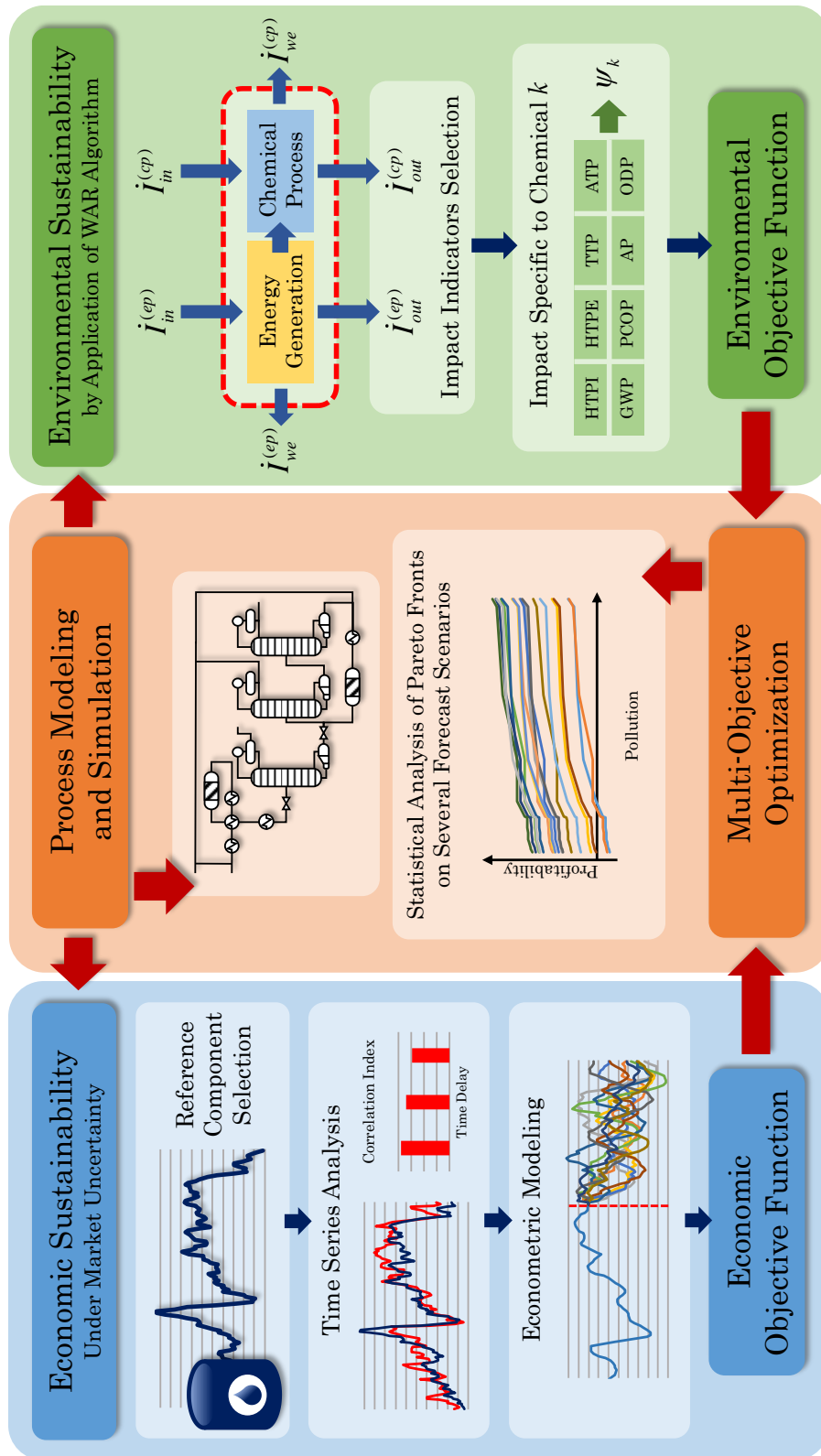


Figure 4: Scope and structure of the work.



# 2 Conceptual design of chemical plants

Conceptual design designates that part of a design project dealing with the basic elements defining a process: flowsheet, material and energy balances, equipment specifications, utility consumption, and economic profitability (Dimian *et al.*, 2014). As already mentioned, conceptual design is particularly relevant to sustainability, as it allows making decisions that feature the minimum implementation cost and the highest potential to influence the behavior of the process during its operation (Ruiz-Mercado *et al.*, 2011). Douglas (1988) developed a systematic procedure that decomposes the design problem into a hierarchy of decision-levels, as follows:

1. Batch versus continuous;
2. Input-output structure of the flowsheet;
3. Recycle structure of the flowsheet;
4. General structure of the separation system;
5. Heat exchanger network.

The decisions are sequential, and quantify at higher detail the features of the flowsheet. The result is not a unique solution but a collection of alternative flowsheets from which an assessment procedure removes the less attractive ones. The evaluation of alternatives relies on the computation of an economic potential that accounts for the positive contribution from selling the products, and the negative terms of capital (CAPEX) and operative expenditures (OPEX). For the sake of exactness, Level-1 decision, which selects between batch and continuous processes, is qualitative, and does not entail any economic potential. Conversely, Level-2 decision is based on an economic balance between the revenues achieved by selling the products and/or using the byproducts, and the expenditures from buying the raw materials. The definition of Level-2 economic potential is almost trivial:

$$EP2 = (Products\ Price + Byproducts\ Value) - (Raw\ Materials\ Cost) \quad (1)$$

It is pretty evident that  $EP2$  must be plentifully positive to make the plant economically attractive, and continue with its design. Level-3 to Level-5 economic potentials call for a more in-depth analysis of the CAPEX and OPEX terms:

$$EP3 = EP2 - Reactors\ and\ Compressors\ Costs\ (CAPEX + OPEX) \quad (2)$$

$$EP4 = EP3 - Separation\ Costs\ (CAPEX + OPEX) \quad (3)$$

$$EP5 = EP4 \pm Heat\ Exchangers\ Costs\ (CAPEX + OPEX) \quad (4)$$

The necessary condition to move from Level-3 up to Level-5 is that the previous economic potential is positive. The CAPEX term for each process unit can be estimated using cost correlations corrected with appropriate cost indexes (*e.g.*, M&S, Nelson-Farrar, CEPCI, VAPCCD). For instance, Guthrie's formulas estimate the purchase and installation costs of process units by considering their characteristic dimension(s), building material(s), and operating pressure.

The OPEX terms, *i.e.* the ongoing costs for running the plant, depend on the prices/costs of raw materials, (by)products, and utilities. Douglas (1988) assumes that those prices/costs are constant throughout the operational life of the plant (*i.e.* several years and even decades). This hypothesis is not representative of reality, since the prices/costs of raw materials, final products, and utilities may vary significantly according to demand and offer fluctuations, and market uncertainty.

## 2.1 Fluctuations and uncertainty

Douglas (1988) used as a case study the hydrodealkylation (HDA) process that converts toluene into benzene, and provided for both components some fixed cost and price. However, Figure 5 shows the continuously crossing trends of benzene price and toluene cost over a long-term horizon.

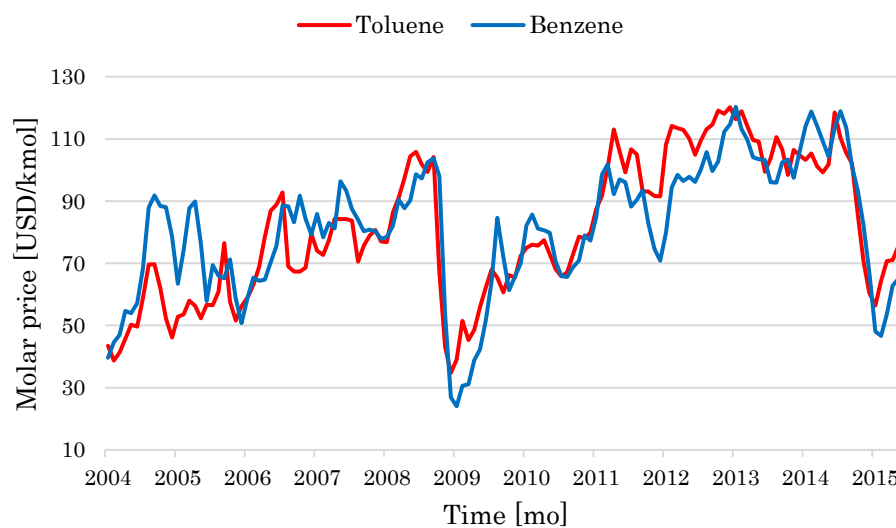


Figure 5: Monthly quotations of toluene and benzene in the 2004-2015 period.

Table 2 shows some interesting results. Over the 2005-2010 period, the averaged quotations of toluene and benzene make the *EP2* marginally

negative. Conversely, by using the spot monthly prices of toluene and benzene (for instance March and December 2008) the  $EP2$  assumes respectively quite positive and quite negative values.

Table 2: Benzene and toluene prices and corresponding  $EP2$  values for the HDA plant based on the productivity data of Douglas (1988). Adapted from Manca (2015).

Time	Benzene price [USD/kmol]	Toluene price [USD/kmol]	$EP2$ [ $10^6$ USD/y]
2005-2010 period	70.16	72.19	-2.0318
March 2008	107.79	84.18	51.122
December 2008	19.41	41.17	-40.589

It is straightforward deducing that the  $EP2$ , which sets a necessary condition for the plant feasibility, changes sign repeatedly, and oscillates between positive and negative values as soon as the benzene price is respectively higher or lower than the toluene cost.

This point is unacceptable as it would subvert any deduction based on Douglas' methodology. In fact, Douglas (1988) does not find an optimal solution capable of satisfying price fluctuations and market uncertainty. On the contrary, a number of distinct solutions result from the continuously changing quotations of commodities and utilities.

To prove this point, Barzaghi *et al.* (2016) performed the optimization of a styrene monomer plant according to Douglas' methodology for the whole set of prices shown in Figure 6(a). The optimal plant layout maximizes the objective function represented by the sum of the  $EP4$  throughout the operational life of the plant measured by  $nMonths$  sampling times:

$$Cumulated\ EP4 = \sum_{t=1}^{nMonths} EP4_t = nMonths \cdot EP4 \quad (5)$$

With  $EP4$  in USD/mo,  $nMonths$  in mo, and  $Cumulated EP4$  in USD. According to the hypothesis of fixed prices, the  $EP4_t$  terms are constant and the summation in Equation (5) becomes a straightforward multiplication. Based on the ten-year quotations of Figure 6(a) and monthly sampling of prices/costs, the life span of the plant is 120 mo. Figure 6(b) shows that the hypothesis of fixed prices determines different optimal solutions as a function of the set of quotations. This would lead to forecast a completely wrong economic potential respect to the real one attained at the end of the life span of the plant.

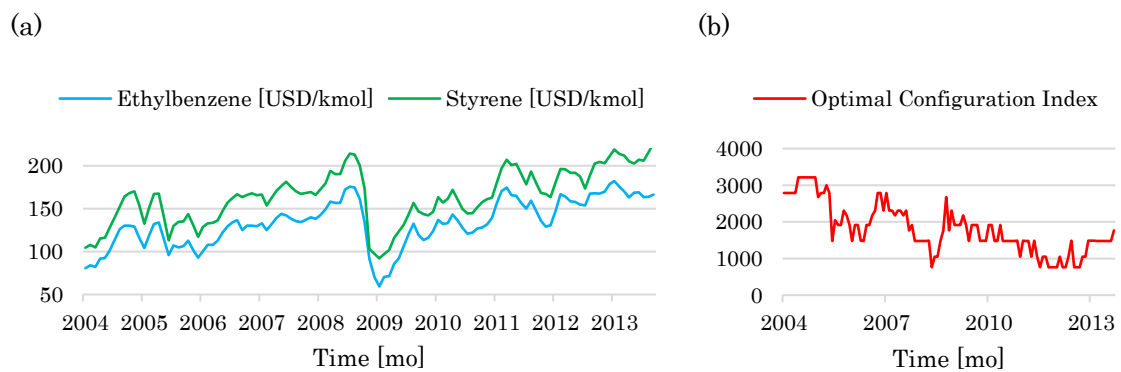


Figure 6: Monthly quotations of styrene (*i.e.* product) and ethylbenzene (*i.e.* raw material) over the 2004-2013 period (a), and effect of price fluctuations on the optimal configuration index (b). Such an index is an integer number that univocally identifies the optimal plant layout among 3872 different layout alternatives (Barzaghi *et al.*, 2016).

In addition, Barzaghi *et al.* (2016) identified a functional dependence of commodity and utility prices from the quotations of crude oil, which is the precursor of each commodity and utility involved in the styrene process. By analyzing the profile of  $Cumulated EP4$  as a function of crude oil quotations, it is possible to determine the existence of a crude oil quotation threshold beyond which the plant is not profitable. This point is remarkable, as in the past decade crude oil quotations have experienced important oscillations with alternating bullish and bearing trends (Figure 7).

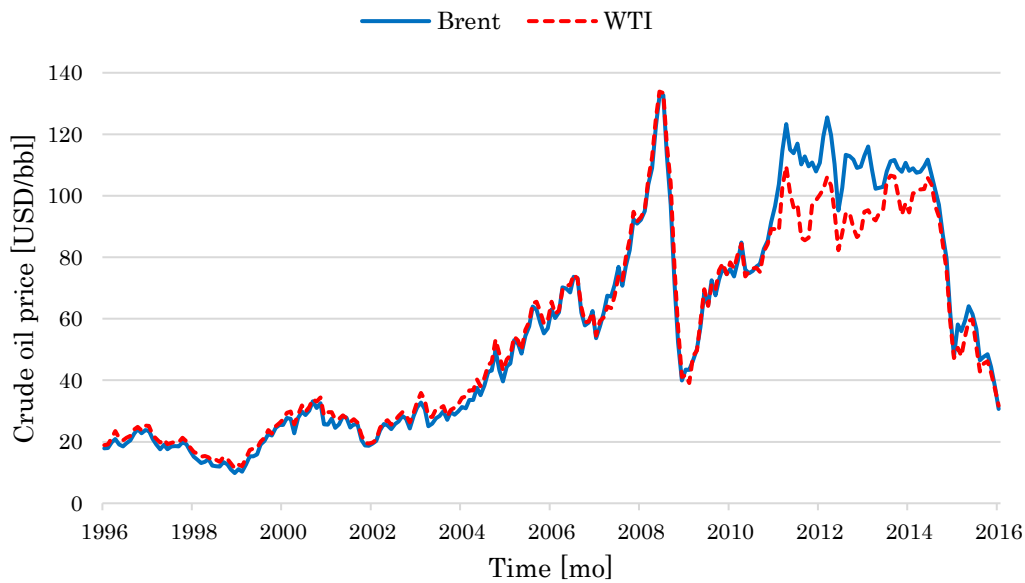


Figure 7: Brent and WTI monthly quotations from January, 1996 to January, 2016.

In fact, a number of political, economic, and financial events have happened worldwide with significant consequences on crude oil markets. The first noteworthy event of recent crude oil quotation history is the financial crisis of 2008. Indeed, Figure 7 shows the tremendous financial and economic calamity that was triggered by the US subprime mortgage crisis in the second semester of 2008. After having trespassed the 145 USD/bbl value in July 2008, WTI crude oil price crashed to 36 USD/bbl in December 2008, and eventually bounced back to 76 USD/bbl in November 2009.

Brent and WTI quotations were tightly intertwined until 2011, after which they lost their mutual consistency (Figure 7). For the sake of clarity, Brent and WTI are the most important crude oil benchmarks, whose quotations specialize in European and American markets respectively (Liu *et al.*, 2015). The divergence between Brent and WTI quotations involved a number of distinct but correlated reasons (Manca and Depetri, 2016). In particular, the sudden abundance of American and Canadian shale oil produced a substantial discount of WTI respect to Brent quotations (Liu *et al.*, 2015). In fact, the

significant increase of crude oil quotations at the beginning of 21<sup>st</sup> century stimulated the interest in shale oil exploitation, which was even more supported by the introduction of new extraction technologies. Indeed, the opportunity of reducing the political and strategic dependence on OPEC (*i.e.* Organization of the Petroleum Exporting Countries) pushed the USA to test and implement new extraction methods, such as advanced hydraulic fracturing, and horizontal drilling. By doing so, the extraction of shale oil in the USA increased from 5.1 Mbb/d in 2008 to 9.6 Mbb/d in 2015 (EIA, 2016). In response, the Middle East producers decided not to cut their quotas at the end of 2014 to maintain their production competitive, and the highest authorities of Saudi Arabia declared acceptable that crude oil prices remained low for long periods if that could reduce the investments in shale oil. As a result, the second semester of 2014 saw a sharp drop of WTI price from 103.59 USD/bbl to 59.29 USD/bbl, and in the first quarter of 2015 the price plummeted from 73.2 to 48.5 USD/bbl (Figure 7). The anthropic events that further upset the crude oil markets are extensively discussed in Manca and Depetri (2016).

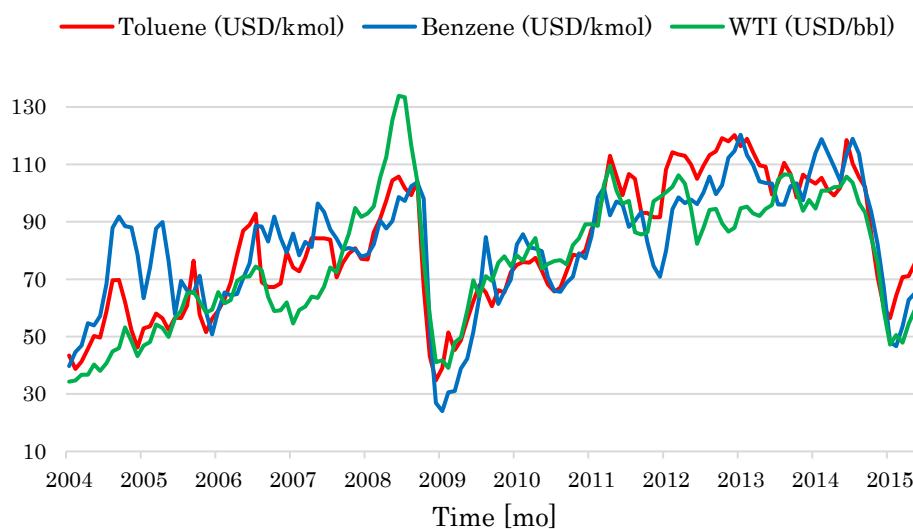


Figure 8: Monthly quotations of toluene, benzene, and WTI crude oil over the 2004-2015 period.

As already mentioned, crude oil quotations affect a number of industrial commodities, *i.e.* distillates and petrochemical derivatives (Mazzetto *et al.*, 2013; Rasello and Manca, 2014; Mazzetto *et al.*, 2015), and utilities (Manca *et al.*, 2011; Manca, 2016). For instance, Manca (2013) tracked the prices and costs of the main components involved in the HDA process, and showed the significant dependence of benzene price and toluene cost on crude oil quotations over a long-term period (Figure 8).

As far as utilities are concerned, Manca (2016) focused on the price of electric energy, which plays a significant role in the economic assessment of industrial plants. However, electric energy follows a complicated behavior respect to crude oil quotations, which means that there is not a direct proportionality as it happens for fuel oil and steam (Barzaghi *et al.*, 2016). In fact, electric energy price is primarily affected by the contract typology signed between the end user and the producer/seller, and subject to the fluctuations driven by meteorological, geographical, political, and social events. To give an idea of how much the electric energy price changes on different time scales, Figure 9 shows a typical trend of the hourly price of Italian electric energy for a given day of the year. It is possible to observe the typical M-shaped trend of electric energy prices, which covered the 43.34-82.38 €/MWh interval in that day. It is worth underlining that both the maximum and minimum values change every day not only in terms of absolute values but also in terms of time position. In fact, minima and maxima shift back and forth, and may assume rather different values as a function of the season, meteorological and climatic conditions, and also political, economic, and financial circumstances. Most recent years saw modifications and movements in the electric energy quotations mainly due to the significant development of renewable sources with the major role played by photovoltaic production (Manca, 2016).

All these issues show how the economic sustainability of industrial processes depends significantly on price/cost volatility and market fluctuations, and

prove that the conventional approach to conceptual design, which is based on the hypothesis of fixed prices/costs of commodities and utilities, is intrinsically unreliable for design optimizations and feasibility studies of chemical plants.

