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Influence of market fluctuations on the computational design of a chemical plant

Process Systems Engineering Lab

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*Science's models are not true, and that's exactly what makes them useful.
They tell simple stories that our minds can grasp.
They are lies-to-children, simplified teaching stories, and none the worse for that.
The progress of science consists of telling ever more convincing lies to ever more
sophisticated children.*

[Terry Pratchett - The Science of Discworld II: The Globe - 2002]

List of Acronyms and Symbols

- BTZ	“Basso tenore di zolfo” - Low sulfur content
- CAPEX	Capital expenses
- CD	Conceptual design
- CO	Crude oil
- DCD	Dynamic conceptual design
- DEP	Dynamic economic potential
- DoF	Degrees of freedom
- E_a	Activation energy
- EB	Ethylbenzene
- EE	Electric energy
- EP	Economic potential
- FEHE	Feed effluent heat exchanger
- HDA	Hydrodelachilation of toluene
- IRR	Internal rate of return
- LP	Low pressure
- MA	Moving average
- M&S	Marshall and Swift index
- NPV	Net present value
- OPEX	Operative expenses
- PCD	Predictive conceptual design
- PSE	Process systems engineering
- R	Pearson-Bravais correlation index
- RTO	Real time optimization
- SSE	Sum of square errors
- WTI	West Texas Intermediate (crude oil)
- ΔG_R^0	Gibbs standard free energy of reaction

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Abstract

This thesis is divided into five chapters.

Chapter 1 introduces Luyben's Conceptual design approach (based on Economic Potential levels, on CAPEXs and OPEXs) and its possible improvements. This method for economic plant evaluation will be adopted to study a styrene plant, which will be described in detail with regard to chemical substances, kinetics, and pieces of equipment involved.

Chapter 2 explains the four degrees of freedom of the plant. With respect to Luyben (2011), also a splitting factor of the "LP Steam" flowrate will be considered. For each degree of freedom the dependence of different plant's design variables will be found. After this preliminary part, economic study on the plant will follow a Conceptual Design evaluation, based on the choice of the optimal configurations.

Chapter 3 is focused on the choice of the best algorithm to optimize the styrene plant. Different options will be compared, in particular customized grid methods and optimizers already included in *MATLAB*[®]. Another decisive matter is the choice of the best way of collecting data: the decision awards the link between *UniSim*[®] *Design Suite* and *MATLAB*[®], in order to have easily controllable data, rather than using these two softwares separately.

Chapter 4 passes from traditional Conceptual Design (CD) to Dynamic Conceptual Design (DCD) and to Predictive Conceptual Design (PCD). The differences among them will be underlined and econometric models on plant raw materials and commodities will be implemented. PCD will lead to the modeling and calculation of different scenarios for the possible future prices. The optimization of the different degrees of freedom will be studied for DCD and PCD.

The final chapter, Chapter 5, summarizes the conclusions drawn from Conceptual Design, Dynamic Conceptual Design and Predictive Conceptual Design on the styrene plant. In addition to this, some further improvements to the plant and to the thesis work will be suggested.

Chapter 1

Conceptual design of a styrene plant

This first chapter concerns the main properties of styrene and its importance in terms of production worldwide in the present and future industry. A general description of styrene process, with involved reactions, and an overview on the most adopted plant solutions (from ethylbenzene) are provided. Pieces of information regarding styrene history and industrial processes development mainly come from Ullmann's (2011), Turton et al. (2003), and some specific websites on styrene chemistry. The basis for the plant configuration represented in this work came from Vasudevan et al. (2009), Luyben (2011) and Barzaghi and Conte (2015). Conceptual Design approach and improvements to it are introduced to explain how styrene plant will be studied from an economic point of view.

1.1 Introduction to Conceptual Design

Under the “Conceptual Design” (CD) definition some methods for optimization of an industrial plant are included. In fact, the possible process configurations to obtain a product are theoretically infinite, but only a very little number of ideas (usually <1%) are operable and profitable on industrial scale (Douglas (1988)). The aim of Conceptual Design approach is to find the best plant configuration, estimating the best design variables values and operative conditions.

The final goal of CD is to maximize profits, always respecting law constraints on pollution and safety, and to reach the best available configuration of the process. Conceptual Design approach is based on simplified step-by-step calculations in order to easily provide intermediate results, ending the evaluation once the profit starts to become too low or becomes negative. Following this strategy becomes affordable to try many more configurations because in a few step it is already clear if a case study is correct or not. The hierarchy in Conceptual Design consists of five analysis levels, which will be explained in more detail in Paragraph 2.2.1. At each level some specific decisions have to be made and the entire plant design is obtained by joining them at the end of the analysis.

Decisions are based on economic indexes that depend on two main factors:

- CAPital EXpenses (CAPEXs): purchasing and installation of equipment that will be amortised during the plant's life
- OPerative EXpenses (OPEXs): raw materials, commodities, and utilities cost and values that influence the plant while it is running

This first analysis, if the process is economically convenient, is then deepened by considering other essential aspects, such as safety, environmental limits/constraints, and controllability performing the final design in detail.

Conceptual Design approach is largely used in industry because of its immediacy: a little number of calculations allow the designer to draw conclusions on the most relevant plant choices. They depend on economic levels, which are based on simple balances (algebraic sums) between incomes (products value) and expenses (CAPEXs, utilities and commodities). However, the main disadvantage of Douglas' work is that quotations are assumed fixed and constant, whereas real market prices can vary significantly due to the supply and demand law (Manca and Grana (2010); Sorknæsa et al. (2015); Manca et al. (2015)). In this thesis work, economic potential indexes will follow the Douglas' approach, by considering the real historical trend of quotations instead of constant prices: the aim is improving the accuracy of estimations of the traditional Conceptual Design approach and pointing out the differences in the two methodologies. The implementation of possible future price trends and scenarios will also be investigated and the introduction of econometric models for the main raw materials/commodities involved will be discussed in Chapter 4. All these elements contribute to the economic optimization of the chemical plant considered. For this purpose, the styrene production process was chosen and this thesis work mainly focuses on the economic evaluation with CD, Dynamic CD, and Predictive CD methods. The best strategy to minimize the calculation time will also be analyzed.

1.2 Styrene



Figure 1.1: Styrene molecule representations (taken from SIGMA-ALDRICH 2016 and Wikipedia 2016).

Styrene [100-42-5] is a clear and colorless liquid. Its IUPAC name is phenyl ethylene, but it is also known as vinyl benzene and phenyl ethene. It is an aromatic monomer, which boils at 145 °C and solidifies at -31 °C. Being rather volatile and having a flash point of 32 °C, styrene is classified as a flammable substance, which may form flammable or explosive vapor-air mixtures. It is soluble in acetone, benzene, ether, n-heptane, and ethanol. It is synthesized for commercial use from petroleum and natural gas by-products.

Styrene is used all over the world as a raw material to create high-performance plastics, composites, and other products. Styrene-based resins are included in some artefacts like hospital and school supplies, boats, automobile parts, and durable lightweight packaging of all kinds. Styrene also occurs naturally in the environment and is an inherent component in small concentrations of many foods and beverages, such as coffee and strawberries.

Styrene world production is about 26.5 million of tons per year, which means that it is one of the most important products of the organic chemical industry sold in the world.

Major styrene manufacturing regions in Europe include Benelux, France, Germany, Italy,

1.2. Styrene

and Spain. In Asia, principal styrene interests can be found in Japan, China, Korea, and Malaysia. Areas in the United States with significant styrene production include California, Indiana, New York, Pennsylvania, Ohio, and Texas.

For all these reasons, studying how a styrene plant works and improving a styrene plant are crucial issues in chemical engineering.

Figure 1.2 explains how styrene is exploited in industry:

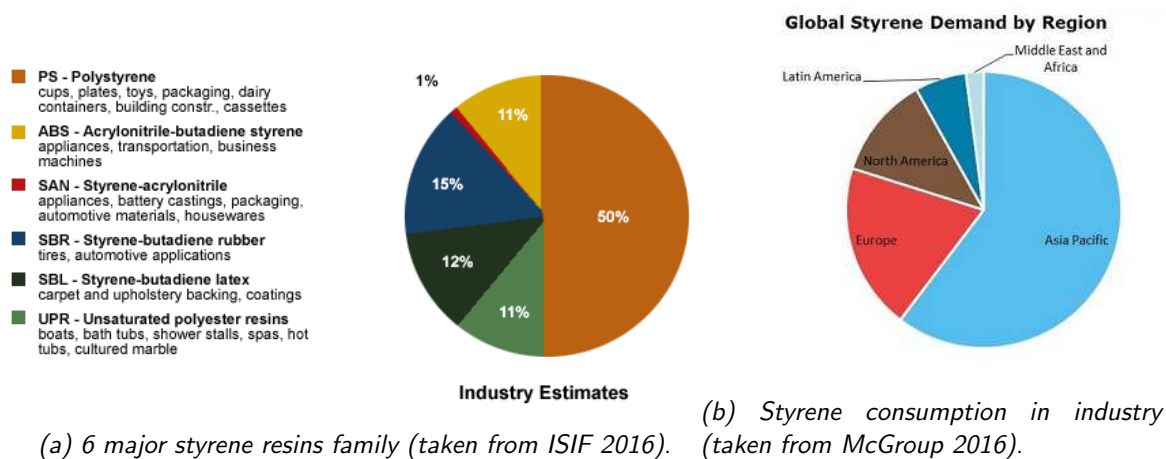


Figure 1.2: Styrene in industry.

1.2.1 Health risks associated to styrene

Styrene is classified as a “hazardous chemical”, especially in case of eye contact, but also in case of skin contact, of ingestion, and of inhalation. Styrene oxide is considered toxic, mutagenic, and possibly carcinogenic. The U.S. EPA does not have a cancer classification for styrene, but it has been the subject of their Integrated Risk Information System (IRIS) program. Styrene affects the nervous and respiratory system in workers who breathe the chemical in conditions of inadequate protection or ventilation. Symptoms include mucous membrane irritation, muscle weakness, tiredness, nausea, eye, nose, and throat irritation. There is little information regarding the acute effects of ingesting styrene, but animal studies showed that long-term ingestion of styrene can damage the liver, kidneys, brain, and lungs. Chronic exposure to styrene can cause central nervous system problems, such as headache, fatigue, weakness, depression, problems with memory and intellectual function, and hearing loss.

1.2.2 Styrene history

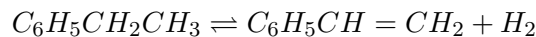
Styrene name originates from styrax balsam, the resin of Liquidambar trees. In the 19th century, styrene was isolated by distillation of the natural storax balsam. Styrene production in significant quantities started in the 1930s, but the real increase happened in the successive decade, when it found large use for synthetic rubber production.

After the Second World War, styrene became essential because of the development of polystyrene production. Other products derive from styrene, however, such as styrene-butadiene copolymer, and styrene-butadiene rubber.

1.3 Plant scheme

1.3.1 How styrene is produced: dehydrogenation of ethylbenzene process

About 90% of styrene is obtained from the ethylbenzene dehydrogenation process¹. On the other hand, 10% of styrene is provided from the co-production of propylene oxide, by using the so-called POSM or SM/PO process. In this route, ethylbenzene is treated with oxygen to form the ethylbenzene hydro-peroxide. This hydro-peroxide is then used to oxidize propylene to propylene oxide. After that, a dehydrogenation gives styrene. Dehydrogenation of ethylbenzene is the most relevant process to produce styrene. The reason is that benzene and ethylene are available in very large quantities and they are cheap. The main reaction to produce styrene is:

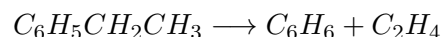
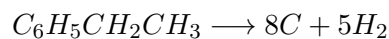
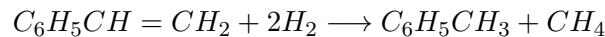


This reaction is endothermic, so it better performs at high temperatures. It happens at about 550-600 °C and the $\Delta G_R^0 = 0$ is reached at about 700 °C.

The upper limit in temperature is mainly due to the catalyst stability and working above it may cause a premature deactivation of the catalyst.

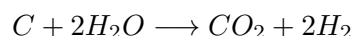
The reaction is also non-equimolar, thus it is better operated at low pressure in the range 1-3 bar with the co-feed of superheated steam to further decrease the partial pressure.

The catalyst for this reaction contains some major active ingredients, a stabilizer, and an alkali-metal promoter. Common commercial catalysts contain iron oxide (Fe_2O_3) promoted by potassium (K_2CO_3) and a structural stabilizer (Cr_2O_3). Potassium is a very effective promoter and increases the reaction rate by an order of magnitude. The catalyst becomes less efficient in time, but increasing temperature (in a suitable range) helps to use it for a longer period. In general, this kind of catalyzers lasts about 2 years. Catalyst's costs are not considered in this thesis work, but they are not negligible at all while running the plant. The main byproducts of reaction are toluene, benzene, and carbon dioxide (deriving from carbon). They are formed by the following parasite reaction:



Other byproducts are methane, ethylene, cumene, xylene, carbonic anhydride, tars, and other aromatics, which are critical because their separation from styrene is difficult and affects styrene purity.

Superheated steam plays an important role in styrene production and serves several purposes: it is introduced directly into the reactor in large molar excess to provide part of the necessary heat to drive the endothermic reaction and make the adiabatic reactor feasible. It serves as an oxidant to maintain the iron oxide catalyst in the appropriate oxidation state and removes carbonaceous deposits from the catalyst through the water-gas shift reaction:



It reduces the partial pressure of hydrocarbons, thereby styrene conversion increases. Optimum conversion is determined by the balance between the advantage of increased conversion

¹Ethylbenzene is almost exclusively (>99%) used as an intermediate for the manufacture of styrene monomer: 50% of the world's benzene production is consumed for this purpose. Less than 1% of the ethylbenzene produced is used as a paint solvent or as an intermediate for other chemicals.

1.3. Plant scheme

and the cost of increased steam. Over the last two decades, improved processing has permitted a continual decrease in the molar ratio of steam to hydrocarbon. The ratio is between 6 and 12, with 65-70% conversion and 90-95% selectivity. Over 75% of styrene plants operate adiabatically in multiple reactors or reactor beds operated in series. Table 1.1 shows a typical crude styrene from the dehydrogenation process.

Table 1.1: Typical crude styrene composition.

Products	T_{boil} [°C]	Products %
Benzene	80	1
Toluene	110	2
Ethylbenzene	136	32
Styrene	145	64
Others	Unknown	1

The separation of these components may become very complicated due to the residence time and the temperature at which styrene is found in the columns. Styrene starts to polymerize near its boiling point so it could cause serious problems in the reboilers of the columns. For these reasons, styrene needs to be separated as soon as possible and the distillation column should be under vacuum with some inhibitors of polymerization like sulfuric compound (in the past) or aromatics with amino, nitro, or hydroxyl groups. Usually, the separation of these components is performed in a train of three columns with two different configurations (Figure 1.3).

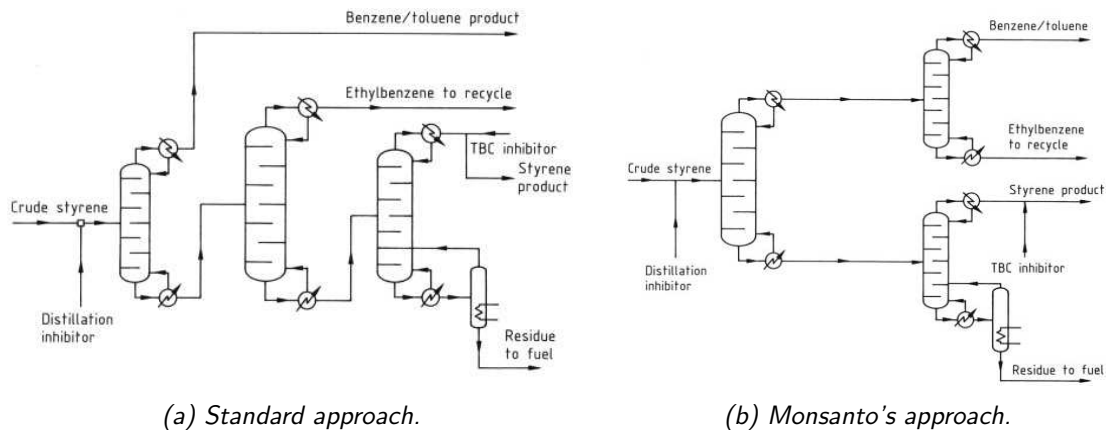


Figure 1.3: Styrene different separation approach (taken from Ullmann's (2011)).

In the standard approach, Fig. 1.3a, benzene and toluene are separated first and then ethylbenzene from styrene in an under vacuum column. In the Monsanto approach, Fig. 1.3b, the major separation is performed first between ethylbenzene (T_{boil} 136 °C) and styrene (T_{boil} 145 °C), and then ethylbenzene is separated from benzene and toluene. Benzene and toluene in both cases can be separated and sold, or benzene can be recycled to the entrance of the benzene to ethylbenzene plant².

²Currently, almost all ethylbenzene is produced commercially by alkylating benzene with ethylene, via two routes: in the liquid phase with aluminum chloride catalyst or in the vapor phase with a fixed bed of either a Lewis acid or a synthetic zeolite catalyst.

1.3.2 Styrene Plant overview

The plant that has been used in the present thesis is the one described in Figure 1.4.

The inlet streams are ethylbenzene and low pressure steam. The ethylbenzene is supposed to come from a previous ethylbenzene plant, which has ethylene and benzene as raw materials, at a constant rate of 132.8 kmol/h. This value has been chosen by Luyben (2011), Vasudevan et al. (2009), and Barzaghi and Conte (2015) to achieve a styrene productivity of around 100,000 ton/y (above 110 kmol/h). This choice corresponds to a low productivity plant. As written in Ullmann's (2011), a single-train plant can reach a productivity of 150,000 t/y.

The fresh ethylbenzene is mixed with the recycled one with a stream of low pressure steam (whose absolute pressure is 300 kPa) superheated at 200 °C. The feed is initially preheated in the feed effluent heat exchanger (FEHE) E-2 using the reactor effluent, stream 80, and the remaining LPS is superheated in the furnace E-1 to a higher temperature to meet the reactor inlet temperature between 535 and 565 °C.

Industrially, the reactor inlet temperature is chosen between 550-680 °C but the use of kinetics in the "Power Law" form (Tables 1.2, 1.3) forces us to operate a lower temperature to work near the optimum. All these considerations have already been discussed in Barzaghi and Conte (2015) and the study performed in this work is focused on the economical evaluation of the process, so the optimization of the real process is not the primary objective. The approach that is used to evaluate the profitability instead, is the major topic of this thesis.

Observing the activation energy in Table 1.3 of the first reaction, it is notable that the direct reaction is higher than the inverse one. Therefore, the reaction is endothermic and works better at higher temperature, but an excessive increase of the reaction temperature leads also to an increase of the side reactions. For these reasons, we need to find an optimum in the reactors inlet temperature.

Table 1.2: Reactions

(1)	Styrene production	$C_6H_5CH_2CH_3 \rightleftharpoons C_6H_5CH = CH_2 + H_2$
(2)	Ethylene-Benzene reaction	$C_6H_5CH_2CH_3 \longrightarrow C_6H_6 + C_2H_4$
(3)	Toluene-Methane reaction	$C_6H_5CH_2CH_3 + H_2 \longrightarrow C_6H_5CH_3 + CH_4$
(4)	Carbon monoxide reaction	$2H_2O + C_2H_4 \longrightarrow 2CO + 4H_2$
(5)	Carbon monoxide reaction	$H_2O + CH_4 \longrightarrow CO + 3H_2$
(6)	Carbon dioxide reaction	$H_2O + CO \longrightarrow CO_2 + H_2$

Stream 50 is then fed to the two adiabatic PFRs, in series with a heater in between, in which the production of styrene takes place following the reactions of Table 1.2.

The reactor effluent is cooled in the FEHE and further cooled up to 40 °C in the cooler E-4 with water, before being sent to the three-phase separator, where the light gases (mainly hydrogen) are removed, and water and the organic phase are removed separately. The intermediate organic layer is sent to a set of distillation columns for styrene separation from the other components.

This decanter operates at 40 °C and takes advantage of the miscibility gap between the organic phase and water as can be seen in the ternary diagram of Figure 1.5.

The first column (product column C-1) is operated under vacuum to prevent styrene polymerization. Polymerization inhibitors, that do not modify significantly the relative volatility

1.3. Plant scheme

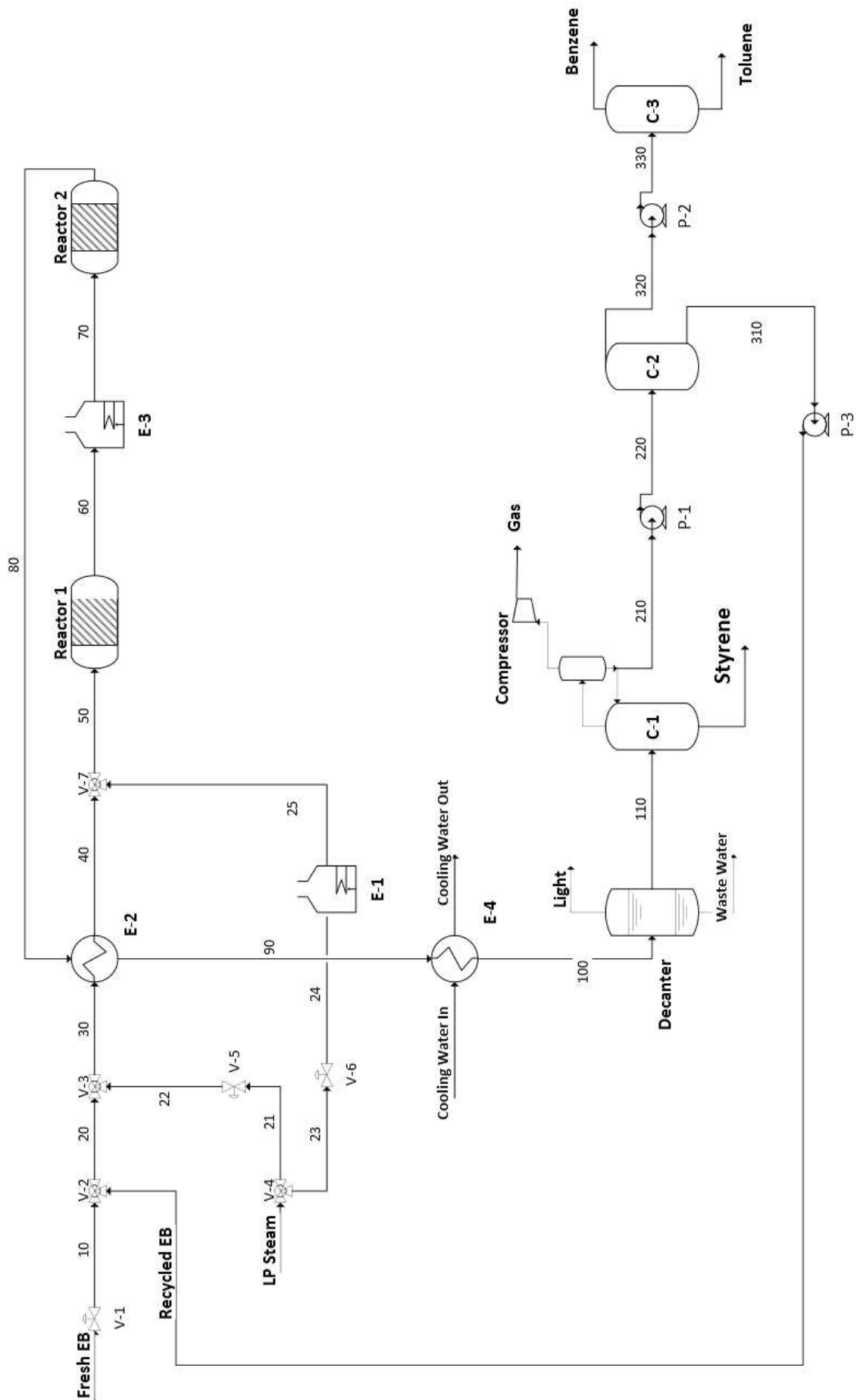


Figure 1.4: Process flow diagram of the styrene plant considered.

Table 1.3: Reaction kinetics.

Reaction	k	E_a [kJ/kmol]	Reaction kinetics [$\text{kmol}/\text{m}^3/\text{s}$]
1 direct	0.044	90,981	$kP_{Eb} \exp\left(-\frac{E_a}{RT}\right)$
1 inverse	6E-8	61,127	$kP_{Sty}P_{H_2} \exp\left(-\frac{E_a}{RT}\right)$
2	27,100	207,989	$kP_{Eb} \exp\left(-\frac{E_a}{RT}\right)$
3	6.484E-7	91,515	$kP_{Eb}P_{H_2} \exp\left(-\frac{E_a}{RT}\right)$
4	4.487E-7	103,997	$kP_{H_2O}P_{C_2H_4}^{0.5} \exp\left(-\frac{E_a}{RT}\right)$
5	2.564E-6	6,723	$kP_{H_2O}P_{CH_4} \exp\left(-\frac{E_a}{RT}\right)$
6	1,779	73,638	$kP_{H_2O}P_{CO} \exp\left(-\frac{E_a}{RT}\right)$

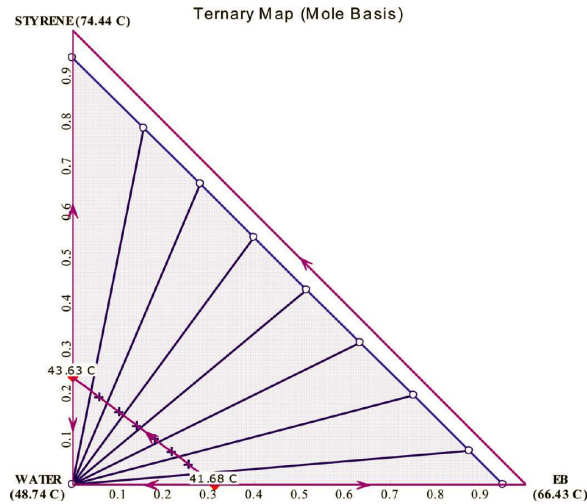


Figure 1.5: Ternary map water-styrene-ethylbenzene at 10 kPa (taken from Luyben (2011)).

between styrene and ethylbenzene, are also added in addition to the vacuum operation (10 kPa at top and 50 kPa at bottom). This first column is made of 80 theoretical stages and is filled with a packed bed to lower the pressure drop to its minimum.

Styrene is removed as the bottom product with a molar composition of 99.75% (industrial specification), and the top product is sent to a second column (recycle column C-2) to separate the unreacted ethylbenzene (EB) from the two byproducts, toluene and benzene.

The unreacted EB is then recycled back and the stream of benzene and toluene, coming from the top, is distilled in a third column (C-3). Benzene-toluene separation is almost ideal, which means that it is a separation that needs only a small number of trays.

In particular, this column has 21 trays and the feed is at 11th tray. This third column was not taken into consideration by Luyben's approach and in this work has been added to confirm whether or not its capital and operative costs are negligible as first approximation in the economic evaluation (see Chapter 2).

Chapter 2

Selection of the degrees of freedom

This section deals with the description of the four chosen degrees of freedom (DoFs) for the plant design, each with its own feasibility and physical limits. As expected, each of the DoFs affects the plant both on a process and on an economic point of view. Since aim of the whole thesis is the economic optimization of a styrene plant, the focus is on this side. Then, Conceptual Design method is explained and deepened. Some suitable calculations are run to provide numerical results: they help selecting the DoFs values which make the plant as most profitable as possible under the tight hypothesis of fixed prices conditions as stated by the conceptual design theory of Douglas (1988).

2.1 Degrees of freedom

The analyzed styrene plant has four degrees of freedom. They can assume only a limited range of values because of physical constraints needed to fall within suitable feasibility conditions. Each degree of freedom affects other optimization variables and, as a consequence, the economic potential of the whole plant.

In particular, the four degrees of freedom are:

- Low pressure (LP) steam inlet flow
- Inlet temperature to the reactors (same for each reactor)
- Reactor volume (same for each reactor)
- Splitting factor of the “LP Steam” flow

The first three mentioned degrees of freedom are the same as those adopted by Luyben (2011), whereas the splitting factor is a further step for plant optimization and is a peculiar feature of this thesis.

Reactor volume are design variables and are fixed throughout the plant life, unless the reactors are physically revamped/substituted. The reactor volume that can be found in this work is always referred to the volume of a single reactor. On the contrary, steam flow, inlet reactor temperature, and the splitting factor can be modified while the plant is running. These three variables are both a design variable, giving specification on the unit operations sizes, and act as set-point for the manipulated variables when operated on-line. By varying on-line these DoFs, it is possible to manage a real time optimization (RTO) after the plant design, which allows increasing furthermore the profitability of the plant during its operation. This aspect has not been considered in this thesis work for the evaluation of the Dynamic and Predictive Conceptual Design value (Chapter 4.4), but can be investigated thanks to the use of a heuristic method, as will be discussed in Paragraph 3.1.3.

2.1.1 Bounds and influence of LP steam flow

Low pressure (LP) steam inlet flow has to be considered as a degree of freedom because the design implies that a certain amount of steam has to be provided to the plant to make it work (as seen in Paragraph 1.3.1). It must be remembered that the action of steam acts as thermal sink, decreases partial pressure of ethylbenzene (shifting equilibria), and avoids coke formation in the reactors. As a consequence, the quantity of steam has to be controlled and can also be varied, accordingly to different conditions that can occur.

The interval proposed here is between 2000 and 5000 kmol/h as proposed by Luyben (2011) and expanded by Barzagli and Conte (2015), to fall in the range of an EB/LP Steam ratio of 12-17 as proposed in Vasudevan et al. (2009), Sheel and Crowe (1969). This DoF has a discretization step size of 100 kmol/h, which makes it quite good in case of RTO and increases a lot the precision in case of optimal plant design.

In order to highlight the effect of low pressure steam flow variations, the remaining degrees of freedom are kept fixed and the main process variables are reported in Figure 2.1.

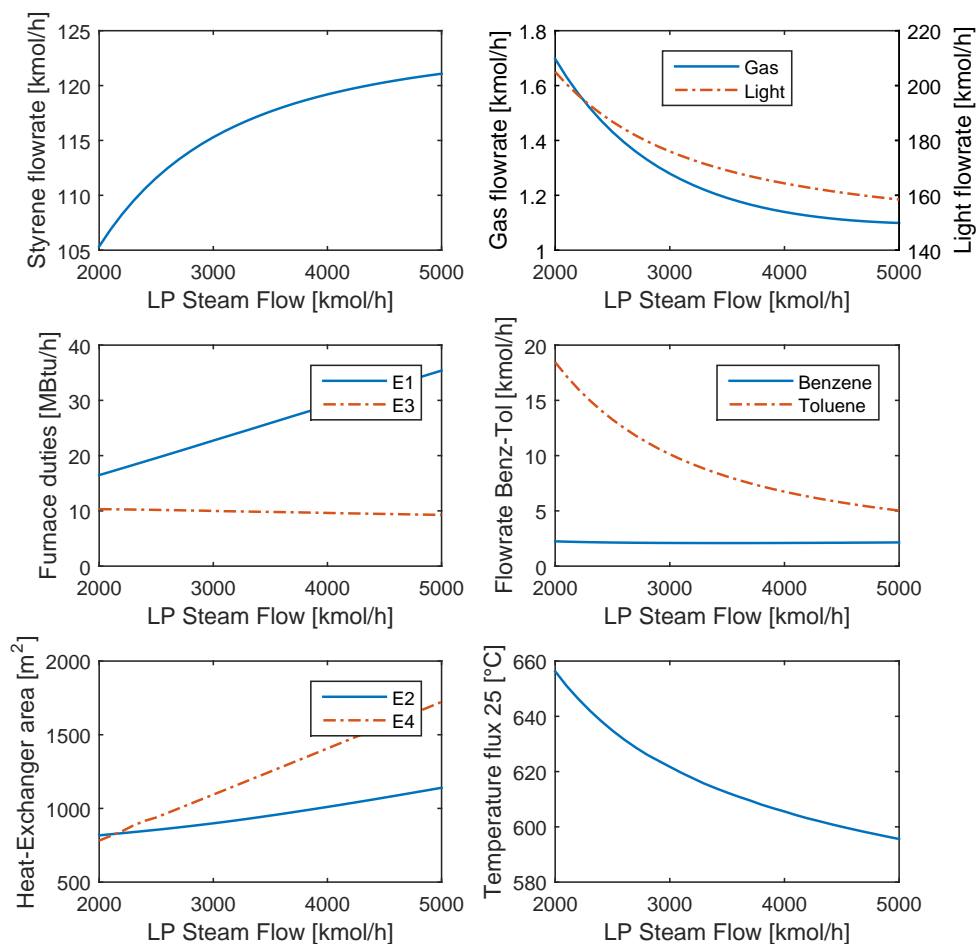


Figure 2.1: Effect of LP steam flowrate on main process variables. Inlet temperature, reactor volume, and the splitting factor are respectively fixed at 541 °C, 42.76 m³ and 0.5 [-].

Varying only the LP Steam flow among the four DoFs implies an increase of about 15-20 kmol/h in styrene flowrate production as shown in the top-left of Figure 2.1. On the

2.1. Degrees of freedom

contrary, benzene, gaseous, and light products follow an opposite trend. In the considered range, the amount of benzene reduces to a fourth of the initial quantity (from about 20 kmol/h to 5 kmol/h), whereas the molar flows of other undesired products decrease at around 1 kmol/h from the initial 1.5 kmol/h. The increase of LP Steam flow has a beneficial effect on the selectivity and conversion of the reaction, because more styrene and less byproducts are obtained.