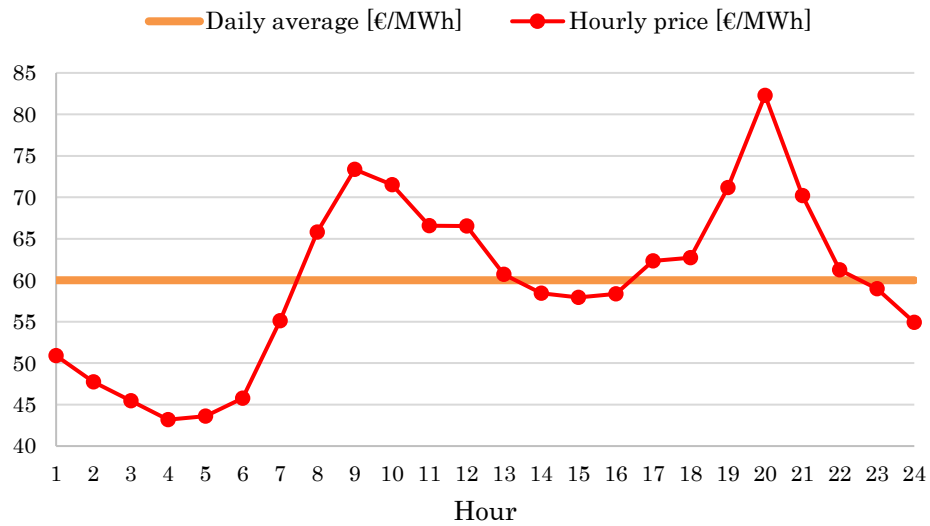


Figure 9: Hourly price of Italian electric energy for a given day of the year (19-Oct-2016). Adapted from GME (2016).



# 3 The cumene manufacturing process

The cumene molecule can be visualized as a straight-chain propyl group having a benzene ring attached at the middle carbon (Figure 10).

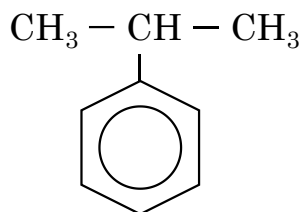


Figure 10: The cumene molecule.

Cumene is produced from benzene and propylene, accounting for 20% of benzene demand and 4% of propylene demand (IHS Markit, 2016). Cumene is made primarily for phenol and acetone production. Phenol/acetone production consumes approximately 98% of all cumene globally, so cumene demand is very closely tied to the phenol market. Cumene can also be used as a blending component in the gasoline pool, especially to avoid benzene restrictions in gasoline. When cumene and its feedstocks become undervalued relative to

energy, gasoline blenders can use cumene as a blending component, since it has a high-octane rating. Other uses for cumene are as a thinner for paints, lacquers and enamels, and as a constituent of some petroleum-based solvents. It is also used in manufacturing polymerization catalysts, catalyst for acrylic and polyester type resins, and as a raw material for peroxides and oxidation catalysts (ICIS, 2016). Table 3 reports some chemical and physical properties of pure cumene.

Table 3: Chemical and physical properties of pure cumene (adapted from IARC,2016).

IUPAC name	Isopropylbenzene
Common name	Cumene
Molecular formula	C <sub>9</sub> H <sub>12</sub>
Molecular mass	120.2 g/mol
Description	Colorless liquid with a sharp, penetrating, aromatic odor
Boiling point	152 °C
Melting point	-96 °C
Density	0.86 g/cm <sup>3</sup> at 20 °C
Vapor pressure	3.2 mmHg at 20 °C; 4.6 mmHg at 25 °C
Flash point	31 °C; upper and lower explosive limits, 6.5% and 0.9% respectively
Stability	Reacts violently with acids and strong oxidants, causing fires and explosions; can form explosive peroxides
Auto-ignition temperature	420 °C

The cumene market is driven by phenol market dynamics. Phenol is used mostly to make bisphenol A (BPA), phenol-formaldehyde (PF) resins, and nylon-KA (ketone-alcohol) oil. Nearly half of global phenol consumption is for the production of BPA. BPA, in turn, is driven primarily by demand for polycarbonate resins. Polycarbonate has been a rising market over the past few years, keeping steadily above GDP growth rates. This market is expected to

continue to grow at almost 3% per year in the next five years. The second-largest market for phenol is the production of PF resins, which accounted for about 28% of phenol demand in 2015. PF resins are used mainly in the construction industry. Nylon-KA oil is the third-largest market for phenol, making up about 13% of the global market (IHS Markit, 2016).

The pie chart of Figure 11 shows the world consumption of cumene as in 2015. Regionally, the largest cumene market is Northeast Asia (43%), followed by North America, and Western Europe. The Middle East will be one of the fastest-growing markets, with consumption increasing at an average annual rate of almost 15%. Capacity is expected to grow even faster, at an average annual growth rate of approximately 18.5% to 2020 (IHS Markit, 2016).

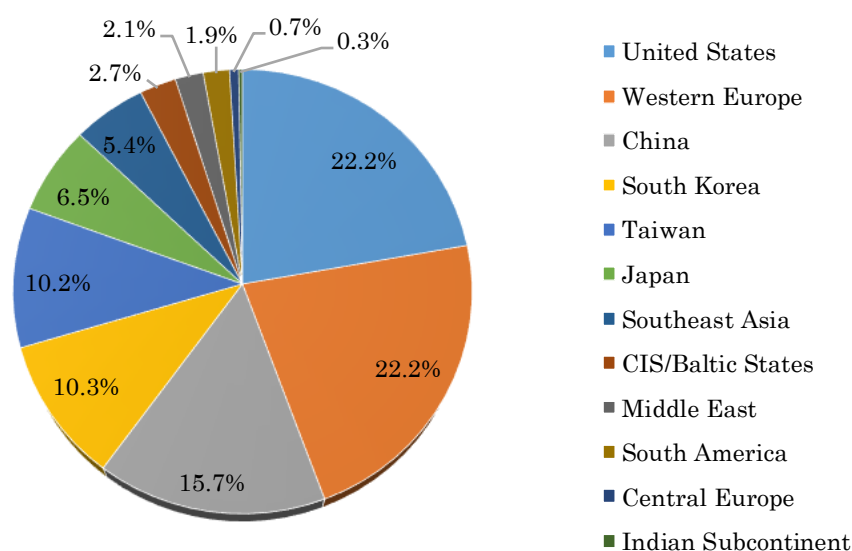


Figure 11: World consumption of cumene in 2015 (adapted from IHS Markit, 2016).

### 3.1 Recent developments in commercial processes

Cumene is produced by the Friedel-Crafts alkylation of benzene and propylene over a catalyst. Catalysts may include solid phosphoric acid (SPA), or one of the new generation of zeolite catalysts. In a typical alkylation process, refinery-

or chemical-grade liquid propylene and benzene are introduced to a fixed-bed alkylation reactor, where the propylene is consumed completely by the benzene. The effluent from the alkylation reactor is sent to a column to remove propane, which enters in small quantities with the propylene. The bottoms from this column are sent to a benzene column where unreacted benzene is distilled and recycled. Effluent from this column proceeds to a cumene separation column to recover the cumene product as an overhead stream. The byproduct from the cumene column is diisopropylbenzene (DIPB). The DIPB is separated from a small quantity of heavy hydrocarbon byproduct and recycled along with benzene to a transalkylation reactor, where the DIPB reacts with benzene to produce additional cumene.

Prior to 1992, virtually all cumene was produced by propylene alkylation of benzene using either SPA or aluminum chloride ( $\text{AlCl}_3$ ) as catalysts (Degnan Jr. *et al.*, 2001). The SPA process was developed in the 1940s primarily to produce cumene for aviation fuels. The SPA catalyst consists of a complex mixture of orthosiliconphosphate, pyrosiliconphosphate, and polyphosphoric acid supported on kieselguhr. To maintain the desired level of activity, small amounts of water are continuously fed into the reactor. The water continually liberates phosphoric acid ( $\text{H}_3\text{PO}_4$ ) causing some downstream corrosion. Besides, it is known that the SPA catalyst is not able to transalkylate DIPB, similar to free sulfuric acid and amorphous silica-alumina gels (Perego and Ingallina, 2004). On the contrary,  $\text{AlCl}_3$  is able to do it. As a matter of fact, in the 1980s Monsanto introduced a technology based on  $\text{AlCl}_3$  with the aim of improving cumene yield by DIPB transalkylation.

Unfortunately, SPA and  $\text{AlCl}_3$  are highly toxic and corrosive. They are dangerous to handle and transport as they corrode storage and disposal containers. In addition, because the reaction product is mixed with acids, the separation at the end of the reaction is often a difficult and energy-intensive process. Usually, these acids are neutralized at the end of the reaction, and

therefore the corresponding salts have to be disposed of. In order to avoid these problems, many efforts have been devoted to the search for solid acids that are more selective, safe and environmentally friendly. Among the different solid acids, zeolites have been extensively evaluated for such a purpose (Anastas *et al.*, 2000). The first industrial demonstrations of cumene technologies based on zeolite catalysts were started-up in 1996 by Mobil-Raytheon, EniChem, and UOP, independently (Perego and Ingallina, 2004). In all these cases, existing plants were revamped by substituting the old SPA catalyst with new zeolite catalysts. According to Degnan Jr. *et al.* (2001), fourteen cumene units were already operating worldwide in 2001 with zeolite catalysts. The zeolite-based processes produce higher cumene yields than the conventional SPA process because most of the DIPB byproduct is converted to cumene in separate transalkylation processes. Operating and maintenance costs are reduced because there is no corrosion associated with the zeolite catalysts. Finally, environmental concerns associated with the disposal of substantial amounts of phosphoric acid or  $\text{AlCl}_3$  are eliminated by the use of zeolites because they can be regenerated and safely disposed of by means of digestion or landfilling.

### **3.2 Case study**

The cumene manufacturing process provides an interesting example of plantwide design optimization subject to some classical engineering tradeoffs. A number of authors used the cumene process to illustrate plantwide economic optimization (Luyben, 2009; Gera *et al.*, 2012; Norouzi and Fatemi, 2012), but only few included environmental considerations (Sharma *et al.*, 2013). Most studies drew inspiration from the basic flowsheet of Turton *et al.* (2008), where the DIPB byproduct is removed and used as fuel. However, the use of a transalkylation reactor is a standard practice nowadays in conventional cumene manufacturing processes (Zhai *et al.*, 2015). For this reason, this work



kmol/h and 105.3 kmol/h, respectively. Fresh propylene contains 5% propane impurity, which is inert and has to be removed from the process. Since the separation of propylene and propane is difficult (Luyben, 2009), process economics favors high propylene conversion, which can be achieved by either increasing the reactor volume or operating at high temperature. The latter alternative increases the production of the undesired byproduct, revealing the critical conflict between conversion (favored at high temperature) and selectivity (favored at low temperature).

Table 4: Chemical reactions and kinetic scheme of the cumene process (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.  $R$ : 8.316 kJ/(kmol·K). Concentrations are in kmol/m<sup>3</sup>. Reaction rates are in kmol/(m<sup>3</sup>·s). For transalkylation, both forward ( $f$ ) and backward ( $b$ ) reaction rates are reported.

Reactions		Kinetics
1	Cumene reaction $C_3H_6 + C_6H_6 \rightarrow C_9H_{12}$	$r_1 = 2.8 \cdot 10^7 \exp[-104,181 / (RT)] C_B C_P$
2	DIPB reaction $C_3H_6 + C_9H_{12} \rightarrow C_{12}H_{18}$	$r_2 = 2.32 \cdot 10^9 \exp[-146,774 / (RT)] C_C C_P$
3	Transalkylation $C_{12}H_{18} + C_6H_6 \rightleftharpoons 2C_9H_{12}$	$r_{3,f} = 2.529 \cdot 10^8 \exp[-100,000 / (RT)] x_B x_D$ $r_{3,b} = 3.877 \cdot 10^9 \exp[-127,240 / (RT)] x_C^2$

As shown in Figure 12, fresh reactants are mixed with the benzene recycle, vaporized in E1, and preheated in two heat exchangers. The feed effluent heat exchanger recovers heat from the hot reactor outlet stream, while E2 heats the reactor inlet stream to the reaction temperature. The packed bed reactor recovers additional energy by generating high pressure steam from the exothermic reactions. For the sake of completeness, Sharma *et al.* (2013) proposed an alternative heat integration system. However, the optimization of the heat exchanger network is out of the scope of this work.

The cooled reactor effluent is sent to a sequence of three distillation columns where the lightest component is separated first, according to the heuristics of Douglas (1988). Column T1 separates inert propane and any unreacted propylene (with a little benzene) as vapor distillate. The bottom from T1 is sent to column T2 that separates the unreacted benzene to be recycled. Finally, column T3 separates nearly pure cumene as distillate and DIPB as bottom. The DIPB stream is mixed with a fraction of the benzene recycle, heated, and fed to the transalkylator, whose effluent is sent to column T2 to recover benzene and cumene.

Pathak *et al.* (2011) recommend adopting a heuristic approach to design the transalkylator, whose economic impact is limited as the inlet stream is relatively low (9.73 kmol/h in the base case). Pathak and coauthors set the inlet temperature at 240 °C (to avoid cumene dealkylation), the benzene to DIPB ratio at 2 (which provides good equilibrium conversion while controlling the benzene recycle), and the single pass conversion at 75% (which is low enough to avoid an excessive increase in the reactor size). Thus, the smallest possible transalkylator has 100 packed tubes, and is 1.6 m long.

### **3.2.1 Feasibility study**

As anticipated in Chapter 2, the approach to conceptual design proposed by Douglas (1988) is not reliable for the feasibility study of chemical plants as it assumes that the prices/costs of commodities and utilities are constant throughout the operational life of the plant. As shown in Figure 13, this hypothesis does not reflect the real fluctuations of the prices/costs of raw materials and final product, and can lead to significant errors in the conceptual design procedure.

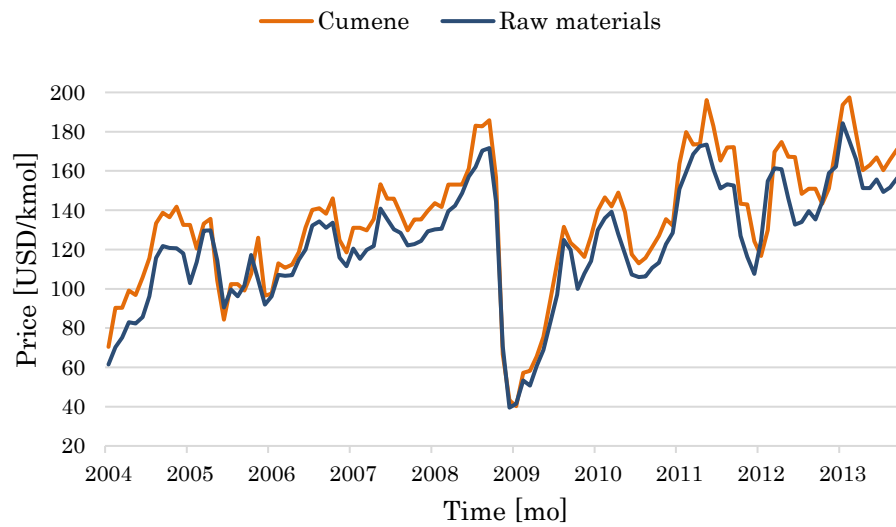


Figure 13: Monthly quotations of cumene and raw materials over the 2004-2013 period. Raw material cost is obtained by addition of benzene and refinery-grade propylene costs on a molar basis. Past values of cumene price were available only up to October 2013 (ICIS, 2016).

As already observed for the HDA process, the  $EP2$  changes sign repeatedly and fluctuates between positive and negative values as soon as cumene price is either higher or lower than benzene and propylene cost (Figure 14).

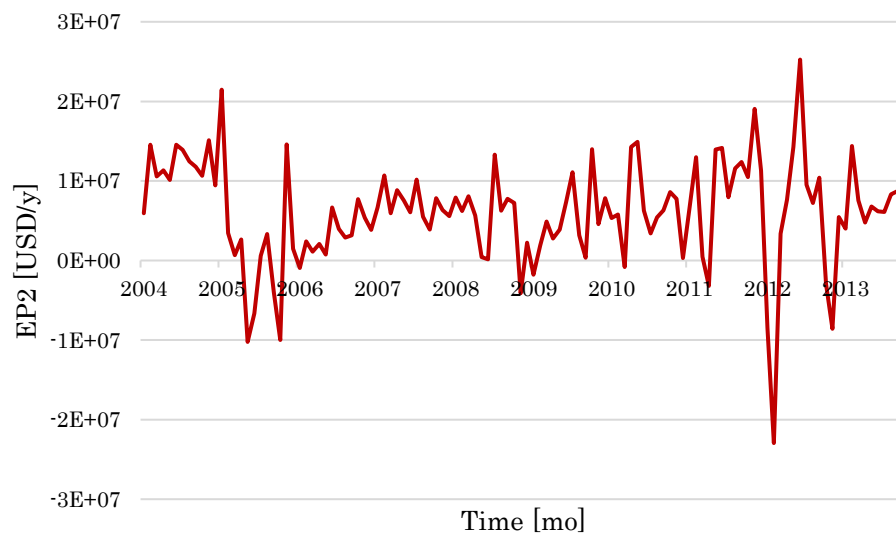


Figure 14:  $EP2$  values for the cumene process based on the process flow diagram of Pathak *et al.* (2011).

It is worth observing the significant oscillations of  $EP2$  with peaks, ridges, and narrow valleys in rather short time intervals. This point is even more disturbing as far as the *Cumulated EP4* of Equation (5) is concerned. As already mentioned, the CAPEX terms can be estimated using the Guthrie's formulas, which are briefly reported in Table 5.

Table 5: Cost correlations for each process unit of the cumene process (Douglas, 1988; Pathak *et al.*, 2011). The  $M \& S$  index is assumed equal to 1457 (Barzaghi *et al.*, 2016).  $D$ ,  $L$ , and  $A$  are the process unit diameter, length, and area, respectively.  $H$  is the tray stack height.  $F_p$  and  $F_m$  depend on the operating pressure and building material, respectively.  $F_t$  and  $F_s$  depend on the tray type and spacing, respectively.  $F_d$  depends on the type of heat exchanger.  $P$  and  $Q$  are the pump outlet pressure and duty, respectively.

Process unit	Cost correlation
(Trans)alkylation reactor	$CAPEX_{Reactor} = \left( \frac{M \& S}{280} \right) 101.9 D^{1.066} L^{0.802} (2.18 + F_c)$ $F_c = F_p \cdot F_m$
Distillation column	$CAPEX_{Vessel} = \left( \frac{M \& S}{280} \right) 101.9 D^{1.066} L^{0.802} (2.18 + F_c)$ $CAPEX_{Trays} = \left( \frac{M \& S}{280} \right) 4.7 D^{1.55} H F_c$ $F_c = F_t + F_s + F_m$
Heat exchanger	$CAPEX_{Heat\ exchanger} = \left( \frac{M \& S}{280} \right) 101.3 A^{0.65} (2.29 + F_c)$ $F_c = (F_d + F_p) F_m$
Pump	$CAPEX_{Pump} = C_p (1.8 + 3.624 F_p)$ $\log(C_p) = 3.5793 + 0.3208 \log(P) + 0.0285 \log(P^2)$ $F_c = 0.1682 + 0.3466 \log(Q) + 0.4841 \log(Q^2)$

The OPEX terms are evaluated by considering the specific prices/costs of inlet/outlet flow rates (Figure 13) and utilities from rigorous steady-state mass

and energy balances. The main utilities used in the cumene plant are electric energy (Figure 15) and high-pressure steam.

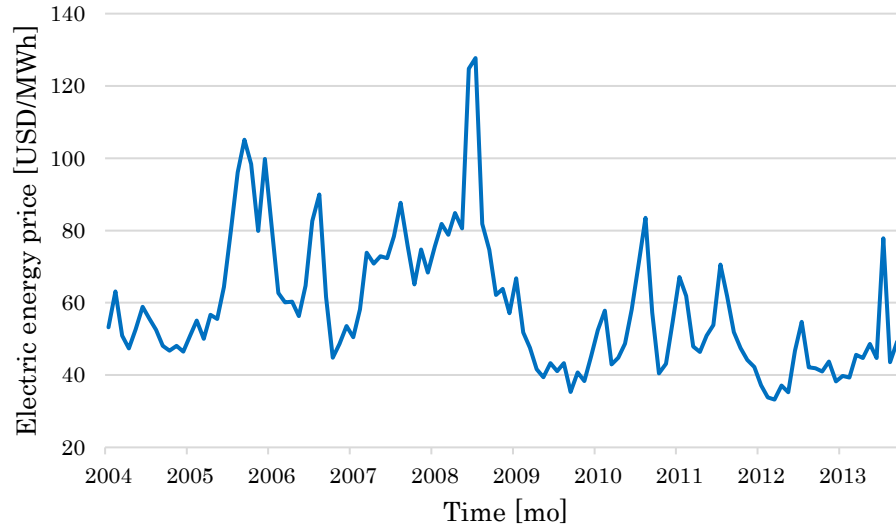


Figure 15: Monthly quotations of electric energy over the 2004-2013 period.

The steam price is assumed proportional to that of the fuel used in the boiler. The Steam System Modeler Tool provided by DOE (2016) allows to determine the amount of fuel energy required to produce steam with specified properties at a given flow rate using general boiler operational characteristics.

Table 6: Assumptions in the calculation of the fuel energy required to produce steam. Combustion efficiency is the percentage of fuel energy that is directly added to the feedwater and not lost. Blowdown rate is the percentage of inlet feedwater flow rate that leaves the boiler as a saturated liquid at boiler pressure.

Fuel type	Natural gas
Combustion efficiency	85%
Blowdown rate	3%
Deaerator pressure	1 atm

This work used the assumptions made by Idris *et al.* (2016) and reported in Table 6. From the calculations, it was estimated that the production of 1 klb/h (*i.e.* 453.6 kg/h) of steam requires 1.2 MBtu/h of fuel energy. As a result:

$$P_s = 0.003 \frac{\text{MBtu}}{\text{kg}} P_{NG} \quad (6)$$

Where  $P_s$  is the steam price in USD/kg, and  $P_{NG}$  is the natural gas price in USD/MBtu (Figure 16).

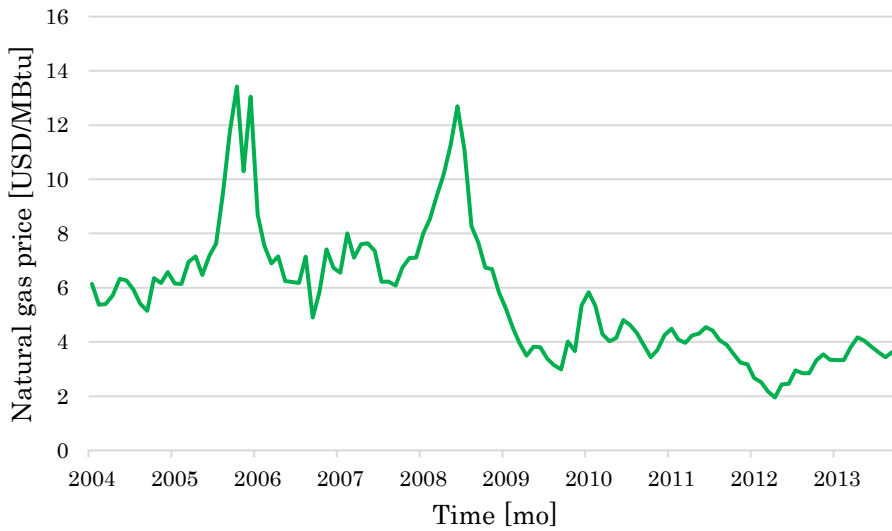


Figure 16: Monthly quotations of natural gas over the 2004-2013 period.

Based on the quotations of Figure 13, Figure 15, and Figure 16, the life span of the cumene plant is 118 mo, *i.e.* the  $nMonths$  term of Equation (5) is equal to 118. Figure 17 shows how the *Cumulated EP4* strictly depends on the specific set of historical prices and spans from a minimum of -119 MUSD to a maximum of 142 MUSD.

Therefore, the economic sustainability of the cumene plant is heavily conditioned by price/cost volatility and fluctuations. This calls for a novel

systematic procedure to account for market uncertainty in the conceptual design of chemical plants.

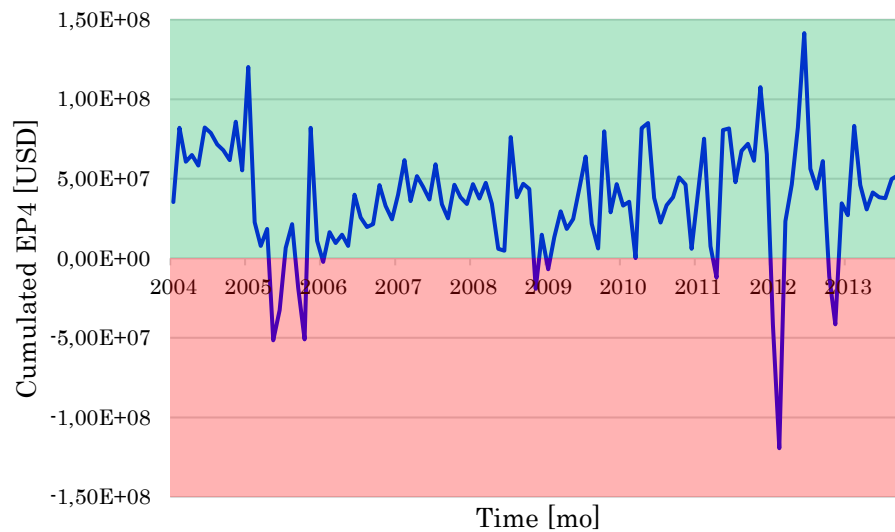


Figure 17: Effects of price fluctuations on plant profitability. The green area shows the profitable economic region; the red area shows the not profitable one.



# 4 Predictive conceptual design

Paragraphs 2.1 and 3.2.1 showed how the economic sustainability of chemical processes depends significantly on the price volatility of raw materials, final products, and utilities. This Chapter proposes and discusses a dynamic approach to the economic assessment of chemical plants that is primarily based on econometric models and dynamic trajectories of prices/costs. Indeed, this innovative approach to conceptual design, christened Predictive Conceptual Design (PCD) by Barzaghi *et al.* (2016), considers the OPEX terms as a function of price fluctuations, and introduces a direct time dependence in the formulation of Douglas' economic potentials, which result in the Dynamic Economic Potentials (DEPs). PCD uses econometric models to devise a set of possible future scenarios of commodity and utility prices, and finds an optimal plant configuration for each possible scenario. Based on the future price/cost scenarios, PCD moves from a deterministic approach, characterized by fixed prices/costs of commodities and utilities, to a probabilistic approach that provides a distribution of DEPs for a specific process/plant.

The building of econometric models for forecasting purposes can go along with the following sequence of actions:

1. Identification of a reference component;
2. Identification of the sampling time and time horizon for the economic assessment;
3. Identification of an econometric model of the reference component;
4. Identification of econometric models of the raw material(s) and (by)product(s) (as a function of the reference component, whenever possible);
5. Identification of econometric models of the utilities (as a function of the reference component, whenever possible);
6. Use of the identified econometric models to dynamically assess the economic sustainability of the process/plant under design.

As hinted by Sepiacci and Manca (2015), this procedural methodology allows covering the assessment of economic sustainability for the following activities:

- Design of new chemical plants;
- Revamping, retrofitting of existent plants;
- Process intensification;
- Scheduling, planning of production;
- Supply chain management;
- Product and process design.

#### **4.1 The reference component**

The identification of a reference component is not mandatory but highly recommended. Instead of tracking the dynamics of every OPEX term involved in the process, it is possible to define a reference component and quantify the

OPEX term respect to that component. By doing so, the dynamics of commodity and utility prices will be a suitable function of the time series of the quotation of the reference component. As extensively discussed in Manca (2013), the reference component must be chosen according to the market field of the chemical plant. It should be a key component for either the chemical process or the sector where the plant operates. The availability of frequent and updated values of the reference component is a further recommended feature. For instance, as far as the O&G sector is concerned, crude oil is a good candidate to the role of reference component. Indeed, it is the raw material and precursor of a number of chemical processes. Besides, its price is well known, largely available, and periodically updated on the main trading markets. Finally, crude oil, besides being a reference component for all its derived commodities, plays a similar role also respect to industrial utilities, *e.g.*, steam, electric energy, diathermic oil, refrigeration systems (Manca, 2016). By identifying future price trajectories of crude oil, it is possible to assess the corresponding price trajectories of both the commodities and utilities that play a role in the PCD framework.

#### 4.1.1 The correlation role

To numerically assess the economic dependence between the quotations of the reference component and the price of commodities and utilities, it is worth considering the covariance statistical index that measures the interaction intensity between variables  $X$  and  $Y$ :

$$\sigma_{X,Y} = \text{cov}(X,Y) = E[(X - \mu_X)(Y - \mu_Y)] \quad (7)$$

$\sigma_{X,Y}$  allows understanding if there are any correlations between the fluctuations of  $X$  and  $Y$  respect to their expected (*i.e.* average) values  $\mu_X$ ,  $\mu_Y$  (Manca, 2012). To better understand the interaction between  $X$  and  $Y$

variables, the correlation index measures in a non-dimensional way the interaction between those variables:

$$\text{corr}(X, Y) = \frac{\text{cov}(X, Y)}{\sqrt{\text{var}(X)\text{var}(Y)}} = \frac{\sigma_{X,Y}}{\sigma_X\sigma_Y} \quad (8)$$

Where  $\text{corr}(X, Y) \in -1, \dots, +1$ .  $\text{corr}(X, Y)$  allows assessing quantitatively the dependence of commodity and utility prices on the quotation of the reference component. The higher the correlation index (between each single commodity or utility price,  $Y$ , and the reference component quotation,  $X$ ) the better the identification of the reference component and, eventually, the functional dependence of commodity and utility prices on the quotation of the reference component (Manca, 2012). Values of the correlation index higher than 0.7 mean a rather good correlation between the variables (Manca, 2013).

#### **4.1.2 Time dependence**

Once the dependence of commodity and utility prices on the quotation of the reference component has been assessed, it is necessary to determine if there are any time delays between the corresponding time series. Indeed, possible time delays play a role in the definition of the functional dependence between  $X$  and  $Y$  series (Manca, 2013). Correlograms can be of real help in quantifying the time lag (*i.e.* time delay) between those series. Correlograms are diagrams that report the correlation index of the time series  $X$  and  $Y$  as a function of the time lag introduced between them. For instance, Manca (2012) showed that the price of toluene mainly depends on the price of crude oil at the same month and at the previous one based on the correlogram of toluene respect to crude oil for the monthly prices of the 2005-2010 period.

A further step towards the definition of the functional dependence of commodity and utility prices on the quotation of the reference component consists in understanding if there is any autocorrelation for each time series of

commodity and utility prices. In other words, the question is about the dependence of commodity and utility prices from their previous quotations. For the sake of clarity, Stock and Watson (2003) define the  $j$ -th autocorrelation of a series  $Y_t$  as the correlation between  $Y_t$  and its  $j$ -th lag,  $Y_{t-j}$ :

$$\text{corr}(Y_t, Y_{t-j}) = \frac{\text{cov}(Y_t, Y_{t-j})}{\sqrt{\text{var}(Y_t) \text{var}(Y_{t-j})}} \quad (9)$$

For instance, Manca (2012) showed that the price of toluene loses any memory of the past quotations after 4-5 months.

## 4.2 Time horizon and sampling time

As shown in Paragraph 1.3, the time horizon of a PSE problem depends on the phenomenon to be studied. Indeed, the time horizon taken for the economic assessment can cover a short-, medium-, or long-term period. For instance, the time horizon is usually few days/weeks in case of tactical allocation of resources (Manca, 2015). In case of strategic problems, the time horizon may be some weeks or a few months (generally no more than a quarter). In case of PCD, the time horizon can be even decades (*i.e.* the expected lifetime of the plant to be designed).

As already mentioned, PCD uses econometric models to devise a set of possible future scenarios of commodity and utility prices. These models are time-discrete, so depend on a suitable fraction of the time horizon, *i.e.* the sampling time, which is based on (i) the availability of real prices/quotations, which can be gathered daily, weekly, monthly, quarterly, or yearly, and (ii) the number of steps that the model can forecast consistently. In case of PCD, the sampling time is usually assumed to be one month (Sepiacci and Manca, 2015). In fact, monthly price/cost series feature a sufficiently detailed texture to capture

short-run movements over time without adding unnecessary complexity to the analysis (Villar and Joutz, 2006).

### 4.3 Econometric model of the reference component

As anticipated in Paragraphs 2.1 and 4.1, crude oil is a good candidate to the role of reference component. The scientific literature has shown interest in forecasting the variations (*i.e.* shocks) of crude oil prices over different time horizons, and has provided a plethora of economic and econometric models (Kaufmann *et al.*, 2004; Déés *et al.*, 2007; Kaufmann and Ullman, 2009; Kilian, 2009; Ye *et al.*, 2009; Cifarelli and Paladino, 2010; Zagaglia, 2010; Salisu and Fasanya, 2013; Chen, 2014; Chevallier, 2014). For the sake of clarity, economic models simulate the crude oil market trend by means of the physical, economic, and financial features involved in the supply-and-demand law. Econometric models do not consider the forces that cause price fluctuations, but simulate market uncertainties and possible price evolutions by the statistical analysis of past price shocks. Hence, economic and econometric models differ for the mechanism used to both generate the simulated prices and explain their trend (Table 7).

Table 7: Intrinsic nature of economic and econometric models.

Economic models	Econometric models
<ul style="list-style-type: none"> <li>✓ Follow the historical market price trends;</li> </ul>	<ul style="list-style-type: none"> <li>✓ Follow the historical market price trends;</li> </ul>
<ul style="list-style-type: none"> <li>✓ Consider physical variables (<i>e.g.</i>, GDP, demand, inventories, production);</li> </ul>	<ul style="list-style-type: none"> <li>✗ Neglect the physical features involved in the supply-and-demand law;</li> </ul>
<ul style="list-style-type: none"> <li>✗ Are inadequate to long-term forecasts.</li> </ul>	<ul style="list-style-type: none"> <li>✓ Can cover short-, medium-, and long-term horizons.</li> </ul>

As observed in Manca and Depetri (2016), the use of economic models on long-term horizons is difficult to carry out, as there would be the need for long-term

forecasts of the levels of supply, demand, capacity storage, technical advances in exploration and production of hydrocarbons, political dynamics or changes in collective behaviors, and both national and international legislations. Instead, process designers and plant managers look for reliable models characterized by a simple structure and reduced number of parameters. For these reasons, econometric models are more suitable for PCD applications (Barzaghi *et al.*, 2016).

The identification of econometric models of crude oil prices requires the acquisition of historical price data and the statistical analysis of both price series and shock series. Indeed, if one performs an analysis of the relative price variations between a time unit (*e.g.*, one month) and the next one, a set of values that are representative of the price volatility is obtained. The study of price series is mainly concerned with decomposing the variation of a series  $X_t$  into components that represent trend  $T_t$ , seasonal variation and other incidental cyclic changes  $S_t$ , and irregular fluctuations  $I_t$  due to stochastic contributions over time  $t$ :

$$X_t = T_t + S_t + I_t \quad (10)$$

Barzaghi *et al.* (2016) suggest using moving-averaged values of crude oil price (with four-month time spans) to eliminate most of the high-frequency fluctuations and catch the trend followed by the prices (Figure 18). For the sake of clarity, Johnston *et al.* (1999) define the simple moving average  $m$  of  $n$  values as:

$$m = \frac{1}{n} \sum_{i=0}^{n-1} X_{t-i} \quad (11)$$

As shown in Figure 18, the simple moving average introduces a time delay between historical and averaged prices that depends on  $n$  terms. In this case

(i.e.  $n$  equal to four monthly quotations), the time delay is approximately 2 mo, which is acceptable for long-term forecasts as in PCD applications (Manca *et al.*, 2015).

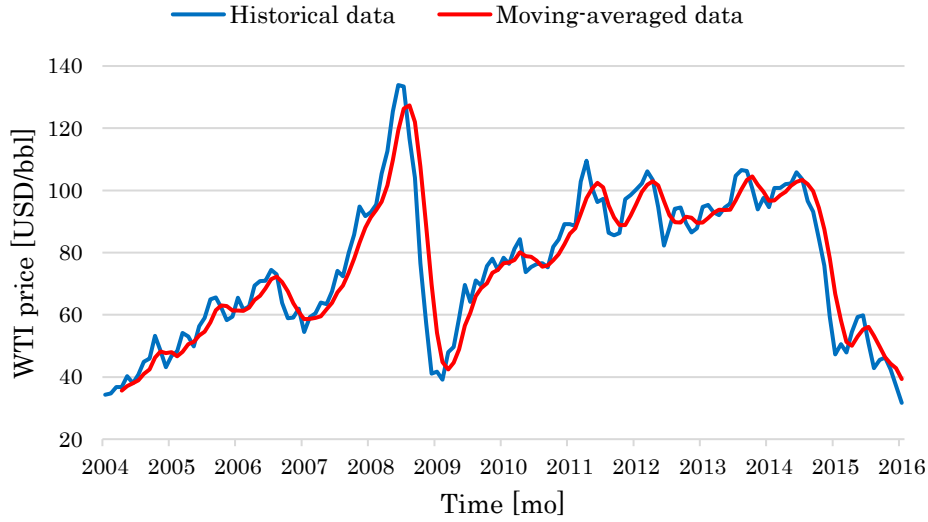


Figure 18: Comparison between historical and moving-averaged values of WTI monthly quotations over the 2004-2016 period.

The following step is to verify whether crude oil shocks depend on previous historical values or change stochastically starting from the last value. Barzaghi *et al.* (2016) denoted a crude oil shock as:

$$Shock_t = \frac{P_{CO,t} - P_{CO,t-1}}{P_{CO,t-1}} \quad (12)$$

Where  $P_{CO,t}$  and  $P_{CO,t-1}$  are the trend components of crude oil price at times  $t$  and  $t-1$ , respectively. As hinted in Paragraph 4.1.1, the correlation index allows assessing quantitatively the dependence of crude oil shocks on previous historical values. Figure 19 shows the diagram that reports the autocorrelation of crude oil shocks as a function of the time lag introduced between them. It is evident that crude oil shocks depend on previous historical values (especially

for time lags equal to 1-2 mo), thus cannot be assimilated to a stochastic variable.

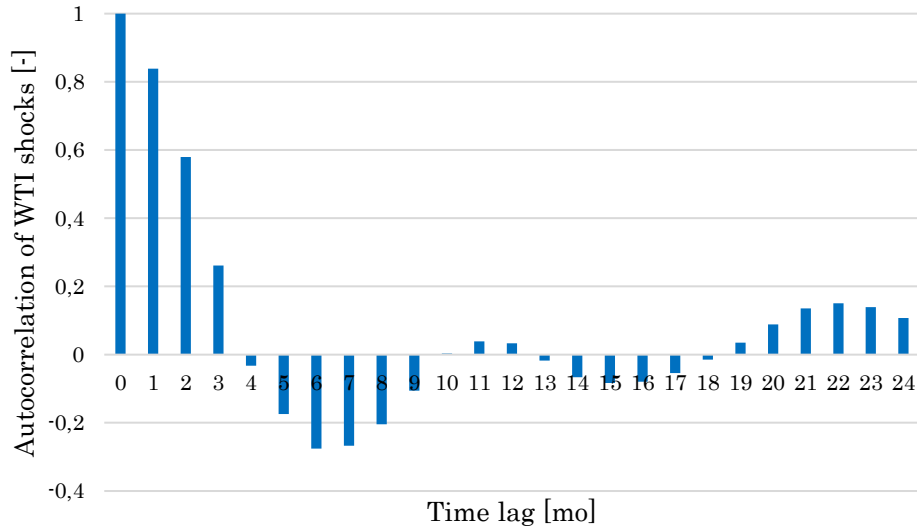


Figure 19: Autocorrelogram of WTI shocks.

These findings allow using autoregressive (AR) models to model past quotations and determine future prices as a function of the previous ones. The candidate AR model assumes the following general structure:

$$X_t = a_0 + a_1X_{t-1} + a_2X_{t-2} + \dots + a_qX_{t-q} \quad (13)$$

The number of lagged values  $q$  is the order, or the lag length, of the autoregression (Stock and Watson, 2003). According to the evidence of Figure 19, the AR model of crude oil price can be formulated as follows:

$$P_{CO,t} = a_0 + a_1P_{CO,t-1} + a_2P_{CO,t-2} \quad (14)$$

Where  $P_{CO,t-1}$  and  $P_{CO,t-2}$  are the trend components of crude oil price at times  $t-1$  and  $t-2$ , respectively;  $a_0$ ,  $a_1$ , and  $a_2$  are linear regression coefficients. The rather simplified model of Equation (14), based on only two lagged values

of crude oil price, is chosen to (i) keep the things as simple as possible (while satisfying the findings of the correlation analysis), and (ii) avoid overfitting problems produced by possible overparameterizations of the identification model.

The evaluation of the adaptive coefficients  $a_0$ ,  $a_1$ , and  $a_2$  goes through a linear regression procedure based on the minimization of the sum of the squared errors between real quotations and model values:

$$\min_{a_0, a_1, a_2} \sum_{t=1}^N \left[ P_{CO,t}^{Real} - (a_0 + a_1 P_{CO,t-1} + a_2 P_{CO,t-2}) \right]^2 \quad (15)$$

Where  $P_{CO,t}^{Real}$  denotes the real trend of crude oil price referred to  $N$  past quotations.