With regard to the temperature of the flow exiting the furnace E-1, a significant reduction of temperature of more than 60 °C is observed as a consequence of the increased LP Steam flow. On the other hand, the size of furnace E-1 needs to increase due to the higher flowrate passing through that process unit and so a higher cost of the fuel oil is expected in the global economic assessment.

The heat-exchanger areas have both a monotonically increasing trend with steam flow, and their areas increase significantly due to the increase of the flowrate in those units. Consequently, their capital expenses are higher.

2.1.2 Bounds and influence of reactors inlet temperature

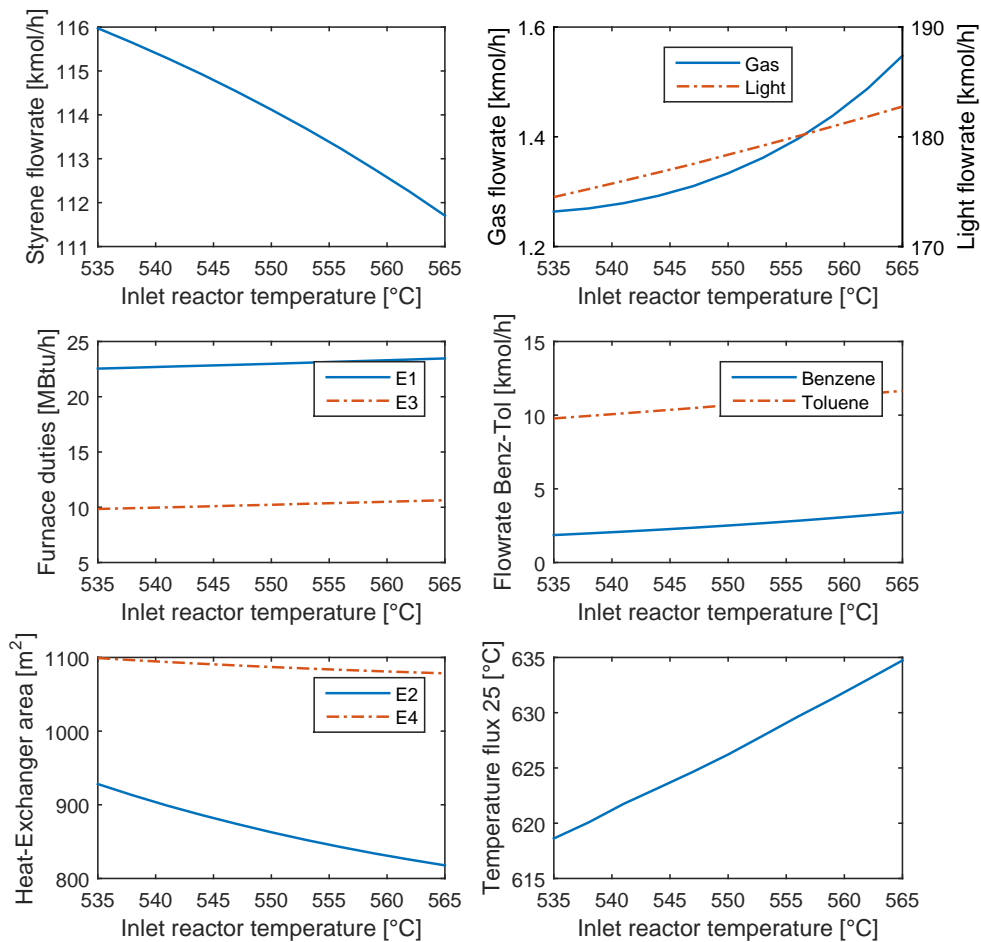


Figure 2.2: Effect of reactors inlet temperature on main process variables. LP steam flow, reactor volume, and the splitting factor are respectively fixed at 3000 kmol/h, 42.76 m³ and 0.5 [-].

The inlet reactor temperature is another essential degree of freedom for the styrene plant because it influences the conversion and selectivity of styrene production reaction. Obtaining high selectivity means that the whole plant is awarding for the user, because the styrene would be in large percentages and with little amounts of undesired byproducts, whose treatment calls for further expenses. On the contrary, high selectivity implies low conversion and, as a consequence, higher recycle ratios and bigger pieces of equipment. For these reasons, plant optimization is important to find the best compromise that maximizes the yield. Since styrene reaction is endothermic, the first conclusion would be running the reaction at the highest possible temperature. This is correct, but all physical limits (for example mechanical pipes resistance) have to be considered. In other words, temperature has to be investigated and optimized. The main assumption in this work is that the reactor inlet temperature is the same for both the adiabatic reactors, as already proposed by Luyben (2011). This allows to collapse two degrees of freedom in one (choosing only one temperature instead of two different values), increasing the computational efficiency. The temperature bounds considered in this study are 535-565 °C as already reported in Paragraph 1.3.2 and in Barzaghi and Conte (2015) with a step size of 3 °C, very tight in this case, but realistically good in case of RTO.

With the other DoFs fixed and varying only the inlet temperature in its range, styrene flowrate slightly decreases, whereas gaseous and light products increase, although in an almost negligible way. Identical considerations are valid for benzene and toluene flowrates. Costs related with products and byproducts are not heavily influenced by variations in inlet reactor temperature. The heat-exchanger E-2 area decreases more than that of E-4. The temperature of stream 25 is directly proportional to the inlet temperature as expected, once the other DoFs are fixed. Furnaces E-1 and E-3 duties are not affected significantly by the increase of reactor temperature.

2.1.3 Bounds and influence of reactor volume

Reactor volume is a degree of freedom that is closely related to reactor temperature, selectivity, and conversion. In addition, volume affects CAPEXs, because building too long plug-flow reactors would increase costs and make them unaffordable. This means that the reactor volume (which immediately implies also its size and its diameter) has to be sufficient to reach the optimal yield, conversion, and selectivity for the styrene and not excessive in order not to leave such a maximum. As for the inlet temperature, has been considered two equal size reactors, collapsing two degrees of freedom in one, as done in Luyben (2011), Vasudevan et al. (2009), with the purpose to make them interchangeable with an additional improvement. The limits for this degree of freedom are from 21.38 to 72.70 m^3 , as in Barzaghi and Conte (2015). This choice is made by setting in UniSim the reactor diameter equal to of 3.3 m (Luyben (2011)) and varying the length from 2.5 m to 8.5 m with a step size of 0.5 m, which is a compromise between accuracy and number of iterations.

Reactor volume variations produce different effects than what happens by increasing LP steam flowrate or the inlet temperature at each reactor. Figure 2.3 shows that styrene flowrate decreases only of few kmol/h by almost triplicating reactor volume. A heavy variation in the reactor CAPEXs does not imply a corresponding improvement of styrene production. Byproduct amounts have contrasting trends: as it happened with the other DoFs, benzene is little influenced and its amount remains rather constant, whereas toluene quantity almost doubles, light byproducts increase and gaseous products reach a minimum point before increasing again. E-2 heat-exchanger area, whose decrement is more evident than the one of E-4, makes the corresponding CAPEX term more advantageous.

2.1. Degrees of freedom

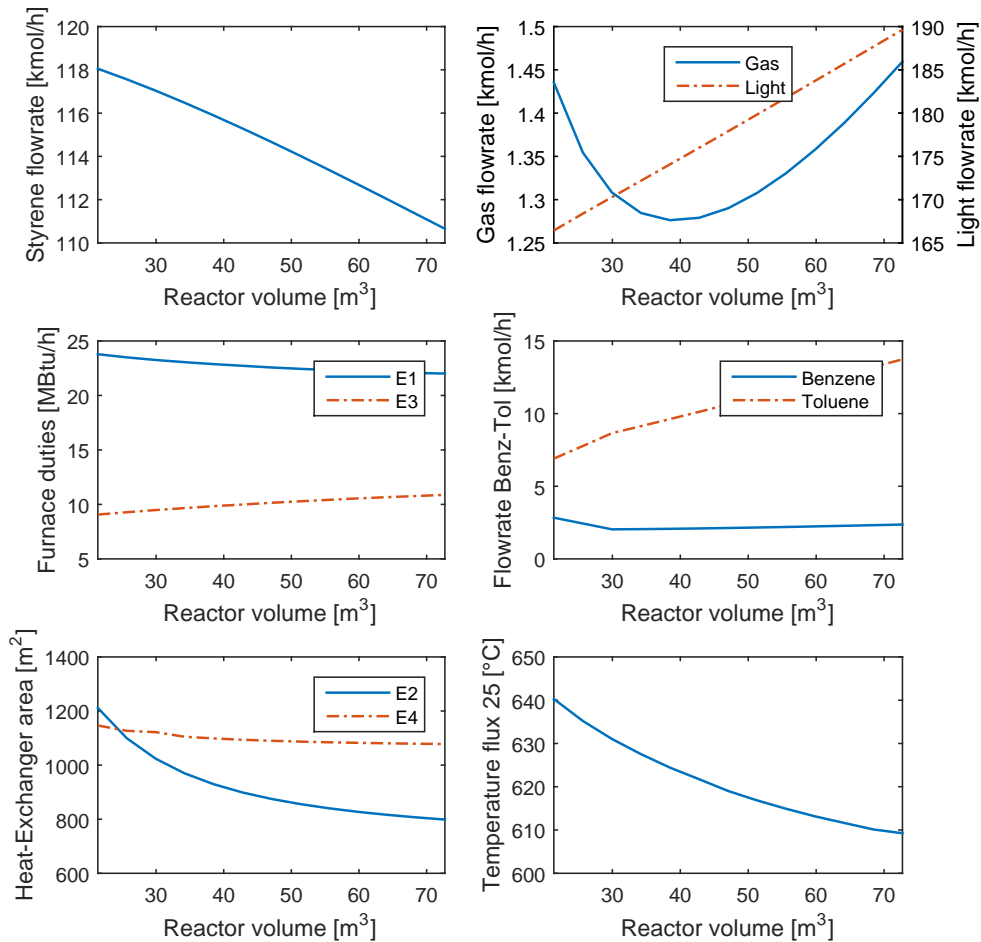


Figure 2.3: Effect of reactor volume on main process variables. LP steam flow, inlet temperature, and the splitting factor are respectively fixed at 3000 kmol/h, 541 °C, and 0.5 [-].

2.1.4 Bounds and influence of splitting factor

By looking at the plant (Figure 1.4), one aspect that has not been studied yet is how LP steam flow splits into flows 21 and 23 by the three-way valve V-4. Vasudevan et al. (2009) and Luyben (2011) chose to keep it constant to at 18% (of total LP steam in flux 21) and later utilize that DoF as manipulated variable in controller's configuration. Optimizing this splitting factor is crucial, because of the heat fluxes involved: in fact, depending on the other two degrees of freedom (LP steam flowrate and reactor inlet temperature), the furnace E-1 will be bigger or smaller (in terms of CAPEX) and will consume more or less fuel (in terms of OPEX). By just changing the heat flows and the splitting factor, also heat exchanger E-2 changes in size and influences the profitability.

These hints suggest that there should be an optimal ratio to split LP Steam into flows 21 and 23, which will be called the splitting factor of LP Steam flow.

By increasing the splitting factor, opposite phenomena happen: on one hand, E-4 area increases. On the other hand, CAPEX and fuel flow of furnace E-1 decrease initially and then stay constant. These phenomena are not visible in Figure 2.5 because the suitable physical constraints on duties are evaluated in a second phase, this constraints will be seen

later. In addition to these conflicting issues, it must be considered that the fuel prices are extremely variable over long-term horizon, which further complicates the problem.

This point suggests that it is not possible a priori to foresee where the best splitting factor value is placed. Therefore, the splitting factor can be assumed as the fourth degree of freedom in the styrene plant.

In Vasudevan et al. (2009), they assumed a variability of the splitting factor between 0.1 and 1 as the manipulated variable within the plantwide control procedure. Mostly, they explain that the splitting factor is a dynamic optimization variable: starting from this consideration and assuming it as a *controlled variable*, the on-line investigation on the splitting factor would search of its ideal set-point.

As discussed before, the splitting factor becomes the fourth DoF.

Since the splitting factor is a ratio between two flows, its bounds are 0 and 1. In order to find the optimum value, the whole range has to be investigated.

In this work different physical limits have been considered:

1. The furnace E-1 must not go below a minimum dimension: in this case, it has been assumed that its limit coincides with the limit reported in Douglas (1988) formulas to evaluate its CAPEX. So a minimum duty of 20 MBtu/h has been assigned as the inferior duty limit for CAPEX evaluation (all furnaces with lower duty will have a capital expenses equal to the one of 20 MBtu/h).
2. With reference to the duty, a furnace of 20 MBtu/h will need a minimum flowrate of fuel oil, just to remain switched “on”. By looking in literature (KLM Technology Group) can be found that the minimum turndown ratio of a furnace consists on a value of 2. By definition, the turndown ratio is “*The range of input rates within which a burner will operate*” (Wheeler (2013)). The maximum a burner can fire depends on how the burner is designed. The minimum the burner will “turn down” is based on that peculiar value. Some burners can have as much as a 50 or more turndown ratios while other types of burners are designed for only 2 or 3 turndown. For this thesis purpose a turndown ratio of 2 has been chosen, meaning that a furnace designed for a duty of 20 MBtu/h needs at least a fuel flow, to work efficiently and remain on, correspondent to a duty supply of 10 MBtu/h (a dense oil flow of 263 kg/h).
3. A further physical constrain consists in the maximum temperature that can be found in stream 25 (Figure 1.4). UniSim does not account for a limiting temperature, so it has to be monitored later during the data post-processing. Supposing that the material constituting the pipe of stream 25 is stainless steel, a limit temperature of 750 °C can be assumed to remain as much conservative as possible (Teadit North America (2008), British stainless steel association (2016) and ASM (1978)).
4. By setting all the previous constrains in a UniSim simulation, the minimum stream flow through furnace E-1 can be calculated and it corresponds to 497.3 kmol/h. This produces the maximum value of the allowed splitting factor between 75% and 90% (Figure 2.4) in function of the LP steam flowrate.

All the previous considerations suggest setting the splitting factor bounds between 10% and 90%, and chose the step size as 10% to get an acceptable precision on results.

Variations of the splitting factor do not change the styrene flowrate production, and this is

2.1. Degrees of freedom

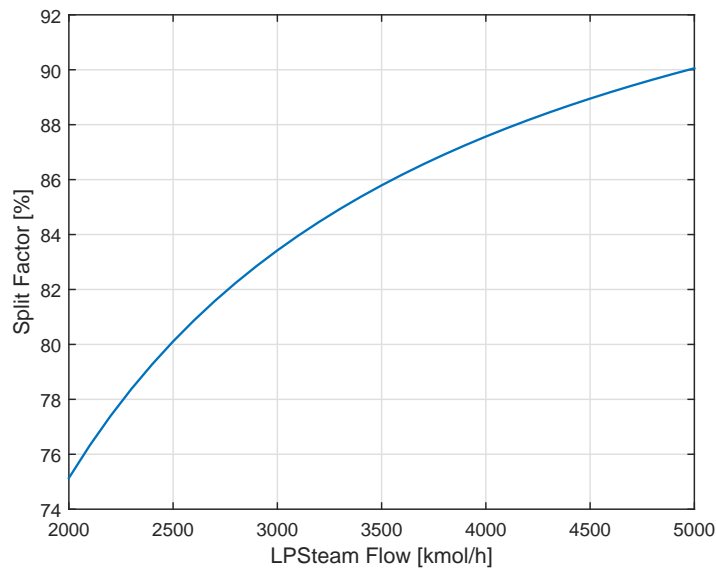


Figure 2.4: Splitting Factor upper bounds as a function of LP steam flow.

obvious because LP steam is just “distributed” in two different flows. As said before, the splitting factor influences only the heat fluxes: for this reason, the duty to the furnace E-1 decreases linearly when the splitting factor increases, because less flow enters the furnace, so a smaller furnace and lower fuel flow will be needed. E-2 heat-exchanger area increases significantly with high values of the splitting factor, because more flow enters in it. On the contrary, no effect is noticed on the heat furnace E-4, since it is not involved directly in this split. The temperature of the flux 25 out of the E-1 furnace after a value of 0.4-0.5 of the splitting factor starts increasing very quickly, because less flow enters the furnace and it needs to be heated at very high temperature to satisfy the energy balance and to achieve an inlet reactor temperature of 541 °C (in this configuration). Nevertheless, a feasibility limit on materials exists: over 750 °C, stainless steel undergoes mechanical resistance problems: this means that the values of the splitting factor over 0.8 are not consistent, because the corresponding temperature would be too high. Consequently those unfeasible values are removed in the economic evaluation of the plant.

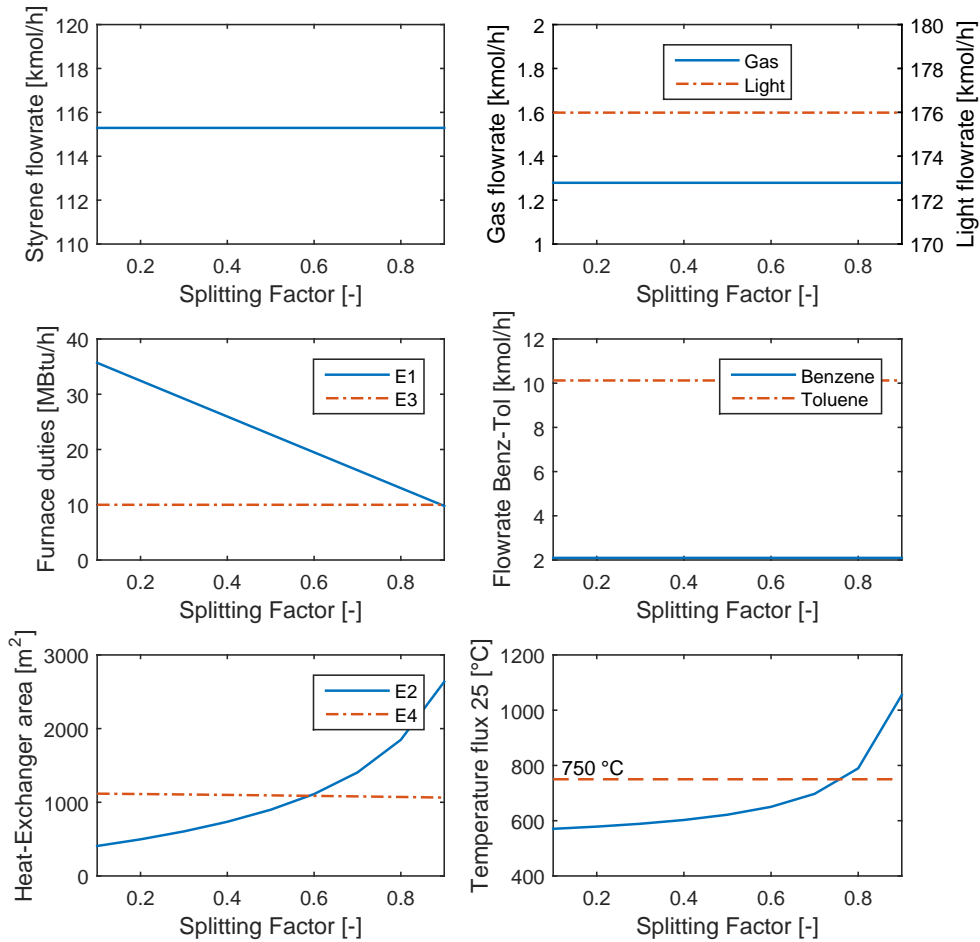


Figure 2.5: Effect of the splitting factor on the main process variables. LP steam flow, inlet temperature, and reactor volume are respectively fixed at 3000 kmol/h, 541 °C and 42.76 m³

2.2 Economic potential evaluation

2.2.1 Conceptual Design

Conceptual design is one of the methods available to analyze the economic potential (EP) of a plant as introduced in Paragraph 1.1. By using this method, it is possible to know how much money the plant will produce, after considering both the most important items of expenditure and the items of income.

Douglas suggests dividing the analysis into 5 different levels:

Level 1 - EP1: choice between batch and continuous process

This choice is the first important decision to make. The criterion is considering the requested productivity of the plant:

- if it is below 500 t/y, the process has to be considered discontinuous (batch). This

2.2. Economic potential evaluation

is usual in pharmaceutical industry, where different products are made during a year. The same plant has to be flexible for different kind of productions, which last short periods of time, usually months

- if it is more than 5000 t/y, the plant will be run continuously, which means that the plant works continuously but the maintenance periods, producing the same and only product in large quantity. This is typical of petro-chemical industry

For the styrene plant investigated in this work, the process is considered as continuous. Luyben (2011) reports hourly styrene production of 115.6 kmol, which is equal to about 12 t/h. By multiplying this quantity by 8000 h/y, which is the mean yearly time of operation of the plant, the whole produced amount of styrene is about 96,000 t/y. This value is clearly in the region of continuous processes, also because real plants in Europe and in the whole world produce on average 10 times more than what Luyben reported.

Level 2 - EP2: input-output process structure of the flowsheet

Purchasing raw materials is a significant item of expenditure: in fact, they cover 30-80% of the overall cost of the process. At this level of analysis, the separation section of the plant is considered as ideal, which means that its efficiency is equal to 1. In particular, to avoid any losses, the unreacted raw materials have to be separated, recovered, and recycled. It is highly recommended to recover more than 99% of the valuable compounds. At level-2, calculations are simplified by moving the specification from 99% to 100%.

For this reason, this approach is still conservative. The economic assessment of Level-2 takes into account only the Input and Output streams. Any internal and recycle streams are neglected.

The mathematical equation which describes this level of EP analysis is:

$$EP2 = \sum_{i=1}^{N_{Outlets}} Value_i \cdot Flowrate_i - \sum_{i=1}^{N_{Inlets}} Price_i \cdot Flowrate_i$$

EP2 is measured in USD/y.

In styrene plant, sold products are styrene, benzene, toluene, and gas. Styrene, benzene, and toluene are really sold, whereas gas is burnt instead of fuel and allows saving money. Expenses are due to inlet flows: low pressure steam and ethylbenzene fresh feed.

Level 3 - EP3: reactors, compressors, recycle

To get a more detailed analysis of the process under design and achieve an improved economic assessment, it is necessary to consider the structure of the recycle streams. At this level, also CAPEXs and OPEXs of reactors and compressors (if any) are considered. Recycling costs are the main item of expenditure in EP3, because they affect reactor and compressor flows, dimensions, and duties. The separation section is still not considered at this level.

$$EP3 = EP2 - [CAPEX_{Reactors+Compressors} / (YearsOfOperation)] - [OPEX_{Reactors+Compressors}]$$

The measure unit for CAPEXs are USD, whereas OPEXs and the EP3 itself are measured in USD/y. In order to make unit measures consistent, it is necessary to divide CAPEXs into the number of years of plant operation. In the present thesis work, 10 years life is considered.

At level 3, EP2 is reduced because of the yearly CAPEXs of reactor and compressor and the electricity costs needed to make the compressor work. In case of styrene plant, the reactors are adiabatic so they do not call for any OPEX.

Level 4 - EP4: separation system

At the 4th level of economic potential, the hypothesis of ideality for the separation system is removed.

Separation costs depend on the efficiency of the separation systems. These expenses are not negligible at all and, obviously, they reduce the earnings calculated as EP3.

For each year, EP4 is calculated as follows:

$$EP4 = EP3 - [CAPEX_{Separation}/(YearsOfOperation)] - [OPEX_{Separation}]$$

EP4 is always less than EP3 because of columns, decanter, heat-exchangers and furnaces CAPEXs, and low-sulphur fuel oil, water and steam utility OPEXs (in the styrene plant).

Level 5 - EP5: Heat-exchanger network

In general, the economic potential analysis stop at 4th level, because further investigations become more complex and they are not essential in this work. In truth, to complete the EP calculations by following Douglas analysis, a 5th level should be considered.

EP5 is calculated as follows:

$$EP5 = EP4 \pm [HeatExchangerNetwork_{changes}]$$

In the present thesis work, EP5 level is not calculated. Heat-exchangers in terms of duty, commodities and investment costs involved are already investigated in the previous EP levels. No considerations have been done, on the contrary, on aspects which are needed for a detailed EP5 analysis, such as the search for best heat-exchangers network configuration.

Cumulated EPn

It has to be noticed that OPEXs are always considered as constant in Douglas work and this is the heaviest limitation of CD. Both Barzaghi and Conte (2015) and the present manuscript overcome this limit by considering the historical price series of commodities involved in the styrene plant as extensively discussed in Chapter 4.

To evaluate the cumulated economic potential it is necessary to pass from a yearly subdivision of CAPEX to a monthly base. This happens because quotations are available monthly and result more accurate on monthly bases with respect to yearly based ones.

By summing the monthly EPn (n from 1 to 4) the cumulated EPn is found, as follows:

$$EPn_{Cumulated} = \sum_{i=1}^{N_{months}} EPn_i$$

The overall cumulated EPn says how much money has been earned (or lost) at the end of the useful life of the plant.

Since in this first analysis all prices have been considered constant in time, its formulation is trivial:

$$EPn_{Cumulated} = EPn \cdot N_{months}$$

2.2. Economic potential evaluation

with N_{months} = number of months considered for the plant life (in our case 120, which are 10 years).

2.2.2 CAPEX and OPEX evaluation

For the CAPEXs evaluation, Guthrie's formulae (Guthrie (1969)) allow evaluating the equipment cost of either investment or installation. They take into account also the material and the operating conditions of the equipment to be quoted. The general formulation is:

$$CE_{inv/inst} = a \cdot \left(\frac{M\&S}{280} \right) \cdot L_1^b \cdot L_2^c \cdot d_1 \cdot d_2$$

- CE is the Equipment cost (either investment or installation)
- a is a suitable constant whose value allowed determining the real cost of the equipment when the formula was proposed in 1969 by Guthrie
- $M\&S$ is the Marshall and Swift index at present time
- 280 was the Marshall and Swift index in 1969
- L_1 and L_2 are two characteristic dimensions of the piece of equipment (L_2 can also be missing)
- d_1 is an expression that usually takes into account the working pressure
- d_2 is an expression that takes into account the building material

Detailed formulations for each process unit of the styrene plant can be found in Appendix A. Chemical plant cost indexes are dimensionless numbers which update capital cost required to erect a chemical plant from the past to present, following changes in the value of money due to inflation and deflation.

A cost index is the ratio of the actual price in a time period compared to that in a selected base period (a defined point in time or the average price in a certain year), multiplied by 100. Raw materials, products and energy prices, labor, and construction costs change at different rates, and plant construction cost indexes are actually a composite, able to compare generic chemical plants capital costs. Cost index adopted in the thesis work is Marshall and Swift Cost Index, also known as M&S. It was established in 1926 with a value of 100. It summarizes two major components: process-industry equipment average and all-industry equipment average. Some industries considered in the process-industry equipment average are chemical, petroleum products, rubber, and paper. The all-industry average encompasses 47 different types of industrial, commercial, and housing equipment. The index is published monthly in each issue of Chemical Engineering, unfortunately not for free for the last year quotations. Since attempts of extrapolating a reliable value of M&S index based on other cost indexes (e.g., NPV, CEPCI...) were not effective, the most recent available value has been used, although it is referred to six years ago. In 2010, M&S index was equal to 1457.4. For the OPEXs evaluation in Douglas approach all prices are kept constant as a configuration in the past. In next section will be discuss the different feasible configurations for the past decade (from January 2004 up to June 2015) based on real historical quotations.

2.2.3 Economic Potential considerations

The economic analysis starts with the evaluation of the EP4 of the plant based on some quotations recorded in the past prices quotations. All the variables useful for the CAPEX and OPEX evaluation are taken from *UniSim[®] Design Suite*, via *MATLAB[®]*, as explained in detail in Chapter 3.

This study, performed with the plant described in Figure 1.4, will lead to an excessive overestimation of the steam consumption. Steam price has been evaluated with the formula in TM Swagelok Company (2011) and in U.S. Department of Energy (2013) as will be said in Chapter 4. This overestimation is due to the absence of any economizing equipment. For this reason two main approximations have been introduced:

- High pressure steam (15 bar) used as steam utility in the reboilers of columns C-1, C-2 and C-3 is laminated to 3 bar and heated up to 200 °C thanks to the first section of heat-exchanger E-4. Heat-exchanger E-4 cannot be used as steam generator, otherwise, under those pressures and temperature conditions, flux *90* would start a phase change and a temperature cross would occur in the pipes
- The hot exhausts from furnaces E-1 and E-3 are used to generate low pressure steam at 3 bar and 200 °C as it will be described later

Before evaluating the amount of steam that can be produced from the exhausts from of the two furnaces, the flue gas produced by the combustion needs to be calculated according to Forgiione and Di Marco (2002):

$$a_{theoretical} = 11.56 \cdot x_C + 34.48 \cdot x_H + 4.31 \cdot x_S + 4.31 \cdot x_O$$

$$a_{real} = a_{theoretical} \cdot AirExcess$$

Where:

- $a_{theoretical}$ is the theoretical air to fuel ratio [kg_{air}/kg_{fuel}]
- a_{real} is the real air to fuel ratio [kg_{air}/kg_{fuel}]
- *AirExcess* is the percentage of air excess. For the thesis purposes, it is equal to 1.5 and this constant accounts also for the non-ideality of combustion
- x_C Carbon percentage in fuel composition
- x_H Hydrogen percentage in fuel composition
- x_S Sulfur percentage in fuel composition
- x_O Oxygen percentage in fuel composition

Once evaluated the quantity of air, its temperature should be known. Thumb rules found in Turton et al. (2003) suggest that the flue air temperature is around 140-195 °C above the feed inlet temperature.

Thanks to these considerations it is possible to obtain the quantity of steam from the hot exhausts from the furnaces.

Figure 2.6 shows how much both these hypothesis will impact on LP steam price.

The economic recovery of LP steam (price in blue vs price in green in Figure 2.6) guarantees a non-negligible saving in terms of its cost. With steam utility price and flue gas steam costs almost constant in time, but strongly dependent from the others DoFs, this difference in LP Steam price is, at its minimum, equal to 500 USD/mo, which means about 60,000 USD in the 10 year horizon of interest.

Thanks to these two hypotheses, EP4 can be evaluated and some preliminary analysis can be performed.

Now that the economic evaluation can be performed, it is possible to find whether or not Luyben's hypothesis of omitting column C-3 is valid or is a too strong approximation.

2.2. Economic potential evaluation

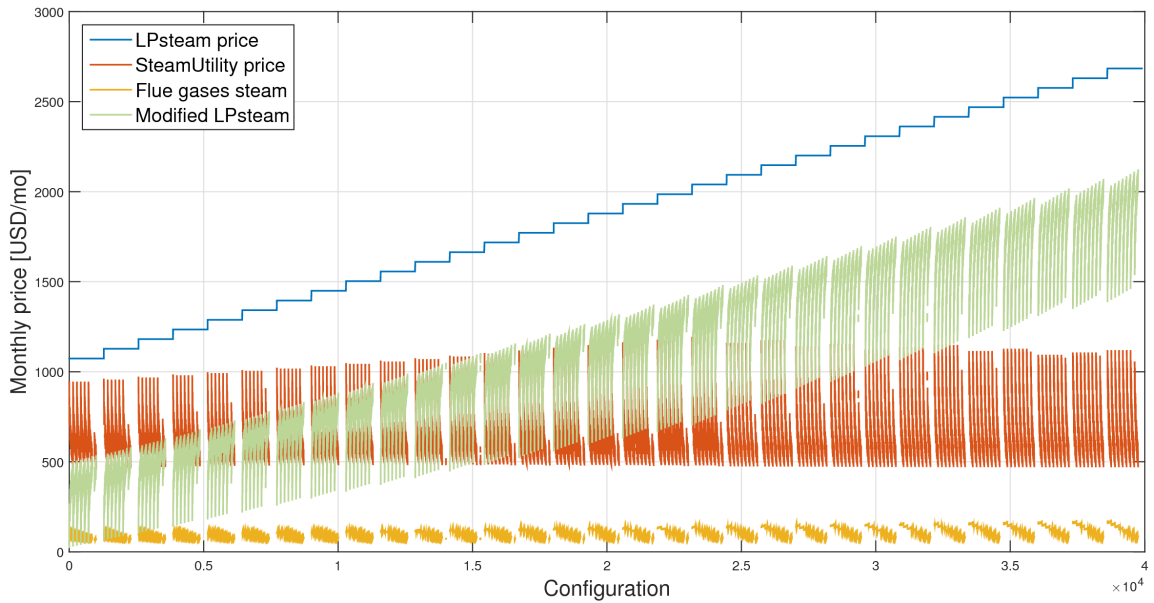


Figure 2.6: LP steam prices with and without economic recovery. The prices have been evaluated with the model described in Chapter 4 with June 2015 historical prices. The configurations are ordered to better show the results, increasing first temperature, then volume, then splitting factor and eventually LP steam (following normal grid routine).

Figure 2.7 shows how the CAPEXs and OPEXs of column C-3 affect the economic potential. The main item of expenditure is the steam utility (as already stated above steam is critical in this plant) and its contribution brings the total impact column 3 to an order of magnitude of 10^4 USD/mo respect to a calculated EP4 of 10^6 USD/mo.