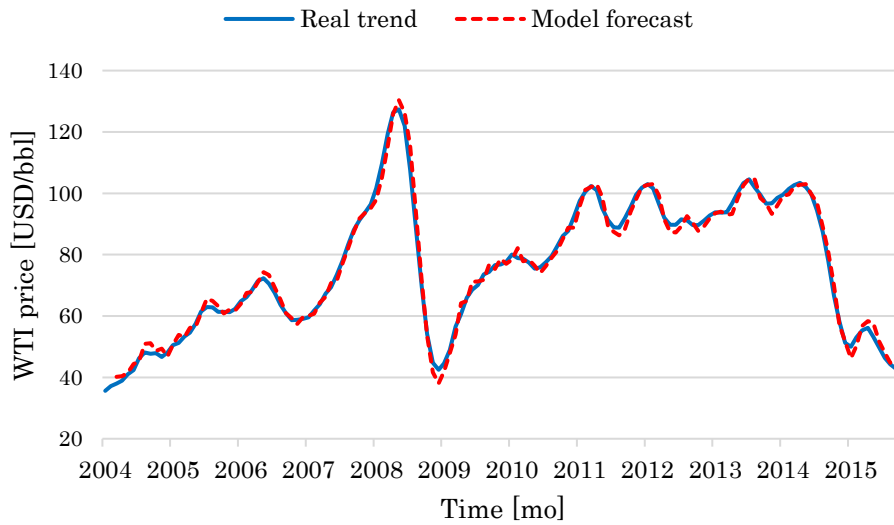


Figure 20: Comparison between the real and model trend of WTI quotations.

Regarding the experimental data (gathered from the market monthly quotations of the Jan-2004 to Jan-2016 period), it is a good operating rule to run the identification procedure (*i.e.* the linear regression) on a subset of data (*e.g.*, 70-80%) and leave the remaining ones (*i.e.* 20-30%) to the cross-validation

procedure (Manca, 2013). Figure 20 shows a comparison between the real trend of crude oil price and the model forecasts, where the validation initial time is October 2013. There is a good agreement in the dynamic model of crude oil price, as measured by the coefficient of determination  $\bar{R}^2$  (Table 8).

Table 8: Parameters of the linear regression for the crude oil price. For the sake of clarity,  $\bar{R}^2$  is the adjusted coefficient of determination as defined by Stock and Watson (2003).

$a_0$ [USD/bbl]	3.3207
$a_1$ [-]	1.8286
$a_2$ [-]	-0.8711
$\bar{R}^2$ [-]	0.9813
$\sigma_{CO}$ [-]	0.0313
$\bar{X}_{CO}$ [-]	-0.0028

Since fluctuations and uncertainty are intrinsic to crude oil quotations, it is necessary to introduce stochasticity in the AR model of Equation (14):

$$P_{CO,t} = (a_0 + a_1 P_{CO,t-1} + a_2 P_{CO,t-2}) (1 + RAND \cdot \sigma_{CO} + \bar{X}_{CO}) \quad (16)$$

Where  $RAND$  is a random function that produces a normal distribution of real numbers with average value 0 and standard deviation 1;  $\sigma_{CO}$  and  $\bar{X}_{CO}$  are the standard deviation and the average value of the relative errors reported in Figure 21.

Equation (16) includes both a deterministic and a stochastic term. The former describes the functional dependence of future prices on the previous ones. The latter allows simulating unexpected variations as random fluctuations. The time-discrete model of Equation (16) has to be used step-by-step over the prediction horizon to forecast possible price trajectories, as shown in Figure 22.

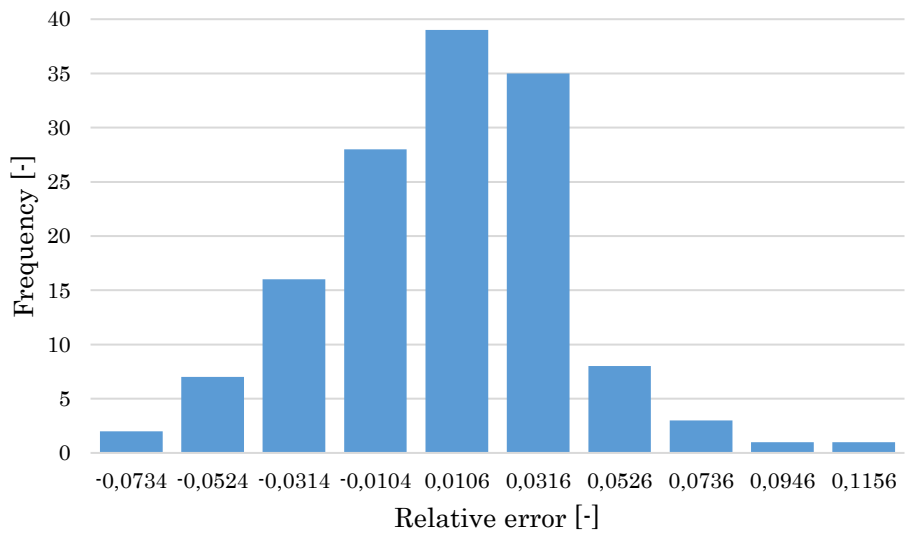


Figure 21: Relative errors between real and model values of WTI quotations.

It is recommended to evaluate a large number of price trajectories, so to make the economic assessment more robust.

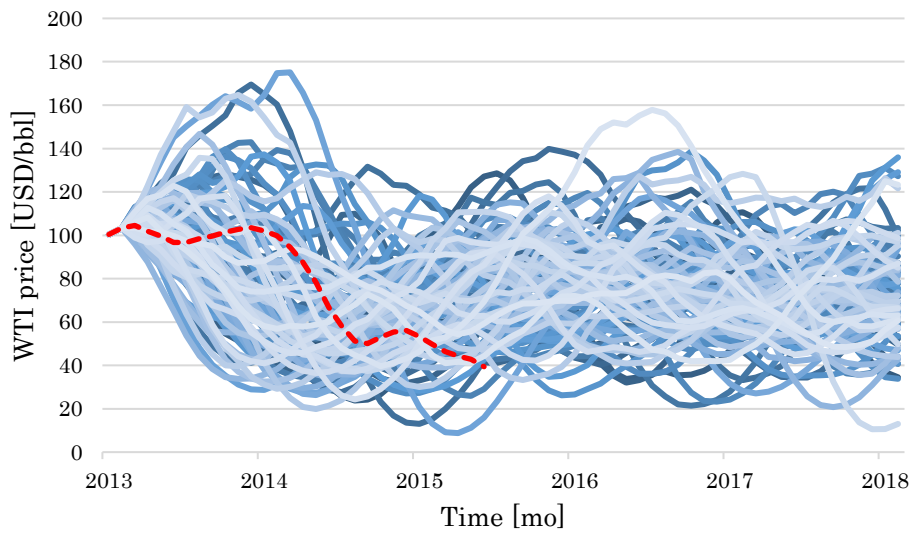


Figure 22: 100 WTI future-price trajectories over a five-year horizon. The red dashed line shows the real trend of WTI quotations up to January 2016. October 2013 corresponds to the initial forecast time.

## 4.4 Econometric models of raw material(s) and (by)product(s)

As already remarked, crude oil plays a central role in commodity pricing. This is a straightforward assumption for the O&G sector. For instance, the main components involved in the cumene process, *i.e.* benzene, propylene, and cumene, depend significantly on the crude oil quotation (Figure 23). Nonetheless, Mazzetto *et al.* (2013) showed that crude oil can be taken as reference component also in the strategic design of bioethanol supply chains where biomaterials are used as raw inlet streams.

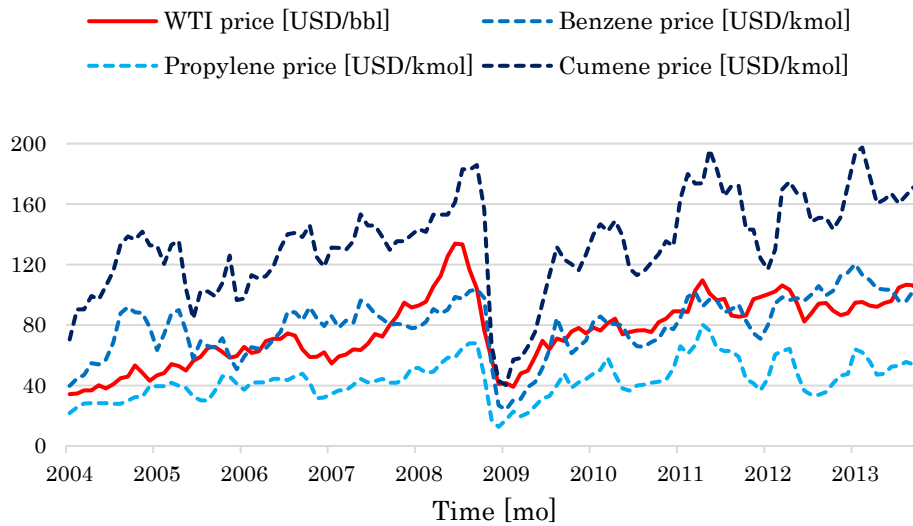


Figure 23: Monthly values of benzene, propylene, cumene, and WTI quotations over the Jan 2004-Dec 2013 period.

The candidate econometric models of raw material(s) and (by)product(s) assume the following general structure:

$$Y_t = a_0 + a_1 X_{t-1} + a_2 X_{t-2} + \dots + a_q X_{t-q} + b_1 Y_{t-1} + b_2 Y_{t-2} + \dots + b_p Y_{t-p} \quad (17)$$

Where  $X_t$  and  $Y_t$  are the prices of the independent (*i.e.* crude oil) and dependent (*i.e.* the specific commodity) variables at time  $t$ , respectively;  $q$  and

$p$  are the number of lagged values of  $X_t$  and  $Y_t$ , respectively. Equation (17) is chosen for its formulation that is linear, keeps the single contributions separate, and neglects any direct interactions (*i.e.* neither rectangular nor quadratic terms are provided). According to the econometric terminology, it depicts an Autoregressive Distributed Lag (ADL) model (Stock and Watson, 2003). The generality of Equation (17) makes the ADL model a good candidate to cover a large number of chemical products over different time intervals (Manca, 2015).

As anticipated in Paragraphs 4.1.1 and 4.1.2, the number of  $X_t$  and  $Y_t$  terms in Equation (17) depends on a correlation and autocorrelation analysis that suggests, in terms of quantitative diagrams, how detailed the econometric model should be. As shown in Paragraph 4.3, the evaluation of  $a$  and  $b$  parameters is achieved by a linear regression procedure that minimizes the sum of squared errors between real quotations and model values. Once the econometric model has been identified over a suitable past time interval, it can be used to forecast future-price trajectories.

#### **4.4.1 Price models of benzene, propylene, and cumene**

As shown in Paragraph 3.2.1, the economic sustainability of the cumene plant is heavily conditioned by the fluctuations of benzene, propylene, and cumene prices. In fact, the  $EP2$  changes sign repeatedly and fluctuates between positive and negative values as soon as the cumene price is either higher or lower than benzene and propylene cost (Figure 14). This calls for specific price models of benzene, propylene, and cumene to forecast the price trajectories throughout the life span of the plant.

Figure 24 shows that the highest correlation between the crude oil quotation and benzene, propylene, and cumene price occurs for time lags of 0-1 mo. The negligible values of the autocorrelation index for time lags of 4-5 mo shows that

the price of benzene, propylene, and cumene loses memory of the past after such a time interval.

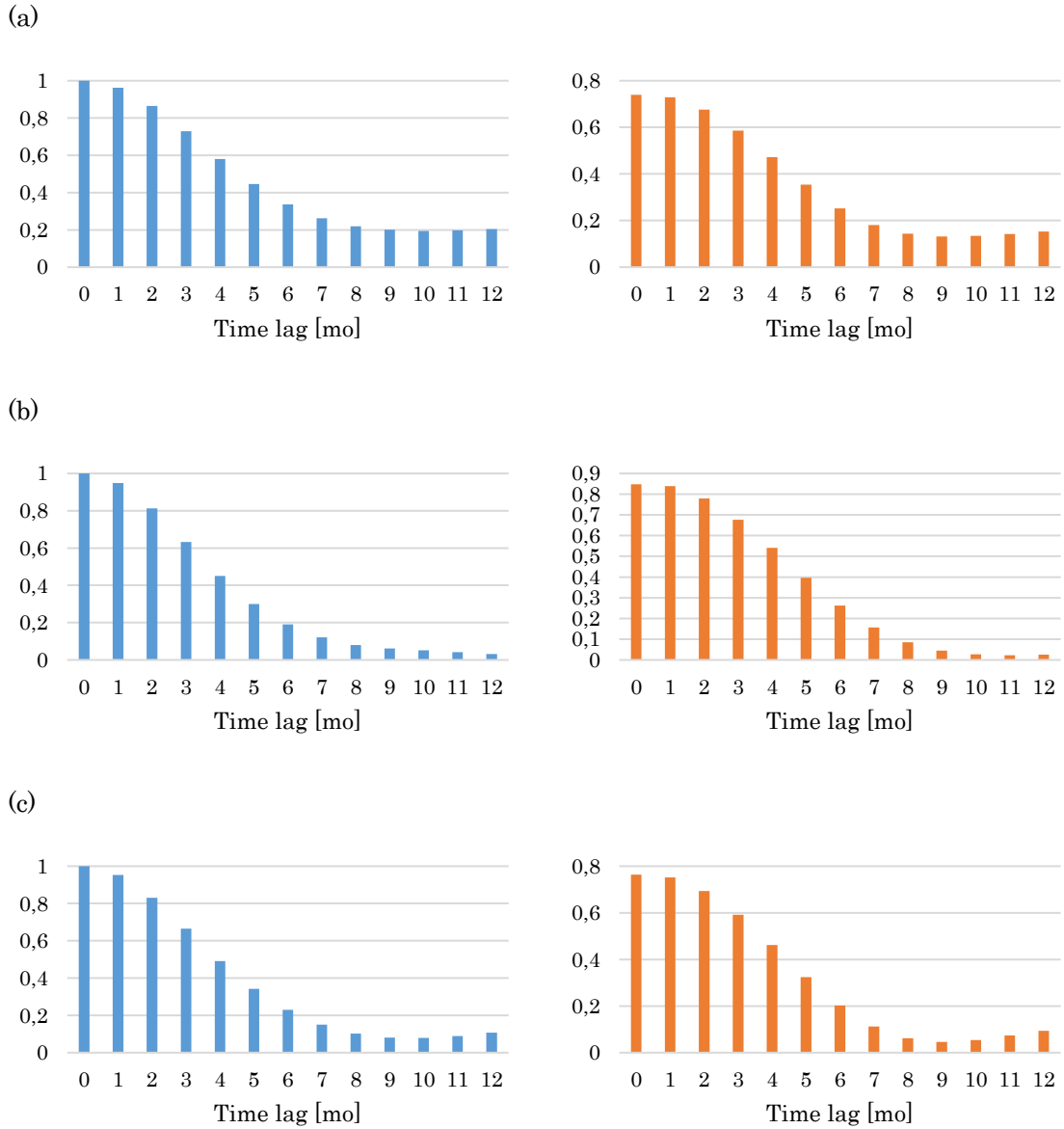


Figure 24: Benzene (a), propylene (b), and cumene (c) price autocorrelation (left) and correlation with the crude oil price (right).

According to the results of Figure 24, the econometric models of benzene, propylene, and cumene assume the following formulations:

$$P_{B,t} = a_0 + a_1 P_{CO,t} + b_1 P_{B,t-1} \quad (18)$$

$$P_{P,t} = a_0 + a_1 P_{CO,t} + b_1 P_{P,t-1} \quad (19)$$

$$P_{C,t} = a_0 + a_1 P_{CO,t} + b_1 P_{C,t-1} \quad (20)$$

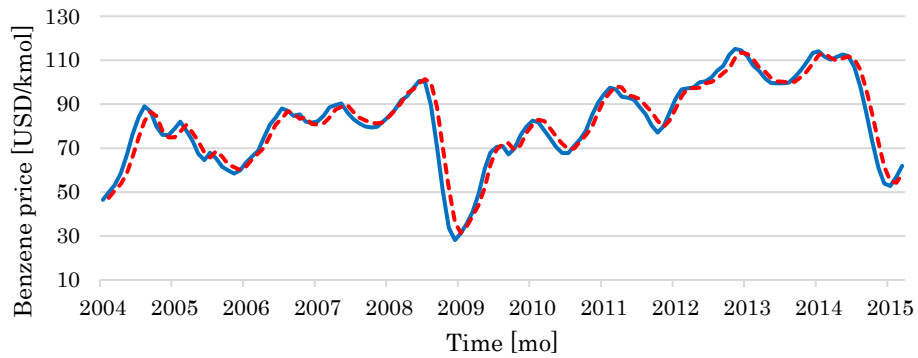
Where subscripts  $B$ ,  $P$ , and  $C$  refer to benzene, propylene, and cumene, respectively.  $a$  and  $b$  parameters of the linear regression are reported in Table 9.

Table 9: Parameters of the linear regression for the price models of benzene, propylene, and cumene.

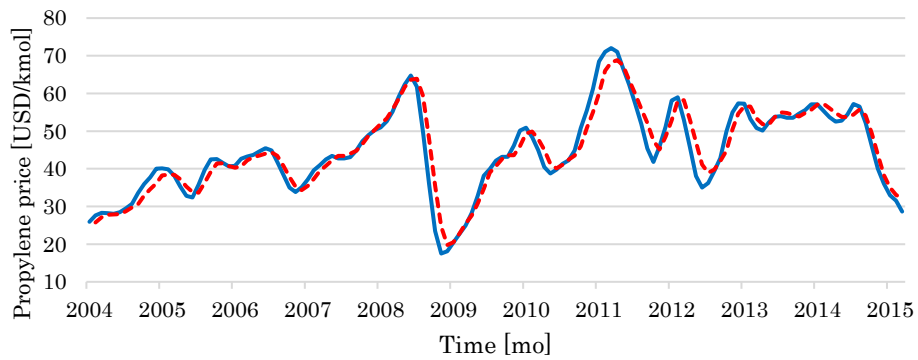
Commodity	$a_0$ [USD/kmol]	$a_1$ [bbl/kmol]	$b_1$ [-]	$\bar{R}^2$ [-]	$\sigma$ [-]	$\bar{X}$ [-]
Benzene	2.6984	0.0754	0.9012	0.9407	0.0843	-0.0098
Propylene	1.3533	0.1124	0.7792	0.9201	0.0885	-0.0113
Cumene	6.7938	0.1924	0.8447	0.9138	0.0880	-0.0068

There is a good agreement between real and model prices (Figure 25), as measured by the coefficient of determination  $\bar{R}^2$  (Table 9). Time lags of few months between real and model prices do not play a significant role in the economic assessment of chemical plants over long-term horizons (Manca, 2013). Besides, Equations (18)-(20) are used to simulate a set of possible economic scenarios where the discrepancy between real and model prices is negligible respect to larger variations due to stochastic fluctuations. Figure 26 shows 100 different price scenarios generated from the econometric models of Equations (18)-(20) based on the standard deviation  $\sigma$  and the average value  $\bar{X}$  of the relative errors between real and model prices (Table 9). It is worth observing that these scenarios are much more irregular (*i.e.* realistic) than those depicted for the crude oil price (Figure 22) thanks to the stochastic contribution (*i.e.* random fluctuations) from both the crude oil and the specific commodity.

(a)



(b)



(c)

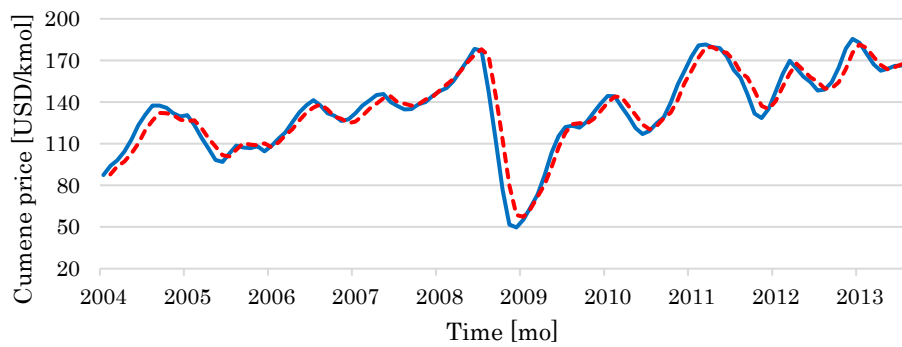
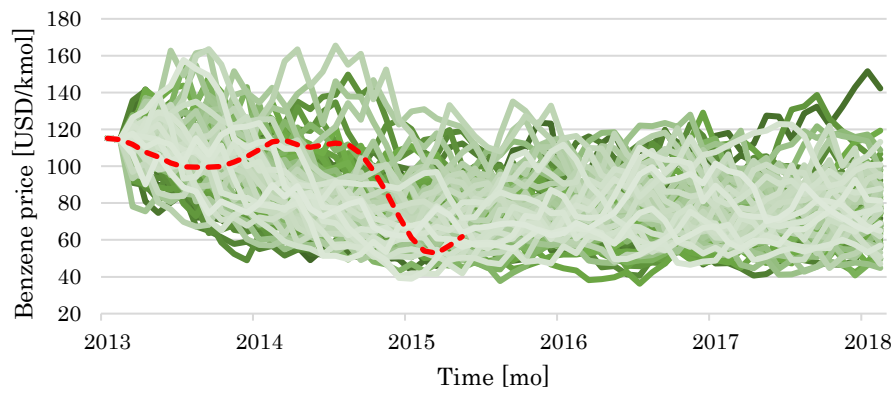
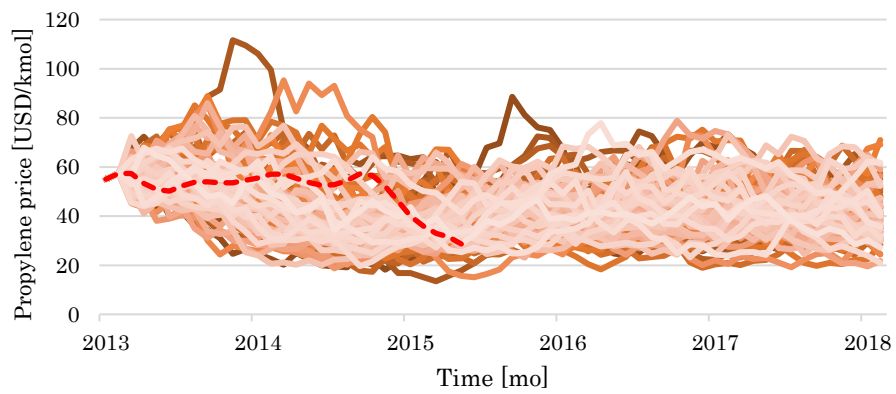


Figure 25: Comparison between the real (blue solid line) and model trends (red dotted line) of benzene (a), propylene (b), and cumene price (c). The validation initial time is April 2013 for the price model of benzene and propylene, and December 2011 for that of cumene.

(a)



(b)



(c)

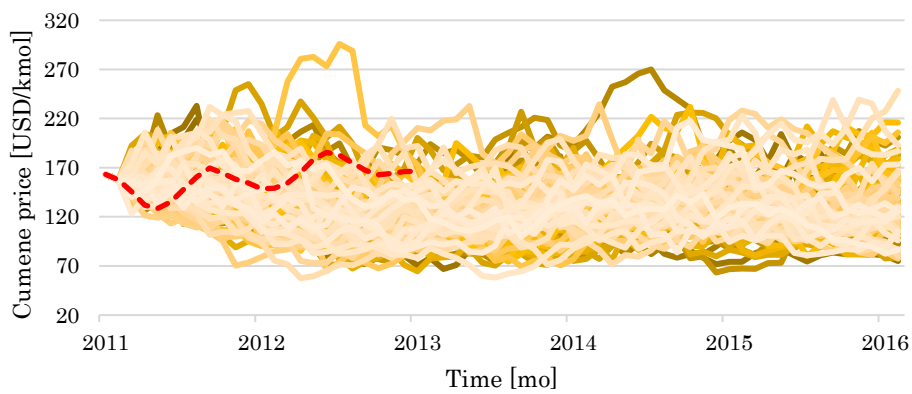


Figure 26: 100 possible benzene (a), propylene (b), and cumene (c) future-price scenarios over a five-year horizon. The red dashed line shows the real price trend of each commodity. The forecast initial time is April 2013 for the price of benzene and propylene, and December 2011 for that of cumene.

The recommended number of scenarios to accomplish a robust economic assessment is a few thousands (Figure 26 shows only 100 scenarios for the sake of drawing clarity).

## 4.5 Econometric models of utilities

Even though there are several utilities that are used in chemical plants, such as electric energy, steam, fuel oil, cooling water, and diathermic and cryogenic fluids, for the sake of brevity this Paragraph focuses on the ones involved in the cumene production process, *i.e.* electric energy and steam.

### 4.5.1 Price model of electric energy

Manca (2016) analyzed in detail how the price of electric energy can oscillate periodically with different characteristic times, *i.e.* from days to weeks, and even up to seasons. In addition, for the Italian market, he found a significant correlation and time delay between electric energy and crude oil price, with the time delay approximating an average value of 3 mo, *i.e.* a quarter. Manca (2016) proposed Equation (21) to forecast the price of electric energy as a function of crude oil quotations:

$$P_{EE,i,j} = a_j + b_j P_{CO,i-t_d} + c_j \sin\left(\frac{2\pi i}{T_j} + \varphi_j\right) \quad (21)$$

Where:

- $P_{EE,i,j}$  is the electric energy price at the  $i$ -th discrete time for the  $j$ -th interval of the day (*i.e.* morning, afternoon, evening, night);
- $a$  and  $b$  are linear regression coefficients that try to catch the long-term dependency of electric energy from crude oil prices;

- $c$  is the proportional constant of the seasonal term based on the  $T$  period and  $\varphi$  phase;
- $t_d$  is the time delay between electric energy prices and crude oil quotations  $P_{CO}$ .

Whenever a model of electric energy price depends explicitly on the crude oil quotation, it is advisable to contextualize it by considering the specific regional values that affect the electric energy price. For instance,  $P_{EE,i,j}$  refers to the Italian market, while  $P_{CO}$  refers to the Brent quotations (which have the highest influence on European markets). The cumene plant described in Paragraph 3.2 is assumed to operate in North America, thus Equation (21) should implement the WTI quotations (Figure 27).

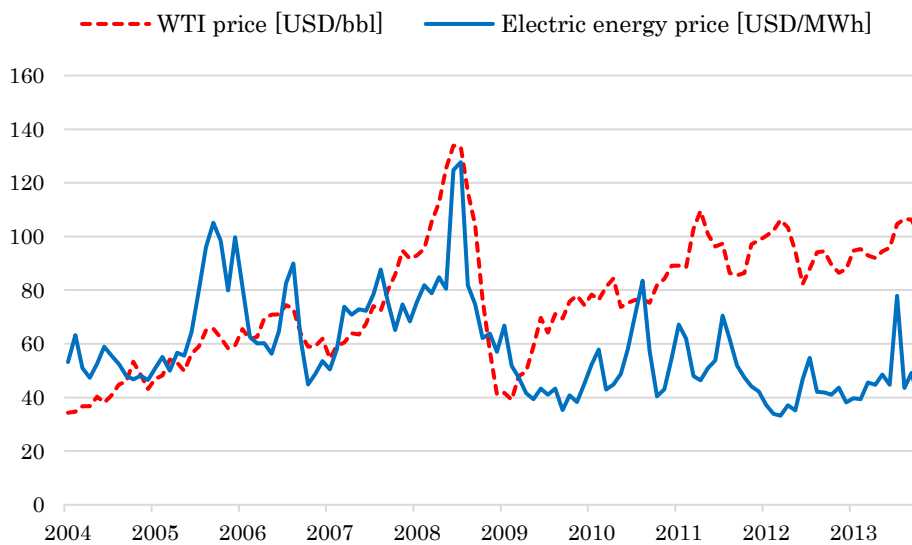


Figure 27: Dynamics of electric energy and WTI prices in the 2004-2013 period.

Unfortunately, Figure 28 shows that there is not a significant correlation between US electric energy and WTI prices. This is probably because less than 1% of all the electric energy in the USA has been generated from crude oil derivatives (*e.g.*, residual fuel oil, petroleum coke) since 2010 (EIA, 2016).

Conversely, nearly 24% of the US electric energy was fueled by natural gas in 2010, while in 2015 natural gas was used for about 33% of the 4 trillion kWh of electric energy generated in the USA (EIA, 2016).

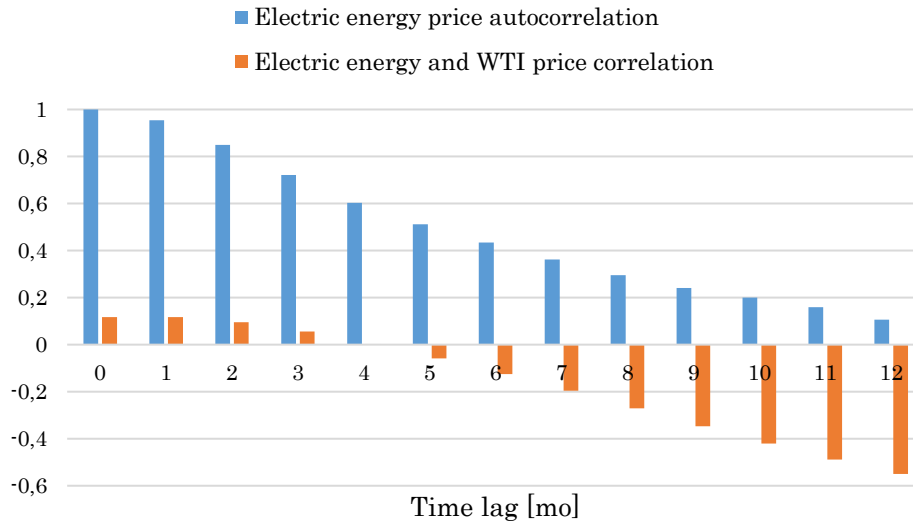


Figure 28: Electric energy price autocorrelation and correlation with WTI quotations.

Figure 29 shows the significant correlation between electric energy and natural gas prices based on the monthly quotations of Figure 15 and Figure 16 over the 2004-2013 period. For the sake of clarity, this work uses the Henry Hub price of natural gas, which is the most widely quoted price in the USA (Brown and Yücel, 2008).

The findings of Figure 28 and Figure 29 call for specific price models of both electric energy and natural gas. Indeed, the price of natural gas can act as the independent variable in the price model of electric energy.

For the sake of consistency, it would be convenient to refer the price of natural gas to the quotation of crude oil, *i.e.* the reference component (Paragraph 4.1). Economic theory suggests that natural gas and crude oil prices should be related because natural gas and crude oil are substitutes in consumption, and complements, as well as rivals, in production (Villar and Joutz, 2006).

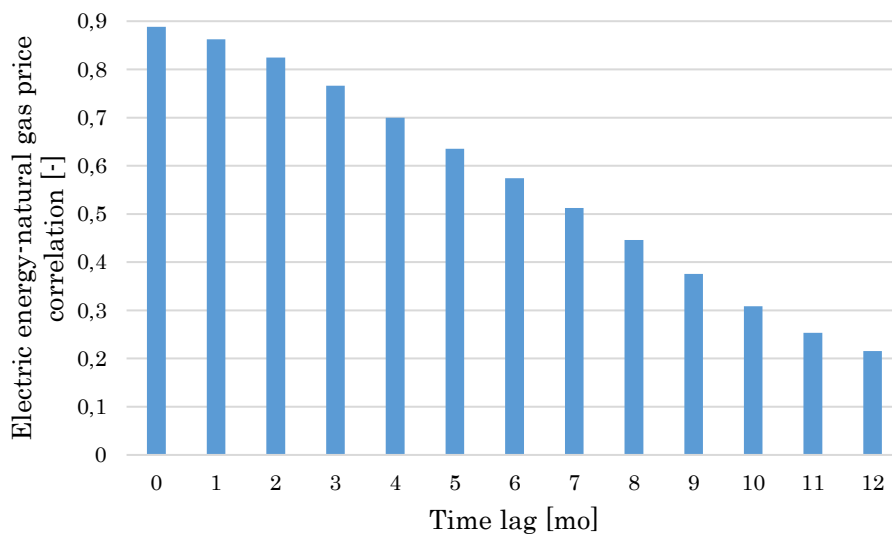


Figure 29: Correlation between electric energy and natural gas prices.

However, there have been periods when natural gas and crude oil prices have appeared to move independently (Figure 30). For instance, natural gas prices rose above their historical relationship with crude oil prices in the 2000-2005 period, after which they fell below (Brown and Yücel, 2008).

In fact, natural gas production expanded by over 20% between 2007 and 2012 thanks to the discovery of shale gas resources and the introduction of new extraction technologies, *i.e.* fracking and horizontal drilling (CME Group, 2014). With a much larger supply, natural gas prices fell by over 50% from 2006 to 2013. Natural gas prices averaged over 7 USD/MBtu during the 2003-2008 period, and dropped below 4 USD/MBtu between 2010 and 2013. Based on Figure 30, natural gas prices are expected to be poorly correlated with WTI quotations, as shown in Figure 31.

However, this should not be considered as a deterrent for further analyses. On the contrary, this suggests increasing both the attention and capability to gather the changes in price and identify the causes (Villar and Joutz, 2006; Brown and Yücel, 2008; Hartley *et al.*, 2008; Atil *et al.*, 2014).

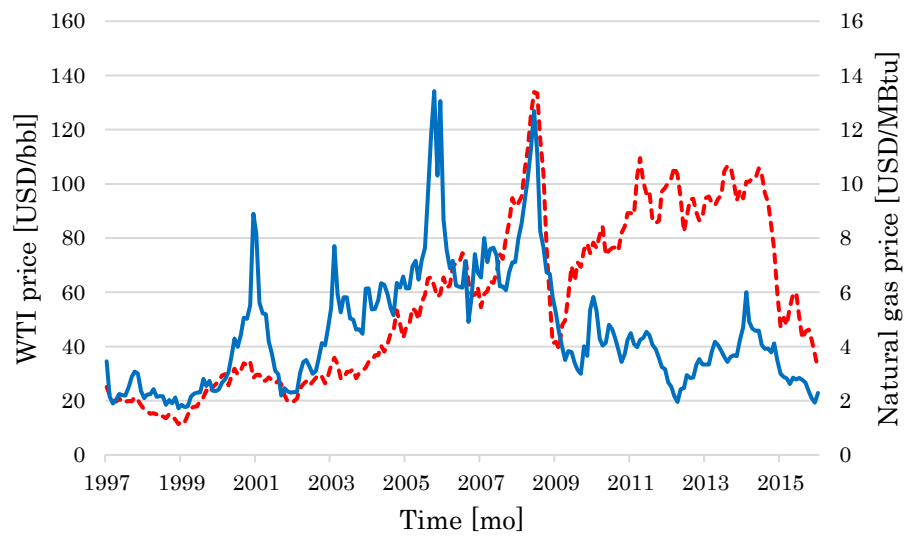


Figure 30: Dynamics of natural gas and WTI prices in the 1997-2015 period.

For now, the econometric model of natural gas can be traced back to the AR models described in Paragraph 4.3.

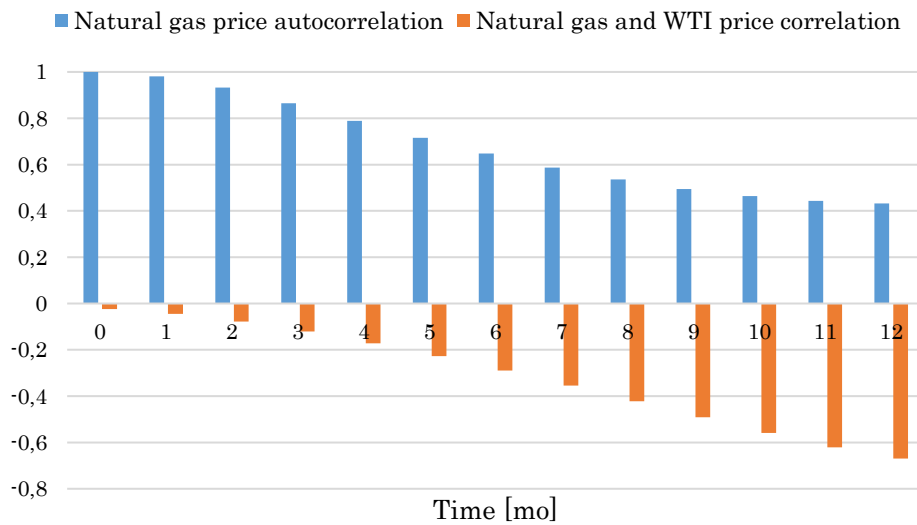


Figure 31: Natural gas price autocorrelation and correlation with WTI quotations over the 2004-2015 period.

According to the results of Figure 31, the AR model of natural gas price assumes the following structure:

$$P_{NG,t} = a_0 + a_1 P_{NG,t-1} + b_1 P_{NG,t-2} \quad (22)$$

The  $a$  and  $b$  parameters of the linear regression are reported in Table 10.

Table 10: Parameters of the linear regression for the price model of natural gas.

$a_0$ [USD/MBtu]	0.2106
$a_1$ [-]	1.7442
$b_1$ [-]	-0.7820
$\bar{R}^2$ [-]	0.9619
$\sigma_{NG}$ [-]	0.0436
$\bar{X}_{NG}$ [-]	-0.0087

There is a good agreement between real and model prices (Figure 32), as measured by the coefficient of determination  $\bar{R}^2$  (Table 10).

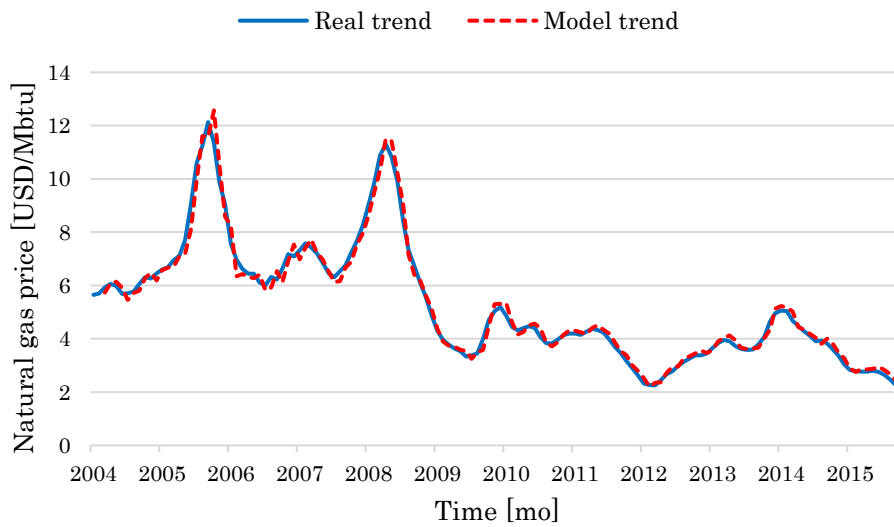


Figure 32: Comparison between real and model trend of natural gas prices over the 2004-2015 period. The validation initial time is October 2013.

Figure 33 shows 100 different price scenarios generated from the econometric model of Equation (22) based on the standard deviation  $\sigma_{NG}$  and the average value  $\bar{X}_{NG}$  of the relative errors between real and model prices (Table 10).

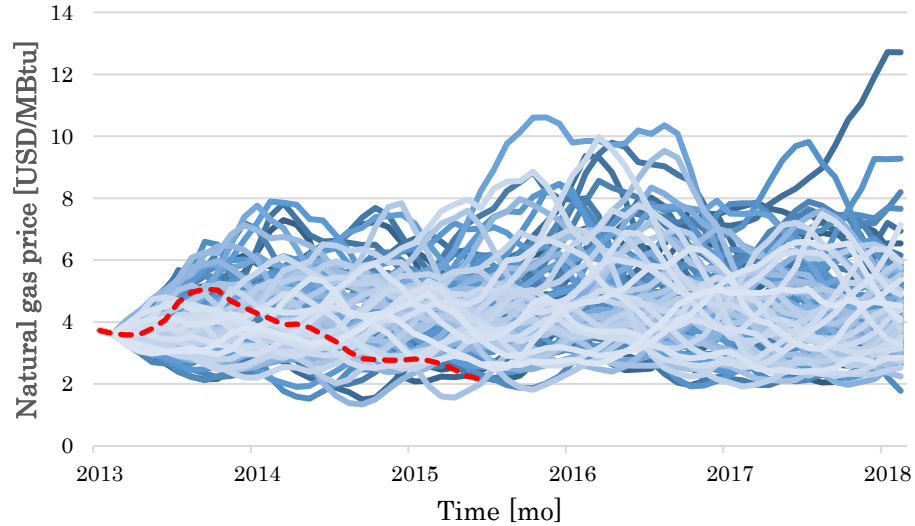


Figure 33: 100 possible natural gas future-price scenarios over a five-year horizon. The red dashed line shows the real price trend. The forecast initial time is October 2013.

Differently from Manca (2016), this work adopts an ADL model to forecast the price of electric energy based on the monthly quotations of the US market. According to the results of Figure 28 and Figure 29, the price model of electric energy can be formulated as follows:

$$P_{EE,t} = a_0 + a_1 P_{NG,t} + b_1 P_{EE,t-1} \quad (23)$$

Where the subscript  $EE$  refers to electric energy. Table 11 reports  $a$  and  $b$  values of the linear regression. There is a good agreement between real and model prices (Figure 32), as measured by the coefficient of determination  $\bar{R}^2$  (Table 11). Figure 35 shows 100 different price scenarios generated from the econometric model of Equation (23) based on the standard deviation  $\sigma_{EE}$  and

the average value  $\bar{X}_{EE}$  of the relative errors between real and model prices (Table 11).

Table 11: Parameters of the linear regression for the price model of electric energy.