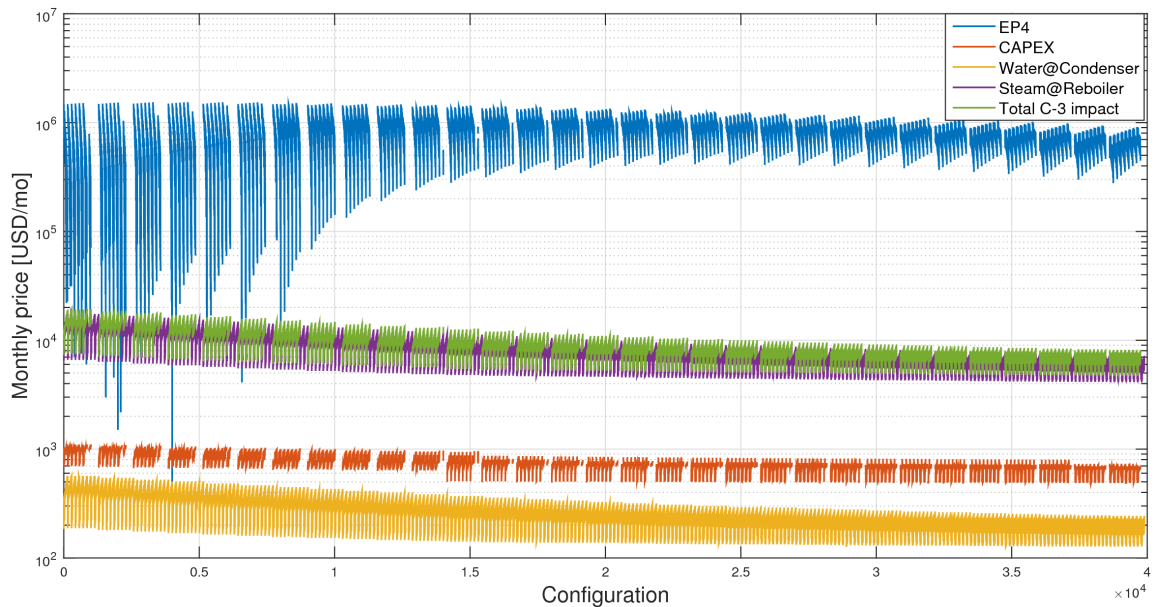


Figure 2.7: Impact of C-3 column on the economics for every plant configuration, with prices evaluated at June 2015. The configurations are ordered to better show the results, increasing first temperature, then volume, then splitting factor and eventually LP steam (following normal grid routine).

These data do not provide a complete comprehension of the impact of column C-3. For this reason the total impact of column C-3 has been compared with the other two columns C-1

and C-2 in Figure 2.8.

This plot shows that the other two columns affect the economic balance by an order of magnitude, or two, more than column C-3. Luyben's first approximation of neglecting column C-3 can be confirmed, but it must be cleared that the steam utility has a high impact on the overall EP4 evaluation, so for a fluctuating steam price accounting for that column, allows achieving a more detailed and consistent economic assessment.

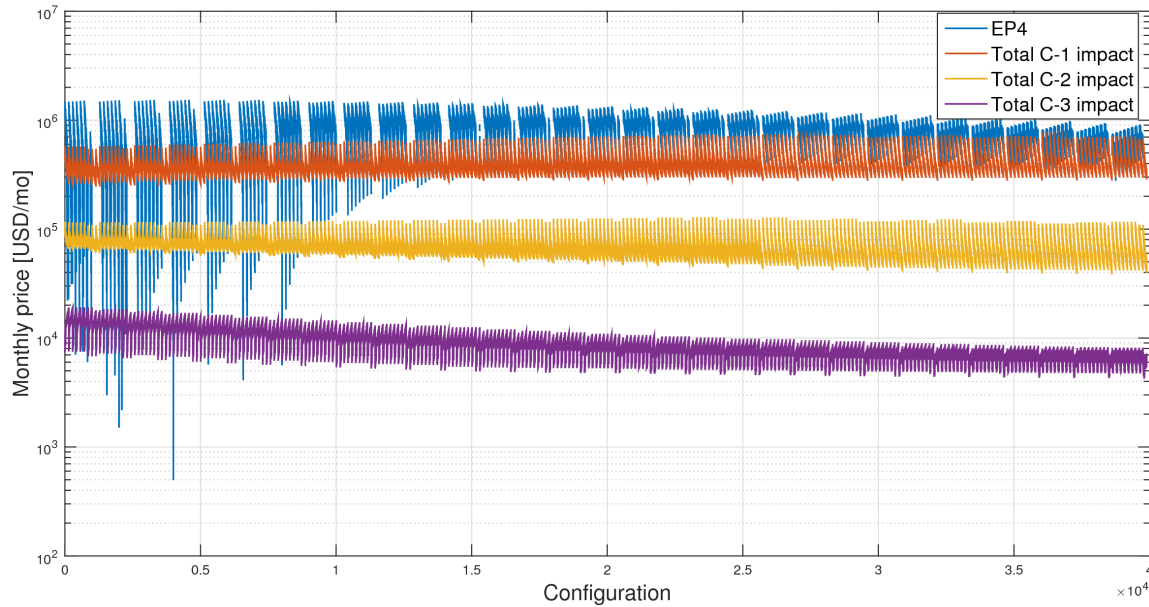


Figure 2.8: Impact of columns C-1, C-2, and C-3 over the economics for every plant configuration, with prices evaluated at June 2015. The configurations are ordered to better show the results, increasing first temperature, then volume, then splitting factor and eventually LP steam (following normal grid routine).

After the previous considerations the $EP4_{Cumulated}$ can be calculated for each configuration and for each past historical price data from January 2004 to June 2015.

The total amount of configurations obtained with the degrees of freedom specified above is equal to 39,897.

This number is the product of:

- the 9 different values of the splitting factor
- the 11 different values of the reactor inlet temperature
- the 13 different values of the reactor volumes
- the 31 different values of the LP steam flow

Among these 39,897 configurations:

- for 451 points UniSim simulation does not converge
- for 7301 points temperature of flow 25 is too high (above 750 °C)

As a consequence, among 39,897 points only 39,446 are suitable to perform the economic evaluation and 7752 points are neglected.

Not all historical prices have been found in literature, so some utilities have been evaluated by following the formulas that can be found in Chapter 4.

In particular, these data are:

2.2. Economic potential evaluation

- Water
- Steam (low and high pressure)
- Electric energy

Two different solutions can be drawn at this stage:

- One solution using the data and the econometric formulas proposed in this manuscript
- Another solution using a quite low and fixed steam price of 16.27 USD per 1000 kg. This hypothesis has been made to see whether or not Luyben's approach produces results similar to the ones with modeled steam prices and to better comprehend steam impact on EP. The steam price expressed above is reported in Turton et al. (2003).

For each month a maximum value of the $EP4_{Cumulated}$ has been found relative to those month's prices. For that maximum there is a corresponding optimal DoF's vector.

Figure 2.9 shows the 4 degrees of freedom of the maximas for each month and for the two different cases specified above.

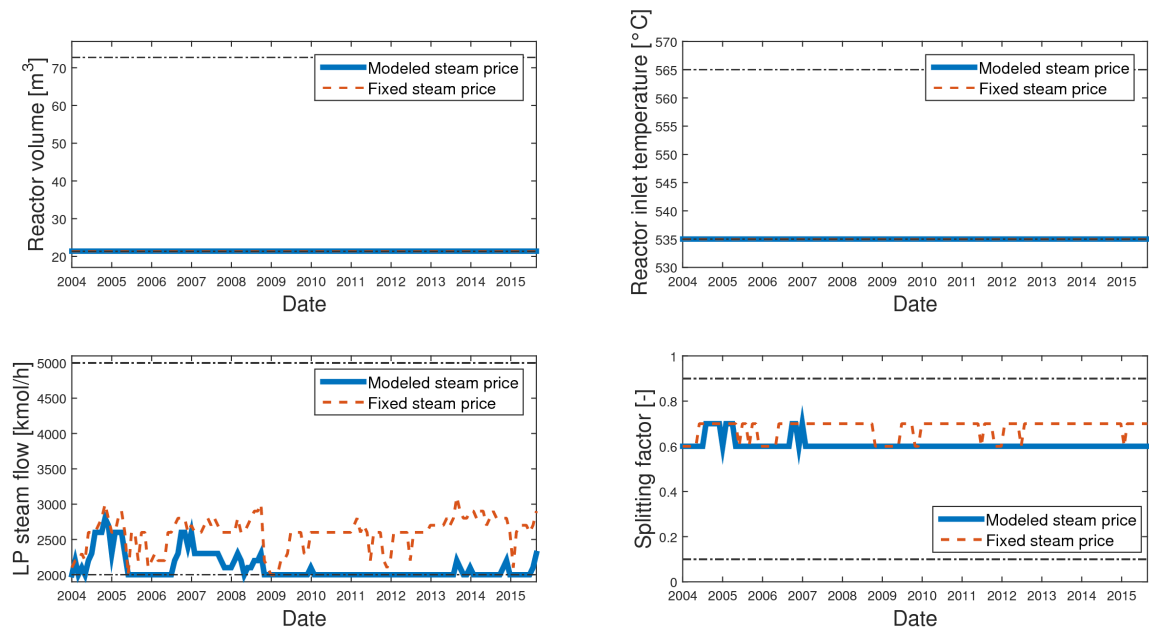


Figure 2.9: Optimal configuration for maximum $EP4_{Cumulated}$ value for each DoF. In the graphs are plotted also the bounds (black lines). Can be noticed how for volume and temperature the maximum always corresponds to the lower bound.

It can be seen that the lower bounds for the reactor volume and temperature correspond to the optimal configuration for both cases, this can be attributed to the limit in the “power law” kinetics, as already discussed in Chapter 1, and a further decrease of temperature risks to move the solution too distant from real plant analysis. Lowering the reactor volume will increase too much the ethylbenzene reflux ratio, that will increase the flux passing from the reactor and its velocity. By doing so, the mathematical computation performed may lead to significant errors under different fluid dynamics conditions with a more relevant error increase in the rate of reaction (the most critical aspect in the calculation).

Considerations are different for the LP steam flowrate. The optimal point is usually low (due to the high cost of steam) and varies significantly between the two cases. This happens because a lower steam cost allows a higher flow and its benefits outclass the price.

The new degree of freedom added in this work, the splitting factor, is found to be as high

as possible for a low steam flowrate. As a consequence of LP steam increase, the splitting factor rises from 0.6 to 0.7, these are the maximum feasible splitting factor values (as can be seen in Figure 2.4) with the addition of the other physical limit described in Paragraph 2.1.4.

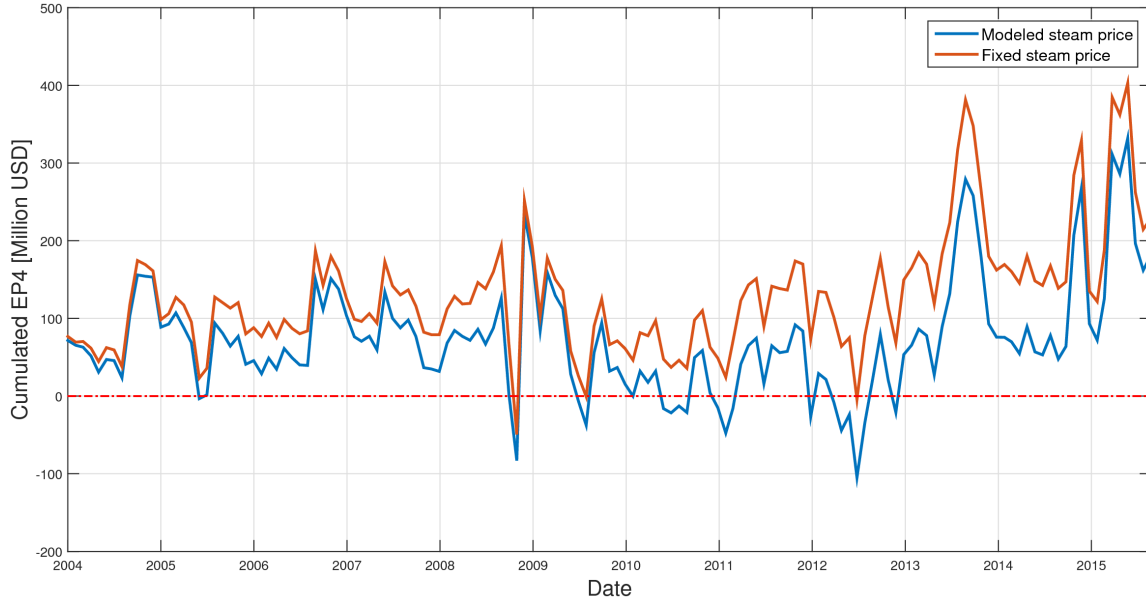


Figure 2.10: Maximum $EP4_{Cumulated}$ (over 10 years) obtainable for each monthly prices.

Figure 2.10 shows the maximum $EP4_{Cumulated}$, the EP4 multiplied for 120 months, obtainable for each month's historical prices with both approximations.

The two curves follow the same fluctuations but it can be clearly seen how the curve made with a fixed steam price is always higher and tends to overestimate the $EP4_{Cumulated}$ value. In some periods, for example from 2009 to 2013, EP4 decreases until becoming strongly negative (negative peak is about -100 Million USD). This is due to market fluctuations. In general, however, an overall $EP4_{Cumulated}$ positivity suggests that the process is profitable for the majority of past real prices.

The dynamic economic potential and its optimal configuration will be evaluated in Chapter 4. This further step of evaluation allows deepening the economic evaluation over the past prices.

Chapter 3

Algorithms and data collection

This chapter focuses on the best methods to both collect data and solve the optimization problem. Data collecting exploits an opportune link between UniSim[®] Design Suite and MATLAB[®]: the reasons for this choice will be explained and some hints on how this link works will be provided. Different paths would be available for the optimization: some algorithms are provided by MATLAB, but it is also possible to implement heuristic methods. They are more suitable than traditional MATLAB optimizers, as a result of a comparison of advantages and disadvantages, for example on CPU time. In addition, the algorithms used and some important considerations on the convergence in UniSim for the case study are also discussed.

3.1 Algorithms

3.1.1 Optimization methods

The present section carries out an analysis of optimization methods. The choice of the most suitable optimization method for the styrene plant is absolutely crucial, because the aim is obtaining the highest possible profitability and, on the other hand, different kinds of scenarios are investigated after solving the maximization and optimization plant. The choice of the best optimization method for these purposes takes into account two main aspects:

- the capacity of the optimization method to converge, independently of the starting point
- the time requested to reach the solution

Several different optimization methods have been tested to make the right choice. The initial considerations are that the present work concerns a mono-objective optimization problem: the search of the maximum cumulated value of DEP4 (see Paragraph 4.4). This objective function is absolutely non-linear, and significantly far from a quadratic approximation. In addition, the variables involved are several, 4 DoFs. For this kind of problems, MATLAB features a few optimization algorithms.

3.1.2 Optimizers

Among the optimization algorithms present in MATLAB's Optimization Toolbox, a preliminary selection with reference to the problem's features was carried out. Only 3 routines seem to be adapt for this optimization and will be discussed with their pros and cons.

The main disadvantages, which prevent from implementing these optimization methods in this thesis, will be explained briefly at the end of this subsection.

fminsearch and fminunc

These algorithms search for the maximum of unconstrained functions. Since the present objective function is constrained, these methods need the implementation of an appropriate penalty function in order to respect the assigned limits. In other words, the penalty function consists in an adequate weighting if the DoFs of the objective function (in this work the optimization of the economic potential) exceed their bounds. In this way the economic potential would results decreased and the optimization routine would not find the optimum point in that region of the domain.

Some problems could rise after the addition of the splitting factor as a further degree of freedom (see Chapter 2) because it has its own physical limits and even the MATLAB routine should take them into account. These routines are already automatized in MATLAB and look for the optimal solution varying the DoFs vector. If the penalty function is not well structured, it could pass a value out of the feasibility limits (above 1 or below 0). Another additional problem could rise if an unfeasible value (unknown to us, because due to UniSim calculations) causes an error in the PFD calculation in UniSim and the whole optimization would stop.

Anyway, some calculations¹ have been performed with these two routines and an average iteration time was found to be 170 min for *fminsearch*, and 9 min for *fminunc*.

The value calculated with the two algorithms looks very close to the starting point and not to the actual solution. This could denote that the function evaluated in UniSim have a high number of local maxima and the optimizers by themselves risk to remain stuck in local maxima solution. This can be avoided using *GlobalSearch* solver, but this would slow down even more the CPU time. *fminsearch* seems to perform better in finding the real optimal solution thanks to its simplex method routine.

fmincon

This method is a constrained method and could avoid the problem of defining a penalty function, as for unconstrained routines, giving our constrained optimization problem directly to the solver.

It finds the maximum not in a very precise way for the thesis purposes, because the optimum is too influenced by the choice of first attempt point variables value. This algorithm has an average evaluation time of 10 min, depending on the algorithm chosen. The algorithm choice is among *Interior Point*, *SQP*, *Active Set*, and *Trust Region Reflective* as specified in the Mathworks Documentation and depends also on the precision and the general setting of the problem.

3.1.3 Heuristic methods

Instead of using an optimization algorithm it is possible to use a heuristic (direct) method like *Random search (Montecarlo)*, *Univariate research*, or *Grid search*. In particular, the last consists of dividing the domain of the degrees of freedom in a multidimensional grid and evaluating the objective function in each joint. This is a so called “brute force” method. The grid method is reliable but has a point of weakness on the precision: each iteration

¹All this preliminary calculations to select the optimization routine between algorithms and heuristic methods have been done with the process simplified, with only 3 degrees of freedom (no splitting factor) and with a low performance notebook, so all the measured CPU time may be reduced by a a factor of 2 and even 3.

3.1. Algorithms

step is pre-determined and values in between these points are not calculated. On the other hand, an advantage is that all the DoF domain can be analyzed without the danger of being stuck in a local minimum solution. Heuristic methods in general are strong but less precise than an optimization routine, they are a lot slower to achieve the same precision but they could be the best choice for the evaluation of a very large number of scenario, as will be better clarify later.

For the purpose of Predictive Conceptual Design (PCD), as will be better said in Chapter 4, a large number of different economic scenarios (3000 in this work) need to be evaluated. At first sight, calculating a grid is much more time-consuming (an order of magnitude of few days with 4 DoFs) than adopting an available optimizer from MATLAB (order of magnitude of hours). This initial disadvantage is eliminated when the grid is complete. The calculation of each scenario (Step 2 in Figure 3.1) in the order of magnitude of seconds: it is much quicker than “traditional” MATLAB algorithms (each scenario follow the “Optimizer approach” in Figure 3.1). This advantage becomes very significant by remembering that styrene plant calls for the simulation/implementation of thousands of economic scenarios to be studied properly. To these remarks, it must be added that MATLAB optimizers have not negligible defects (the most significant are summarized in Paragraph 3.1.2), whereas Barzaghi and Conte demonstrated in their work that grid methods are consistent even if they suffer from low sensitivity problems.

The following graph shows how the time consumption affects the achievement of results in short time.

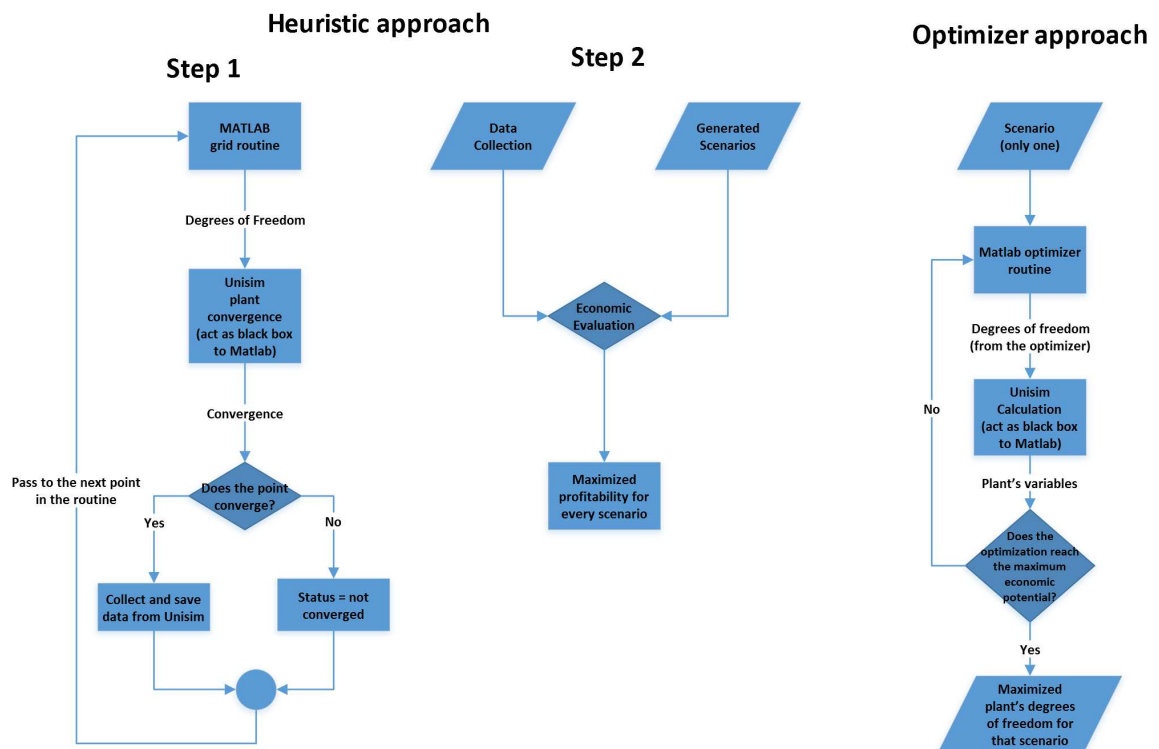


Figure 3.1: Block diagrams of the different approaches: optimizer and heuristic.

Figure 3.1 shows how the two routines, algorithm versus hierarchic method, differ one from the other: algorithm method can compute one scenario at a time, whereas grid method needs to inspect all the domain before any evaluation. Procedure called “Step 1” in Figure 3.1 needs to be completed in order to evaluate one scenario.

The algorithm is chosen considering that the use of an optimizer looks convenient for a low number of scenarios, whereas for a high number of scenarios a grid method is the best option, as can be seen in Figure 3.2.

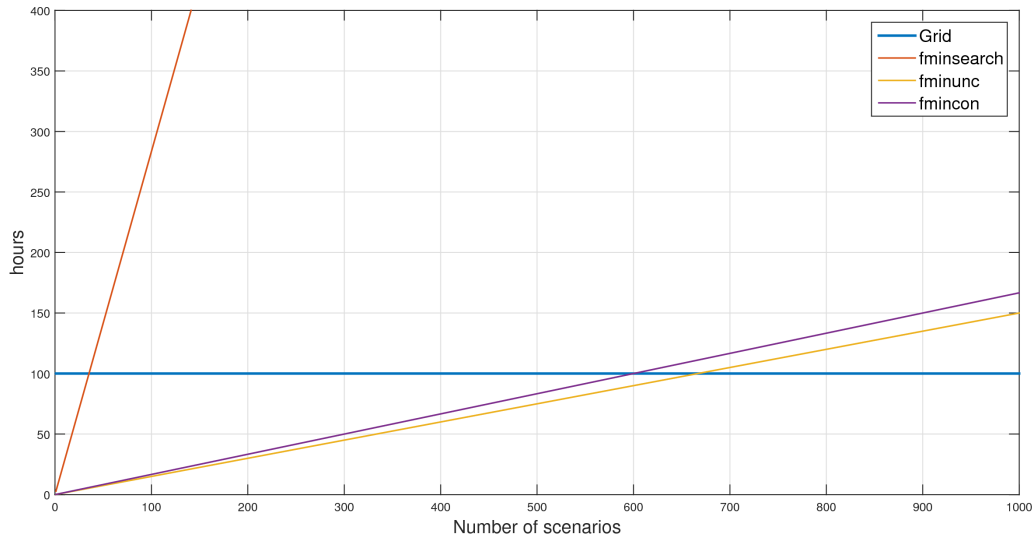


Figure 3.2: Algorithms and grid method's time in function of scenarios number.

It is evident that after just 700 scenarios all the algorithms take more time than the grid method for computation, having the disadvantage of their computation complexity, problems in precision with more than 2 degrees of freedom, local maximum problem, and as ulterior disadvantage these algorithms do not leave trace of the data taken. This means that a database containing all the possible variables (e.g. fluxes, equipment sizing ...) cannot be built and the influence of all the degrees of freedom on the process cannot be investigated.

3.1.4 Implementation of grid iteration steps

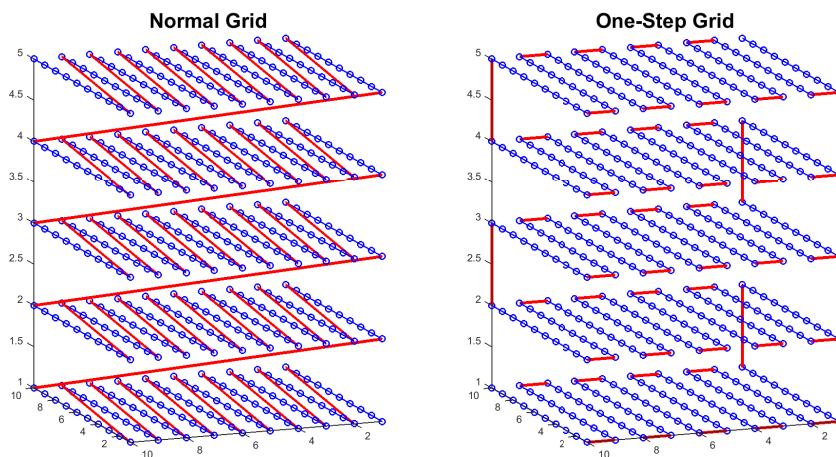


Figure 3.3: Example of different iteration routine studied to collect grid data.

A different route to collect the data using the brute-force approach can be the one-step grid method (see Figure 3.3, right). This algorithm is thought as the normal grid method already used in Barzaghi and Conte (2015), but with a difference: the normal grid method considers

3.1. Algorithms

each degree of freedom by increasing it up to its upper limit and then reset the variable from its minimum. On the contrary, the one-step grid method proposed here starts from the hypothesis that an iteration step will differ from the following (and from the previous) only from one step size degree of freedom (see Table 3.1). In theory, this new kind of grid promises to be advantageous because, for each iteration step, the plant simulator (UniSim) will change the configuration of the degrees of freedom changing only one variable, of its minimum step size. On the contrary, when using a traditional grid method could happen, for some points, that the simulator changes 2 or 3 degrees of freedom at a time (red lines in Figure 3.3, left). As a consequence, the one-step method is promising because it is able to guarantee at least equal accuracy and stability in comparison to a normal grid method.

Table 3.1: Example of the differences between the two iterations routine. The difference between iterations are highlighted in bold, can be seen that for one-step grid change only one DoF at a time, whether for normal grid more than one DoF could change.

# Iteration	Normal				One-Step			
	SF	LPSteam	Temp	Lenght	SF	LPSteam	Temp	Lenght
3061	0.1	5000	565	2.5	0.1	5000	565	2.5
3062	0.2	5000	565	2.5	0.2	5000	565	2.5
3063	0.3	5000	565	2.5	0.3	5000	565	2.5
3064	0.4	5000	565	2.5	0.4	5000	565	2.5
3065	0.5	5000	565	2.5	0.5	5000	565	2.5
3066	0.6	5000	565	2.5	0.6	5000	565	2.5
3067	0.7	5000	565	2.5	0.7	5000	565	2.5
3068	0.8	5000	565	2.5	0.8	5000	565	2.5
3069	0.9	5000	565	2.5	0.9	5000	565	2.5
3070	0.1	2000	535	3.0	0.9	5000	565	3.0
3071	0.2	2000	535	3.0	0.8	5000	565	3.0
3072	0.3	2000	535	3.0	0.7	5000	565	3.0
3073	0.4	2000	535	3.0	0.6	5000	565	3.0
3074	0.5	2000	535	3.0	0.5	5000	565	3.0
3075	0.6	2000	535	3.0	0.4	5000	565	3.0
3076	0.7	2000	535	3.0	0.3	5000	565	3.0
3077	0.8	2000	535	3.0	0.2	5000	565	3.0
3078	0.9	2000	535	3.0	0.1	5000	565	3.0

On the basis of the considerations mentioned above, the one-step grid method seems more suitable than the normal grid. However, the two methods have to be compared in terms of CPU time, which is as essential as a comparison on numerical values accuracy and robustness. If the two algorithms provide similar results, which will be discussed in Paragraph 3.2.2, the choice should go to the quickest method.

Numerical results obtained from normal grid and one-step grid are presented as follows in Figure 3.4.

Obtained results are partially different from what was expected in theory. In particular, with 3 degrees of freedom (reactor inlet temperature, reactor volume, LP steam flow) in Figure 3.4a, the one-step method takes less computation time than the normal grid with an overall mean of the difference ($CPUTime_{One-Step} - CPUTime_{Normal}$) of 1.4 s and a median of 0.6 s. This is coherent with the fact that in the first case the solver passes through equidistant points, with shorter and more performing steps than the normal grid.

On the contrary, the addition of a fourth degree of freedom, the splitting factor, leads to an

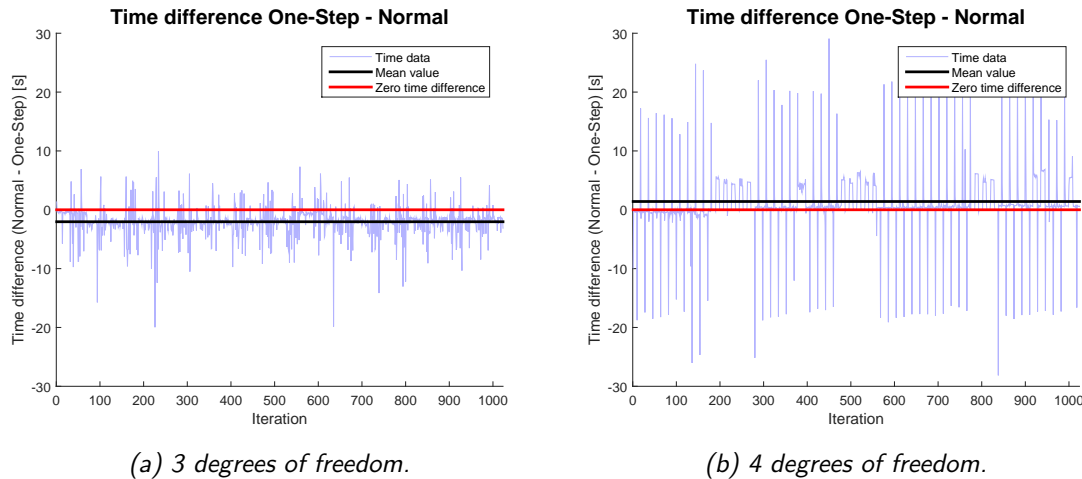


Figure 3.4: Time difference between methods evaluated as Time of one-step grid minus time for normal grid, step by step for the first 1000 points.

opposite result: the normal grid is faster than the one-step grid with a mean and a median of the difference equal to -2 s.

This conclusion could be explained in different ways:

- The problem could be in the splitting factor computation. This degree of freedom is placed in a peculiar place (Chapter 2.1.4) and its computation causes UniSim to re-evaluate only the heat section, for this reason it is the fastest respect the PFD simulation (it takes only a few seconds) but can be the critical one.
- A deeper analysis on UniSim's computation methods and rules could support more reasons for this peculiar behavior.

It must be cleared that the real reason would deserve a more careful investigation, which is not the main topic of this thesis. However, as a further analysis on this aspect would be interesting, it could be a useful point to follow in future improvements of the plant optimization, as it will be discussed in Chapter 5.

3.2 Data Collection

The styrene plant has been solved both with UniSim and MATLAB linked together via ActiveX feature of the Microsoft Windows environment, already implemented both in the simulator and in the numerical computing environment. The link is biunivocal: MATLAB can both read and write variables in UniSim Design, as can be seen in Figure 3.5. An extract of the source code used can be found in Appendix B.

3.2. Data Collection

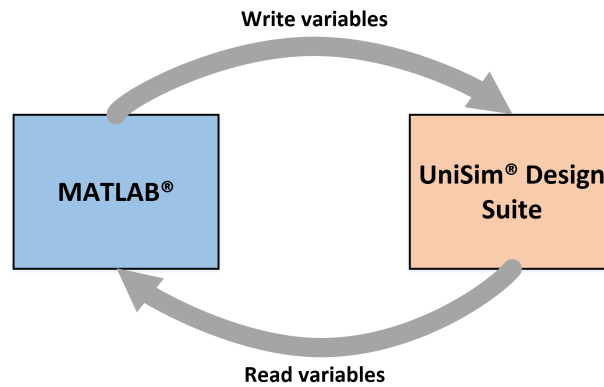


Figure 3.5: Scheme of biunivocal UniSim-MATLAB link.

3.2.1 Pros and cons of linking UniSim and MATLAB

UniSim has less accurate optimizers than MATLAB. UniSim's use is to obtain a steady state simulation of the process and from that solution get all the variables needed for the economic evaluation. In other words, UniSim is essential to obtain the convergence of the simulated PFD, which is absolutely crucial for the feasibility of the plant itself. In addition, the internal optimizer of UniSim is not that performing and, for rather complex problems, most of the times either fails or does not converge properly. Alternatively, one could use UniSim manually by means of brute-force methods but this would be a non-sense and absurd activity both in terms of huge efforts spent and poor, if any, results obtained.

On the contrary, MATLAB is ideal to solve optimization problems for any given objective function, even with a black box approach as in this case. It is possible to implement different optimization methods and to choose the best performing one in terms of both accuracy of the results and CPU time.

This link has been devised to improve the control of the results provided by the calculations. UniSim is essential to design the layout of the plant correctly and to import the accurate results from it (equipment details, flows, temperatures, pressures, compositions).

Another advantage of the connection is that UniSim and MATLAB do not work at the same time, because MATLAB waits until all useful data from UniSim are calculated and that the system has converged.

When MATLAB "calls" UniSim and passes to it the current degrees of freedom, UniSim recognizes the call and activates. It starts solving the plant to make it converge:

- If the plant converges, the requested data are provided to MATLAB, which activates and solves the user-assigned objective function.
- If there are any convergence problems, MATLAB "understands" that any piece of equipment in UniSim have not converged (usually columns C-2 and C-3) and it will not import the simulated data. This fact is then memorized in an appropriate status vector. In this way, all iterations are controllable. All the 451 not converged points (as said in the previous chapter) are located on the margin of the domain (see Figure 3.6) so the domain collected is continuous and limited.

For these reasons, the strategy followed for the overall optimization procedure consists of exporting all the useful and converged plant data from UniSim, which has calculated them, to MATLAB. These data become input values for the economic evaluation and the further

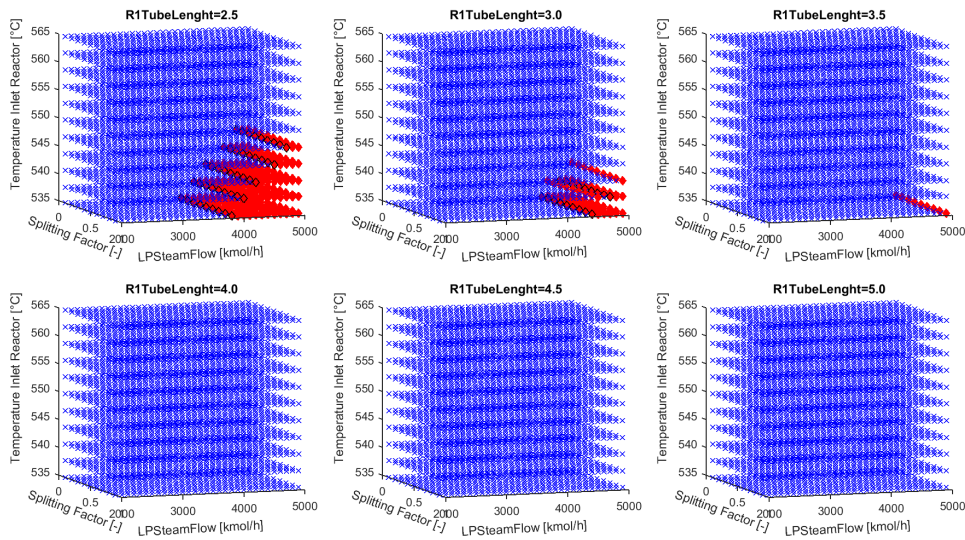


Figure 3.6: Schematic representation of the not converged points (red dots) above all degrees of freedom. For reactors length above 3.5 meters all points converged.

search for the best plant configuration.

Using two different software instead of just one at a time means that these different tools must intercommunicate perfectly and all the interruptions should be avoided, addressed, and eliminated. For example, by implementing an auto-save of the plant configuration each time, all the degrees of freedom that already converged remain saved and no data will be lost if any error occurs. By doing so, if a configuration has not converged, the next step evaluation will be done on the last converged plant, decreasing the time calculation and avoiding convergence errors due to the columns, which often have a very unstable and erratic behavior.

The main problems can be found in UniSim computation methods, so additional precautions have to be taken. During the iterations, UniSim works internally and it is impossible to see the plant's variables for each configuration, so it is important to study in advance the different problems that can be found and take precautions on them, for example as we advise for the splitting factor variable in Paragraph 2.1.4.

3.2.2 Problems on tolerances in UniSim

In order to reach the plant convergence with accurate results, choosing the most suitable tolerance values has been one of the most critical aspects for the plant calculations in UniSim. First of all, each piece of equipment has its own convergence tolerance. In truth, this is not a real problem because only the recycles really affect the results. This conclusion has been drawn by testing a large number of modifications on columns, reactors, and recycles tolerances. Modifying the first two does not imply any significant change on the results, whereas the most relevant impact comes from changes in the recycle tolerances.

First of all, each time a material stream (only material and not energetic) returns to the plant, a "Recycle" operation has to be conferred in UniSim. This unit simply takes the entrance stream and places it to its outlet. In this way, the calculator knows the composition of that stream and can account for it. In the plant described in Figure 1.4 only one recycle unit needs to be placed between the bottom of column C-2 and the *Recycled EB* stream.

The problem in this operation is that UniSim starts calculating the whole plant. When

3.2. Data Collection

the solver reaches the recycle, it updates the value of the outlet stream and restarts the calculations. It continues until the difference between the inlet and the outlet is below the assigned tolerance or until it reaches the limit of iterations.

Once having noticed this first aspect, the aim is finding the right compromise between a sufficiently narrow tolerance and a reasonable CPU time.

Default values for recycle are all expressed in terms of absolute tolerances, the only exception is the flow tolerance, which is relative rather than absolute. All the values can be found in Table 3.2.

Table 3.2: Default recycle tolerances in UniSim.

Variable	Internal Tolerance
Vapour Fraction	0.01
Temperature	0.01
Pressure	0.01
Flow	0.001
Enthalpy	1.00
Composition	0.0001
Entropy	0.01

UniSim recycle option shows the multiplier applied for these default tolerances. The default multiplier value is 10 for each physical dimension considered.

For example, the internal tolerance for Temperature is 0.01 (see Table 3.2) and the default multiplier is 10, so the absolute tolerance used by the Recycle convergence algorithm is $0.01 \cdot 10 = 0.1$. Therefore, the assigned temperature and the calculated value must be within 0.1 °C.

In the present work, this multiplying factor has been significantly reduced from 10 to 0.001, which means that tolerances were narrowed of 3 orders of magnitude on all the variables of Table 3.2. The choice of having the same multiplier for all the physical dimensions is not mandatory. It must be noticed that the aim is to have very accurate values on compositions. For other dimensions (especially temperatures and pressures), the requested precision would have been less compelling, because a precision on the tenths of Celsius/Kelvin degree or kPa is not required and it does not produce a significant impact on the results.

Having very tight tolerances is in fact essential for two main reasons: obtain accurate results and, most of all, determine convergence values that are independent from the starting point of the iteration.

For this reason, the results taken from the two different iteration routines have been studied: normal grid and one-step grid and their difference in terms of economic values (i.e. CAPEX and OPEX over a 10 year horizon) are shown in Figures 3.7, 3.8, and 3.9.

By looking at the bar diagrams, it is evident how much the starting convergence state in the PFD in UniSim will influence the final results. This may be due to the calculation routine already implemented in UniSim and the most important tolerance, as said above, is the recycle one.

The CAPEX evaluation does not have high differences between the methods and an error of $10^2 - 10^3$ USD is negligible over an Economic Potential value of 10^8 USD.

More critical problems occur when OPEX are considered. It has to be said that the maximum error found between the two iteration routines is of about 0.8 kmol/h, which can be considered very low and negligible when evaluating only a single plant configuration with a

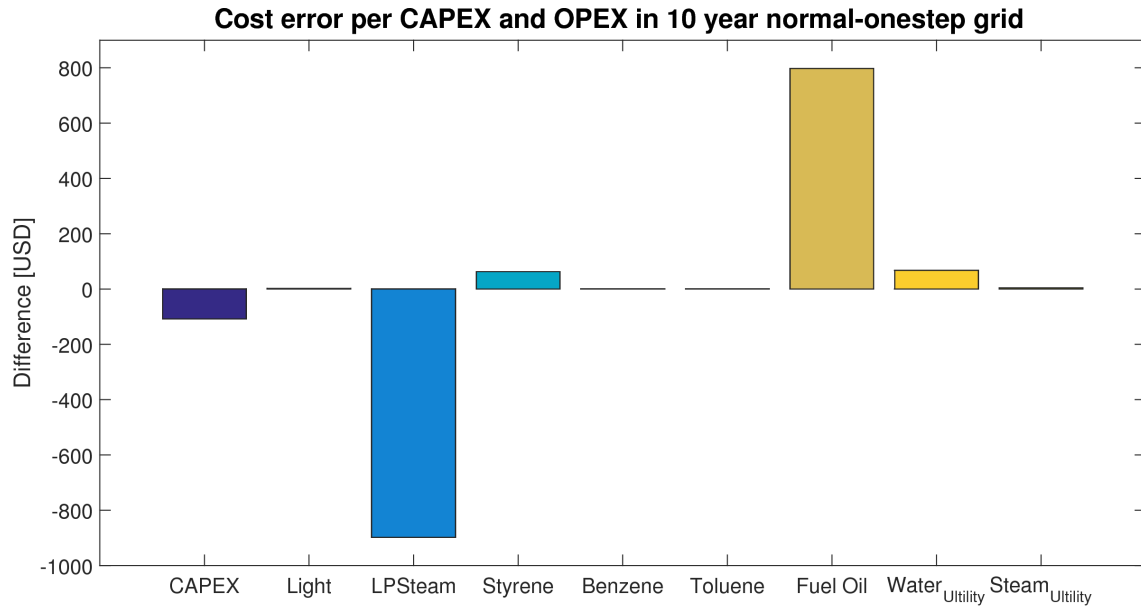


Figure 3.7: CAPEX and OPEX differences for the main streams and all capital expenses with fixed prices at June 2015. This iteration point correspond to a splitting factor of 0.5, a LP steam flux of 3000 kmol/h, a reactors inlet temperature of 541 °C, and a volume of 34.21 m³ for each reactor.

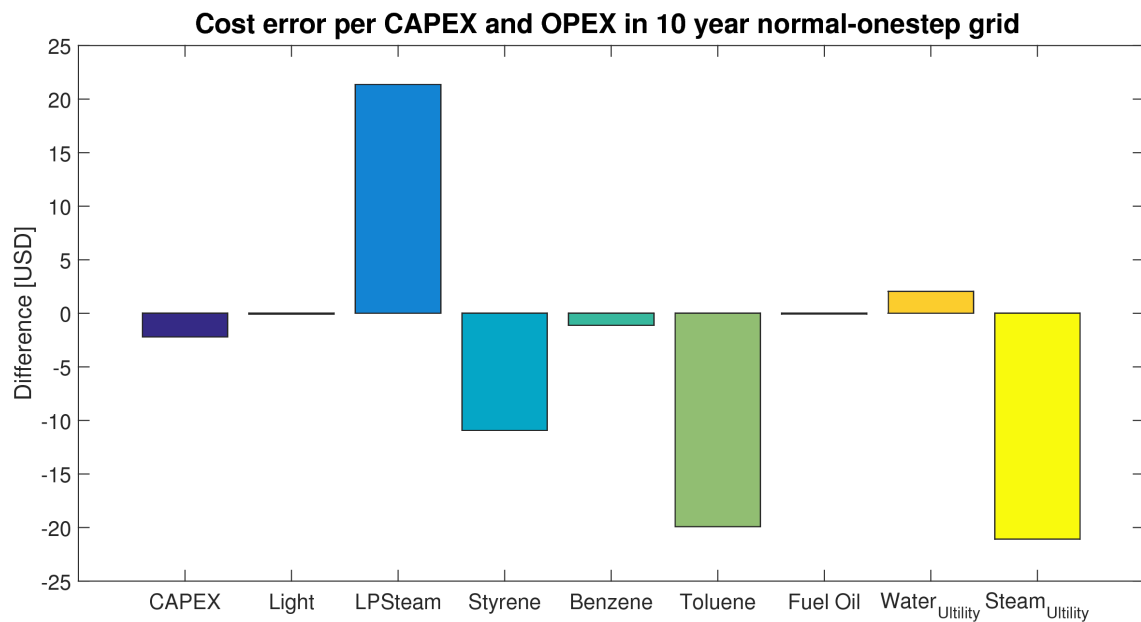


Figure 3.8: CAPEX and OPEX differences for the main streams and all capital expenses with fixed prices at June 2015. This iteration point corresponds to a splitting factor of 0.3, a LP steam flux of 4500 kmol/h, a reactors inlet temperature of 556 °C, and a volume of 25.66 m³ for each reactor.

conventional conceptual design approach. Conversely, that error (i.e. 0.8 kmol/h) cannot be neglected for the development of this thesis.

The reason for which even a very small error could influence our calculation is due to the time horizon considered. Every flow stream data has to be multiplied for its price, which is very low for water and much higher for styrene, and then for 8000 h/y and for 10 y.

At last, a factor of 10⁴ multiplies the convergence error and for styrene, for instance, can

3.2. Data Collection

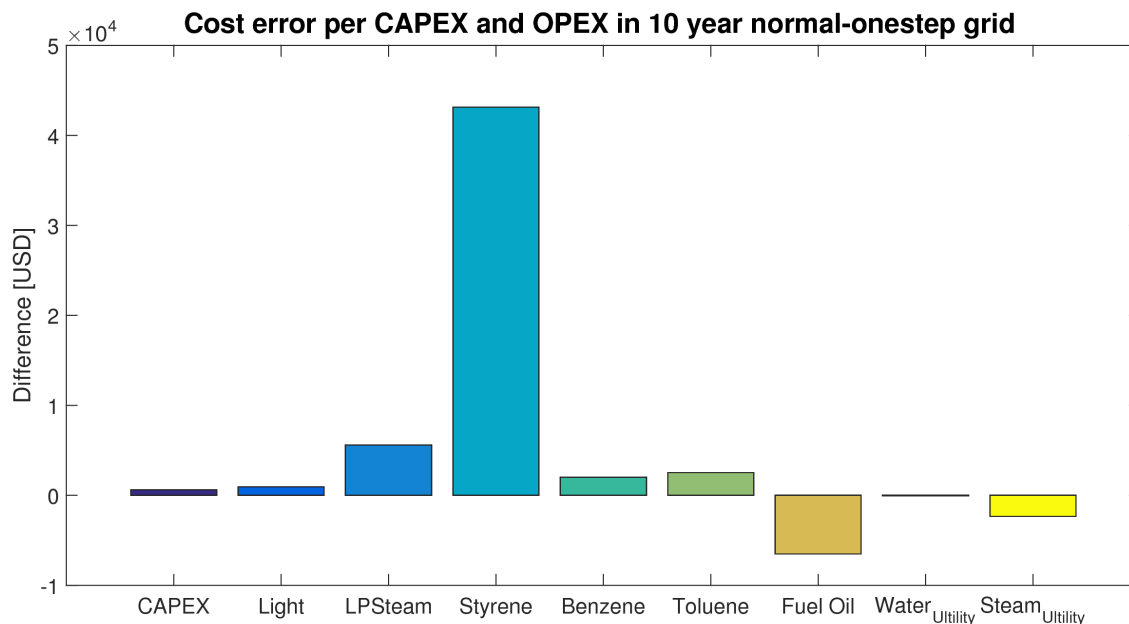


Figure 3.9: CAPEX and OPEX differences for the main streams and all capital expenses with fixed prices at June 2015. This iteration point corresponds to a splitting factor of 0.6, a LP steam flux of 3600 kmol/h, a reactors inlet temperature of 547 °C, and a volume of 34.21 m³ for each reactor.

become 10^7 being its price of 155.51 USD/kmol (June 2015 quotation).

These considerations can be clearly seen in Figure 3.9, where an apparently negligible error on styrene flowrate of 0.00347 kmol/h is significantly amplified by the above-mentioned issue, to become an overall error in the economic potential assessment over a 10 year horizon of 43,131 USD referred to a cumulated EP4 value of $1.30 \cdot 10^8$ USD. This shows how even a small error could lead to high economic differences, which are small in relative terms but become important to have a feeling on the data accuracy.

The distribution of these errors is stochastic and not in all configurations the same variables bring to the same errors (see Figures 3.7, 3.8, and 3.9), making this values unpredictable. It is also important to point out that the correct value is unknown, which implies that both data could be equally correct or wrong/not consistent.

Tightening the recycle convergence up to its limit of 0.001 (above which no improvement is achieved) allows obtaining results with a very low relative error around 0.03%. When this precaution is not taken into account, which means with convergence limits superior of some orders of magnitude, the relative errors on the final results reach a value of 1-2%. This percentage would be significant in absolute terms, on a total EP4 of 10^8 . Such a small relative error allows performing very consistent and stable economic evaluations consequently the results of the overall assessment of CD, DCD, and PCD are correctly and consistently evaluated.

Chapter 4

Dynamic and Predictive Conceptual Design

The following part of the thesis deals with the Dynamic and Predictive Conceptual Design approach, which improves Douglas's Conceptual Design by introducing variable commodities and raw material prices. Based on quotations from 2004 to June 2015, a DCD analysis is performed. Thanks to some historical data, econometric models allow foreseeing future prices trends. The main feature of these models is that they usually depend on raw material prices (e.g. crude oil) and on the previous month quotation of the product of interest. Once having studied accurately the econometric models, the generation of different future price scenarios becomes possible. Eventually, different optimized configurations of the plant are analyzed under Predictive Conceptual Design (PCD) hypothesis. Discussion about the reliability of this approach, best possible configurations, and confutation with DCD results will be included.

4.1 Introduction to Dynamic and Predictive Conceptual Design

An effective approach to the search of the maximum possible earning is considering the problem on a dynamic point of view. This means that product and reactant values vary in time, according to the market quotations. Differently from the conceptual design methodology, dynamic models consider quotations variability and this is a significant improvement in terms of accuracy.

Cumulated DEP are calculated with the following formula:

$$DEP_{nCumulated} = \sum_{i=1}^{nMonths} EP_{n_i}$$

where EP_{n_i} is the economic potential of level n in the i^{th} month.

Two different paths can be followed by adopting a dynamic model:

- performing the Dynamic Conceptual Design calculation, using the historical prices for the past 10-year horizon (from July 2005 to June 2015).
- performing the Predictive Conceptual Design (as proposed in Barzaghi et al. (2016)) using the prices calculated by following econometric models, in a high number of

scenario. In this work, 3000 scenarios were calculated in order to have a sufficiently large pool of data of possible future prices.

The search of the maximum $DEP^4_{Cumulated}$ of the plant can be obtained by no longer considering a unique constant set of prices, but analyzing the historical price series of the last years (e.g., 10-12 years).

Monthly EPn are summed by considering prices at the specific period under analysis. Many $DEP^n_{Cumulated}$ are obtained in this way: the highest value determines the optimum plant configuration for that economic scenario. By applying this method, one optimum configuration can be found for past quotations of all raw materials and commodities involved in styrene production plant.

An intrinsic weakness of this methodology is that prices related to the past are used to infer an optimal configuration for the future. To overcome this critical issue, a better performing method consists of calculating optimal values for the future by maximizing $DEP^4_{Cumulated}$ for each future evolution scenario. Each scenario will depend on considered quotations and these scenarios distributions are shown in Paragraph 4.3.

4.2 Econometric models

4.2.1 Economic vs econometric models

In order to foresee future prices on raw materials and commodities, two different categories of models can be adopted:

- economic models
- econometric models

Economic models consider real price fluctuations, also by analyzing political scenarios, supply and demand trend, and other relevant aspects. On one hand, this approach allows calculating prices based on a real-time evidence, but on the other hand this is an intrinsic limit of the model, for two reasons:

- prices and quotations need continuous updates in order to produce consistent estimations
- these models provide an accurate estimation for the present, but predictions on a long-term horizon are not reliable

On the contrary, econometric models are based on the historical series of prices in the last years for that raw material or commodity. In other words, they are less focused than economic models on the current quotations and fluctuations and they do not investigate in detail the reasons of the current situation. In truth, this is the main advantage of econometric models: since they implement a long period of quotations, although obviously of the past, they are useful for medium- and long-term predictions. Core of econometric models is to forecast the trend of prices for the future, given last years' quotations.

In addition to this, considering somehow the reasons of this trend becomes possible also to force different kinds of scenarios: bullish, bearish, and constant in time.

Since econometric models are more suitable for the purposes of the present thesis, they will be chosen and implemented.

4.2. Econometric models

The purpose of the thesis is calculating the $DEP4_{Cumulated}$ trend of a styrene plant. Therefore, the knowledge and model of styrene price is crucial. In the plant, however, also other commodities and utilities are involved, in particular:

- Crude Oil (CO)
- BTZ Fuel Oil
- Ethylene
- Ethylbenzene
- Benzene
- Toluene
- Electric Energy
- Water
- Steam

To build a robust econometric model, Barzaghi and Conte 4-terms moving average has been kept. This is a lagging statistical indicator calculated as follows:

$$\tau(t) = \frac{1}{m} \cdot [y(t) + y(t-1) + y(t-2) + y(t-3) + \dots]$$

where:

$\tau(t)$ is the value of the moving average

m is the number of terms which were averaged: in this work, Barzaghi and Conte choice of averaging 4 terms is confirmed, as they demonstrated in their thesis work it was suitable for these purposes

y is the value of the price series in a precise time interval

Moving average and real prices trends are coherent. As expected and as it will be seen also for other commodities, the moving average is a smoother curve, because it is obtained with the mean of consecutive values, whereas the real price plot shows peaks frequently.

The present thesis bases the future economic evaluation after June 2015, since the most recent prices were found for that month.

Using moving average, the econometric models can be evaluated by minimizing the sum of square errors between the model and the real prices from Jan-2004 to Mar-2012 and verifying that throughout the domain of interest (up to June 2015) the error remains near zero. The econometric model is in the form:

$$y_i(t) = a_0 + a_1 \cdot y_i(t-1) + a_2 \cdot y_i(t-2) + a_3 \cdot y_i(t) + \dots$$

where $y(t)$ is the price at month t

$y_i, y_j \dots i, j$ are the different commodities

$a_0, a_1, a_2, a_3, \dots$ are the regressors used in the model

It is not true that more regressors are used, better performing is the model, because if the model has too many parameters, it will not be accurate out of the regression interval, and this becomes a critical aspect for predictions in the future. The experimental evidence

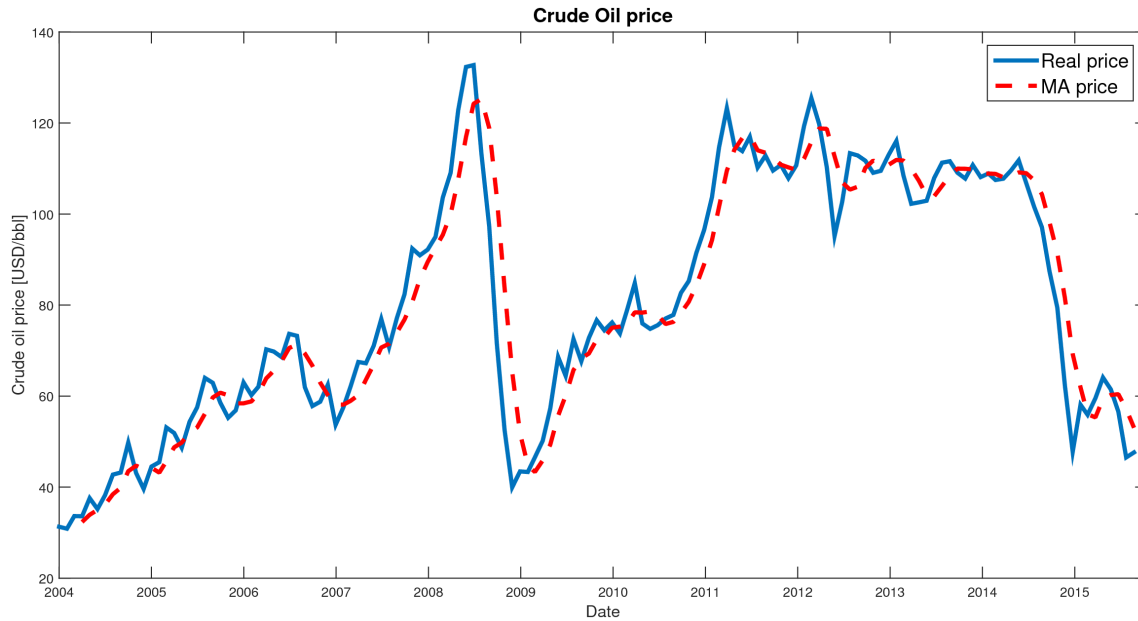


Figure 4.1: Crude oil real price and its moving average (red dashed line).

helps to choose how many regressors are needed.

It is expected that most recent prices in the past will have the greatest influence on present ones. The price of a product always depends on its last month quotation and sometimes on its penultimate. In many cases, but not always, prices depend on other commodities quotations in the same month, or also of one, two or three months before.

The choice of the most suitable econometric model is made by looking at some different parameters, which will be explained in Paragraph 4.3.

Correlograms and autocorrelograms

The preliminary study for an econometric model is based on correlograms and autocorrelograms.

Correlograms are plots that show the relationship between the quotations of a raw material or a commodity and the product of interest. They help in identifying the time dependence and any possible delay between the quotation of the reference component and the ones of the depending commodities. Correlation index varies from -1 to +1.

If it is equal to -1, the trend of the two variables is perfectly opposite.

If it is equal to +1, the correlation is perfectly positive: the two variables follow the same trend and the relationship is linear. In general, the higher the correlation, the greater the influence of that price product on the quotation of the commodity of interest.

Some example of correlograms can be found in Figures 4.8, 4.17, 4.12, 4.23, and 4.27.

Autocorrelograms indicate how the past price of the commodity of interest affects its current price. An autoregressive model connects the current value of the variable to its past values, in order to consider the statistic dependence between observations made at different times.

Pearson-Bravais correlation index and adjusted- R^2

The square of Pearson - Bravais correlation index, which can be named R^2 , is the coefficient used to determine whether a model respects the historical prices correctly or not. This index

4.2. Econometric models

is the ratio between the covariance of the two variables and the product of their standard deviation:

$$R = \frac{\sigma_{xy}}{\sigma_y \cdot \sigma_y}$$

where σ_{xy} is the covariance and is calculated as follows:

$$\sigma_{xy} = \frac{1}{N} \cdot \sum_{i=1}^N (x_{model,i} - \mu_{x_{model}}) \cdot (x_{real,i} - \mu_{x_{real}})$$

where N is the number of data available for the statistical evaluation (size of the pool)

$x_{model,i}, x_{real,i}$ are the variables of the data set

$\mu_{x_{model}}, \mu_{x_{real}}$ are the mean values of the two statistical variables

Covariance measures the linear relationship between statistical variables X and Y.

A more consistent parameter is the so-called *adjusted* – R^2 , which verifies if a parameter addition and a consequent complication of the model really improve it.

The *adjusted* – R^2 is calculated with the following formula:

$$R_{adjusted}^2 = R^2 - (1 - R^2) \cdot \frac{p}{n - p - 1}$$

where R^2 is Pearson-Bravais coefficient

p is the total number of parameters considered

n is the number of data considered

The regressive parameters are calculated by minimizing the sum of squared errors (SSE) between foreseen prices and real prices. This typology of model is one-step ahead, because it uses the past real values in moving average quotations for each prediction. Aim is minimizing this squared sum, which means that the difference between estimations and real values must be as small as possible.

The formula to calculate SSE is:

$$SSE = \sum_{i=1}^{Ndata} (x_{model} - x_{real})^2$$

The optimization formula minimizes the SSE modifying the parameter of the model, as already explained in Paragraph 4.2.1.

Historical series of prices

The modeling of crude oil (CO) quotation is fundamental, even if it does not appear in the process. This is due to the fact of having a reliable reference for all the commodities, for this reason CO appears as an independent variable in all the commodities of interest. In the commodities in which crude oil does not appear directly, its dependence is indirect via other quotations. Under these considerations, the best and most coherent strategy is modeling all the economic scenarios on CO quotation, then evaluating all other streams econometric models (more info about the scenarios are provided in Paragraph 4.3).

The choice of adopting a reference raw material for all econometric models such as crude oil, which is quoted on all international markets, will lead to generate robust and reliable scenarios, as already discussed in Fini and Oliosì (2010), Manca (2013a), Manca (2013b),

and Manca et al. (2015).

Since it was impossible to find a unique plot with all quotations in our decade of interest, historical prices found in this work were taken from different sources online and then merged together to form a continuous plot of monthly quotations. First of all, crude oil quotations were taken from the website of *U.S. Energy Information Administration* and can be seen in Figure 4.2.

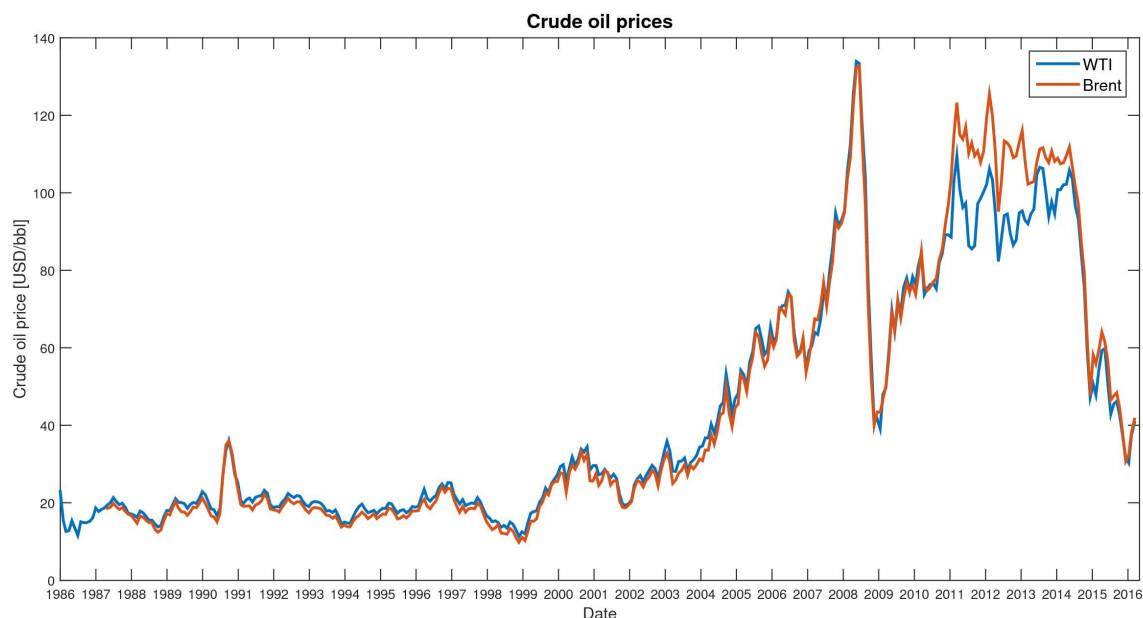


Figure 4.2: Crude oil prices: Brent vs. WTI.

Two main crude oil prices are available: Brent and WTI (West Texas Intermediate). The first is a high quality crude oil (low density and low sulfur content) extracted from North Europe and the second is the American reference one. The trend of prices between 1986 and the first part of 2016 is plotted. In the main part of 1986-2016 period, WTI and Brent prices are very similar. Main price variations are concentrated in the last decade. In particular, after a fast increase between 2006 and 2007, a fall of prices can be found around 2008. This strong decrease is due to the crisis started in the U.S.A. from the bursting of the housing bubble and then leading to the collapse of big institutions and banks like Lehman Brothers. On the other hand, it is also interesting to denote the different trend of the two quotations in the 2010-2014 period. In fact, WTI price is systematically inferior than Brent quotation and this discrepancy is significant, as it can be noticed in Figure 4.2. This difference will influence the evaluation of the econometric models depending on which quotation will be chosen. In this work the Brent quotation has been chosen on the hypothesis of installing the plant in Europe, specifically in Italy as will be pointed out in Paragraph 4.2.2, so the Brent quotation seems the most adapt.

The historical prices of the commodities are not easy to be found for free online. The majority of the databases (Orbichem, ICIS, Platts, IHS ...) are very expensive or do not contain all the data. This could lead to incongruousness. For styrene, benzene, toluene, and ethylene two different databases have been used: for the first 10 year period a free datasheet of presentation of Orbichem containing data from West Europe quotations has been used, getting the data one by one from the plot with the free online software *WebPlot-Digitalizer*. The remaining monthly prices, from November 2013 to June 2015, has been taken from another plot with data from HIS database from January 2013. The two plots were superimposed in the common interval and has been noted that the data taken match

4.2. Econometric models

well, as it can be seen in Figure 4.3.

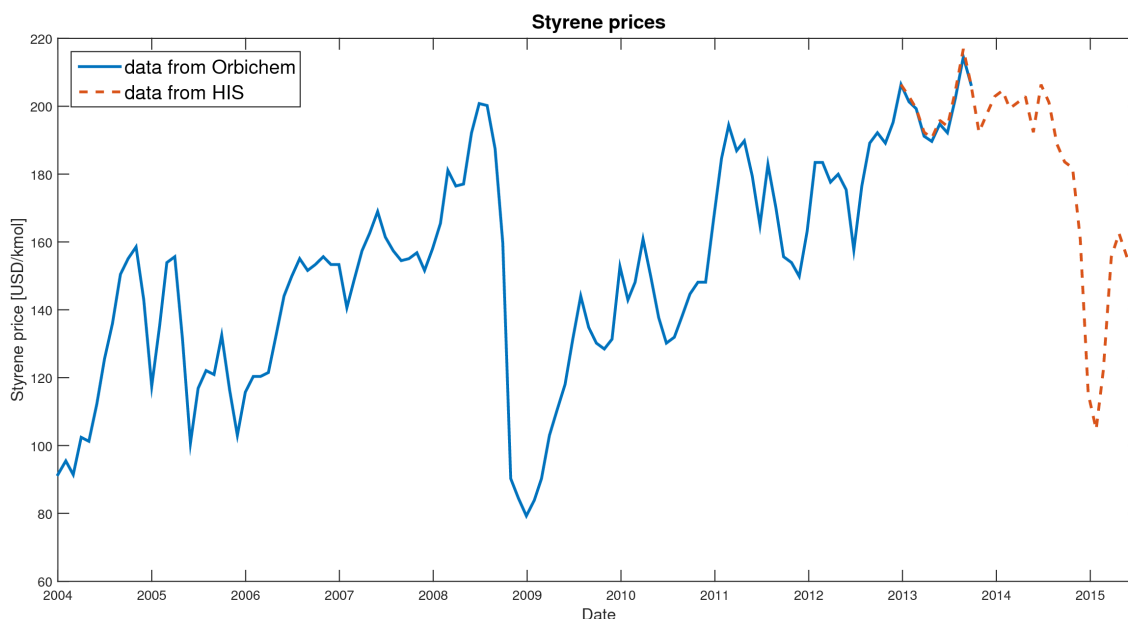


Figure 4.3: Example of data merging (styrene price) from two different datasets.