$a_0$ [USD/MWh]	4.7255
$a_1$ [MBtu/MWh]	2.0285
$b_1$ [-]	0.7209
$\bar{R}^2$ [-]	0.9560
$\sigma_{EE}$ [-]	0.0680
$\bar{X}_{EE}$ [-]	0.0002

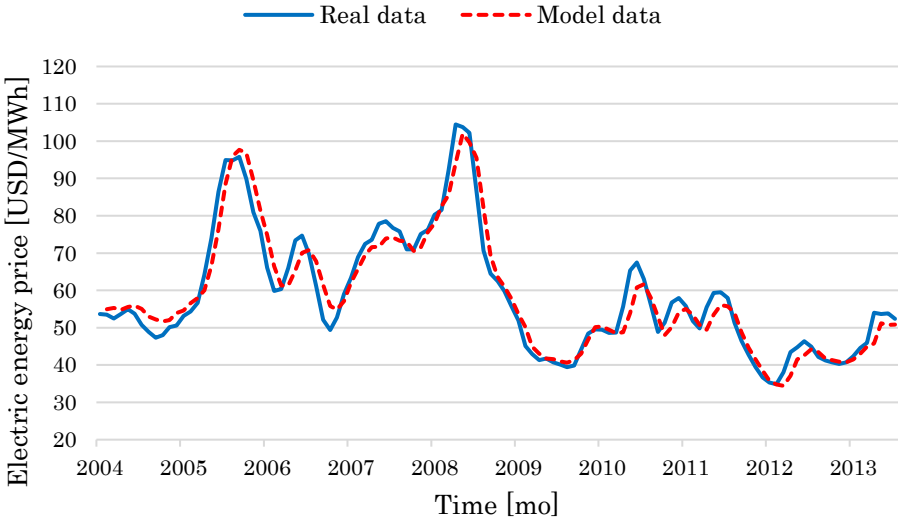


Figure 34: Comparison between real and model trend of electric energy prices over the 2004-2013 period. The validation initial time is December 2011.

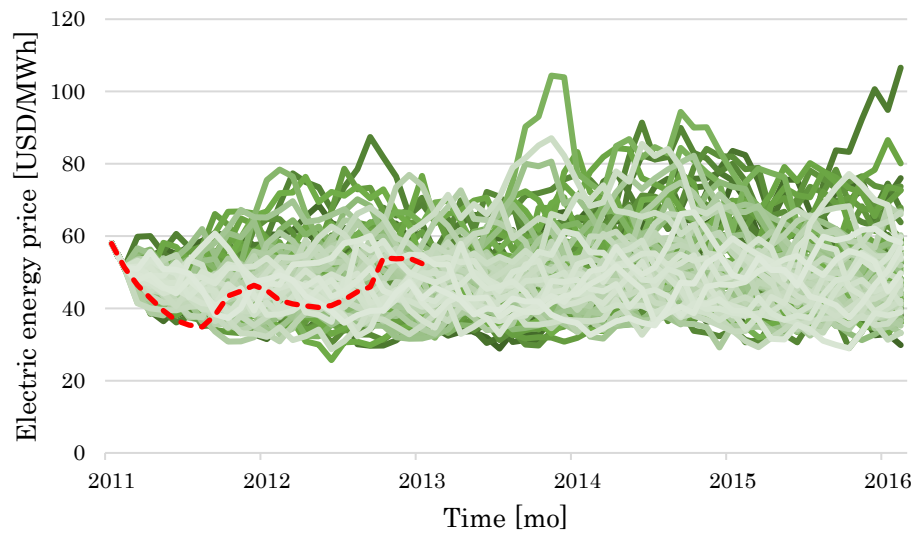


Figure 35: 100 possible electric energy future-price scenarios over a five-year horizon. The red dashed line shows the real price trend. The forecast initial time is December 2011.

#### 4.5.2 Price model of steam

As already mentioned in Paragraph 3.2.1, this work considers the steam cost as proportional to that of the fuel (*i.e.* natural gas) used in the boiler.

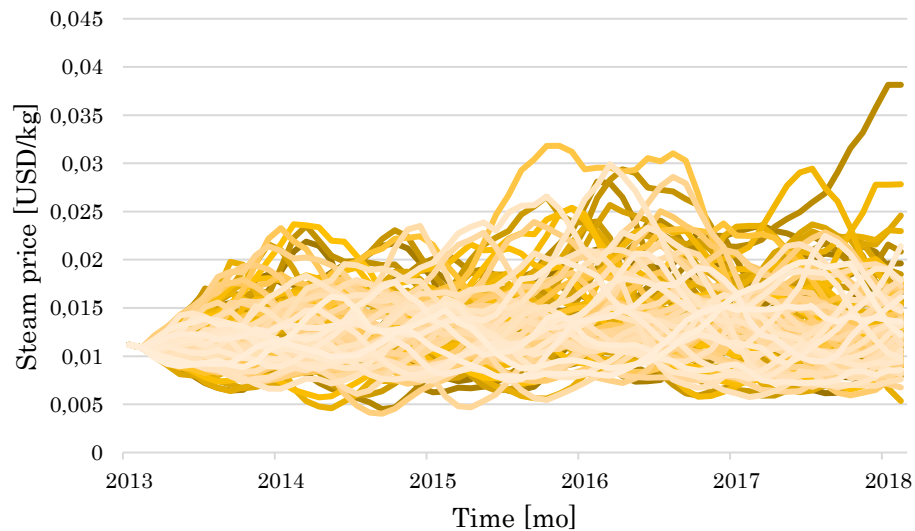


Figure 36: 100 possible steam price scenarios over a five-year horizon. Past price trend was not available.

For the sake of completeness, the effective cost of steam should include the operating costs associated with raw water supply, boiler feed water treatment, feedwater pumping power, combustion air fan power, sewer charges for boiler blowdown, ash disposal, environmental emission control, maintenance, and labor. However, Equation (6) provides a rather good first approximation for the cost of steam generation. Figure 36 shows 100 different economic scenarios generated from Equation (6) based on the econometric model of Equation (22).

#### 4.6 Use of the identified econometric models

Paragraphs 4.3-4.5 showed a systematic approach to finalize the econometric models of raw materials, (by)products, and utilities that contribute to OPEX terms of chemical plants. These models can be used to produce a set of economic scenarios that are distributed according to the modeled fluctuations of dependent variables (*i.e.* commodities and utilities) and the stochastic contribution of the independent variable (*i.e.* the reference component).

As far as PCD is concerned, the economic assessment of OPEX terms can be extended from the original approach proposed by Douglas (1988) by introducing a direct time dependence in the formulation of Douglas' economic potentials, which result into DEPs (Manca and Grana, 2010; Manca *et al.*, 2011).

This work proposes the following DEPs to assess the economic sustainability of the cumene plant described in Paragraph 3.2:

$$\begin{aligned}
 Revenues_{2,t,k} \left[ \frac{USD}{h} \right] &= \max \left[ 0, (P_{C,t,k} F_C - P_{B,t,k} F_B - P_{P,t,k} F_P) \right] \\
 DEP_{2,k} \left[ \frac{USD}{y} \right] &= \frac{\sum_{t=1}^{nMonths} (Revenues_{2,t,k} \cdot nHpM)}{nMonths/12} \quad k = 1, \dots, nScenarios
 \end{aligned} \tag{24}$$

$$DEP3_k \left[ \frac{USD}{y} \right] = \frac{\sum_{t=1}^{nMonths} (Revenues2_{t,k} \cdot nHpM)}{nMonths/12} - \frac{CAPEX_{Reactor}}{nMonths/12} \quad (25)$$

$k = 1, \dots, nScenarios$

$$Revenues4_{t,k} \left[ \frac{USD}{h} \right] = \max \left[ 0, (P_{C,t,k} F_C - P_{B,t,k} F_B - P_{P,t,k} F_P - P_{EE,t,k} W - P_{S,t,k} F_S) \right]$$

$$DEP4_k \left[ \frac{USD}{y} \right] = \frac{\sum_{t=1}^{nMonths} (Revenues4_{t,k} \cdot nHpM)}{nMonths/12} - \frac{\sum_{e=1}^{nEquip} CAPEX_e}{nMonths/12} \quad (26)$$

$k = 1, \dots, nScenarios$

Where  $P$  and  $F$  are the prices/costs of process streams and their corresponding flow rates, respectively;  $nHpM$  and  $nEquip$  are the number of production hours in a month and the number of process units, respectively;  $W$  is the power absorbed by pumps.  $DEP5$  is intentionally not formalized since the optimization performed on the network of heat exchangers, as suggested by Douglas (1988), would not introduce additional bits of information relevant to the PCD framework.

Equations (24)-(26) consider both CAPEX and OPEX terms. The max function summarizes the concept that the plant should be operated only when the revenues are positive, *i.e.* the incomes are higher than the expenditures, whose role in terms of price/costs is updated according to the granularity of the problem (*i.e.* monthly quotations for the cumene case study). However, the proposed economic assessment is quite simplified. For instance, the unavoidable transients produced by the startup and shutdown of the plant are not considered when evaluating the DEPs. The absence of transients assumes that the plant can turn on and off instantaneously. If not, the transients would produce some off-specs on the production quality thus introducing further elements to be discussed and possibly quantified. In addition, no investigation

about the mechanical and thermal stresses on the involved equipment has been performed.

The cornerstone of the PCD methodology is symbolized by the *nScenarios* parameter that calls for quantifying a set of different scenarios subject to the price/cost trajectories obtained by the econometric models through their stochastic contribution. Therefore, the *k* subscript, which connotes every DEP, takes to a probabilistic concept of PCD that is grounded on the distribution of possible economic scenarios for a specific process/plant. A necessary condition for economic sustainability is that DEPs are positive. This condition can be tightened to higher DEP values to meet a user-defined threshold that makes the investment/operation appealing respect to different financial opportunities (Manca, 2015).

# 5 The waste reduction algorithm

Traditionally, the methods devised in PSE, to assist in the design and operation of chemical processes, have concentrated on finding the solution that maximizes the economic performance while satisfying a set of mass balances and capacity constraints imposed by the plant typology (Guillén-Gosálbez *et al.*, 2008). In past years, however, there was a growing awareness of the importance of including environmental concerns in the design of chemical processes (Grossmann and Guillén-Gosálbez, 2010). This trend was motivated by several issues, a major one being the pressure placed on the chemical industry to take charge of climate change, degradation of air, water, and land, depletion of natural resources (*e.g.*, fresh water and minerals), and loss of agricultural land due to deforestation and soil erosion (Bakshi and Fiksel, 2003; Guillén-Gosálbez and Grossmann, 2009).

For these reasons, numerous approaches were proposed in the literature to mitigate the environmental impact of chemical processes. Burgess and Brennan (2001), García-Serna *et al.* (2007), and Abbaszadeh and Hassim (2014) provide extensive reviews of various methods for assessing the

environmental friendliness of products and processes. For instance, LCA is a promising tool to evaluate “*the environmental consequences of a product system or activity, by quantifying the energy and materials used, the wastes released to the environment, and assessing the potential environmental impacts of those energy, materials, and wastes*” (Jiménez-González *et al.*, 2000). However, there are some drawbacks in the application of LCA to the early stages of process design. In fact, LCA is supposed to assess the environmental performance of a product system from the *cradle* of primary resources to the *grave* of recycling or safe disposal (Azapagic, 1999; Clift, 2006), thus well apart from the process section to be designed. A critical point is the large amount of information required over the entire life cycle, and the lack of public data due to legal or intellectual property concerns (Tugnoli *et al.*, 2011). At the early design stage, extensive data related to process alternatives are not available, and the focus is more on excluding the worst alternatives instead of finding the best one (Diwekar and Shastri, 2011). In this respect, a data-intensive approach is not helpful, whereas the estimation of site-specific information becomes feasible and a plausible alternative to life cycle inventory (Jiménez-González *et al.*, 2000).

Indeed, some authors focus on decreasing the environmental impact of production sites, thus performing a *cradle-to-gate* analysis that covers the stages that go only from manufacturing to the factory gate, *i.e.* before products are delivered to the customer (Guillén-Gosálbez *et al.*, 2008; Othman *et al.*, 2010; Ouattara *et al.*, 2012; Ruiz-Mercado *et al.*, 2012; Yue and You, 2013). For instance, the Waste Reduction (WAR) algorithm considers only the manufacturing step of the entire life cycle of a product (Figure 37), thus it neglects raw material acquisition and product distribution, use, disposal, and recycle (Young *et al.*, 2000). However, it is a simple tool to be used by design engineers to evaluate the environmental friendliness of a process (Young and Cabezas, 1999).

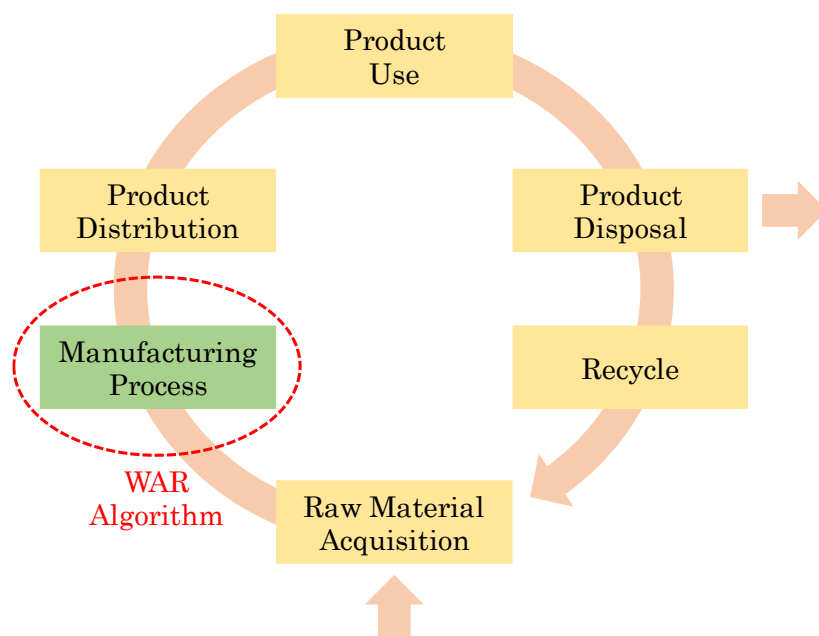


Figure 37: Applicability of WAR algorithm to product life cycle (adapted from Young and Cabezas, 1999).

Recently, the WAR algorithm was used to describe the environmental performance of unit operations (Chen and Feng, 2005; Ramzan *et al.*, 2008), optimize chemical manufacture and recovery (Kim and Smith, 2004; Shadiya *et al.*, 2012), design eco-efficient biodiesel processes (Couto *et al.*, 2011; Marulanda, 2012; Othman *et al.*, 2010), and model industrial utility systems (Idris *et al.*, 2016). This work applies the WAR algorithm to evaluate the environmental impact of both the cumene plant and the energy consumed within the process. For the sake of clarity, Paragraph 5.1 presents a summary of the theoretical background.

## 5.1 Impact balance

The WAR algorithm determines the potential environmental impact (PEI) of a chemical process. The PEI of a given quantity of material or energy can be defined as the effect that this material or energy would have if it were to be emitted into the environment (Young and Cabezas, 1999). This implies that

the PEI of a particular emission is probabilistic in nature, and an average estimate of the effect that this emission is likely to have (Young *et al.*, 2000). Cabezas *et al.* (1999) proposed to consider a balance equation describing the PEI of a manufacturing process to incorporate environmental aspects into process design. Young and Cabezas (1999) improved that balance including the energy generation process (Figure 38). For steady state processes, the PEI balance equation is:

$$\dot{I}_{in}^{(cp)} + \dot{I}_{in}^{(ep)} - \dot{I}_{out}^{(cp)} - \dot{I}_{out}^{(ep)} - \dot{I}_{we}^{(cp)} - \dot{I}_{we}^{(ep)} + \dot{I}_{gen}^{(syst)} = 0 \quad (27)$$

Where  $\dot{I}_{in}^{(cp)}$  and  $\dot{I}_{out}^{(cp)}$  are the input and output PEI to the chemical process,  $\dot{I}_{in}^{(ep)}$  and  $\dot{I}_{out}^{(ep)}$  are the input and output PEI to the energy generation process,  $\dot{I}_{we}^{(cp)}$  and  $\dot{I}_{we}^{(ep)}$  are the output PEI associated with waste energy lost from chemical process and energy generation, and  $\dot{I}_{gen}^{(syst)}$  is the rate of PEI generation inside the system.

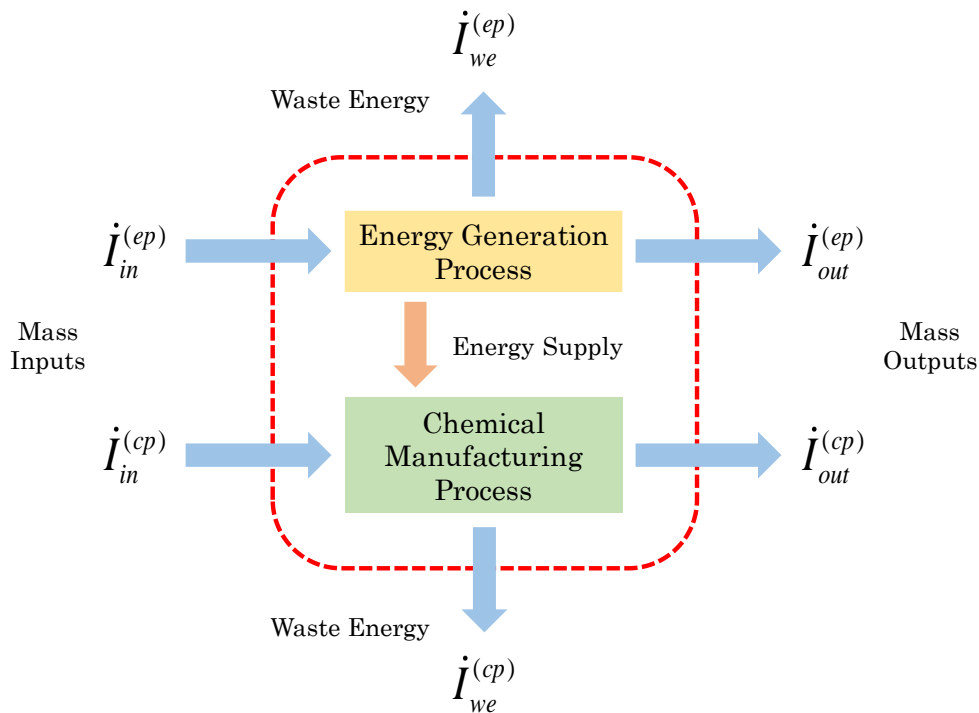


Figure 38: System battery limits for PEI calculation (adapted from Young *et al.*, 2000).

As observed by Young and Cabezas (1999), chemical plants do not emit large amounts of waste energy generally, and the PEI associated with the emission of energy is usually negligible compared to the PEI associated with the emission of mass. This reduces Equation (27) to:

$$\dot{I}_{in}^{(cp)} + \dot{I}_{in}^{(ep)} - \dot{I}_{out}^{(cp)} - \dot{I}_{out}^{(ep)} + \dot{I}_{gen}^{(syst)} = 0 \quad (28)$$

## 5.2 Application to the cumene plant

As already mentioned, this work focuses on decreasing the environmental impact of the cumene production plant (Paragraph 3.2), thus the downstream processes are neglected, while the upstream/input processes are included within the system battery limits. Nevertheless, this spatially reduced approach could be easily extended to include other stages in the life cycle of the product. There are two classes of indicators that can be derived from Equation (28): those associated with PEI generation, and those associated with PEI output. Regarding PEI generation,  $\dot{I}_{gen}^{(syst)}$  would be a useful indicator of the internal environmental efficiency of a process (Young and Cabezas, 1999). In fact, it gives emphasis to the contribution of raw materials to the total PEI. For instance, output indicators do not capture the impact of switching from a non-renewable feedstock to a biomass derivative (Seay and Eden, 2009). However, this is not the case of cumene manufacture, which is a well-established process based on benzene and propylene (Degnan *et al.*, 2001). This consideration does not apply to energy generation as far as renewables are concerned. For now, being natural gas a major contributor to electric energy and steam generation (Paragraph 4.5), the relative importance of  $\dot{I}_{in}^{(cp)}$  and  $\dot{I}_{in}^{(ep)}$  will not be considered. Conversely, this work uses the total rate of PEI output,  $\dot{I}_{out}^{(tot)}$ , to characterize the environmental efficiency of the cumene plant:

$$\dot{I}_{out}^{(tot)} = \dot{I}_{out}^{(cp)} + \dot{I}_{out}^{(ep)} \quad (29)$$

Another way to express the PEI output is to divide  $\dot{I}_{out}^{(tot)}$  by the mass flow rate  $\dot{P}_p$  of product  $p$ :

$$\hat{I}_{out}^{(tot)} = \frac{\dot{I}_{out}^{(tot)}}{\sum_p \dot{P}_p} \quad (30)$$

$\hat{I}_{out}^{(tot)}$  allows comparing different process alternatives based on the PEI emitted by the process per unit mass of products, thus meaning that comparisons can be made regardless of manufacturing plant size. Based on Equation (29), it is necessary to relate  $\dot{I}_{out}^{(tot)}$  to measurable quantities, such as stream flow rates and compositions. For instance,  $\dot{I}_{out}^{(cp)}$  can be formulated as follows:

$$\dot{I}_{out}^{(cp)} = \sum_j^{cp} \dot{M}_j^{(out)} \sum_k x_{kj} \psi_k \quad (31)$$

Where  $\dot{M}_j^{(out)}$  is the output mass flow rate of stream  $j$ ,  $x_{kj}$  is the mass fraction of chemical  $k$  in stream  $j$ , and  $\psi_k$  is the overall PEI for chemical  $k$ . It is worth observing that Equation (31) is a first order approximation that does not include the synergistic effects that can occur when multiple chemicals are present (Cabezas *et al.*, 1999). Young and Cabezas (1999) calculate the overall PEI for chemical  $k$ ,  $\psi_k$ , as:

$$\psi_k = \sum_l \alpha_l \psi_{kl}^s \quad (32)$$

Where  $\psi_{kl}^s$  is the specific PEI of chemical  $k$  for the impact category  $l$ , and  $\alpha_l$  is the weighing factor of the impact category  $l$ . Indeed, the implementation of the WAR algorithm requires the definition of impact categories for which  $\psi_{kl}^s$

can be relatively quantified. Based on the study by Heijungs *et al.* (1992), Young and Cabezas (1999) selected a list of eight environmental impact categories that fall into four general areas of concerns: human toxicity, ecological toxicity, global atmospheric impacts, and regional atmospheric impacts (Table 12).