For the fuel oil utility, a low sulfur content fuel oil has been chosen. It is known as BTZ (“*Basso Tenore di Zolfo*” in Italian) and it has a lower heat of combustion of 9600 kcal/kg (ENI S.p.A. (2015)). All historical prices of this utility were found on the Italian website of *Ministero dello sviluppo economico* and they are expressed in €/ton. A successive conversion to USD/kg (with monthly €/USD conversion ratio) has been performed in order to calculate the econometric model.

For the electric energy price a model proposed by Manca (2016) has been chosen and modified in order to obtain prices in USD/MWh instead of €/MWh, as it will be discussed in detail in Paragraph 4.2.2.

Other utilities like steam and water will be specified at the end of this section.

4.2.2 Models for raw materials, commodities and utilities

Crude oil

For the Oil & Gas sector, a good candidate for the reference component is crude oil, being the precursor of a high number of chemical processes. As a consequence, the price and cost fluctuations of commodities (e.g. styrene, ethylene) are referred to the dynamics of crude oil quotations. Crude oil plays a significant role also respect to a number of industrial utilities, steam, and electric energy in particular. The cost of this raw material is well-known, largely available and periodically updated. Collected price data for the thesis work involve the period between January 2004 and June 2015 with a regression period¹ from Jan-2004 to Mar-2012, whereas the rest of the data set has been used as data check². As already discussed in Barzaghi and Conte, an econometric model based on Markov process (Cai (1994), Abramson and Finizza (1995) and Fong and See (2002)) would not be reliable, so, in this work, different models were tried in order to upgrade the model found in Barzaghi

¹Period in which the regression parameters of the model was modified in order to minimize the *SSE*.

²The values of *Adjusted - R²* and *SSE* used in the model selection are evaluated for the whole period (Jan-2004, Jun-2015)

and Conte, up to May 2016. The last years bring out model to a deep decrease of the crude oil prices, so the regression parameters are quite different from previous evaluations and respect rather well crude oil quotations up to May 2016. Looking at the autocorrelogram in Figure 4.4, two different econometric models can be extracted, demonstrating that the correlation index for a lag time of 2 months is still above a value of 0.9.

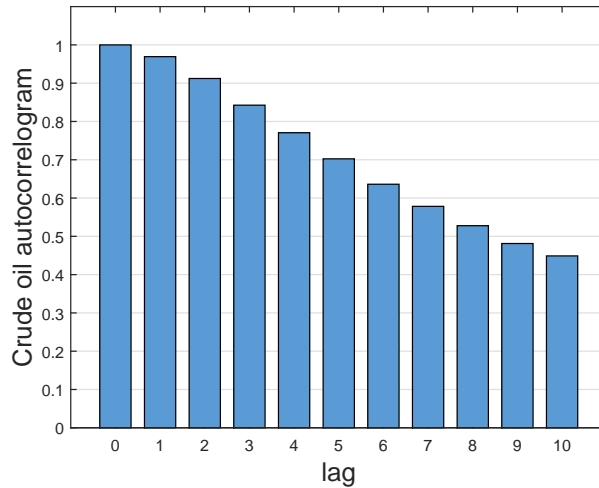


Figure 4.4: Autocorrelogram for crude oil quotations.

Both models were compared to crude oil price trend. Crude oil quotations considered are related to Brent, since styrene plant is thought to be built in Europe.

M1: $P_{CO}(t) = A + B \cdot P_{CO}(t - 1) + C \cdot P_{CO}(t - 2)$

M2: $P_{CO}(t) = A + B \cdot P_{CO}(t - 1)$

M1 depends not only on crude oil price in the month before, but also on the quotations of two months before. By comparing M1 and M2, the results are the following:

Table 4.1: Crude oil models regression parameters.

	A	B	C	SSE	R	R ²	p	n	adjusted - R ²
M1	2.596	1.846	-0.880	464.295	0.996	0.992	3	96	0.992
M2	2.202	0.982	-	2038.245	0.985	0.970	2	96	0.969

Adjusted - R² for M1 is greater than M2's and the SSE is much inferior by using the model 1 than the model 2. Model 1 is chosen, and A, B and C assume the values written in Table 4.1.

The plots for the two models in Figure 4.5, and 4.6 confirm this choice, because model 1 follows the price trend in moving average more accurately than model 2.

4.2. Econometric models

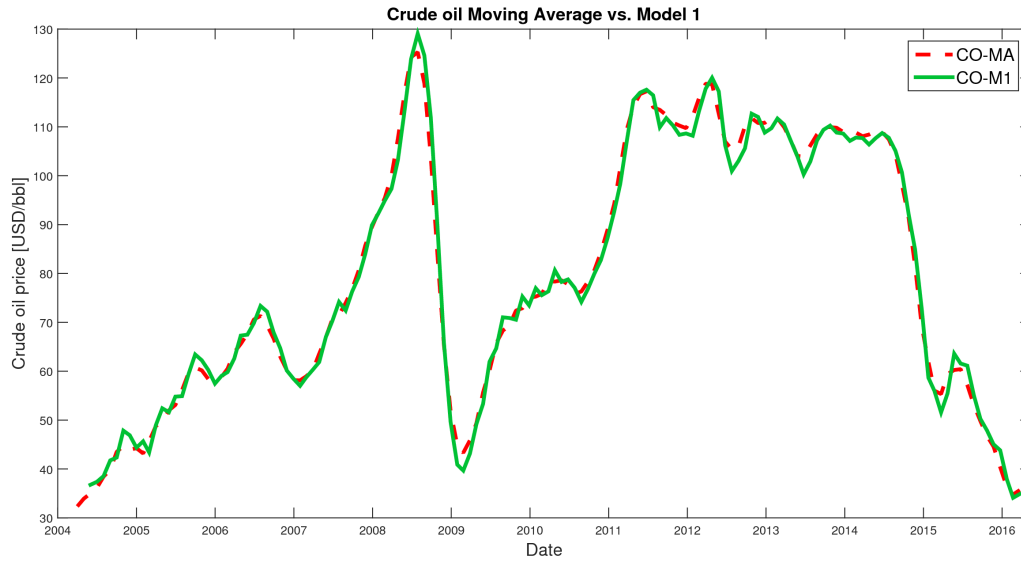


Figure 4.5: Crude oil model 1 vs. moving average.

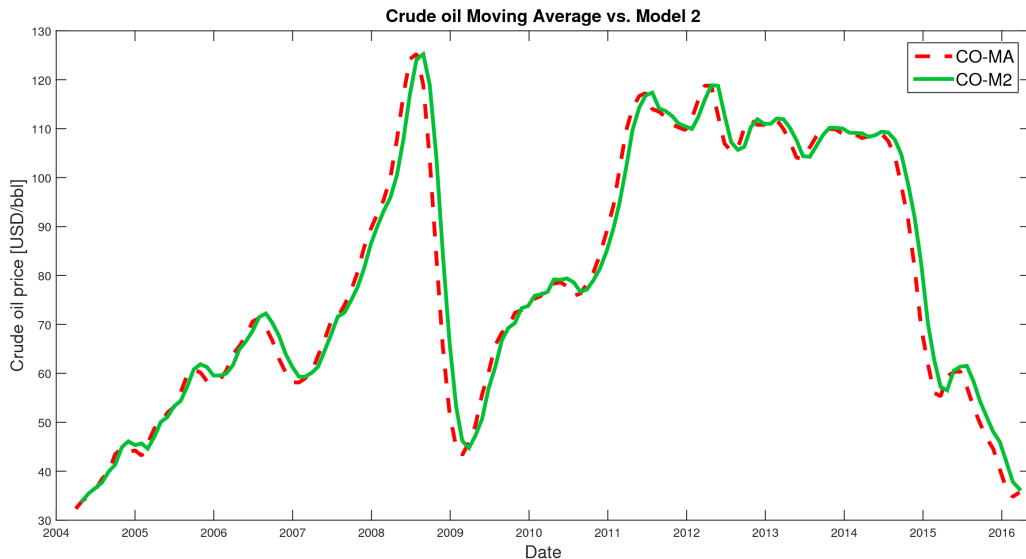


Figure 4.6: Crude oil model 2 vs. moving average.

BTZ fuel oil

BTZ fuel oil is used in the styrene plant. This typology of fuel oil contains less than 1% of sulphur, usually around 0.3%. As a consequence, low-sulphur oil respects environmental laws concerning pollution levels. Its price is low (Figure 4.7) but its importance in the economy of the plant brings it to be a fundamental commodity and its correct modeling can improve the accuracy of the results.

First of all, the moving average model follows the real prices quotations in a satisfying way, with the same considerations expressed for crude oil. From its autocorrelogram (Figure 4.8a), BTZ has a high autocorrelation index up to 3 months lag period; it does not seem so true for the correlation with CO (Figure 4.8b) that has a low correlation even for 0 month lag. It has to be pointed out that a correlation with CO should exist and is also necessary

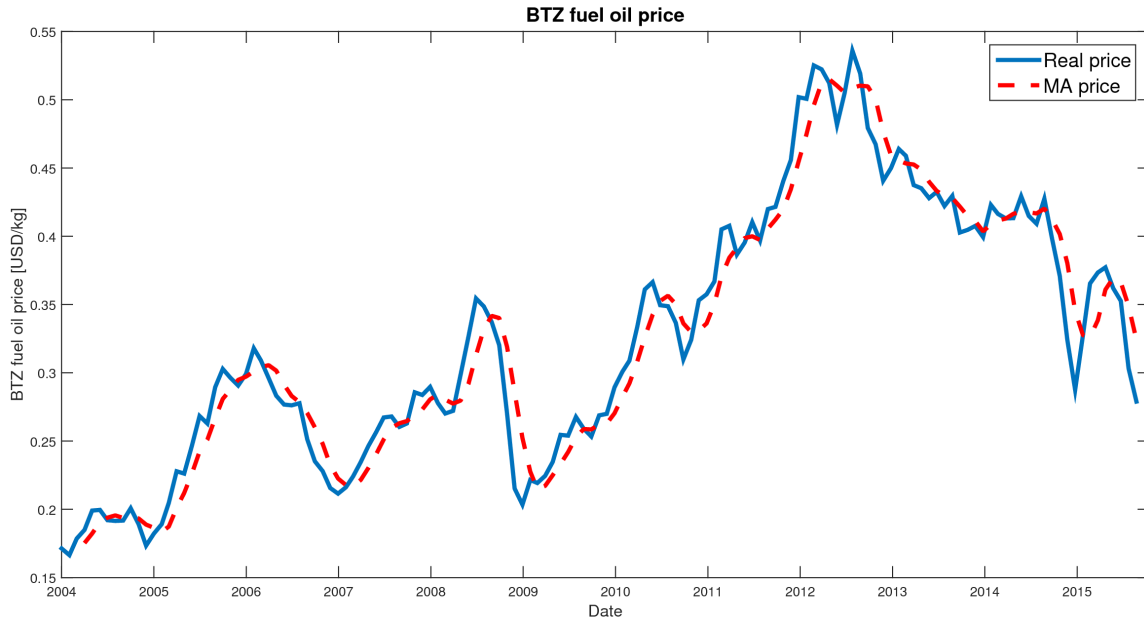


Figure 4.7: BTZ fuel oil real price and its moving average.

for the generation of stochastic scenarios on CO reference. All utilities and commodities need to follow those fluctuations.

For this reason, CO has been included in the scenarios study and four different econometric models were thought for BTZ oil based quotations from January 2004 to May 2016.

M1: $P_{BTZ}(t) = A + B \cdot P_{BTZ}(t - 1) + C \cdot P_{CO}(t) + D \cdot P_{CO}(t - 1)$

M2: $P_{BTZ}(t) = A + B \cdot P_{BTZ}(t - 1) + C \cdot P_{CO}(t)$

M3: $P_{BTZ}(t) = A + B \cdot P_{BTZ}(t - 1)$

M4: $P_{BTZ}(t) = A + C \cdot P_{CO}(t)$

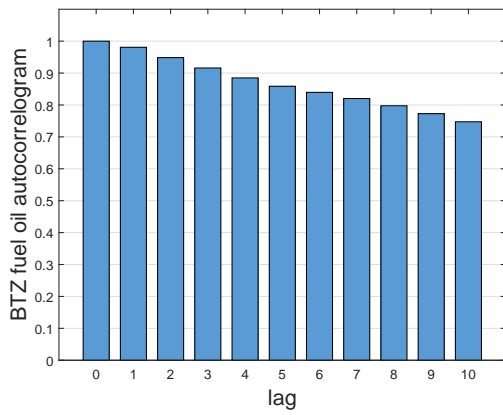
BTZ fuel oil’s cost at time t depends on its cost in the month before the current quotation and on crude oil price. A comparison among the four proposed models is advisable.

Table 4.2: BTZ fuel oil models regression parameters.

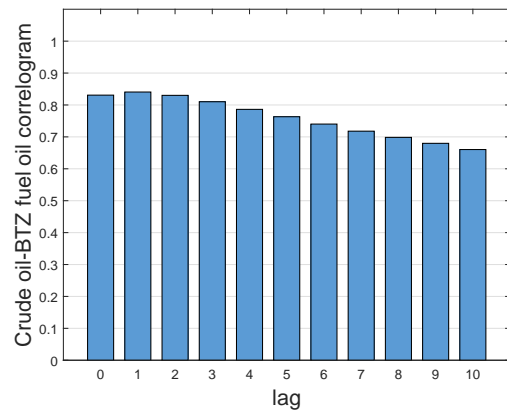
	A	B	C	D	SSE	R	R ²	p	n	adjusted - R ²
M1	9.93E-05	0.978	5.080E-06	1.313E-04	0.0104	0.993	0.986	4	95	0.985
M2	0	0.939	2.763E-04	-	0.00934	0.994	0.988	3	95	0.987
M3	0	1,013	-	-	0.0107	0.993	0.985	2	95	0.985
M4	0.104	-	0.00245	-	0.136	0.839	0.703	2	96	0.697

From *SSE* and *adjusted - R²* results, M4 has to be rejected for its low performance. Model 1, 2 and 3 provide similar results. Model 3 has to be excluded because it does not contain the relationship with CO quotations. The plots in Figure 4.9 and 4.10 show model 1 and model 2. Both follow BTZ fluctuations in a satisfying way. Model 2 looks as the more accurate between them, because it has the lowest *SSE* and the highest *adjusted - R²*. It contains 2 parameters, easy to manage, and considers both crude oil and low-sulphur oil prices. These reasons justify the choice of the model 2 for the forecast of low-sulphur oil quotations, with A, B and C parameters corresponding values.

4.2. Econometric models



(a) Autocorrelogram for BTZ fuel oil.



(b) Correlogram of BTZ with respect to CO.

Figure 4.8: Autocorrelogram and correlogram for BTZ fuel oil.

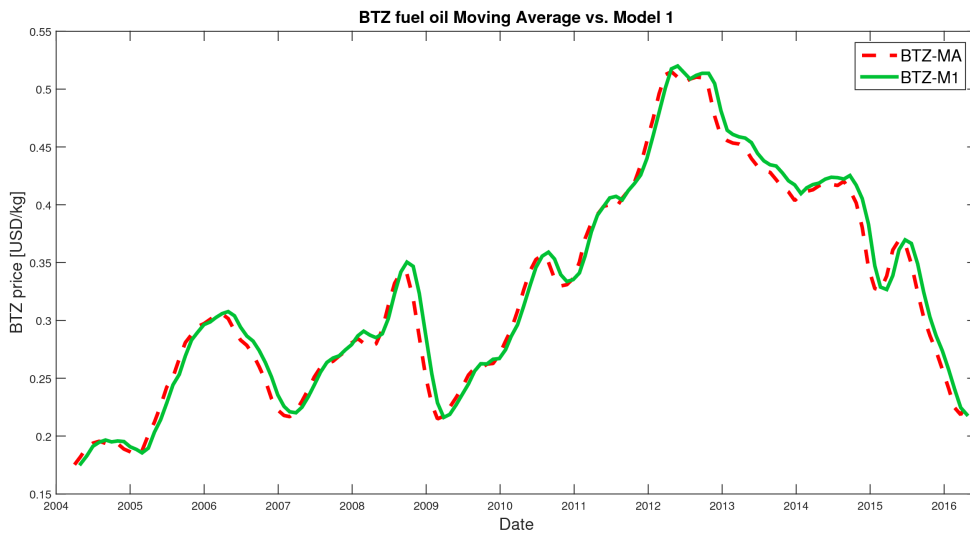


Figure 4.9: BTZ model 1 vs. moving average.

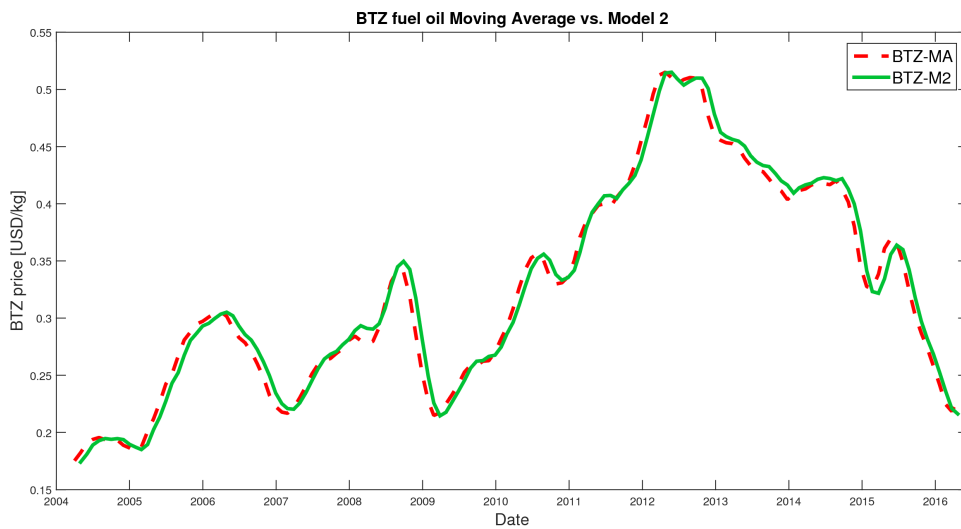


Figure 4.10: BTZ model 2 vs. moving average.

Toluene

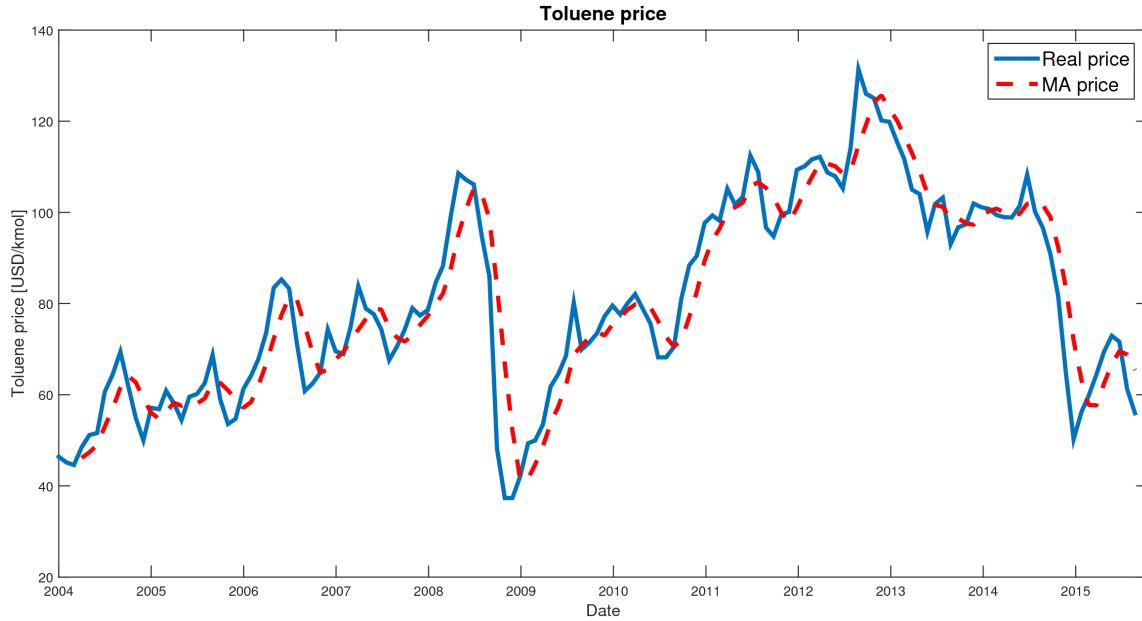
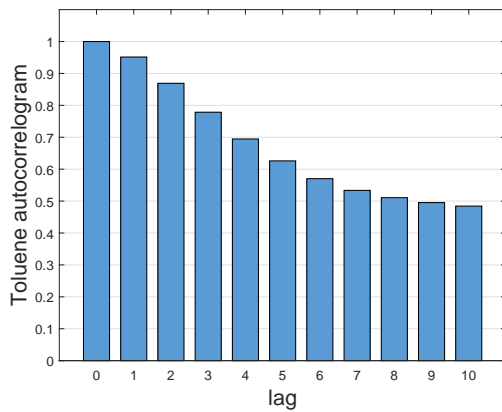


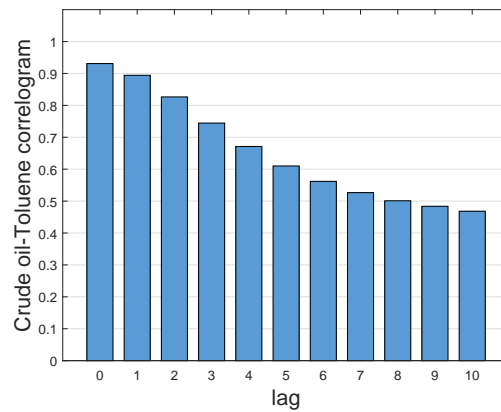
Figure 4.11: Toluene real price and its moving average.

Basing this study on correlograms (Figure 4.12b) and autocorrelogram (Figure 4.12a), it can be noted that toluene is strongly dependent from CO, so no other commodities (as benzene) have to be considered to obtain a reliable model.

Five different econometric models were realized for toluene price trend:



(a) Autocorrelogram for toluene.



(b) Correlogram of toluene with respect to CO.

Figure 4.12: Autocorrelogram and correlogram of toluene.

$$\mathbf{M1:} P_{Tol}(t) = A + B \cdot P_{CO}(t) + C \cdot P_{CO}(t - 1) + D \cdot P_{Tol}(t - 1) + E \cdot P_{Tol}(t - 2)$$

$$\mathbf{M2:} P_{Tol}(t) = A + B \cdot P_{CO}(t) + C \cdot P_{CO}(t - 1) + D \cdot P_{Tol}(t - 1)$$

$$\mathbf{M3:} P_{Tol}(t) = A + B \cdot P_{CO}(t) + C \cdot P_{Tol}(t - 1)$$

$$\mathbf{M4:} P_{Tol}(t) = A + B \cdot P_{CO}(t) + C \cdot P_{CO}(t - 1)$$

$$\mathbf{M5:} P_{Tol}(t) = A + B \cdot P_{CO}(t - 1) + C \cdot P_{Tol}(t - 2)$$

As for previous models a minimization of *SSE* has been performed in order to get all regression parameters' values and results obtained are written in Table 4.3.

4.2. Econometric models

Table 4.3: Toluene models regression parameters.

	A	B	C	D	E	SSE	R	R ²	p	n	adjusted - R ²
M1	6.12	0.53	-0.42	1.26	-0.44	303.23	0.995	0.991	5	96	0,9901
M2	4.26	0.85	-0.77	0.87	-	399.76	0.994	0,988	4	96	0.9877
M3	7.00	0.17	0.74	-	-	1573.71	0.981	0.963	3	96	0.9617
M4	25.45	1.23	-0.58	-	-	2384.14	0.939	0,882	3	96	0.8784
M5	19.68	0.40	0.35	-	-	5141.07	0.932	0,868	3	96	0.8641

Model 1 and Model 2 are the best performing in terms of *SSE* and of *adjusted - R²*. Since their results are quite similar the model with less regressive parameters is chosen in order to simplify calculations. For this reason, model 2 is chosen. Toluene current price depends on previous month toluene price, current crude oil price and on previous month crude oil quotation.

By looking at both plots in Figures 4.13, and 4.14, the choice of model 2 as the toluene econometric model is confirmed, thanks to the good correspondence between moving average and the model itself.

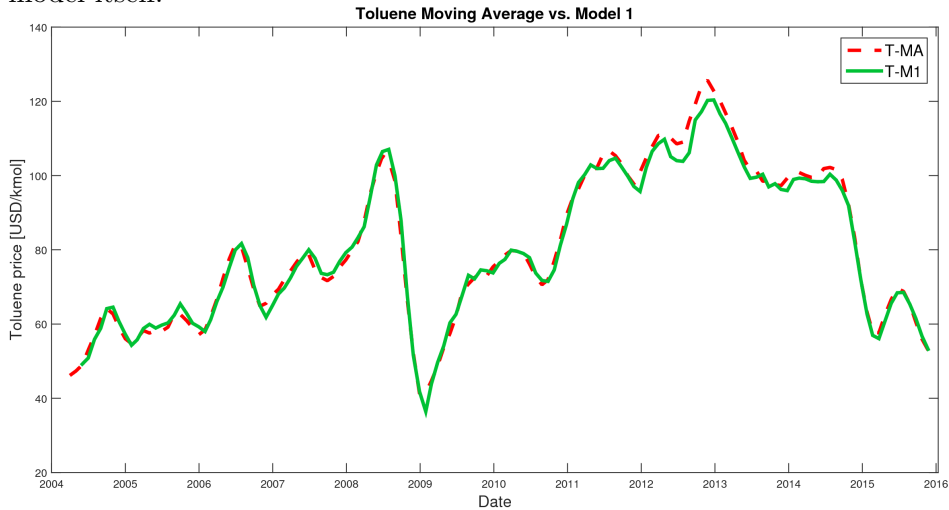


Figure 4.13: Toluene model 1 vs. moving average.

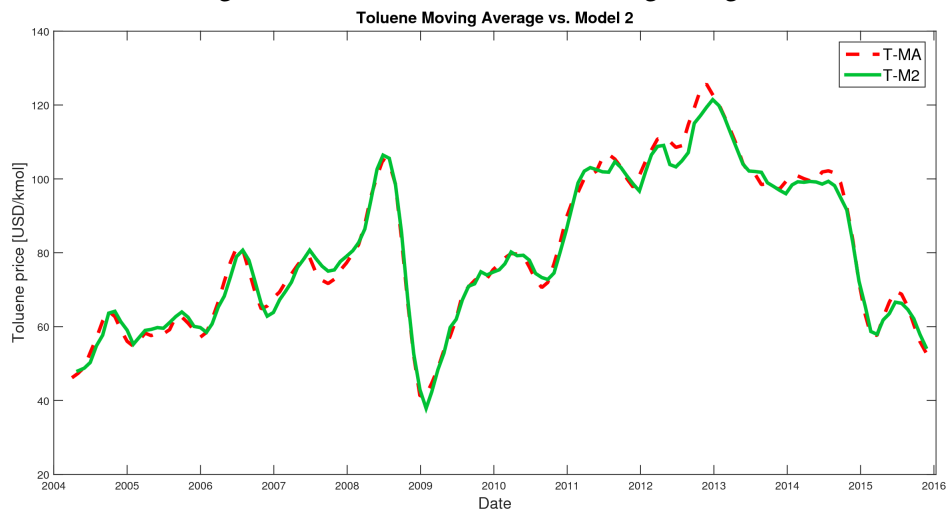


Figure 4.14: Toluene model 2 vs. moving average.

Benzene

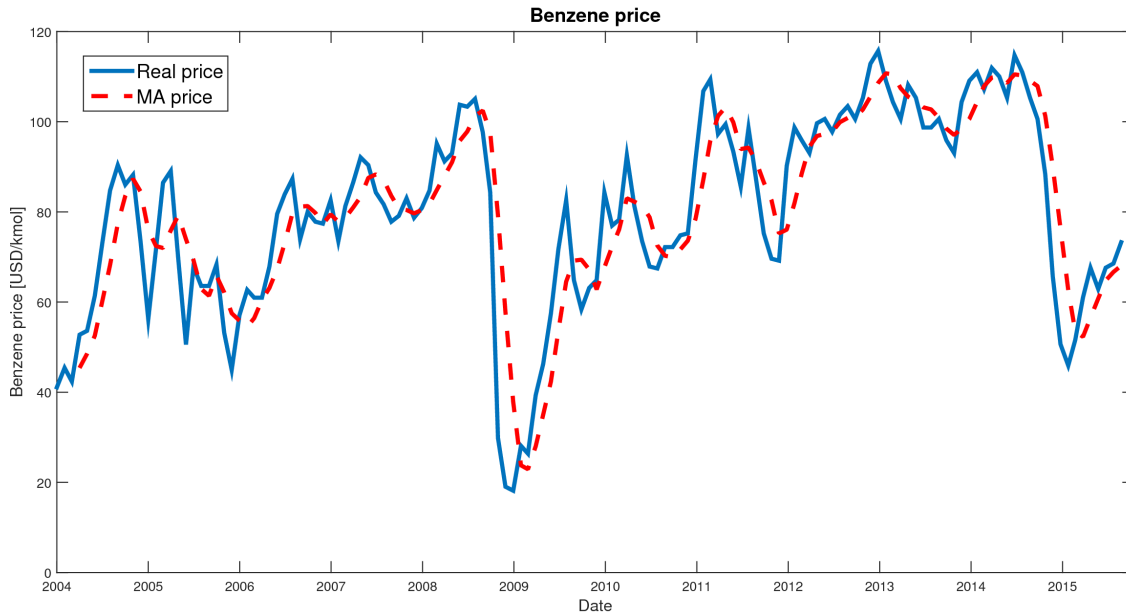


Figure 4.15: Benzene real price and its moving average.

Looking at autocorrelogram (Figure 4.16) and correlograms in (Figure 4.17b), it can be denoted that benzene price has a low correlation with CO, so another component like toluene can be added to the model to improve it.

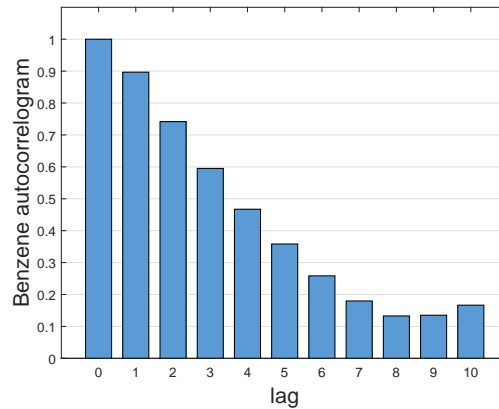


Figure 4.16: Autocorrelogram for Benzene

As a consequence of these considerations, seven different econometric models were tested for benzene:

$$\mathbf{M1:} P_{Benz}(t) = A + B \cdot P_{CO}(t) + C \cdot P_{CO}(t-1) + D \cdot P_{Tol}(t) + E \cdot P_{Tol}(t-1) + F \cdot P_{Benz}(t-1)$$

$$\mathbf{M2:} P_{Benz}(t) = A + B \cdot P_{CO}(t) + C \cdot P_{CO}(t-1) + D \cdot P_{Tol}(t) + E \cdot P_{Tol}(t-1)$$

$$\mathbf{M3:} P_{Benz}(t) = A + B \cdot P_{CO}(t) + C \cdot P_{Tol}(t) + D \cdot P_{Tol}(t-1) + E \cdot P_{Benz}(t-1)$$

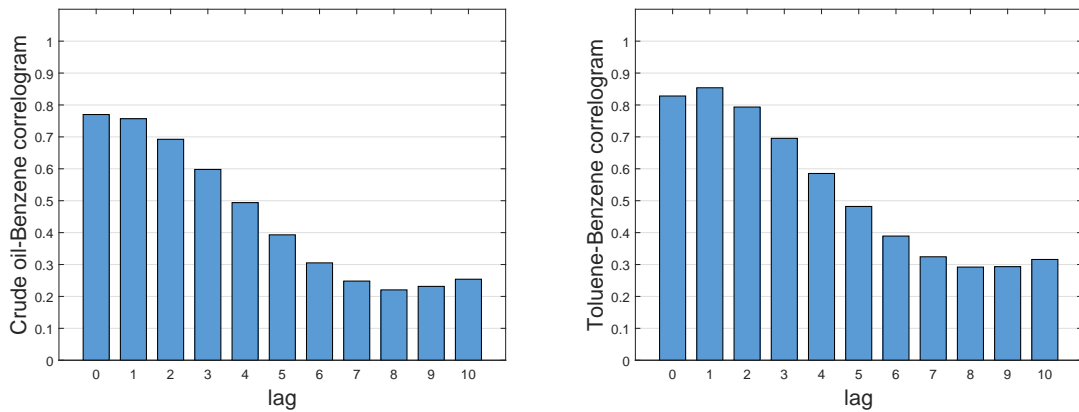
$$\mathbf{M4:} P_{Benz}(t) = A + B \cdot P_{CO}(t) + C \cdot P_{Tol}(t-1) + D \cdot P_{Benz}(t-1)$$

$$\mathbf{M5:} P_{Benz}(t) = A + B \cdot P_{Tol}(t) + C \cdot P_{Tol}(t-1) + D \cdot P_{Benz}(t-1)$$

$$\mathbf{M6:} P_{Benz}(t) = A + B \cdot P_{Tol}(t-1) + C \cdot P_{Benz}(t-1)$$

$$\mathbf{M7:} P_{Benz}(t) = A + B \cdot P_{Tol}(t) + C \cdot P_{Benz}(t-1)$$

4.2. Econometric models



(a) Correlogram of Benzene with respect to CO. (b) Correlogram of Benzene with respect to Toluene.

Figure 4.17: Correlograms for benzene.

The first evidence is that benzene price may depend also on crude oil and it is surely correlated to toluene and previous month benzene price. This remarks the very close correlation between the two utilities due to the HDA process as deeply discussed in Manca et al. (2011), Fini and Oliosi (2010). It can be seen in Figure 4.18 how benzene and toluene prices are strongly interdependent.

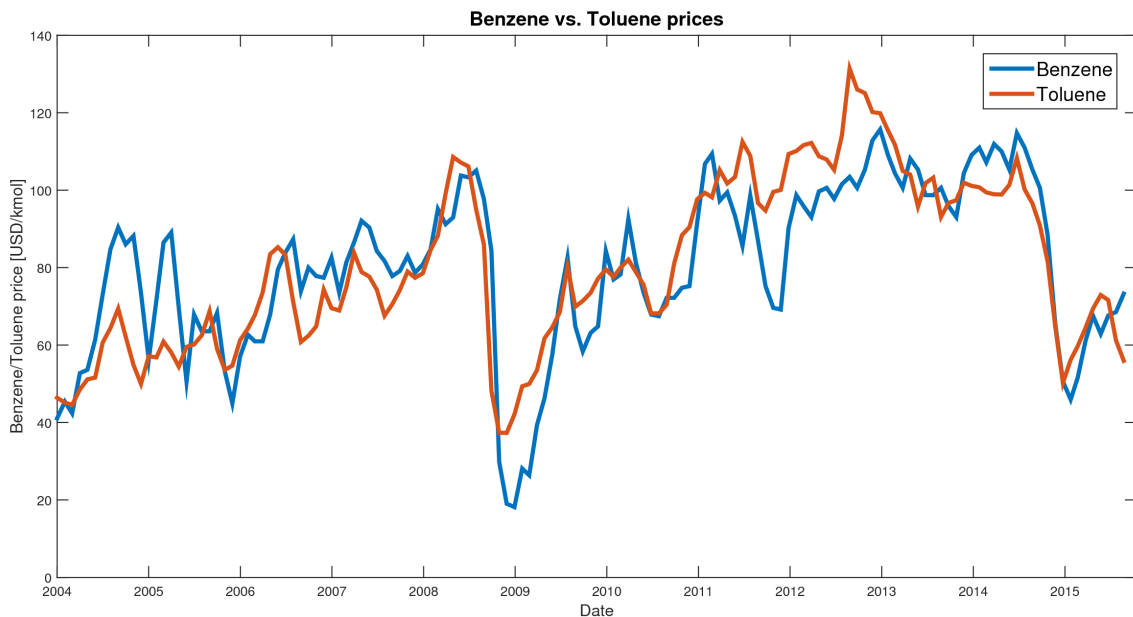


Figure 4.18: Benzene ad toluene price confutation.

The seven models were compared and the results obtained are reported in Table 4.4. The three most suitable models are M1, M3, and M5, because they have the lowest values of SSE and the highest $adjusted - R^2$. Looking at Figure 4.19, 4.20, and 4.21 all the models are very close to the real moving average prices, so the best option is to choose the simplest model to decrease the possible errors and to make evaluation as simple as possible. Model 5 has been chosen as econometric model for benzene prices.

Table 4.4: Benzene models regression parameters.

	A	B	C	D	E	F	SSE	R	R ²	p	n	adjusted - R ²
M1	-5.09	0.35	-0.60	0.42	0.05	0.85	1031.05	6	96	0.98	0.97	0.966
M2	5.22	1.06	-1.63	-1.19	2.69	-	6149.27	5	96	0.88	0.77	0.765
M3	-7.39	-0.26	1.04	-0.57	0.89	-	1194.15	5	96	0.98	0.96	0.962
M4	0.29	-0.15	0.40	0.76	-	-	2719,47	4	96	0.96	0.92	0,923
M5	-1.63	0.95	-0.89	0.96	-	-	1493.82	4	96	0.98	0.97	0.964
M6	3.42	0.16	0.80	-	-	-	2827.06	3	96	0.96	0.93	0.929
M7	0.81	0.23	0.77	-	-	-	2351.55	3	96	0.97	0.944	0.942

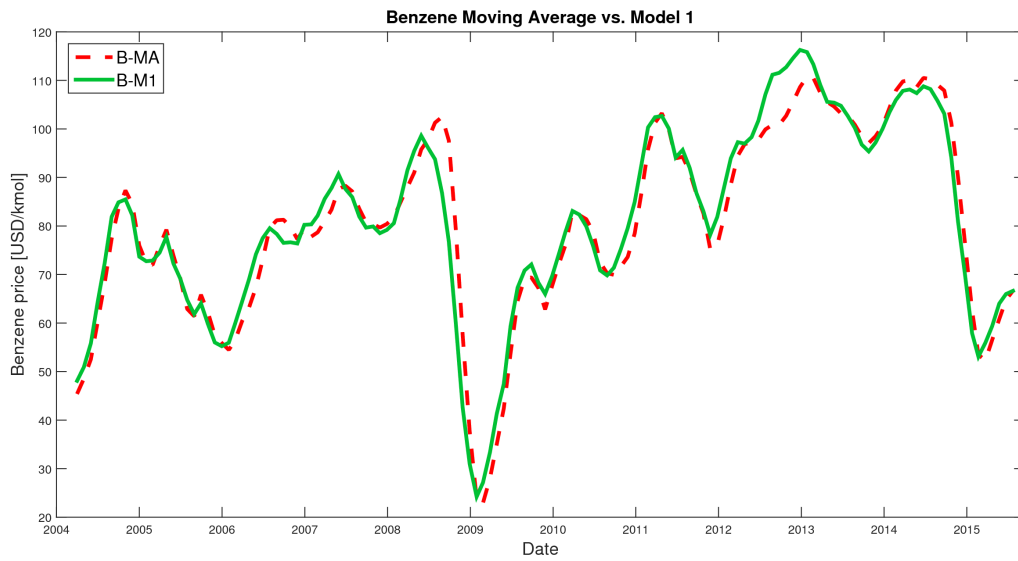


Figure 4.19: Benzene model 1 vs. moving average.

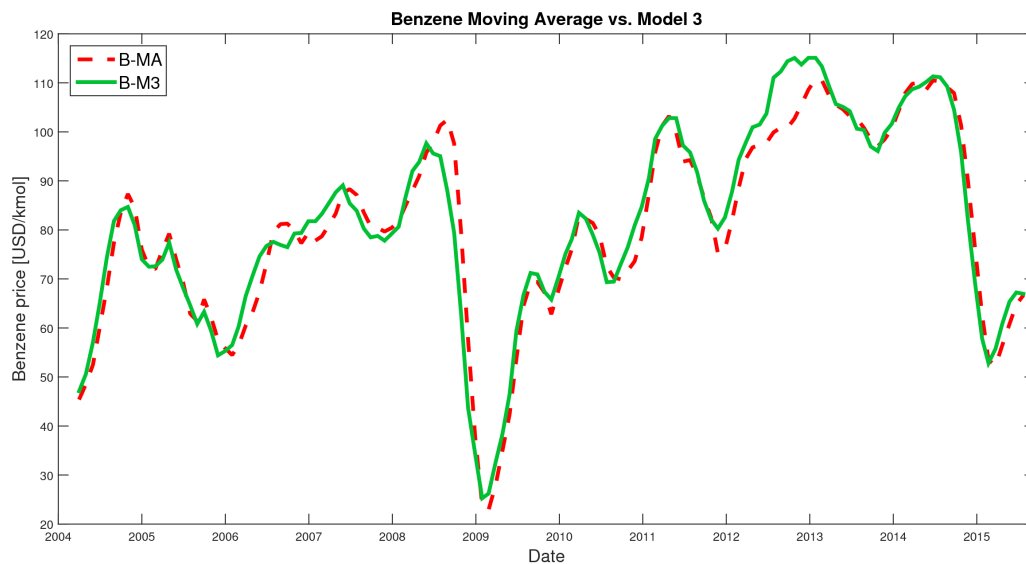


Figure 4.20: Benzene model 3 vs. moving average.

4.2. Econometric models

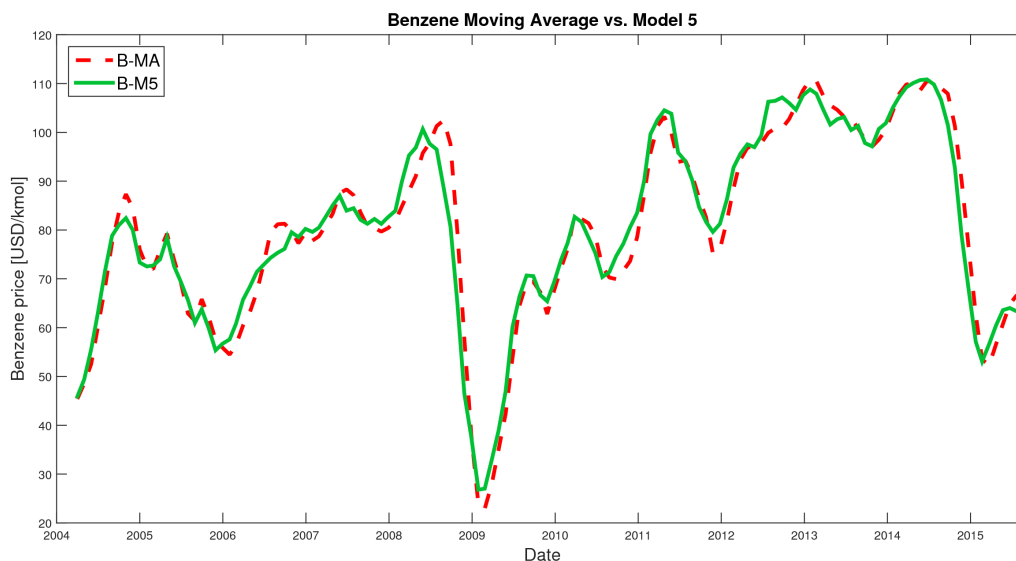


Figure 4.21: Benzene model 5 vs. moving average.

Ethylene

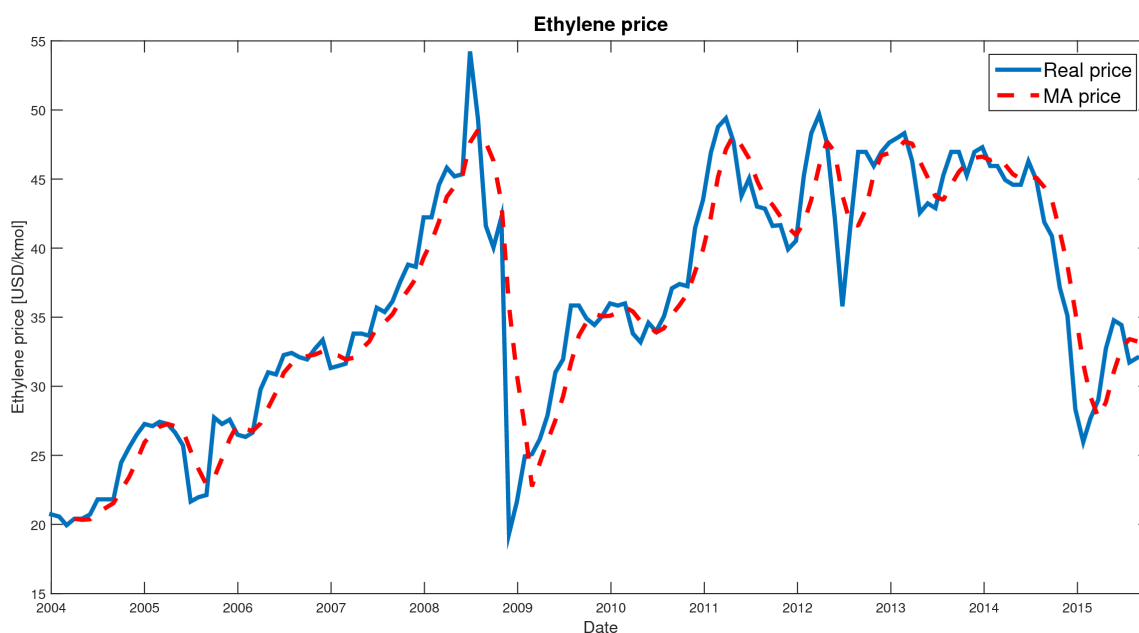


Figure 4.22: Ethylene real price and its moving average.

The considerations already written for other commodities are still valid, but in the ethylene case the prices (Figure 4.22) have peaks which denote a more nervous trend. In fact, real past prices have varied frequently and differ more from moving average prices.

Ethylene can be produced from different raw materials such as naphtha or natural gas (Weissermel et al. (2008)). For this reason, the localization of the plant is important in the formulation of the econometric model. Since the styrene plant has been designed for Europe, ethylene price is not influenced by natural gas quotation. It depends only on crude-oil price, as already found out by Barzaghi and Conte. This dependence can be clearly seen in

the correlogram of Figure 4.23b.

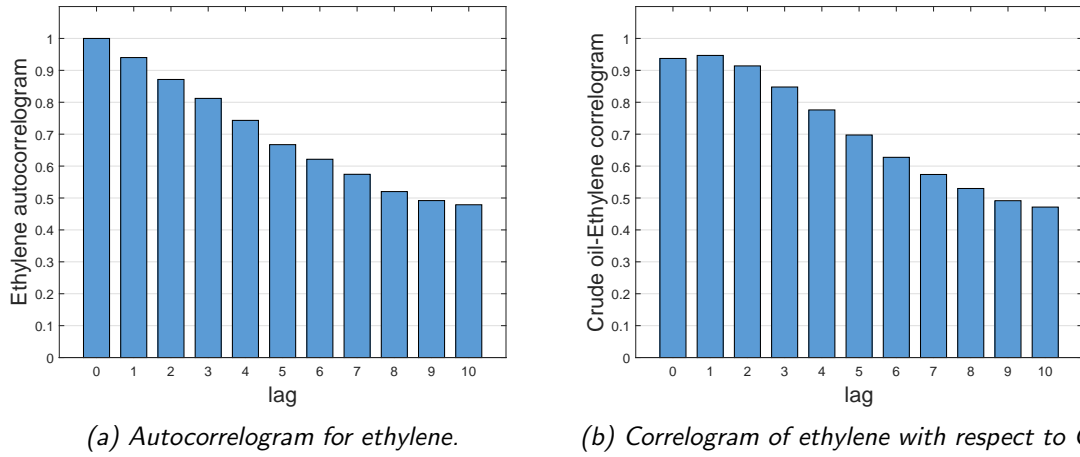


Figure 4.23: Autocorrelogram and correlogram of ethylene.

As a consequence, natural gas prices have not been further investigated. For these reasons the resulting model is:

$$\mathbf{M1}: P_{Ethyl}(t) = A + B \cdot P_{Ethyl}(t - 1) + C \cdot P_{CO}(t)$$

The comparison between moving average and the model proposed in the present thesis work is satisfying, as it emerges by looking at SSE and $adjusted - R^2$ values in Table 4.5 and at the plot in Figure 4.24.

Table 4.5: Ethylene models regression parameters.

	A	B	C	SSE	R	R ²	p	n	adjusted - R ²
M1	3.43	0.678	0.103	136.98	0.9899	0.9798	3	95	0.979

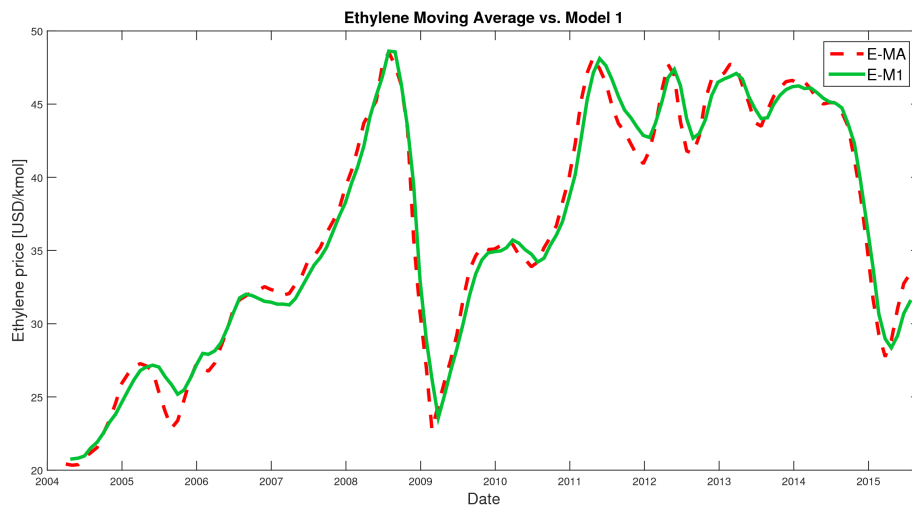


Figure 4.24: Ethylene model 1 vs. moving average.

4.2. Econometric models

Ethylbenzene

Ethylbenzene is the main reactant in this process, but its price cannot be found in literature because a real market for this product does not exist, Kirk-Othmer (2007). Although about 99% of all ethylbenzene produced is used in styrene production (US Environmental Protection Agency (2016)).

As a consequence of these difficulties, a different approach has been used to evaluate it:

$$P_{EtBz}(t) = P_{Ethy}(t) + P_{Benz}(t) + P_{Production}$$

To evaluate the cost of production of ethylbenzene from benzene and ethylene, some pieces of information from a similar dimension plant were exploited. An article from MacDonald et al. (2005) has been used for this purpose. MacDonald et al. perform a detailed analysis on an ethylbenzene production plant with capital and operative expenses. These production costs were estimated in 8.6697 USD/kmol bringing to the price of ethylbenzene that can be seen in Figure 4.25.

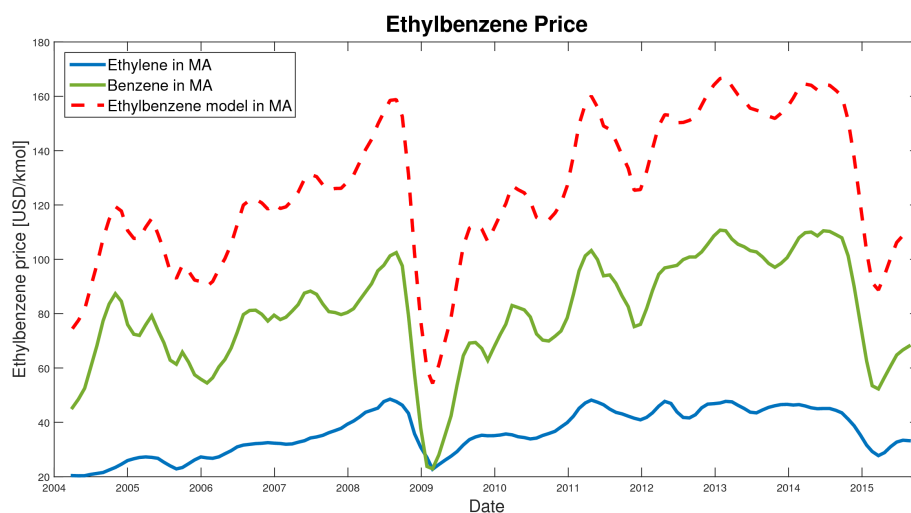


Figure 4.25: Ethylbenzene price in moving average, derived from ethylene and benzene prices in MA.

Styrene

Correlograms and autocorrelogram in Figure 4.27 are needed to determine the structure of styrene models.

The correlations suggest that styrene price is heavily affected from its own price in the month before the current quotation, from benzene price, and from ethylene price. Crude oil does not play a decisive role in the definition of styrene price, as a consequence it is excluded from the econometric model.

Two econometric model were proposed for styrene:

$$\mathbf{M1:} \quad P_{Sty}(t) = A + B \cdot P_{Sty}(t) + C \cdot P_{Benz}(t) + D \cdot P_{Ethy}(t)$$

$$\mathbf{M2:} \quad P_{Sty}(t) = A + B \cdot P_{Sty}(t) + C \cdot P_{Benz}(t)$$

Their correspondent parameters are available in Table 4.6.

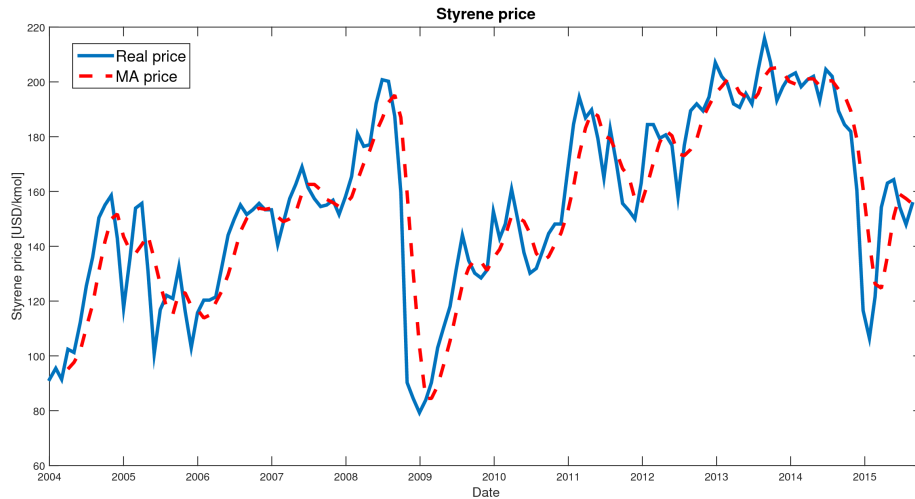
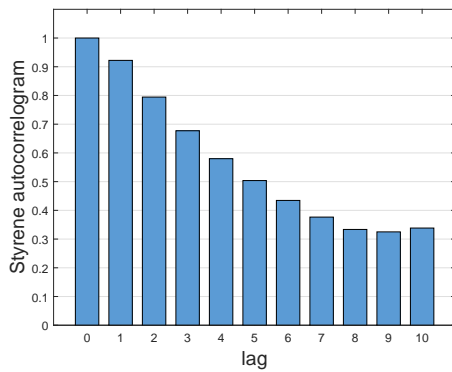
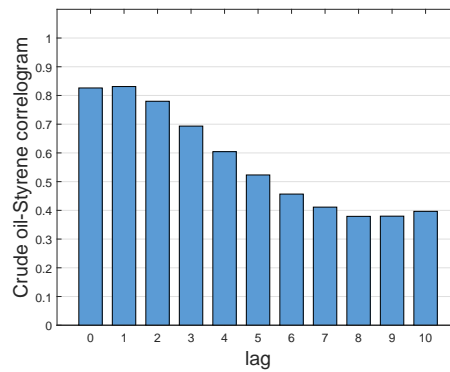


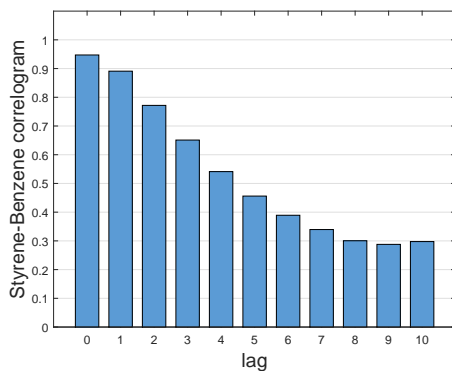
Figure 4.26: Styrene real price and its moving average.



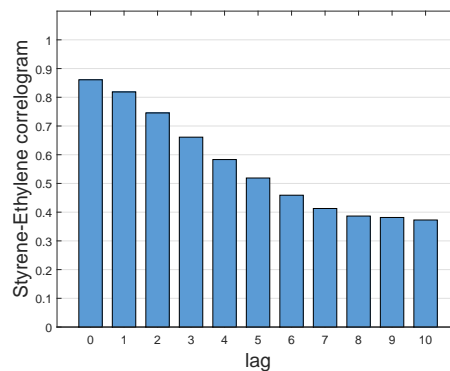
(a) Autocorrelogram for Styrene.



(b) Styrene of ethylene with respect to CO.



(c) Correlogram of styrene with respect to benzene.



(d) Correlogram of styrene with respect to ethylene.

Figure 4.27: Autocorrelogram and correlograms of styrene.

Model 1 is very distant from convergence, as can be seen in the plots in Figures 4.28, and 4.29. Model 2 instead, looks like a nice approximation of styrene prices trend. In addition to this, graphical comparison between the models remove any doubt about the choice of model 2 for styrene prices. The latter is closer to moving average quotations than the former, also from a qualitative point of view.

4.2. Econometric models

Table 4.6: Styrene models regression parameters.

	A	B	C	D	SSE	R	R ²	p	n	adjusted - R ²
M1	16.610	1.55E-06	1.131	1.240	1667.60	0.975	0.950	4	95	0.9481
M2	11.474	0.538	0.735	-	1748.83	0.986	0.972	3	95	0.9707

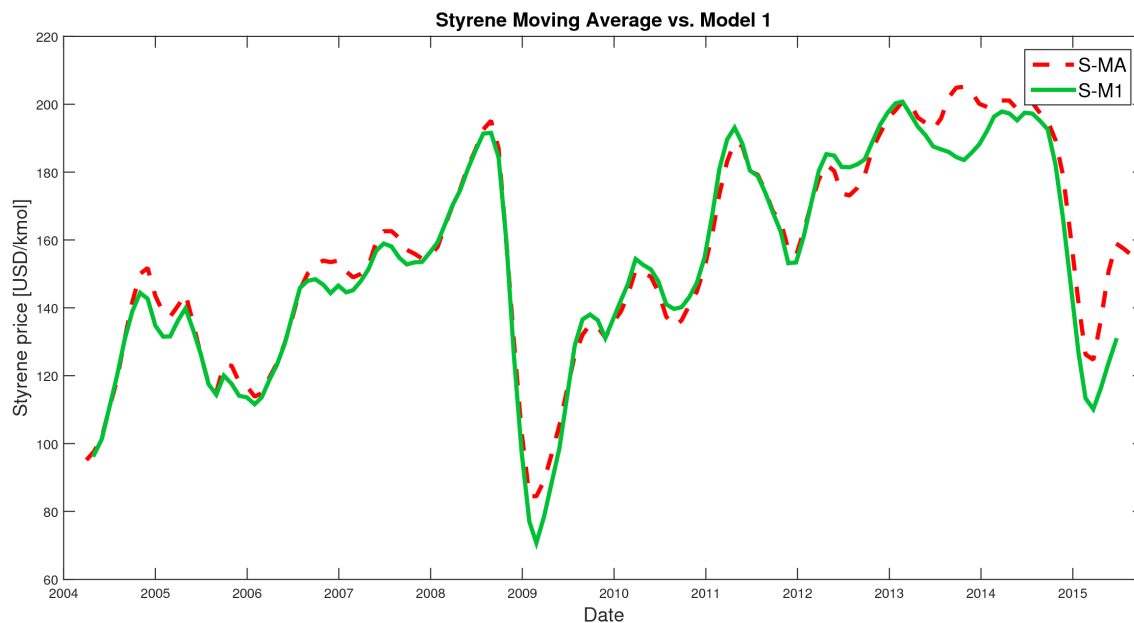


Figure 4.28: Styrene model 1 vs. moving average.

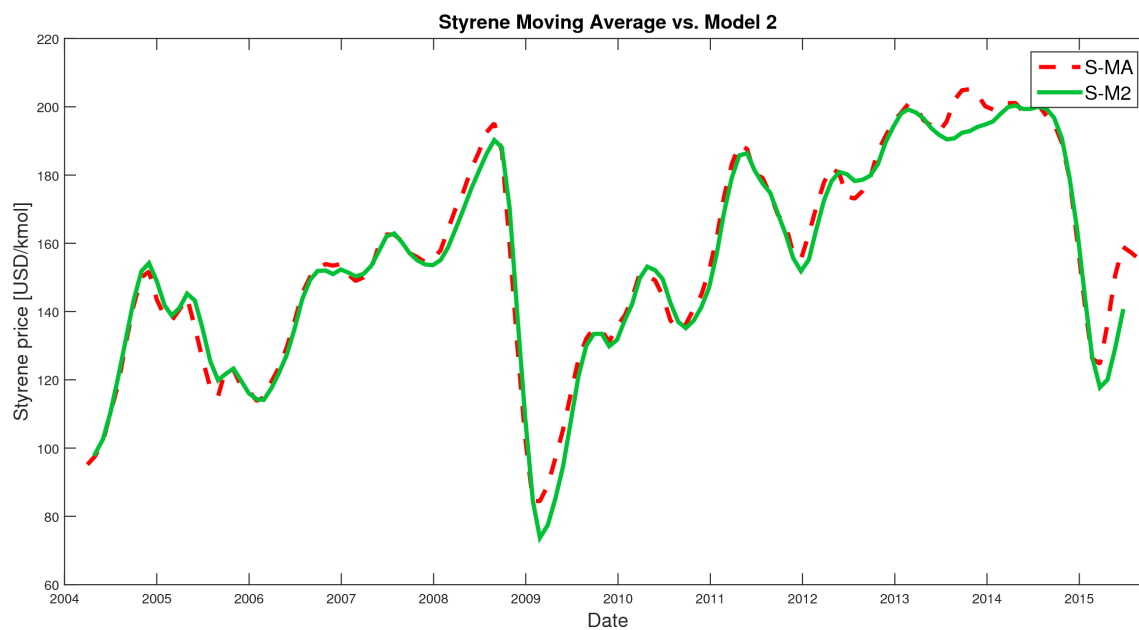


Figure 4.29: Styrene model 2 vs. moving average.

Electric Energy

Electric energy (EE) price is modeled and implemented in the styrene plant because of the costs associated to the compressor. As already discussed in Paragraph 4.2.1, electric energy price has been evaluated on the model proposed in Manca (2016) based on Italian prices of electric energy. To perform a realistic model, it is important to know that the maxima changes from hour to hour and from day to day. In addition, there are differences between working days and holidays and also among seasons. The daily maxima are higher during the summer months. This is due to the fact that in summer the peak for energy production (and therefore its price) occurs during the hottest period of the day, whilst in winter the peak is due to the request for artificial lighting. Some stochastic oscillations in prices are present and by their nature cannot be explained.

Electric energy price is significantly influenced by the crude oil quotations.

There is a time delay between the EE and CO quotations that can be estimated into 10-15 weeks: as a mean, this time delay is set equal to 3 months.

To model the seasonal component a sinusoidal dependency can be introduced bringing to a model of the kind:

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

Where:

- i is the i -th week
- j is the time band (there are four bands in a day: morning, afternoon, evening, night)
- a is a reference value of EE price [€/MWh]
- b : is coefficient for the dependency of EE price from CO [€ bbl/USD MWh]
- t_d is time delay [week] (i.e. number of weeks of delay between the EE and CO prices)
- c is parameter of the periodic component [€/MWh]
- T is period of the sinewave function (the period is expected to be comparable to a season) [week]
- ϕ is the phase of the sinewave function [-]

Since monthly quotations are needed to be consistent with other commodities, electricity price is considered at monthly intervals and it is assumed constant during the weeks of the same month. This is a simplification respect to all the considerations explained above, but it is necessary to council this formula with the other econometric models.

Electric energy price for a specific week has been calculated with a weighted average between the four bands of the day:

Morning includes 5 hours (9-14): 5/24 of a day.

Afternoon includes 3 hours (14-17): 3/24 of a day.

Evening includes 5 hours (17-22): 5/24 of a day.

Night includes 3 hours (22-9): 11/24 of a day.

As a consequence, the formula is written as follow:

$$P_{EE,i} = \sum_{k=1}^{4weeks} \frac{5}{24} \cdot P_{EE,morning,k} + \frac{3}{24} \cdot P_{EE,afternoon,k} + \frac{5}{24} \cdot P_{EE,evening,k} + \frac{11}{24} \cdot P_{EE,night,k}$$

It must be noticed that electric energy price is expressed in €/MWh from the model.

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Conversion to USD/MWh is needed because of the units of measure adopted in the styrene plant. Two different strategies can be followed:

- multiplying the results expressed in €/MWh by a mean conversion factor for the last 12-year period to obtain the value in USD/MWh.
- updating a_j , b_j , and c_j parameters in order to convert their units of measure. This path consists in minimizing the error between the model in USD/MWh and the model expressed in €/MWh and then using the real conversion factor (related to past data) to have quotations in USD/MWh.

The first route is the most comfortable in terms of data search and calculations. By following this path, an average conversion factor of 0.771 USD/€ were found as a mean of the conversion factor from January 2004 to April 2016. for each month the error is evaluated as:

$$Error_i(t) = P_{EE,i}(t) \cdot Change[€/USD] - P_{EE,i}(t) \cdot AverageChange[€/USD]$$

The SSE in this situation is equal to 3084.

The parameters updating is performed minimizing the SSE , by varying the coefficients a_j , b_j , and c_j . This bring to a SSE value of 2514 for the past prices.

Despite these two strategies, the error is not negligible. Anyway, the model with updated parameters is more efficient and in Figure 4.30 can be seen qualitatively the two cases.