Table 12: Impact categories and measures of impact category (adapted from Barrett *et al.*, 2011). For the sake of clarity, LD<sub>50</sub> and LC<sub>50</sub> are respectively the lethal dose and concentration that cause death in 50% of the test specimens. The measure of aquatic toxicity is referred to fathead minnow that is a small fish species. OSHA PEL is the permissible exposure limit established by the US Occupational Safety and Health Administration.

General impact category	Impact category	Measure of impact category
Human toxicity	Ingestion	LD <sub>50</sub>
	Inhalation/dermal	OSHA PEL
Ecological toxicity	Aquatic toxicity	Fathead minnow LC <sub>50</sub>
	Terrestrial toxicity	LD <sub>50</sub>
Global atmospheric impacts	Global warming potential	GWP
	Ozone depletion potential	ODP
Regional atmospheric impacts	Acidification potential	AP
	Photochemical oxidation potential	PCOP

The weighing factors  $\alpha_i$  in Equation (32) are used to express the relative importance of the impact categories. The user should assign the weighing factors according to site-specific concerns. This work discusses an illustrative case study with no specific site in mind, thus the weighing factors for all the categories will be assigned the same unity value.

The  $\psi_{kl}^s$  values are accessible from the WAR algorithm add-in included in the COCO/COFE simulator released by AmsterCHEM in collaboration with the US EPA (Barrett *et al.*, 2011). For the sake of clarity, the  $\psi_{kl}^s$  are normalized within each impact category (Table 13). In fact, a proper normalization ensures that values of different categories contain the same units, and have on average

equivalent scores. In this respect, the unit for both  $\psi_k$  and  $\psi_{kl}^s$  should be PEI/kg of chemical  $k$  (Young and Cabezas, 1999; Young *et al.*, 2000; Kim and Smith, 2004; Chen and Feng, 2005). The weighing factors  $\alpha_l$  should be, of course, dimensionless.

This work considers only the non-product streams in the calculation of  $\dot{I}_{out}^{(tot)}$ . This ensures that the producer is not directly penalized by the production of a chemical that has a high PEI value. However,  $\dot{I}_{out}^{(cp)}$  can account for raw material and product streams as fugitive emissions by means of a 0.001 multiplying factor (Smith *et al.*, 2004), since chemical plants are likely to have relevant fugitive losses (Burgess and Brennan, 2001).

Table 13: Normalized impact scores of the chemicals involved in both cumene production and energy generation as provided by the WAR algorithm add-in included in the COCO/COFE simulator (Barrett *et al.*, 2011). The ODP is omitted as none of the chemicals contributes significantly to that category.

Chemical	HTPI	HTPE	TTP	ATP	GWP	PCOP	AP
Benzene	1.38E-01	2.26E-01	1.38E-01	1.06E-01	-	2.29E-01	-
Propylene	-	8.42E-03	-	-	-	3.83	-
Propane	-	4.02E-03	-	-	-	1.51E-01	-
Cumene	1.57E-01	2.96E-02	1.57E-01	4.11E-02	-	8.11E-01	-
DIPB	1.34E-01	-	1.34E-01	6.50	-	1.13	-
NO <sub>2</sub>	-	8.05E-01	-	-	-	1.57	1.08E-01
Carbon Monoxide	-	1.32E-01	-	-	-	1.73E-01	-
CO <sub>2</sub>	-	8.05E-04	-	-	2.44E-04	-	-
SO <sub>2</sub>	-	5.57E-01	-	-	-	1.47E-01	1.54E-02
Methane	-	1.10E-02	-	-	5.61E-03	4.55E-01	-

Similarly to  $\dot{I}_{out}^{(cp)}$ , the rate of PEI leaving the energy generation process,  $\dot{I}_{out}^{(ep)}$ , can be formulated as:

$$i_{out}^{(ep)} = \sum_j^{ep-g} \dot{M}_j^{(out)} \sum_k x_{kj} \psi_k \quad (33)$$

Where the subscript *ep-g* means that Equation (33) considers only the gaseous output streams, as the PEI of solid outputs can be assumed negligible compared to those of the gas outputs (Young and Cabezas, 1999). For the case study discussed in this work, the predominant emissions from a combined cycle gas turbine (CCGT) and a large wall-fired boiler were used. A CCGT is essentially an electric power plant in which a gas turbine and a steam turbine are used in combination to achieve greater efficiency than would be possible independently (Causey, 2000). A large wall-fired boiler is commonly used to provide large amounts of process steam, and is characterized by multiple individual burners located on a single wall or on opposing walls of the furnace (EPA, 2016). As already mentioned in Paragraph 4.5, natural gas is one of the major combustion fuels used to both generate electric energy and produce industrial process steam. Therefore, Equation (33) considers the emission factors from natural gas-fired turbines and boilers (Table 14) multiplied by the rate of energy input required for the operation of the plant.

Table 14: Emission factors from natural gas-fired turbines and boilers (EPA, 2016). For the sake of clarity, values are referred to uncontrolled turbine and boiler types, and consider a power plant heat rate of 0.010 MBtu/kWh, a fuel heat content of 0.036 MBtu/m<sup>3</sup>, and a fuel energy per mass of steam equal to 0.003 MBtu/kg (EIA, 2016; DOE, 2016).

Chemical	CCGT	Large wall-fired boiler
	Emission factor [kg/MBtu]	Emission factor [kg/m <sup>3</sup> ]
NO <sub>2</sub>	1.45E-01	3.04E-03
Carbon monoxide	3.72E-02	1.34E-03
CO <sub>2</sub>	4.99E+01	1.92
SO <sub>2</sub>	1.54E-03	9.60E-06
Methane	3.90E-03	3.68E-05

Table 15 provides the results for the base case study (Pathak *et al.*, 2011). The  $\psi_k$  values show that DIPB, *i.e.* the byproduct, is the most environmentally unfriendly chemical involved in the process. However, the  $\psi_k$  values depend on the uniform weighing of the impact categories (Table 13). Therefore, if different weighing factors were used, the  $\psi_k$  values would be different. The total rate of PEI output for chemical  $k$ ,  $\dot{I}_{out,k}^{(tot)}$ , can be calculated from either Equation (31) or Equation (33) depending on whether  $k$  leaves the chemical process or the energy generation process.  $\dot{I}_{out,k}^{(tot)}$  shows that DIPB is not likely to realize its PEI as it is almost completely consumed within the transalkylator (Paragraph 3.2). Conversely, propylene is the most significant contributor to  $\dot{I}_{out}^{(tot)}$ .

Based on Table 13 and Table 15, Figure 39 shows the PEI output per unit mass of cumene,  $\hat{I}_{out}^{(tot)}$ , for each impact category as calculated for the base case study.

Table 15: Output mass flow rates, overall PEI, and total rate of PEI output for the chemicals involved in both cumene production and energy generation as calculated for the base case study. Overall PEI and total rate of PEI output result from the uniform weighing of the impact categories.

Chemical	Mass flow [kg/h]	$\psi_k$ [PEI/kg]	$\dot{I}_{out,k}^{(tot)}$ [PEI/h]
Benzene	22.537	0.837	18.863
Propylene	53.473	3.838	205.251
Propane	232.293	0.155	36.010
Cumene	12.682	1.196	15.164
DIPB	0.001	7.898	0.010
NO <sub>2</sub>	3.624	2.483	8.999
Carbon Monoxide	1.594	0.305	0.486
CO <sub>2</sub>	2275.783	0.001	2.387
SO <sub>2</sub>	0.012	0.719	0.008
Methane	0.045	0.472	0.021

As a quick reference, the  $\hat{I}_{out}^{(tot)}$  value for the cumene process as in the base case study is quite low if compared with that of other processes available in the literature, such as acrylic acid production, *i.e.* 0.4 PEI/kg (Young and Cabezas, 1999), and allyl chloride production, *i.e.* 0.3 PEI/kg (Young *et al.*, 2000). However, they involve a higher number of units (*e.g.*, absorbers, extractors, compressors), utilities, and waste streams than that of the cumene plant.

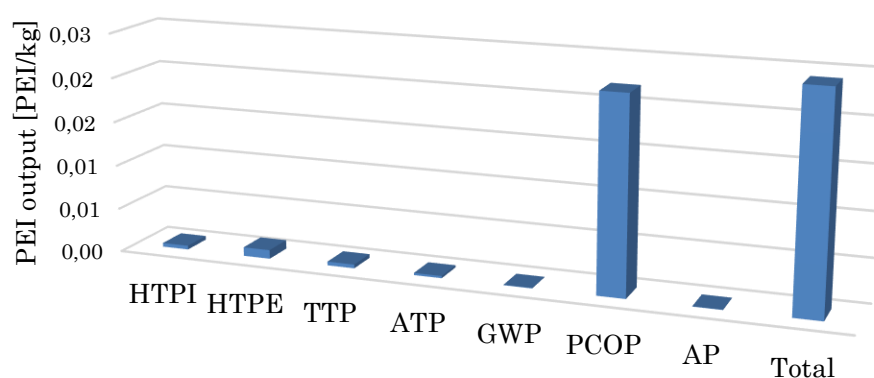


Figure 39: PEI output per unit mass of cumene for each of the impact categories as calculated for the base case study. The ODP is omitted as none of the chemicals contributes to that category.

From Figure 39, it is quite evident that the major concern is PCOP, *i.e.* smog formation (Heijungs *et al.*, 1992). Table 13 shows that propylene plays the most significant role in that category. As a primary improvement, the findings of Table 15 and Figure 39 suggest reducing the loss of propylene by changing the reactor operating conditions. In this respect, the WAR algorithm can be used in conjunction with PCD to design a cumene plant that is environmentally and economically sustainable. Indeed, whenever a process is modified to reduce waste, there is a consequent change in the associated economics. While it is often possible to make environmental improvements from an inspection of the

process flowsheet, there are several situations where a more systematic approach is required (Cabezas *et al.*, 1999). As illustrated in Chapter 6, this can be done by employing the indicators of Equations (26) and (29) as objective functions in a MOO problem.

# 6 Multi-objective optimization

As defined by Marler and Arora (2004), MOO is “*the process of optimizing systematically and simultaneously a collection of objective functions*”. MOO, also known as multi-criteria optimization, is widely applied in both process synthesis and SCM/EWO to quantify the tradeoffs among different conflicting criteria. In this respect, MOO is well suited to incorporate environmental concerns in the optimization of chemical processes, since it allows treating them as decision-making objectives (Grossmann and Guillén-Gosálbez, 2010). For this purpose, the synthesis problem can be formulated as a MOO of the following form:

$$\begin{aligned} \text{Min}_x \quad & F(\mathbf{x}) = [F_1(\mathbf{x}), F_2(\mathbf{x}), \dots, F_n(\mathbf{x})] \\ \text{s.t.} \quad & h_j(\mathbf{x}) = 0 \quad j = 1, 2, \dots, n_e \\ & g_j(\mathbf{x}) \leq 0 \quad j = 1, 2, \dots, n_i \\ & \mathbf{x}_l < \mathbf{x} < \mathbf{x}_u \end{aligned} \tag{34}$$

Where:

- $F(\mathbf{x})$  is the vector of  $n$  objective functions  $F_i(\mathbf{x})$  to be simultaneously optimized;
- $\mathbf{x}$  is the vector of design variables (*e.g.*, flows, operating conditions, equipment sizes) with lower ( $x_l$ ) and upper ( $x_u$ ) bounds;
- $n_e$  and  $n_i$  are the number of equality ( $h$ ) and inequality ( $g$ ) constraints (*e.g.*, mass and heat balances, design specifications), respectively.

In contrast to single-objective optimization, there is no single global solution to a MOO problem, and it is often necessary to determine a set of points that all fit a predetermined definition for an optimum. The predominant concept in defining an optimal point is that of Pareto optimality (Pareto, 1906), according to which “a point,  $\mathbf{x}^* \in X$ , is Pareto optimal if there does not exist another point,  $\mathbf{x} \in X$ , such that  $F(\mathbf{x}) \leq F(\mathbf{x}^*)$ , and  $F_i(\mathbf{x}) < F_i(\mathbf{x}^*)$  for at least one function” (Marler and Arora, 2004), where  $X$  is the feasible design space, *i.e.* the set of vectors  $\mathbf{x}$  that satisfy all the constraints and bounds of Equation (34). In other words, a point is Pareto optimal if there are not any points that improve at least one objective function without detriment to another function. Therefore, some tradeoffs among objective functions are necessary to reach the preferred optimal solution, *i.e.* the optimal flowsheet configuration and its corresponding operating conditions (Guillén-Gosálbez *et al.*, 2008).

## 6.1 Application to the cumene plant

The optimal design of the cumene plant (Paragraph 3.2) offers some opportunities to improve both the economic and environmental performance by decreasing the formation of byproduct, and reducing the loss of raw materials and final product.

As reported by Pathak *et al.* (2011), the most important design variables are the reactor inlet temperature, the reactor size, the reactor pressure, and the

benzene recycle fraction. The reactor inlet temperature affects both conversion and selectivity. In fact, higher temperatures increase reaction rates and consequently the conversion, as shown in Figure 40(a). At the same time, higher temperatures decrease the selectivity, since the activation energy of the undesired reaction is higher than that of the synthesis reaction (Table 4), as shown in Figure 40(b).

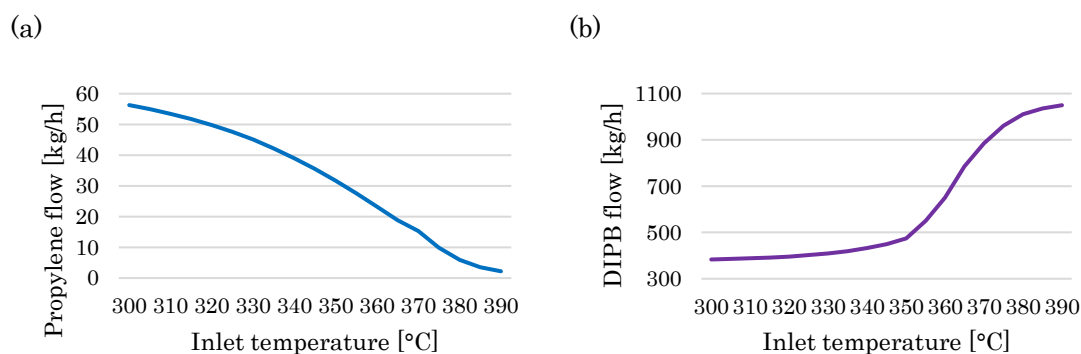


Figure 40: Propylene (a) and DIPB outlet flow (b) as a function of the inlet temperature (for a reactor length of 8 m as an example). It is worth observing that propylene conversion is directly proportional to cumene production since unreacted propylene is not recovered.

The reactor size has a relevant impact on the performance of the system. As the reactor size increases, conversion improves (Figure 41), even though both vessel and catalyst cost increase. However, an increase in the reactor size allows decreasing the reactor inlet temperature, which improves the selectivity. As far as the reactor pressure is concerned, it is worth operating at the maximum allowable pressure as the reaction occurs with a decrease in the number of moles (Table 4). For this reason, in this work the reactor pressure is fixed at 25 bar as suggested by Pathak *et al.* (2011) and not optimized.

Eventually, the recycle of benzene affects a number of important variables. For instance, the production of DIPB decreases as more benzene is recycled, but total capital and energy costs increase due to a larger recycle column (Pathak *et al.*, 2011). In summary, it is possible to improve the selectivity by either decreasing the reactor inlet temperature or increasing the benzene recycle

fraction. For the sake of simplicity and robust flowsheet convergence, this work adopts as design variables only the reactor inlet temperature and vessel length. Such a number of design variables is low if compared to other optimization problems in the literature (Gera *et al.*, 2012; Norouzi and Fatemi, 2012, Sharma *et al.*, 2013). However, this matter is not much relevant, as aim of this work is to illustrate a methodology that can account for both environmental impact and prices/costs volatility to improve the feasibility studies of chemical plants in the direction of both economic and environmental sustainability.

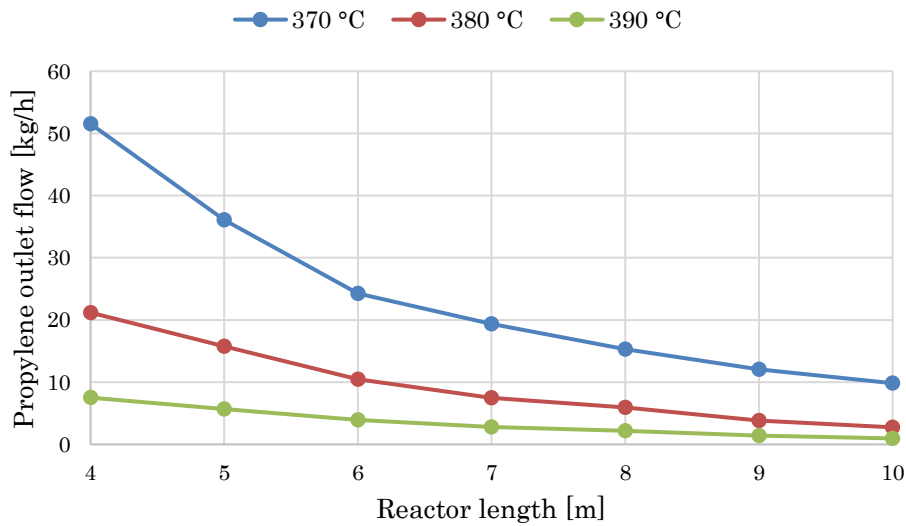


Figure 41: Propylene outlet flow as a function of reactor length at different inlet temperatures.

For the case study discussed in this work, two different objective functions are considered. The first one is the sum of  $DEP4_k$  values for the  $k$ -th economic scenario throughout the operational life span of the plant:

$$Cumulated DEP4_k = \sum_{t=1}^{nMonths} DEP4_{t,k} \quad k = 1, \dots, nScenarios \quad (35)$$

Where the  $DEP4_k$  values are in USD/mo. The second objective function is represented by the sum of  $\dot{I}_{out}^{(tot)}$  throughout the operational life span of the plant:

$$Cumulated\ PEI = \dot{I}_{out}^{(tot)} \cdot nHpM \cdot nMonths \quad (36)$$

Where  $\dot{I}_{out}^{(tot)}$  is in PEI/h as in Equation (29), and  $nHpM$  is in h/mo. The result would be the same if Equation (36) considered  $\hat{I}_{out}^{(tot)}$  multiplied by the mass flow rate of product throughout the operational life span of the plant.

As anticipated in Paragraph 4.6, the intrinsic fluctuations of future price scenarios lead to distributions of  $Cumulated\ DEP4_k$ . Therefore, the optimization algorithm identifies a Pareto optimal set, *i.e.* a set of optimal plant configurations, for each  $k$ -th scenario. For the sake of clarity, the optimization algorithm used in this work is the grid-search method, which can perform a robust and exhaustive evaluation of the objective functions as far as the number of decision variables is reasonably low (Table 16).

Table 16: Lower and upper bounds of the decision variables. The interval bounds are based on those proposed by Pathak *et al.* (2011) and suitably modified to either broaden the search extent or increase the domain discretization.

Design variable	Lower bound	Upper bound	Step size	Steps number
Reactor length [m]	4	10	1	7
Inlet temperature [°C]	300	390	5	19

In addition, the grid-search method allows reducing the overall CPU time whenever a high number of economic scenarios is involved (Barzaghi *et al.*, 2016). Another positive spinoff of the grid-search method consists in the improved convergence of the process simulator that can rely on initial condition values for a new simulation, which are inherited from the previous convergence

point (*i.e.* previous simulation). Indeed, the foregoing simulation of the grid-search method is rather near to the following one as the decision variables, being discretized by a narrow net of values, make the perturbations from the previous point to the next one small.

As a first reference, Figure 42 shows the non-Pareto and Pareto optimal solutions of the MOO problem for an arbitrarily chosen economic scenario. For the sake of clarity, each solution corresponds to a discrete point of the grid-search domain (Table 16), *i.e.* a plant configuration. Indeed, after having simulated all the discrete points of the grid-search domain and having saved the input data (*i.e.* equipment size and process/utility flow rates) necessary for the computation of Equations (35)-(36), both *Cumulated DEP4<sub>k</sub>* and *Cumulated PEI* are calculated for each plant configuration.

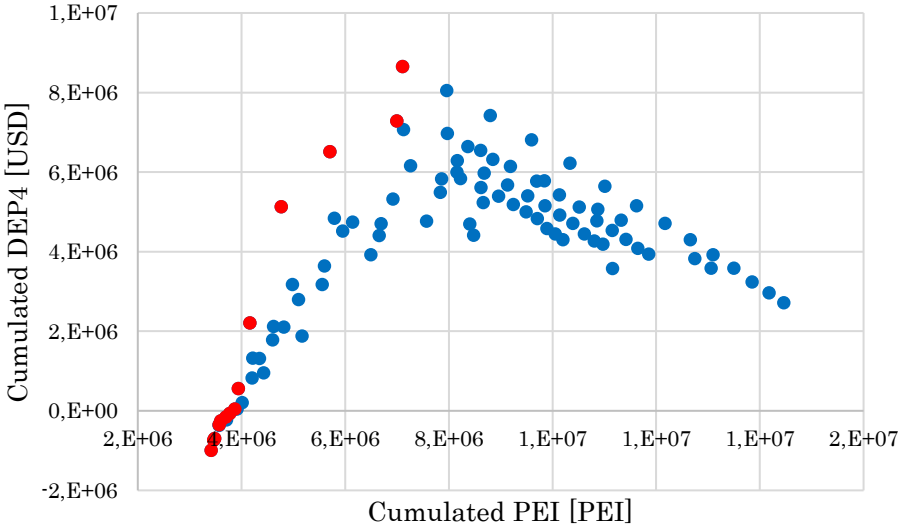


Figure 42: Non-Pareto (blue dots) and Pareto optimal solutions (red dots) of the MOO problem for an arbitrarily chosen economic scenario. Each solution corresponds to a discrete point of the grid-search domain, *i.e.* a plant configuration.

As already mentioned, the Pareto optimal solutions are those for which none of the objective functions can be improved without worsening the value of at least another objective function (Figure 43). Indeed, the plant configuration

that provides the best economic result, *i.e.* the highest *Cumulated DEP4<sub>k</sub>*, is located at the right end of the Pareto optimal set. Conversely, the plant configuration that provides the lowest *Cumulated PEI*, *i.e.* the most environmentally friendly solution, is located at the left end of the Pareto optimal set.

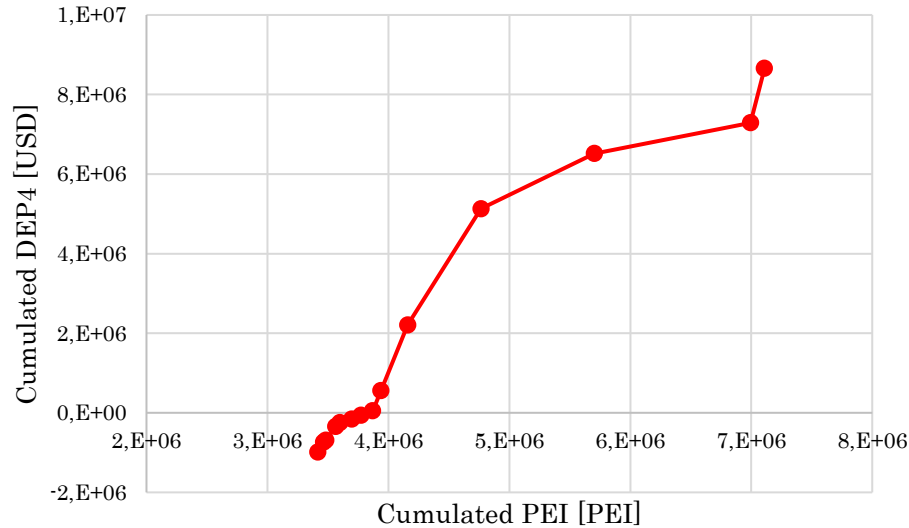


Figure 43: Pareto optimal set for an arbitrarily chosen economic scenario. As none of the objective functions on the Pareto optimal set can be improved without worsening the value of at least another objective function, tradeoffs will take place.

In this respect, Table 17 shows that the right and left-end solutions of the Pareto optimal set differ in the values of the design variables. In fact, both the reactor length and inlet temperature of the plant configuration that provides the lowest *Cumulated PEI* are higher than those of the plant configuration that provides the best economic result. Indeed, as both reactor length and inlet temperature increase, propylene conversion increases as shown in Figure 40(a) and Figure 41, thus  $\dot{I}_{out}^{(tot)}$  decreases as suggested by the findings of Table 15 and Figure 39. However, higher inlet temperatures and reactor lengths lead to higher capital and energy costs, and lower selectivity as shown in Figure 40(b).

Consequently,  $Cumulated DEP4_k$  and  $Cumulated PEI$  tend to be contradictory objectives as illustrated in Figure 43.

Table 17: Right and left-end solutions of the Pareto optimal set for an arbitrarily chosen economic scenario. The configuration index is an integer number that univocally identifies a plant layout among different layout alternatives.

Configuration index	Inlet temperature [°C]	Reactor length [m]	$Cumulated DEP4_k$ [MUSD]	$Cumulated PEI$ [MPEI]
#35	365	7	8.66	7.11
#97	390	10	-0.99	3.42

Figure 44 and Figure 45 show the contour lines of  $Cumulated DEP4_k$  and  $Cumulated PEI$  as a function of both reactor length and inlet temperature (it is worth observing that 27% of the simulations were not successful as only 97 out of the 133 discrete points of the grid-search domain converged). The set of design variables that maximize  $Cumulated DEP4_k$  and minimize  $Cumulated PEI$  are the same of Table 17.

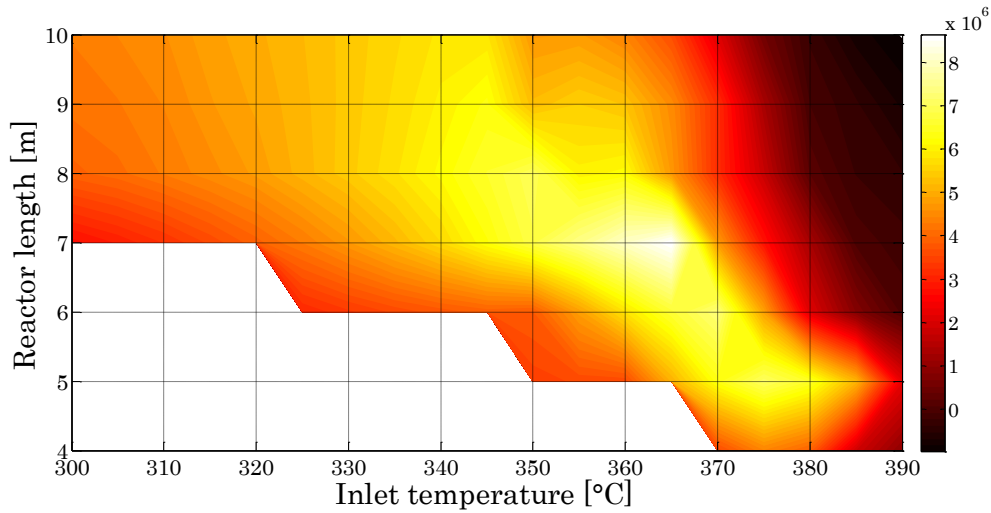


Figure 44: Contour lines of  $Cumulated DEP4_k$  as a function of both reactor length and inlet temperature for an arbitrarily chosen economic scenario.

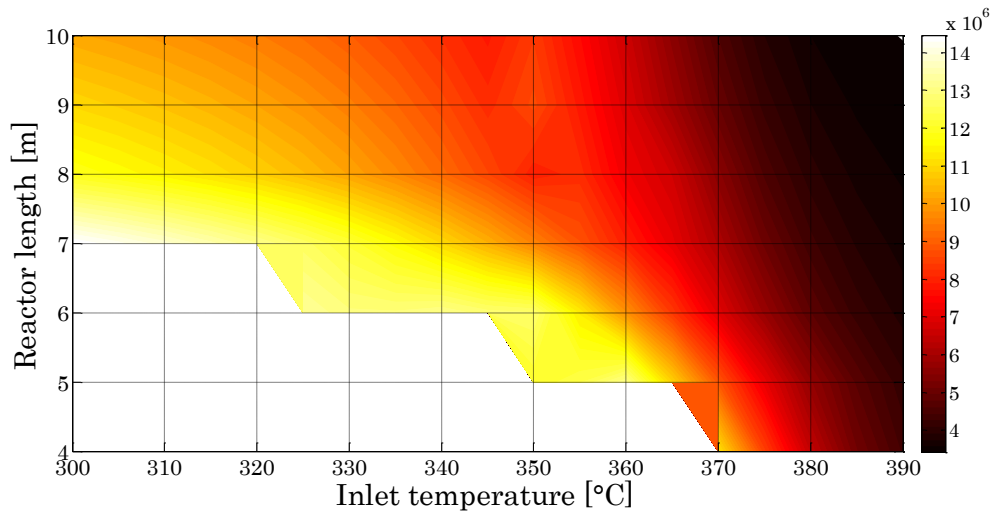


Figure 45: Contour lines of *Cumulated PEI* as a function of both reactor length and inlet temperature for an arbitrarily chosen economic scenario.

Table 18: Pareto optimal solutions of the MOO problem respect to 3000 different price scenarios.

Configuration index	Cardinal number	Inlet temperature [°C]	Reactor length [m]	Cumulated PEI [MPEI]	Average Cumulated DEP4 [USD]	Negative Cumulated DEP4 [%]
#97	1	390	10	3.42	5.69	25.13
#96	2	385	10	3.46	5.98	23.77
#78	3	390	9	3.48	6.02	23.63
#77	4	385	9	3.57	6.41	22.33
#95	5	380	10	3.60	6.53	21.97
#40	6	390	7	3.70	6.60	21.63
#76	7	380	9	3.77	6.73	21.27
#21	8	390	6	3.87	6.82	20.87
#94	9	375	10	3.94	7.43	17.92
#12	10	390	5	4.16	9.19	13.53
#11	11	385	5	4.77	12.40	7.13
#10	12	380	5	5.70	13.92	5.13
#17	13	370	6	6.99	14.79	4.37
#35	14	365	7	7.11	16.27	3.00

While the *Cumulated DEP4<sub>k</sub>* values of Figure 42, Figure 43, Figure 44, and Figure 45 refer to the same arbitrarily chosen economic scenario, Table 18 shows the average *Cumulated DEP4* values respect to 3000 different scenarios. It is evident that the average *Cumulated DEP4* decreases as the *Cumulated PEI* decreases (Figure 46). Indeed, lower *Cumulated PEI* values denote more environmentally friendly plant configurations. Conversely, higher *Cumulated DEP4* values denote better economic results. It is worth observing that the average *Cumulated DEP4* increases by 185.9% along the Pareto optimal set, whereas the *Cumulated PEI* increases by 107.9%.

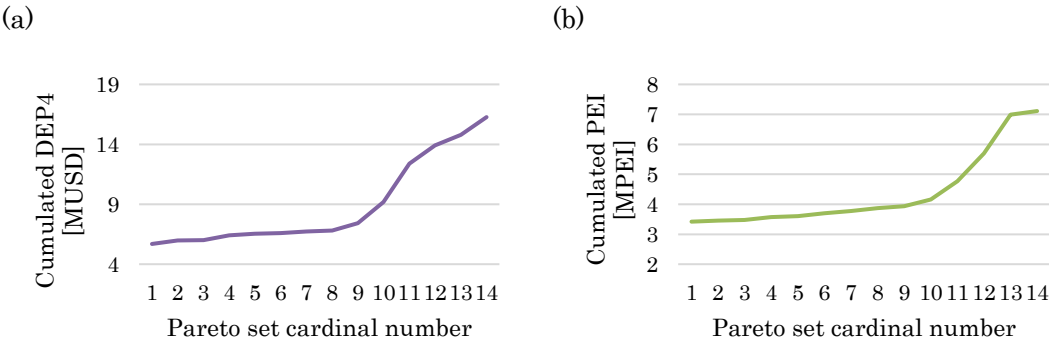


Figure 46: Average *Cumulated DEP4* (a) and *Cumulated PEI* values (b) along the Pareto optimal set.

Most importantly, the occurrence of negative *Cumulated DEP4<sub>k</sub>* values respect to 3000 different scenarios increases from 3.0% to 25.1% along the Pareto optimal set. This point is noteworthy as suggests that the most environmentally friendly configurations are the most likely to be economically unfeasible under market uncertainty and prices/costs volatility. Figure 47 recaps the findings of Table 18 by showing the distribution of *Cumulated DEP4<sub>k</sub>* values for the plant configuration #35 (*i.e.* the economic optimum), #97 (*i.e.* the environmental optimum), and #11 (*i.e.* the equidistant solution from the economic and environmental optima). As expected, the distributions shift to

lower values of  $Cumulated\ DEP4_k$  as we move from the right end to the left end of the Pareto optimal set.

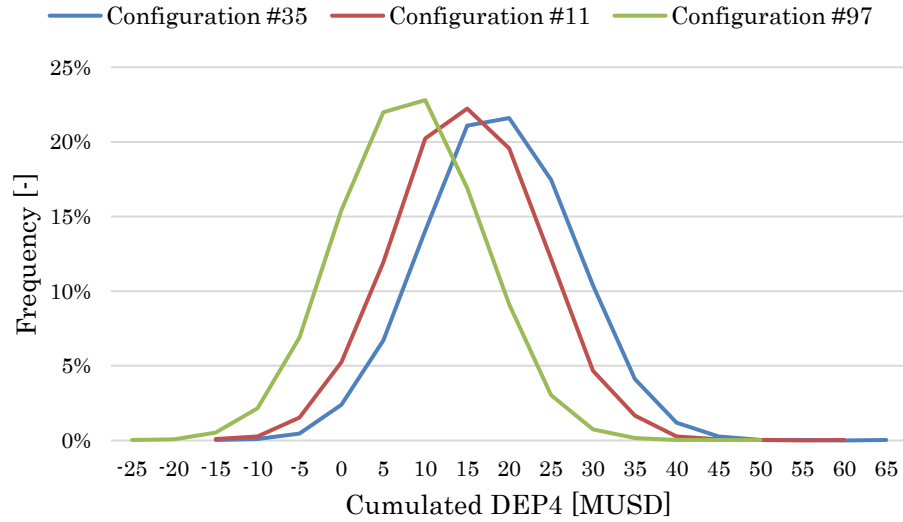


Figure 47: Distribution of  $Cumulated\ DEP4_k$  values respect to 3000 different economic scenarios for three selected Pareto optimal solutions.

Therefore, whenever a modification is proposed to improve the environmental friendliness of a process, it is useful to question its economic viability under market uncertainty. Indeed, the cumene process clearly shows that certain tradeoffs are not economically sustainable for several possible scenarios (Table 18). Consequently, the choice of the optimal flowsheet configuration and its corresponding operating conditions should always rely on a statistical study based on a high number of forecast scenarios.



# 7 Conclusions and future developments

This work presented a methodology that accounts for both environmental impact and price/cost volatility to carry out improved feasibility studies of chemical plants. Indeed, recent global events brought to the realization that substantial changes in the design and operation of products and processes are necessary for the sustainability of industrial systems. For instance, raw material and energy prices have been more volatile than ever in the last decade, and might face higher fluctuations in the future. Unfortunately, conventional feasibility studies base the forecast for incomes and outcomes on the discounted-back approach. This means that prices/costs of commodities and utilities are assumed constant for long periods with the reference point being usually the date when the economic assessment is performed. Clearly, this approach has significant limitations as financial markets are neither stationary nor systematic. For these reasons, this work proposed an innovative approach to conceptual design that considers the OPEX terms as a function of price fluctuations, and uses econometric models to devise a set of possible future scenarios of commodity and utility prices. As far as the O&G sector is

concerned, it is possible to identify a functional dependence of commodity and utility prices on the quotations of crude oil. By identifying future price trajectories of crude oil, it is possible to assess the corresponding price trajectories of raw materials, (by)products, and utilities that contribute to the OPEX terms of chemical plants.

In past years, numerous approaches were proposed in the literature to mitigate the environmental impact of chemical processes. For instance, the WAR algorithm is a simple tool to be used by design engineers to determine the PEI of a chemical process. The PEI is a relative measure of the potential for a chemical to have an effect on the environment, and is calculated by summing the PEI of individual chemicals over eight impact categories that fall into four general areas of concern (*i.e.* human toxicity, ecological toxicity, global atmospheric impacts, and regional atmospheric impacts). Weighing factors are used to combine the PEI categories into a single PEI indicator.

The proposed methodology to account for both environmental impact and price/cost volatility was applied to the conceptual design of a cumene production plant. The economic sustainability of a cumene plant is heavily conditioned by the fluctuations of commodity and utility prices. For instance, the *EP2*, which sets a necessary condition for the plant feasibility, changes sign repeatedly and fluctuates between positive and negative values as soon as the cumene price is either higher or lower than benzene and propylene cost. For this reason, Paragraphs 4.4 and 4.5 showed a systematic approach to finalize the econometric models of the commodities and utilities involved in the cumene process. Paragraph 5.2 focused on decreasing the PEI of the cumene plant. This work considered only the non-product streams in the rate of PEI leaving the chemical process, but accounted for raw material and product streams as fugitive emissions by means of a 0.001 multiplying factor since chemical plants are likely to have relevant fugitive losses. Besides, this work used the predominant emissions from a CCGT and a large wall-fired boiler to

calculate the rate of PEI leaving the energy generation process. As a primary improvement, the findings of Table 15 and Figure 39 suggested reducing the loss of propylene by changing the reactor operating conditions. However, whenever a process is modified to reduce waste, there is a consequent change in the associated economics. In this respect, MOO is well suited to incorporate environmental concerns in the optimization of chemical processes, since it allows to treat them as decision-making objectives.

In contrast to single-objective optimization, there is no single global solution to a MOO problem, and it is often necessary to determine a set of points that all fit a predetermined definition for an optimum. The predominant concept in defining an optimal point is that of Pareto optimality, for which a point is Pareto optimal if there are not any points that improve at least one objective function without detriment to another function. Therefore, some tradeoffs among objective functions are necessary to reach the preferred optimal solution, *i.e.* the optimal flowsheet configuration and its corresponding operating conditions. The different scenarios subject to the price/cost trajectories obtained by the econometric models of Paragraphs 4.4 and 4.5 lead to distributions of the achievable profits. Therefore, the optimization algorithm identifies a Pareto optimal set, *i.e.* a set of optimal plant configurations, for each economic scenario.

This work proved that whenever a modification is proposed to improve the environmental friendliness of a process, it is useful to question its economic viability under market uncertainty. Indeed, the cumene plant showed that certain tradeoffs are not economically sustainable for several possible scenarios, *i.e.* the most environmentally friendly configurations are the most likely to be economically unfeasible under market uncertainty. Consequently, the choice of the optimal flowsheet configuration and its corresponding operating conditions should always rely on a statistical study based on a high number of forecast scenarios.

As far as future developments of this work are concerned, it will be worth considering new processes based on a higher number of design variables to make the optimization procedure more compliant with real plants. In addition, it will be worth implementing economic indicators different from Douglas' economic potentials, such as the net present value and the internal rate of return. Indeed, these indicators are rather different from the economic potentials as they are financially oriented and consider the interest rate in the performance assessment of an economic investment.

A further development could be expanding the boundaries of the study to include the upstream and downstream activities related to the main process, thus considering all material and energy flows from the *cradle* of primary resources to the *grave* of final disposal. Most interestingly, it will be worth accounting for the operational uncertainties associated with the life cycle inventory, *e.g.*, emissions released and resources consumed per unit of reference flow of activity.

As far as the social attribute of sustainability is concerned, it must be recognized that the growing importance of corporate ethics and accountability has made some companies deeply committed to their social responsibilities. However, the linkages between PSE and social performance remain elusive. Indeed, PSE applications to sustainability have so far focused on economic and environmental aspects, with social criteria being considered only very recently. For these reasons, it will be worth developing practical ways to measure social sustainability for both single-site (*e.g.*, process synthesis) and multi-site applications (*i.e.* SCM/EWO).

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- Sepiacci, P., & Manca, D. (2015). Economic assessment of chemical plants supported by environmental and social sustainability, *Chemical Engineering Transactions*, 43, 2209-2214.



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*"Has it been three days? 'Tis true, Peter, time does fly. And so do you, I see."*

*Hook, S. Spielberg, 1991*