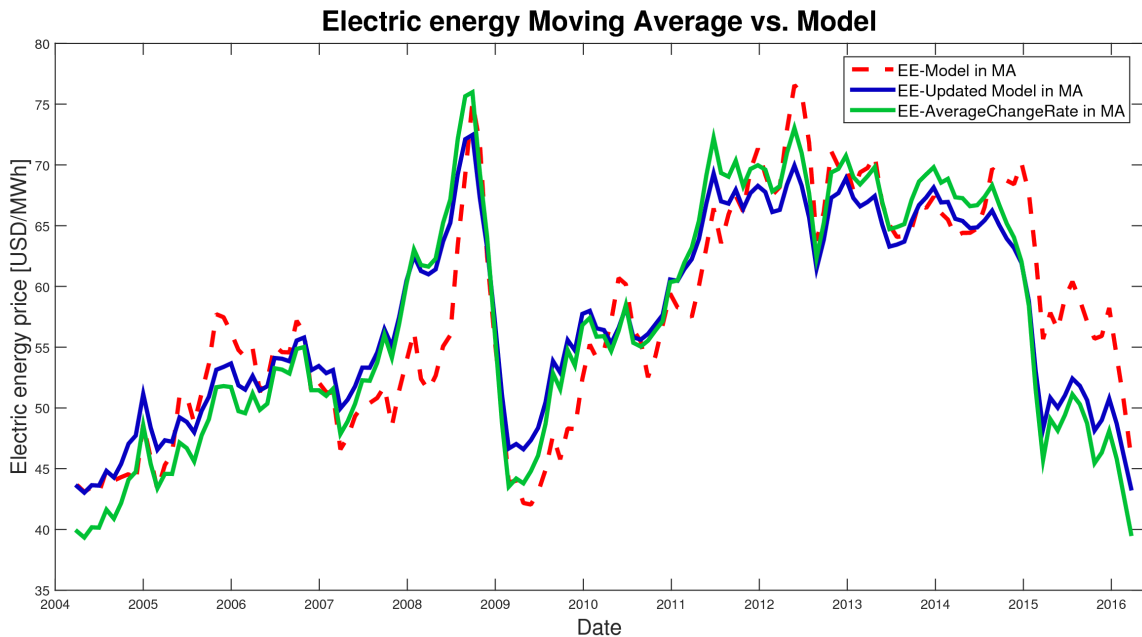


Figure 4.30: Different models for electric energy prevision price.

The error on electricity price is significant (Figure 4.31), because it is at least about 15%. Fortunately, the compressor consumes at most 10 kW, which is about 3 orders of magnitude inferior than MWh. For this reason, compressor costs are almost negligible in comparison to the $EP4_{Cumulated}$ and a small error like the one outlined can be assumed negligible on the overall plant economics.

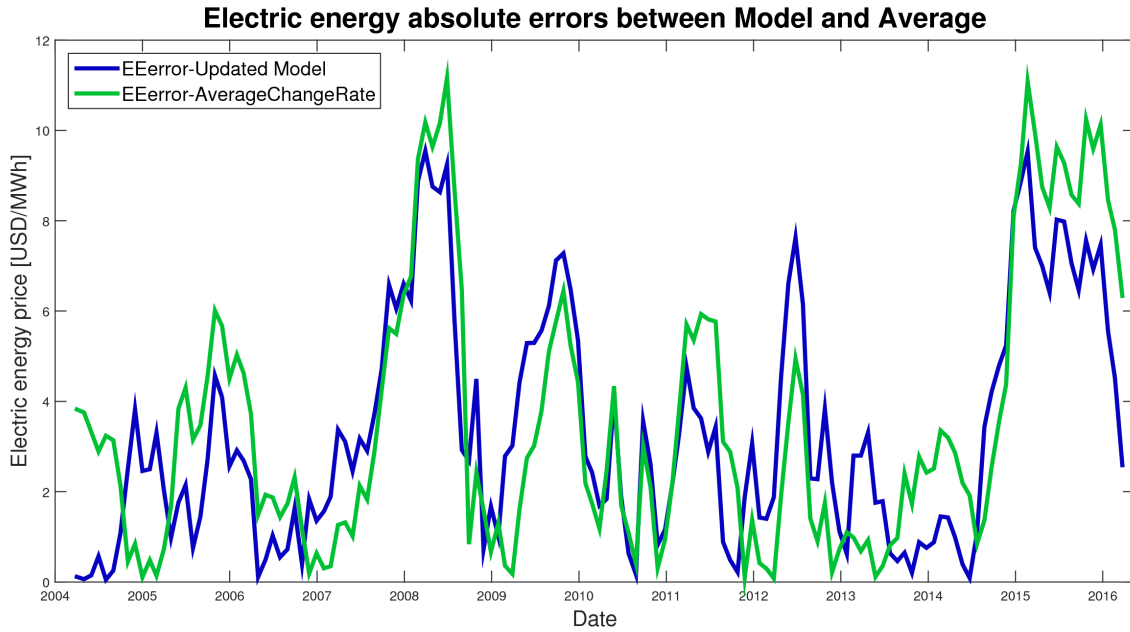


Figure 4.31: Absolute errors with both methodologies.

In the end, the method with an update of the parameters to evaluate EE price in USD/MWh looks like the best option with a cumulated error inferior to the other method, so this approach will be used.

Water

Water price estimation is critical because of the significant variability of its quotations not only in time, but also from country to country, in Italy even from region to region and from district to district. However, providing quotations of water is necessary because of the cooling water input to E-4 heat-exchanger and from water utility at the condensers of the three columns. Cooling water price has been estimated as 0.048 USD/ m^3 (Ulrich and Vasudevan (2006)). In order to have a reliable but conservative estimation, the value has been rounded to 0.05 USD/ m^3 .

Steam

Assuming a constant steam price is a too strong approximation, because steam cost can vary significantly also in short periods. For this reason, steam price is associated to crude oil quotations following the formula of TM Swagelok Company (2011) and U.S. Department of Energy (2013):

$$C_G = C_F + C_W + C_{BFW} + C_P + C_A + C_B + C_D + C_E + C_M$$

Where all costs are:

1. C_F = Fuel
2. C_W = Raw water supply
3. C_{BFW} = Boiler feed water treatment (including clarification, softening, demineralization)
4. C_P = Feed-water pumping power

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5. C_A = Combustion air fan (FD or ID) power
6. C_B = Sewer charges for boiler blowdown
7. C_D = Ash disposal
8. C_E = Environmental emissions control
9. C_M = Maintenance materials and labor
10. C_G = Cost for steam generation

In particular:

$$C_F = a_F \cdot (H_S - h_W)/1000/\eta_B$$

where: a_F = fuel cost [USD/MMBtu]

H_S = enthalpy of steam [Btu/lb]

h_W = enthalpy of boiler feed-water [Btu/lb]

η_B = overall boiler efficiency, fractional

$$C_G = C_F(1 + 0.30)$$

In the constant 0.30 are included all factors reported in the legend from 2 to 9.

Two kinds of steam will be calculated with this formula:

- LPSteam with an enthalpy of formation of 2807.74 [kJ/kg]. This flowrate consists of Low Pressure steam at 200 °C
- Steam utility with an enthalpy of formation of 2774.11 [kJ/kg]. This utility consists of steam at 15 bar, with a boiling point around 200 °C good for column's reboilers

This formula provides accurate results, because it calculates the actualized steam price starting from its raw materials, water and fuel oil, feed to the steam generator. Data evaluated for the historical period are presented in Figure 4.32.

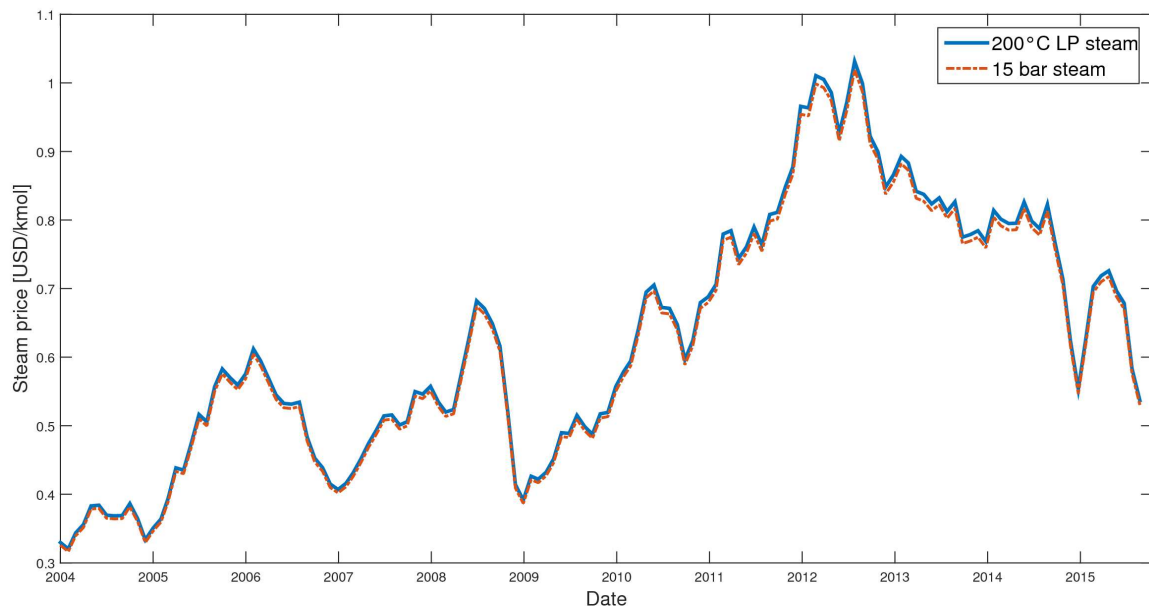


Figure 4.32: Steam prices for the past period, evaluated from historical BTZ price.

4.3 Economic Scenarios

Crude oil scenarios

Once the econometric models have been identified, some scenarios should be generated in order to infer on the possible economic fluctuations of the market in the next 10-year horizon. Future price scenarios generation starts from the crude oil econometric model obtained in Paragraph 4.2.2.

This model allows to foresee the future trend of crude-oil quotation based on 1-month and 2-months before crude-oil quotations. On the other hand, since future results are always uncertain, it is not possible to know the exact crude-oil price at a given future time, but if the model is efficient it is viable to know a realistic and not excessively large range of future quotations. In other words, a high number of scenarios has to be found, instead of just one specific scenario.

In particular, 50 scenarios were considered at a time for each figure of this paragraph. This choice is a compromise between different goals: on one hand, having a significant number of scenarios to make the results analysis efficient (e.g. 10 scenarios would have been a too little number) and on the other hand obtaining a sufficiently clear view of the plotted results (e.g. 100 scenarios plotted together provide results which are very difficult to be visualized).

In the reality of computation, 3000 scenarios were calculated and evaluated in order to exploit a big-data pool and cover the majority of cases.

Different scenarios were calculated with the following formulas, taken from Barzaghi and Conte (2015) and Fini and Oliosi (2010).

$$P_{CO}(t) = [A + B \cdot P_{CO}(t-1) + C \cdot P_{CO}(t-2)] \cdot (1 + \sigma_{P_{CO}} \cdot rand(-1;1) + \mu_{P_{CO}}) \cdot (1 + g(t))$$

Where:

- $\sigma_{P_{CO}}$ is the standard deviation of errors between the model and CO real price in moving average. Its value is 0.031081405 [USD/bbl]
- $\mu_{P_{CO}}$ is the average value of errors between the model and CO real price in moving average. Its value is -0.000172734 [USD/bbl]
- $rand(-1;1)$ is a random number between -1 and +1
- $g(t)$ is a function that adds a *background noise*, making the whole scenario more realistic with the addition of peaks typical of CO price

Without considering the background noise-function $g(t)$, the generated scenarios looks like the one in Figure 4.33 but, thanks to the addition of this peculiar function, they end up like the ones in Figure 4.35, less smoother and with more spikes. In terms of average values the prices remains the same, but the addition of peaks makes the evaluation more correspondent to reality.

$g(t)$ function is modeled in order to account for the stochastic behavior of relative errors between real prices (which are different from the ones calculated with MA approximation) and modeled price. These errors are summarized in Table 4.7 and in Figure 4.34 divided in intervals with their relative frequency of appearance.

Figure 4.34 shows how the errors are not distributed following a Gaussian distribution but a right-tailed one. For this reason, function $g(t)$ takes into consideration this aspect and produces random values that follow a stochastic behavior like this peculiar distribution. In this way, the background noise addition will results in a reduction of the error between the model and the real prices, recreating stochastic peaks with the same frequency as reality.

4.3. Economic Scenarios

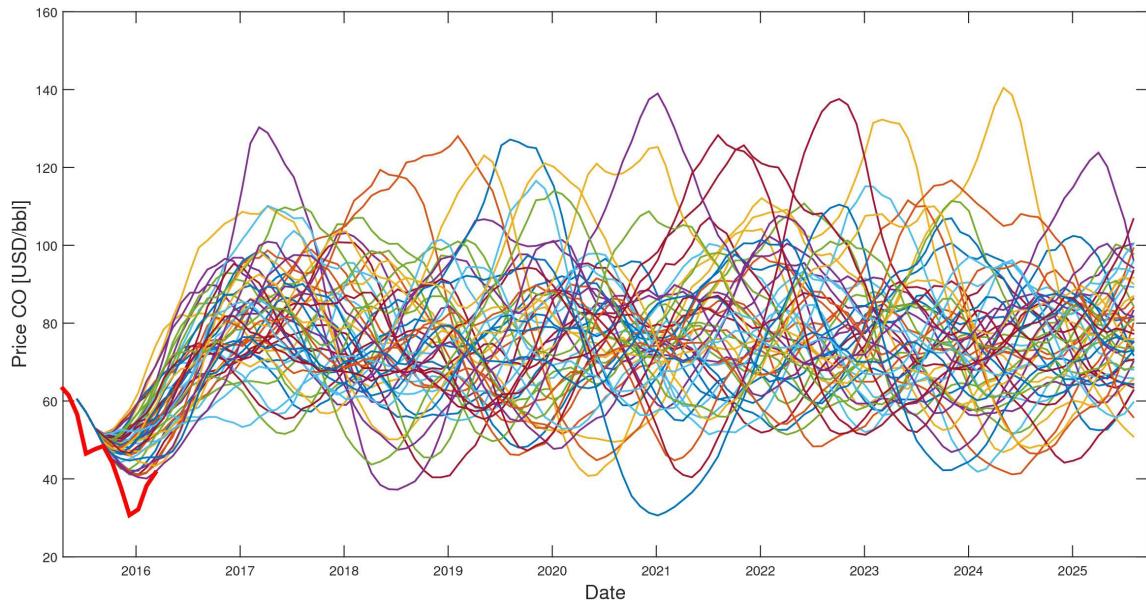


Figure 4.33: 50 scenarios generated without the background noise function for a 10-year future period, these scenarios look very smooth. The red line represents the real prices of CO up to May-2016.

Table 4.7: Relative errors between model and real CO prices.

Stochastic Behaviour				
Interval	Min	Max	Frequency	%
1	-0.12	-0.08	6	4.41
2	-0.08	-0.04	16	11.76
3	-0.04	0	51	37,50
4	0	0.04	38	27.94
5	0.04	0.08	14	10.29
6	0.08	0.12	8	5.88
7	0.12	0.16	2	1.47
8	0.16	0.2	1	0.74
Total			136	100

The scenarios in Figure 4.35 are the ones that will be used as reference for all the other commodities and utilities present in the process.

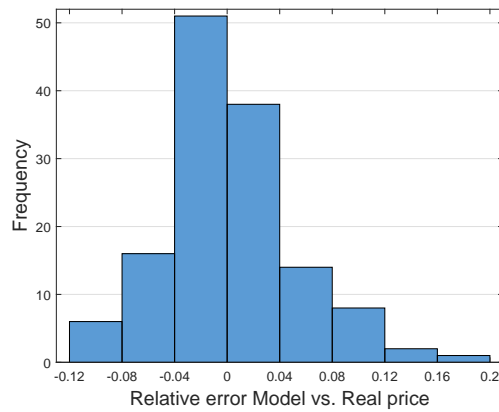


Figure 4.34: Relative errors distribution.

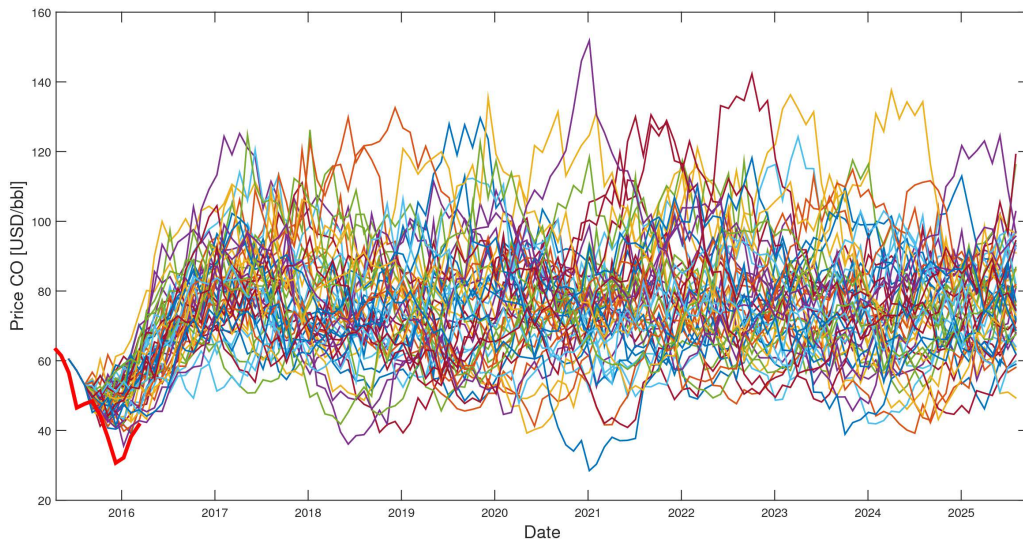


Figure 4.35: 50 scenarios generated with the background noise function for a 10-year future period, these scenarios have peaks like real crude oil quotations. The red line represents the real prices of CO up to May-2016.

commodity and utility scenarios

For each specific scenario, commodity's and utility's trends were evaluated with the formula:

$$P_{Commodities/Utilities}(t) = P_{Model}(t) \cdot (1 + rand(-1, 1) \cdot \sigma_{Commodities/Utilities} + \mu_{Commodities/Utilities})$$

Where:

- P_{Model} is the price evaluated as the econometric model
- $\sigma_{Commodities/Utilities}$ is the standard deviation of the error for that specific commodity or utility between the model and moving average value
- $\mu_{Commodities/Utilities}$ is the average value of the error for that specific commodity or utility between the model and moving average value

It is interesting to notice that each commodity and utility has its own stochastic terms that, summed up with the one deriving from CO scenarios, will increase the variety of the

4.3. Economic Scenarios

system, making the whole economic evaluation more realistic.

Table 4.8 reports the standard deviations and average errors for each model.

Table 4.8: Standard deviation and average values for econometric models.

	$\sigma_{Commodities/Utilities}$	$\mu_{Commodities/Utilities}$
Toluene	0.028867024	-0.0046716
Benzene	0.070056575	0.004779251
Styrene	0.036794306	-0.010971858
Ethylene	0.036412378	0.001505031
BTZ	0.034249484	0.004279642

Bullish, bearish, and constant scenarios

The approach based on the generation of a large number of future scenarios may be more accurate by considering three additional situations, which correspond to a peculiar crude-oil quotation trend that could happen for the law of supply and demand. It can be talked about bullish, bearish, and constant scenarios.

Each kind of trend is obtained by a modification in the econometric model of crude oil. This is performed to be sure that all econometric models will be affected by this modification, following the same trend.

The introduction of a force simulates a no longer completely random trend, because the value of the correcting factor leads the quotations to a precise direction.

In particular, if this factor is greater than 1, bullish scenarios are obtained, and the function is monotonically increasing. On the contrary, this multiplying factor has to be smaller than 1 in bearish scenarios.

If the scenarios are assumed constant, no multiplying factor is introduced, which implies that the obtained quotations are maintained constant and only a background noise is added to the evaluation, useful to evaluate a dynamic economic potential instead of an EP.

Bullish scenarios

On the basis of what has been assumed above, the crude oil econometric model was modified as follows:

$$P_{CO}(t) = [A + B \cdot P_{CO}(t - 1) + C \cdot P_{CO}(t - 2)] \cdot (1 + \sigma_{P_{CO}} \cdot rand(-1; 1) + \mu_{P_{CO}}) \cdot (1 + g(t)) \cdot (1 + 0.00008 \cdot t)$$

The original econometric model has been multiplied by a term equal to $(1 + 0.00008 \cdot t)$ which monotonically increases in time bringing to a continuous increase of prices in the 10-year horizon. The value 0.00008 was found in order to obtain scenarios that did not exceed 130 USD/bbl in 10 years. In this way, the scenarios are more realistic and consistent with the historical prices.

Figure 4.36 shows the scenario distribution obtained with the previous formula.

Under a bullish hypothesis, future 10-year prices for crude oil show that their quotations in the first months follow the real behavior of CO. Later on, the prices start increasing and after 3-4 years the dependence from past prices is completely lost. The time weighted contribution becomes more and more important and dominates over the other terms. At the

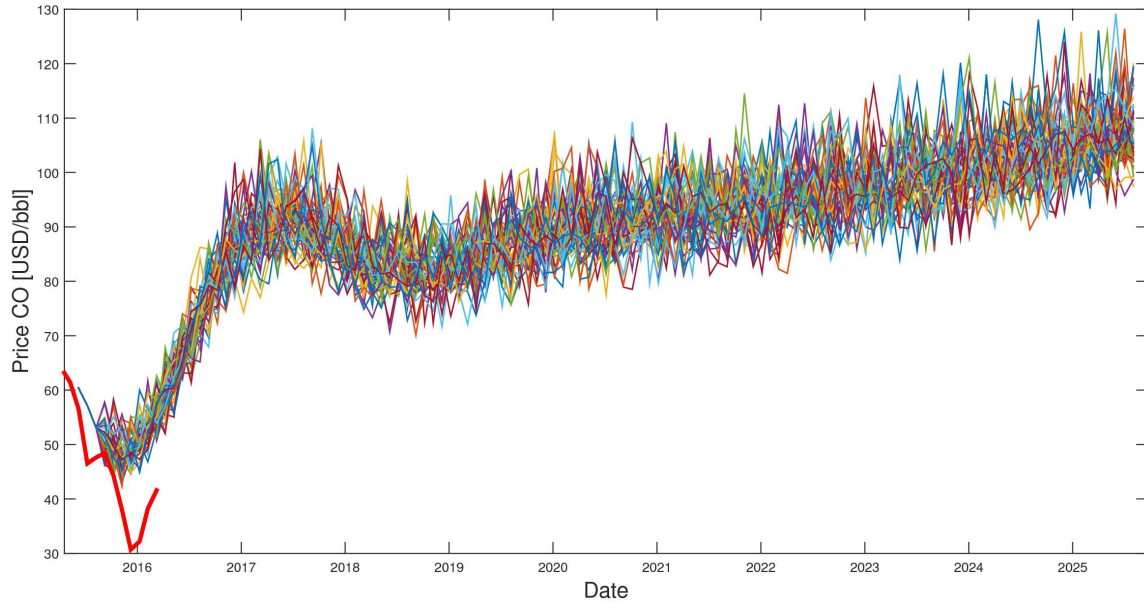


Figure 4.36: 50 bullish scenarios generated in the time horizon of 10 years. The red line represents the real prices of CO up to May-2016.

end of the time-horizon, prices would reach about 120 USD/bbl, overtaking this threshold in some scenarios.

Bearish scenarios

In bearish scenarios, the function will be monotonically decreasing. It must be considered that crude oil quotations decreased until about 30 USD/bbl in the last months of 2015 and at the beginning of 2016. These prices are already so low that introducing further bearish scenarios starting from very low crude oil costs would lead to unrealistic estimations of future prices and economic potentials. Imposing a limit of 20/30 USD/bbl brings to the generation of scenarios constant in time. These considerations can justify the choice of neglecting bearish scenarios from the current styrene plant economic evaluation.

Constant scenarios

Scenarios are considered constant if their mean trend does not change in time (but for stochastic fluctuations).

As a consequence, the expression concerning crude oil becomes:

$$P_{CO}(t) = Constant \cdot (1 + \sigma_{P_{CO}} \cdot rand(-1;1) + \mu_{P_{CO}}) \cdot (1 + g(t))$$

Before starting with the constant scenarios analysis, it is necessary to choose the mean value at which the econometric value refers. This value is chosen by the user *a priori*, being sure that it is a reliable value for crude oil price.

Three constant values were chosen as 30, 60, 120 USD/bbl, and the results are shown in Figures 4.37, 4.38, and 4.39.

Considering CO prices around 30 USD/bbl means staying on a limit situation, because all scenarios are placed where CO quotations remain as low as possible. As a consequence, this hypothesis results robust and also interesting under design point of view.

4.3. Economic Scenarios

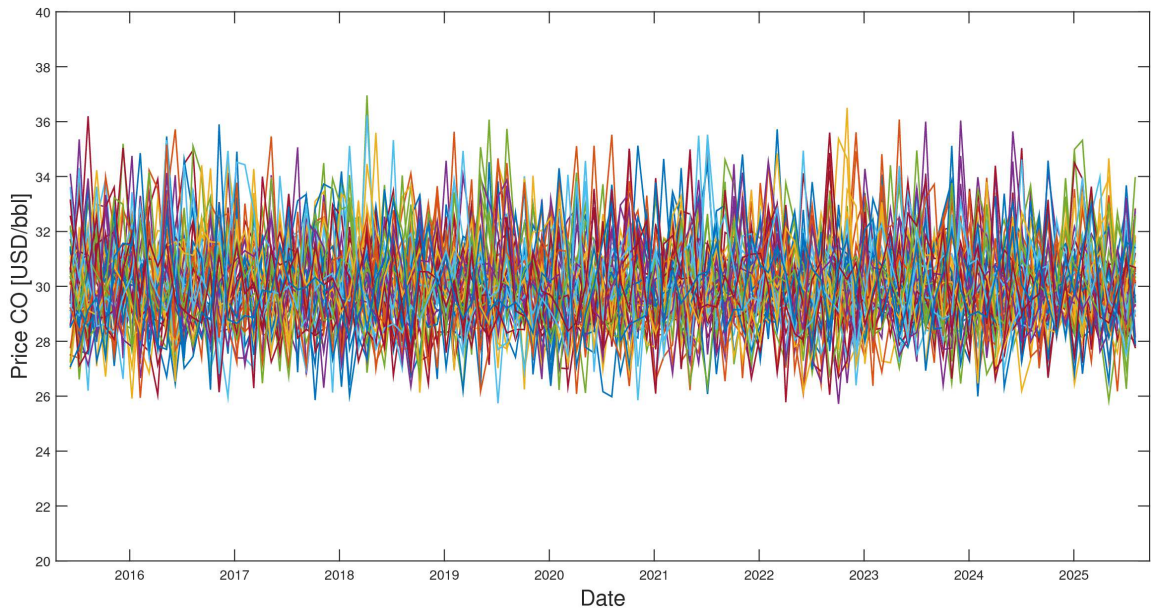


Figure 4.37: 50 constant crude oil scenarios at 30 USD/bbl.

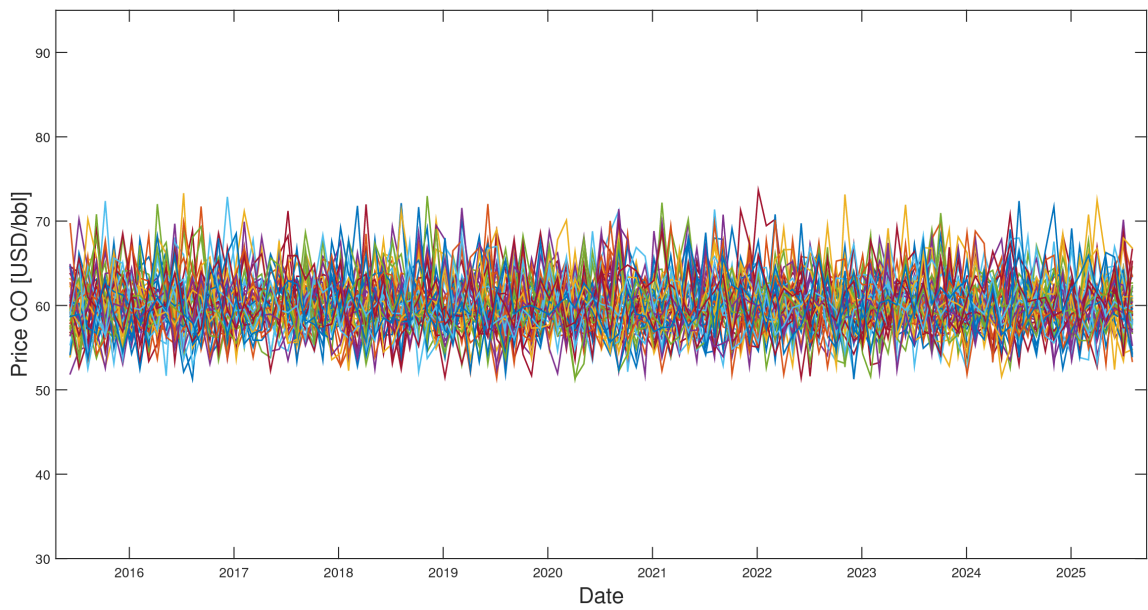


Figure 4.38: 50 constant crude oil scenarios at 60 USD/bbl.

A 60 USD/bbl quotation would maintain crude oil price at a medium price, resulting neither too high nor too low. This plot will permit to notice if the optimal configuration for a medium price will reflect the optimal configuration for the stochastic scenarios.

If crude oil would stay on high selling prices like 120 USD/bbl (as it happened for example in 2007-2009 period, see Figure 4.2), constant scenarios for the next 10 year quotations are very high and also the design will be affected.

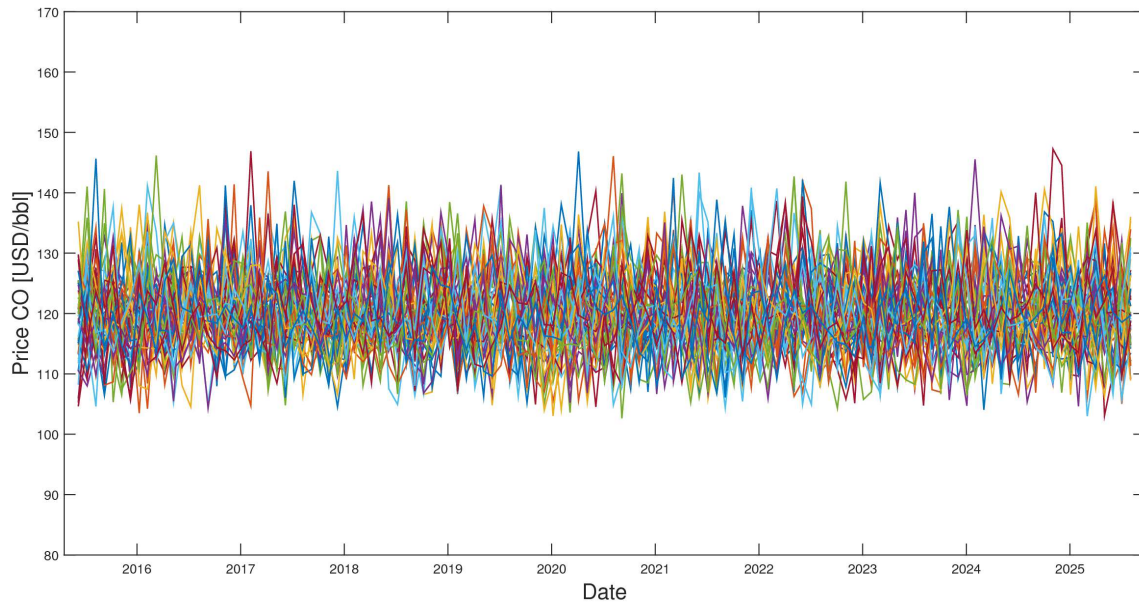


Figure 4.39: 50 constant crude oil scenarios at 120 USD/bbl.

4.4 Dynamic and Predictive Conceptual Design computation

4.4.1 Dynamic DEP_4

The evaluation of DCD for the past months has the purpose to show which were the best plant optimal design variables, in order to maximize the incomes in the 10-year period before proceeding with the analysis on future scenarios. This $DEP_4^{Cumulated}$ is evaluated for both the cases specified in Chapter 2, so for the steam price maintained constant and low (as in Luyben (2011)) and for the steam modeled with the considerations specified at the beginning of this chapter.

The interval of calculation corresponds to 120 months in the decade July-2005, June-2015. The 3-D plots in Figures 4.40, 4.41, and 4.42 show how the dependence from two degrees of freedom at a time affects the analysis of the $DEP_4^{Cumulated}$, in case steam price is variable.

From these plots, some different surfaces are shown:

- some pairs of DoFs (with the other two fixed) show a linearly increasing $DEP_4^{Cumulated}$ in both variables, as for splitting factor versus inlet temperature or reactor's volume.
- the pairs which contain LP steam as the independent variable show a maximum point. This reinforces the hypothesis that steam affects the plant optimization significantly.

For both steam price cases (constant and modeled) a maximum value of the $DEP_4^{Cumulated}$ and its corresponding degrees of freedom configuration were found. These values are expressed in Table 4.9.

In the “modeled steam price” case study all the degrees of freedoms are at their lowest value, except for the splitting factor, which is the highest allowable. On the contrary, if the steam price is maintained constant the optimal configuration will change in the LP steam value, and also $DEP_4^{Cumulated}$ will increase. $DEP_4^{Cumulated}$ difference between these cases is evident, showing almost a doubling of the profitability of the plant in case the steam price is very low.

4.4. Dynamic and Predictive Conceptual Design computation

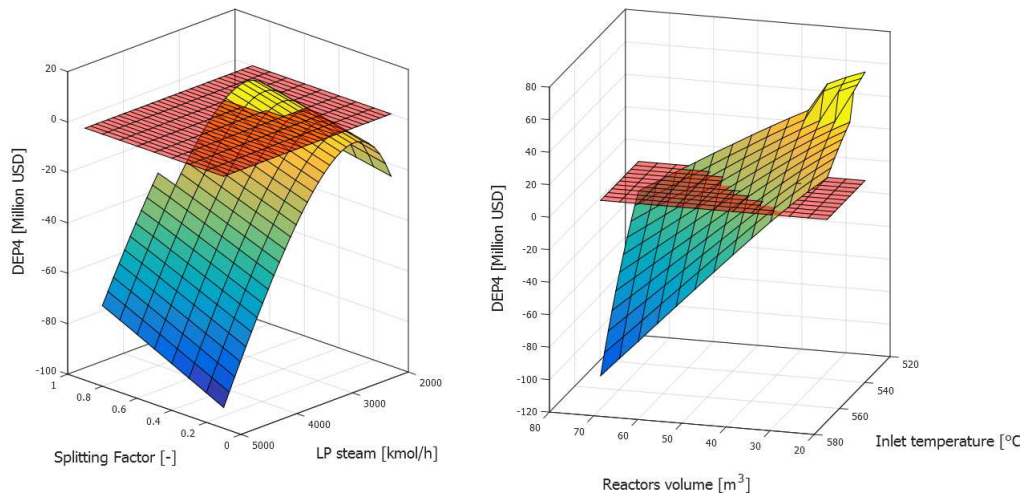


Figure 4.40: $DEP4_{Cumulated}$ value as a function of two degrees of freedom at time. For each 3-D plot, the degrees of freedom considered are written on the axes, whereas the other two DOFs are fixed. In particular, the degrees of freedom not considered are fixed at: splitting factor = 0.6, LP steam flow = 2400 kmol/h, reactor inlet temperature = 533 °C and reactor volume = 42.76 m³. The red plane divides the positive from the negative values.

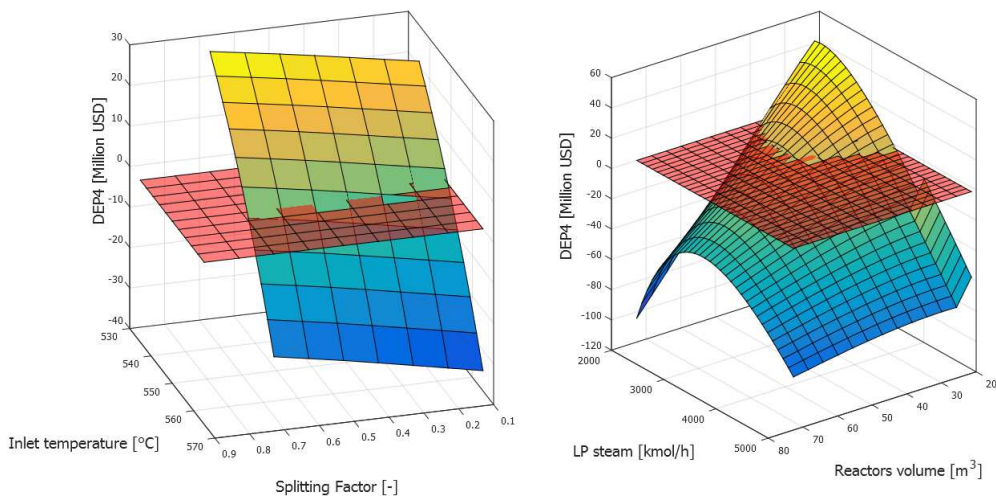


Figure 4.41: $DEP4_{Cumulated}$ value as a function of two degrees of freedom at time. For each 3-D plot, the degrees of freedom considered are written on the axes, whereas the other two DOFs are fixed. In particular, the degrees of freedom not considered are fixed at: splitting factor = 0.6, LP steam flow = 2400 kmol/h, reactor inlet temperature = 533 °C and reactor volume = 42.76 m³. The red plane divides the positive from the negative values.

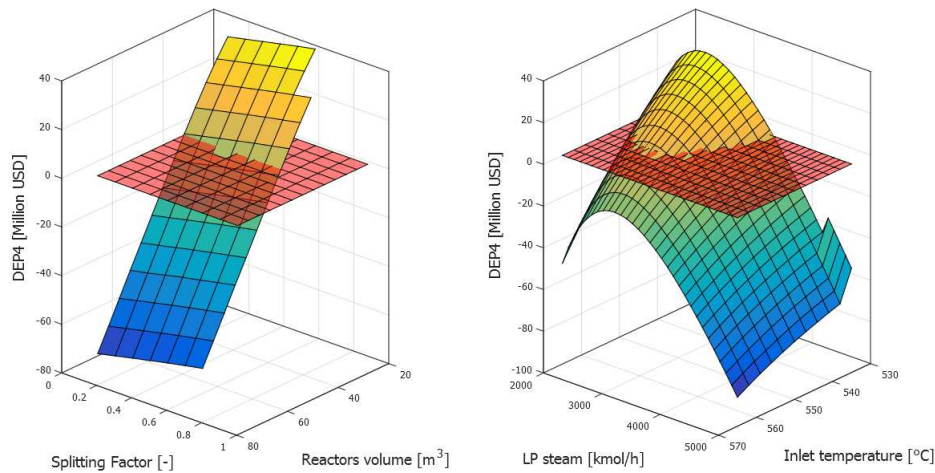


Figure 4.42: $DEP4_{Cumulated}$ value as a function of two degrees of freedom at time. For each 3-D plot, the degrees of freedom considered are written on the axes, whereas the other two DOFs are fixed. In particular, the degrees of freedom not considered are fixed at: splitting factor = 0.6, LP steam flow = 2400 kmol/h, reactor inlet temperature = 533 °C and reactor volume = 42.76 m^3 . The red plane divides the positive from the negative values.

Table 4.9: $DEP4_{Cumulated}$ maximum values and their corresponding configuration.

Steam price	SF [-]	LP steam [kmol/h]	Inlet temperature [°C]	Reactor volume [m^3]	$DEP4_{Cumulated}$ [10^6 USD]
Modeled	0.6	2000	535	21.38	72.699
Constant	0.7	2600	535	21.38	135.694

4.4.2 Predictive $DEP4$

The aim of this thesis is the evaluation of modeled fluctuations of the economic input variables under the hypothesis of Predictive Conceptual Design (PCD). PCD, Barzaghi et al. (2016), consists in the evaluation of the $DEP4_{Cumulated}$ for different scenarios evaluation. It mainly differs from DCD by the fact that DCD evaluates the $DEP4$ for past historical prices, instead PCD evaluates the $DEP4$ using modeled future prices. For this reason, a great number of scenarios need to be investigated in order to have a reasonable data-set of possible market trends. This means that it is not a justified hypothesis maintaining fixed only steam prices. This assumption, proposed in Chapter 3 to understand how much steam price influences the economic evaluation, will be neglected in the computation of the $DEP4_{Cumulated}$ for PCD.

$DEP4_{Cumulated}$ values were shown to be negative in some past cases. For this reason, a new question has to be formulated in the economic assessment of future scenarios:

Could it happen in a styrene plant, as it occurs in the HDA process, that the plant should be switched on and off, depending on market fluctuations?

To accomplish the goal of evaluating this peculiar situation, a physical constrain should be considered: it is not possible to switch on and off the plant for short periods (e.g., one month). This is due to material resistance (e.g., fatigue stress), processistic problems (start-

4.4. Dynamic and Predictive Conceptual Design computation

up and shut-down times) and working problems.

For these reasons, a minimum switch time has been imposed equal to 2 months. If the plant has been shut down for only a month, it has to remain in that state for the following month, *vice versa* if the plant has been started up.

The $DEP4_{Cumulated}$ was calculated for each economic scenario and for each configuration. Then, the optimal configuration that maximizes each scenario was found. In this way, two maximum $DEP4_{Cumulated}$ were found for each economic scenario:

- a maximum $DEP4_{Cumulated}$ for the standard case.
- a maximum $DEP4_{Cumulated}$ when the plant can be switched ON and OFF (with the limitations specified above).

In Tables 4.10 and 4.11, the optimal configurations to obtain the highest $DEP4_{Cumulated}$ are shown with the relative percentage of economic scenarios maximized (over 3000 total scenarios).

In the last row of Table 4.11, all the other maximum configurations, with the degrees of freedoms ranging from the ones specified, are summed up. Each of these are the solution only for no more than 7 scenarios.

Table 4.10: Configurations that maximize the $DEP4_{Cumulated}$ and their abundance.

SF [-]	LP steam [kmol/h]	Temperature [°C]	Volume [m ³]	Percentage of scenarios [%]
0.6	2000	535	21.38	98.27
0.6	2100	535	21.38	1.57
0.6	2200	535	21.38	0.16

Table 4.11: Configurations that maximize the $DEP4_{Cumulated}$ and their abundance (ON-OFF case).

SF [-]	LP steam [kmol/h]	Temperature [°C]	Volume [m ³]	Percentage of scenarios [%]
0.6	2000	535	21.38	82.40
0.6	2100	535	21.38	7.67
0.5	2000	535	21.38	4.40
0.6	2200	535	21.38	1.60
0.4	2000	535	21.38	1.03
0.5	2100	535	21.38	0.83
0.3-0.6	2000-2400	535-562	21.38-25.66	2.07

A different way to visualize the differences between the solutions is to plot all the degrees of freedom that maximize the $DEP4_{Cumulated}$ for each scenario. Figure 4.43 shows the variability of the degrees of freedom with respect to the maximum $DEP4_{Cumulated}$. For the reactor volume and inlet temperature the optimal configuration impacts with the lower bounds (as already seen for the $EP4_{Cumulated}$ in Chapter 3). In PCD case, also the LP steam flowrate of the optimal solutions is around its lower bound with little variations. A slitting factor above 0.6 never maximizes the $DEP4_{Cumulated}$ for each scenario investigated. In case the plant could be started-up and turned-down, whenever is convenient and under the limitations expressed above, the variability of certain DoFs that optimizes the economic evaluation increases. Anyway, under both the hypotheses, the plant has an optimal config-

uration equal to the past $DEP4_{Cumulated}$ one. This assumption is valid for the majority of the scenarios.

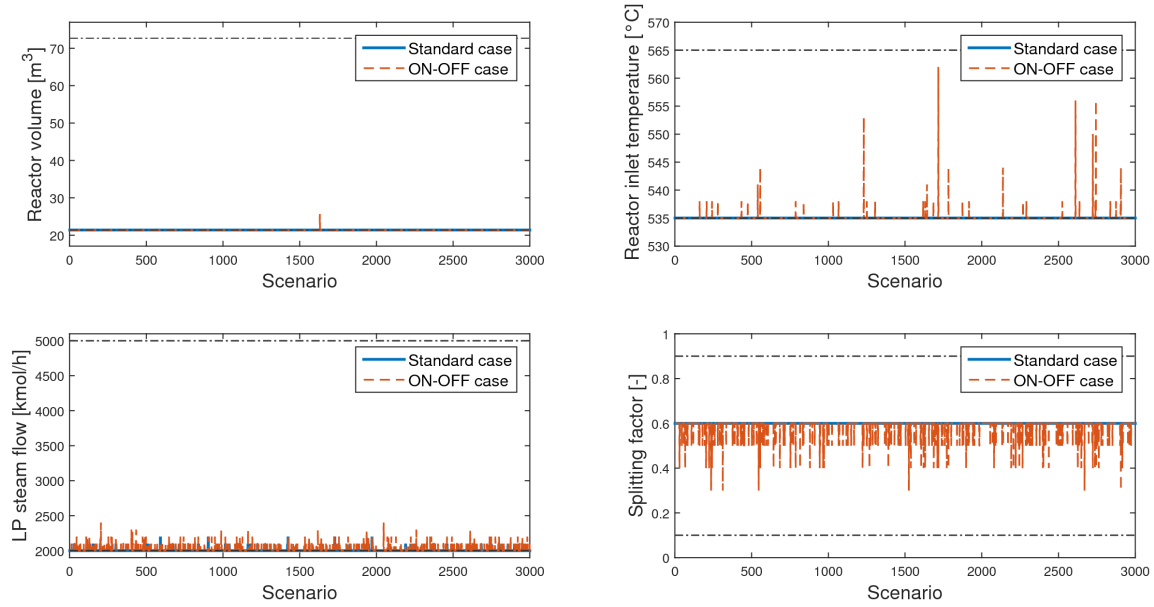


Figure 4.43: Fluctuation of the optimal DoFs configuration for each scenario. In the graphs are plotted also the bounds (black lines).

Some statistical analysis was performed on the data, finding how the optimal $DEP4_{Cumulated}$ are distributed: in Table 4.12 and in Figure 4.44 some results are provided.

In particular, when the plant can be started up and shut down, the $DEP4_{Cumulated}$ distribution passes from a normal type to a strongly asymmetric one with only a few negative data.

The median and the average change in sign passing from one case to the other. For the ON-OFF case, the scenarios where the maximum $DEP4_{Cumulated}$ is negative are just 137 (4.57% of total scenarios) whereas this number rises to 1869 (62.3% of total scenarios) for the standard case.

The minimum value for the newly hypothesized case is one order of magnitude higher. An unexpected behavior can be found for the maximum: the standard calculation finds a higher maximum value than the new one. This is due to the physical constraint imposed above: maybe, for that scenario, the plant remains in a shut-down configuration during some very profitable months, which occurs just after unprofitable one.

Table 4.12: Statistical consideration on $DEP4_{Cumulated}$.

	Standard	ON-OFF
Average	-5.77e6 [USD]	1.55e7 [USD]
Median	-7.48e6 [USD]	1.26e7 [USD]
Skewness	0.329 [USD]	1.267 [USD]
Standard Dev.	2.28e7 [USD]	1.28e7 [USD]
Maximum	8.26e7 [USD]	8.17e7 [USD]
Minimum	-8.69e7 [USD]	-4.92e6 [USD]

Figure 4.45 shows the maximum $DEP4_{Cumulated}$ obtainable for both the cases hypothesized. The data have been ordered in increasing $DEP4_{Cumulated}$ for the “ON-OFF” case.

4.4. Dynamic and Predictive Conceptual Design computation

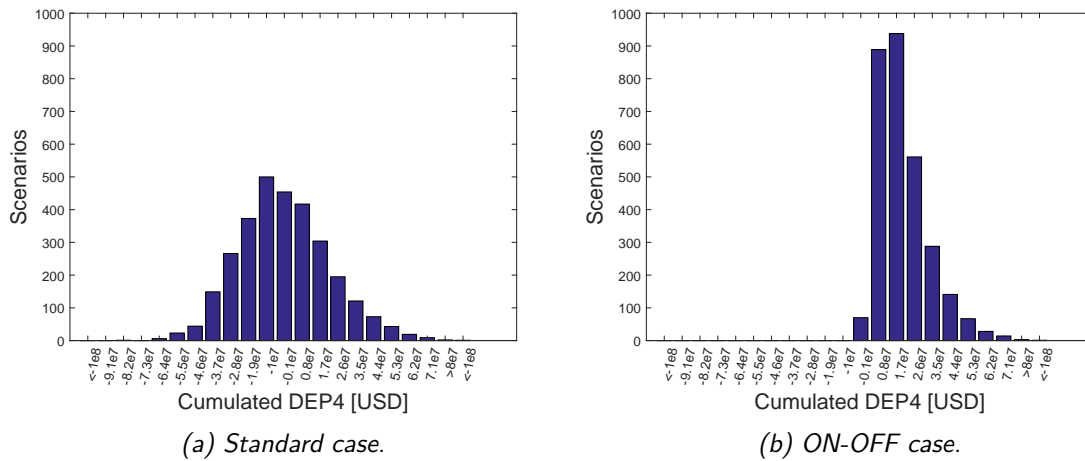


Figure 4.44: Distribution of $DEP4_{Cumulated}$.

Both curves follow the same behavior, which denotes the dependence of economic evaluation from prices, but standard data are highly negative for the majority of scenarios.

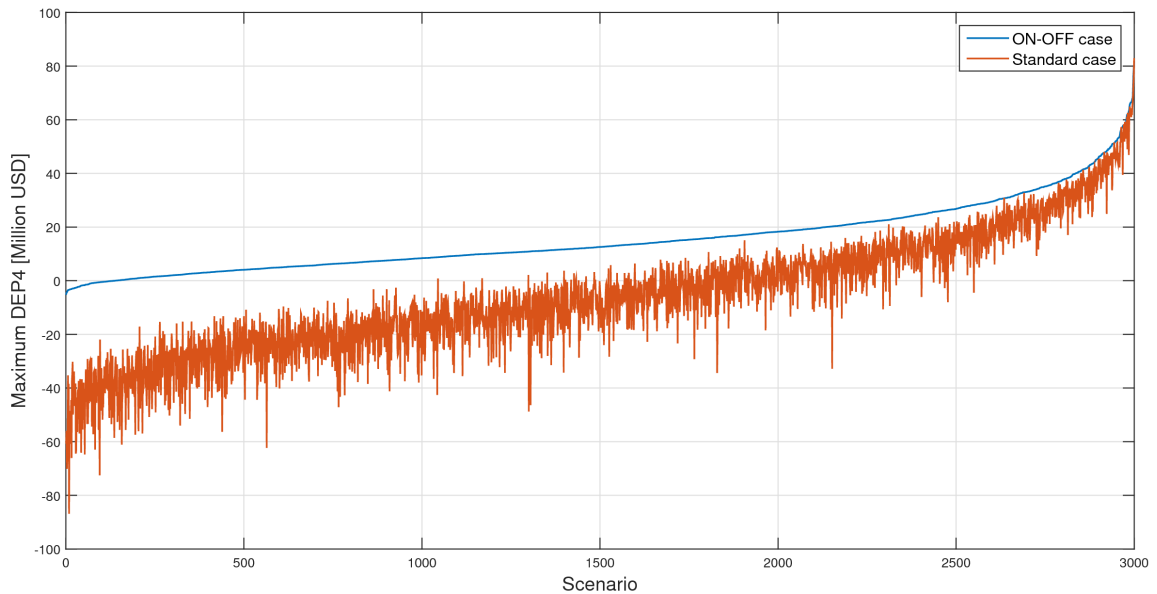


Figure 4.45: Fluctuation of maximum $DEP4_{Cumulated}$ for each scenario: comparison standard case with ON-OFF case. The scenarios have been ordered as increasing $DEP4_{Cumulated}$ for the ON-OFF case, to better show the differences between the cases scenario per scenario.

From the analysis of these results, it is evident than switching ON and OFF the plant whenever is possible seems the best option for the 3000 economic scenarios evaluated. Another question, however, has to be addressed: how long does the plant need to be shut-down during the 10-year period?

If the number of months in which the plant should be shut-down is too high, the profits are expected to be low, and some additional problems could rise related to the operation of the plant (workers payment, supply chain management, ...).

To answer this question it is possible to look at Figure 4.46, where it is shown how many months the plant will stay on, for a period of 120 months.

To better show the number of operative months for each scenario, the scenarios have been

ordered following the increasing months number in which the plant is productive.

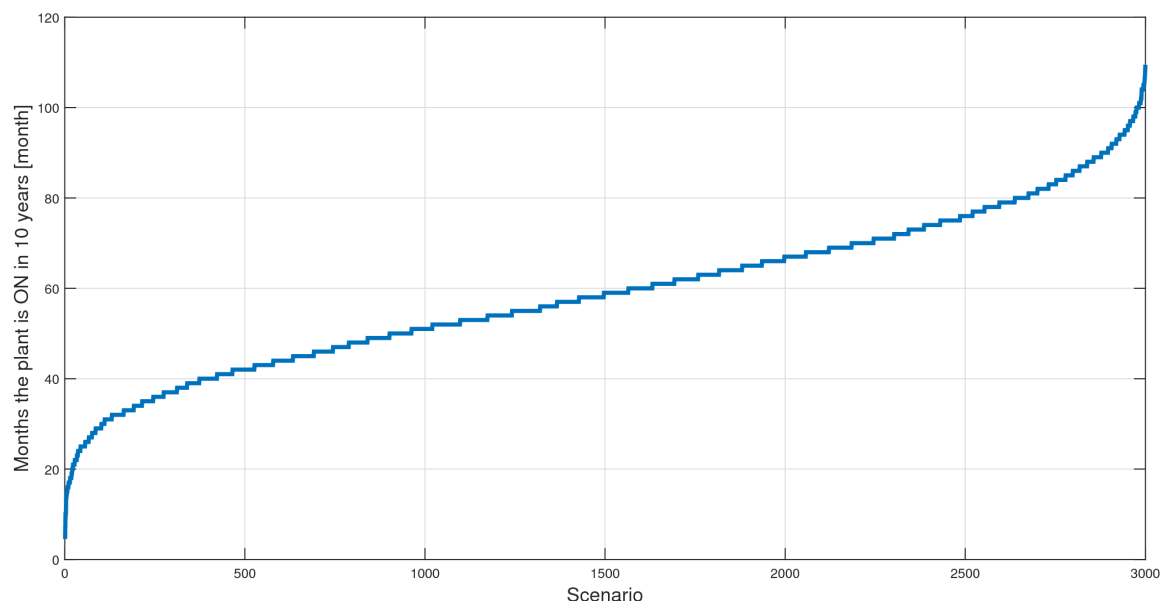


Figure 4.46: Months when the plant is operative. To better show the data, the scenarios have been ordered to have the months when the plant is operative in increasing order.

For around a half of the scenarios (1500 on a total of 3000), the plant is operative just for 60 months, so only for 5 years over 10. This means that the plant would work only for half of its lifespan. In none of the cases the plant is operative for the whole 10 years.

A few more considerations can be explained by looking at Figure 4.47. There, different curves are plotted to show a complete picture of the ON-OFF case. The scenarios are plotted in increasing $DEP4_{umulated}$ order, this has been done to better show the dependence of profitability from the number of months when the plant is operative in its lifespan. The months of activity of the plant follow the $DEP4_{Cumulated}$ curve with some fluctuations. As expected, the most profitable scenarios are the ones where the plant is operative for the majority of its life.

The black line in Figure 4.47 represents the CAPEX value for the optimal configuration³. That line shows that, for about a third of the whole number of scenarios (1000 over 3000), the CAPEX investment done by the buyer is higher than the total income provided by the plant in 10 years. This implies that the investment will not be as profitable as expected from the buyer, and the plant has high economic risk and low profitability.

Buyers of chemical plants expect high profits from the initial investment. If profits themselves become too low, a financial investments is safer and more likable for an hypothetical buyer and the possibility of building a chemical plant will be rejected. For these reasons a detailed analysis of possible market trends, with a high number of scenarios, need to be performed.

For all the reasons explained above, this process seems feasible only in a reduced range of stochastic economic scenarios, and this conclusion reflects in part the market trend that styrene monomer production has followed in the period not covered by historical data, from July-2015 to September-2016. The current trend suggests that styrene monomer price is continuously lowering, as reported by ICIS website, but margins for styrene monomer still

³Optimal for the 82.40% of scenarios for the ON-OFF case. Its DoFs are: splitting factor equal to 0.6, LP steam equal to 2000 kmol/h, inlet temperature equal to 535 °C, and reactor volume equal to 21.38 m³.

4.4. Dynamic and Predictive Conceptual Design computation

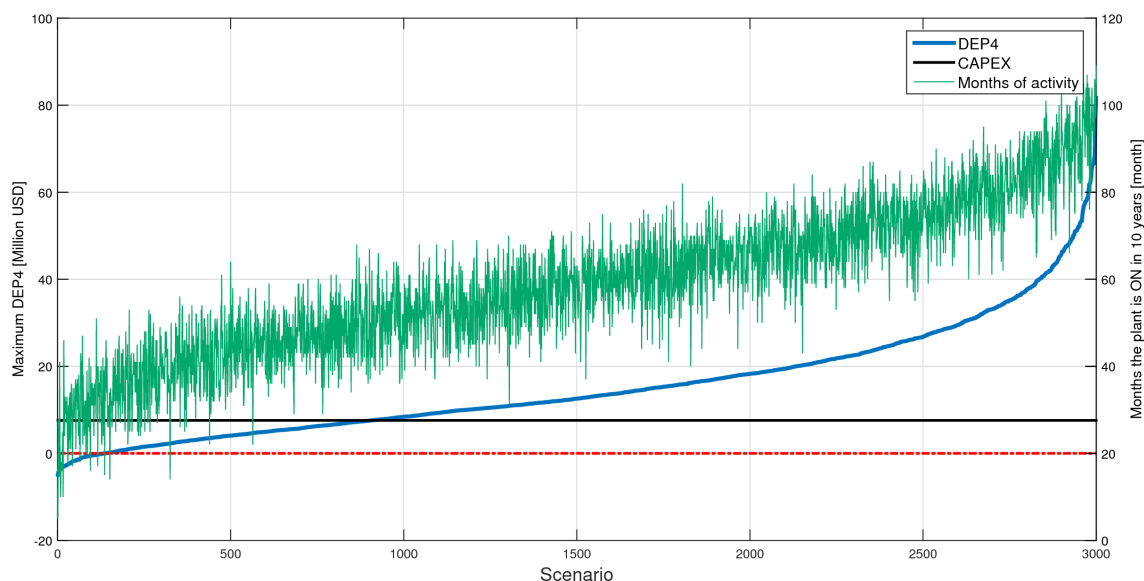


Figure 4.47: Maximum $DEP4_{Cumulated}$ with respect to the months of activity and capital expenses. The scenarios have been ordered as increasing $DEP4_{Cumulated}$ to better show the dependence of operative months from maximum profitability.

do not justify new capacity because they were unable to sufficiently sustain high levels of incomes.

In August 2016, Chris Pappas, CEO of US-based styrenics producer Trinseo, talked about styrene market as follows:

“I don’t think the returns are really that high [...] They have just been better than they had been, better than some very poor histories.”

In the past 30 months, in America, there were about 8 months where styrene margins justified the erection of new plants. In Asian countries, that number has dropped drastically to one month.

From that analysis, it can be concluded that the proposed econometric models reflect the reality of fact and that a styrene process could not be operative for its whole life and yet be profitable and economically sustainable.

4.4.3 Bullish and constant scenarios $DEP4$

The following step of the $DEP4_{Cumulated}$ evaluation consist of studying its different trends by imagining two kinds of future prices scenarios: bullish and constant (bearish scenarios are not considered for the reasons discussed in Paragraph 4.3). This approach is recommended because if the aim is forecasting future trends, the analysis should be as complete as possible. Studying these two different situations helps covering the majority of situation which could occur in future years.

First, bullish scenarios are considered. 50 Bullish scenarios were analyzed and for most of them the optimal design consists in a splitting factor of 0.6, a steam flowrate of 2000 kmol/h, reactor inlet temperature of 535 °C, and reactor volume of 21.38 m^3 . This implies that all the considerations done for stochastic scenarios are still valid in the case a bullish trend in the crude oil quotations for a 10-year period. Some degrees of freedom change a little in order to accomplish the goal of finding the maximum $DEP4_{Cumulated}$. These varia-

tions are on the three independent variables (temperature, steam flow, and splitting factor) that can be changed easily in on-line process control, so they could become RTO variables. It can be noticed how the ON-OFF evaluations are the only feasible way of running the plant and how the net income is very low, making the process uneconomic most of the time. Figure 4.48 shows graphically the different trends of the two approaches.

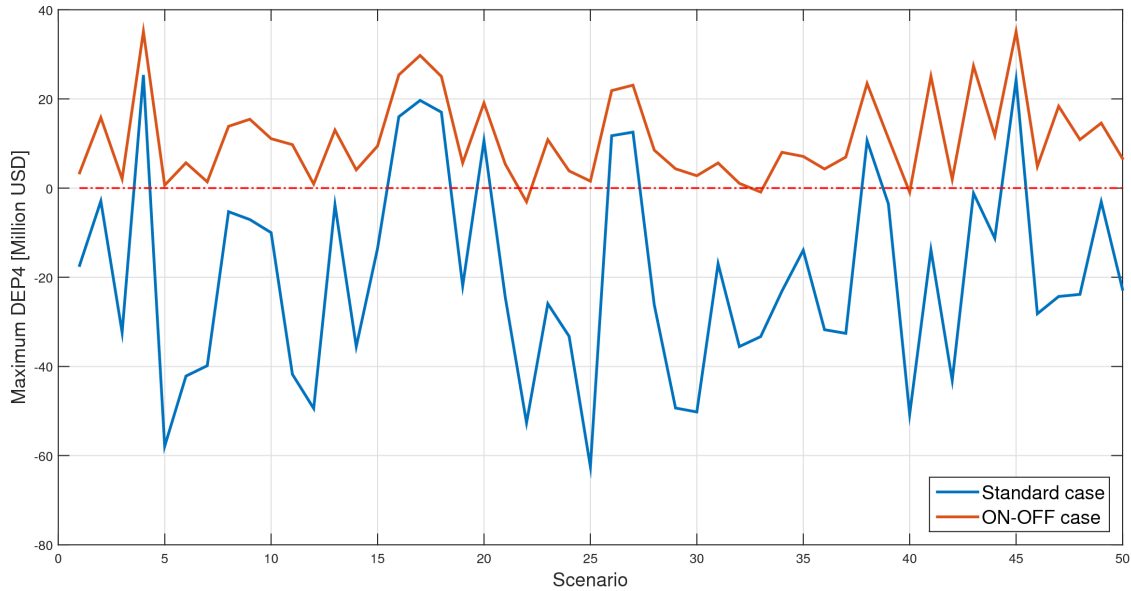


Figure 4.48: Maximum $DEP4_{Cumulated}$ achievable in case crude oil fluctuation follows a bullish trend.

In case of constant crude oil price trend, with little fluctuations, some other considerations can be suggested depending on the value considered. Increasing crude oil prices, the maximum profit achievable in 10 years decreases from 70 Million USD to 40 Million USD. As can be seen in Figures 4.49 and 4.50, a higher dispersion of prices, with more negative scenarios, goes with the increase of crude oil quotations.

In addition, it also can be seen how it is unnecessary to shut-down the plant for low crude oil prices (around 30 USD/bbl), and how the process becomes less and less profitable as it progressively approaches 120 USD/bbl.

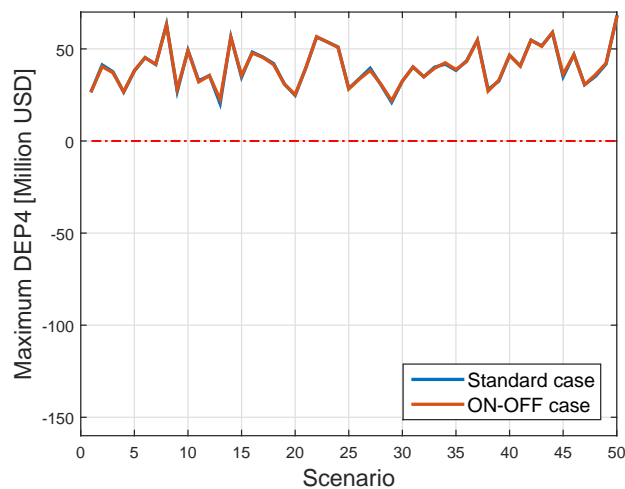
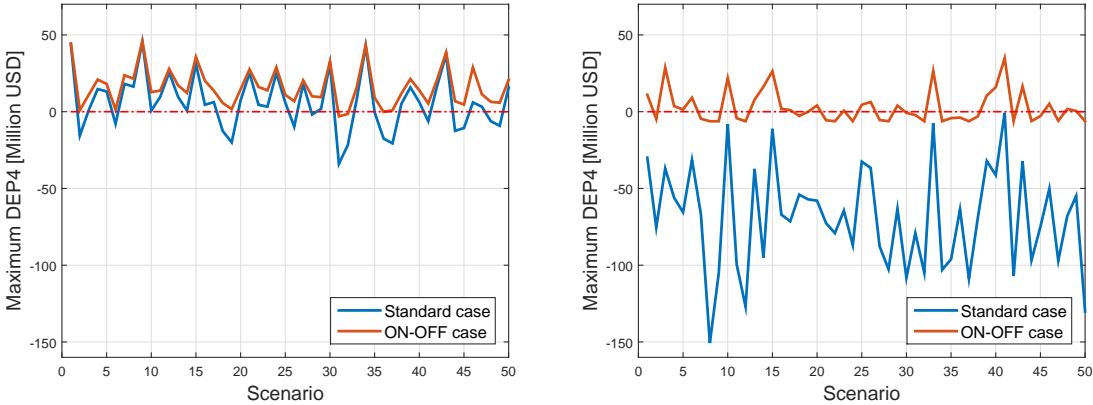


Figure 4.49: Crude oil at 30 USD/bbl.

4.4. Dynamic and Predictive Conceptual Design computation



(a) Crude oil at 60 USD/bbl.

(b) Crude oil at 120 USD/bbl.

Figure 4.50: Max $DEP4_{Cumulated}$ for constant crude oil trends.

Chapter 5

Conclusions and future developments

Purpose of this thesis was to demonstrate that the conceptual design approach (Douglas (1988)) can be improved by mean of dynamic econometric models in the optimization design of a chemical plant.

Dynamic and predictive conceptual design have shown to be robust and, for different crude oil quotations, the styrene plant behaves in different ways in terms of design features. It has been also shown how some simplifications can be correct preliminary but need to be taken into account for a deeper analysis (e.g., column C-3 was neglected in Barzaghi and Conte (2015) and Luyben (2011)).

As improvements to the plant, some modifications could be theoretically implemented, but they would affect the CPU time and the real styrene plant optimization was not the main goal of this thesis.

The computational design takes long times and some erratic behaviours have been found. It could be challenging to know the exact reason, if exists, of the opposite behavior of normal grid and one-step grid methods when the degrees of freedom of the plant increase from 3 to 4. Some hypotheses have been formulated in Chapter 3, but they would require further investigations to be either confirmed or rejected.

A further application of the data collected thanks to the link between Unisim Design Suite and MATLAB can be their use as a database of possible plant configurations to accelerate a future real time optimization of the installed plant, once the reactor volume have been assigned. By doing so, a rough first approach of the plant operation can be provided to the buyer once the plant is installed.

Another possible improvement could be adopting a multi-objective optimization to consider the environmental impact of the styrene plant. The aim would be trying to concile both the maximization of production ($DEPA_{Cumulated}$ value) and the minimization of pollution (with opportune models based on massive fractions).

About the scenarios modeling, it could be interesting to see whether the use of different models, not only based on previous prices (econometric models) but for example economic models based also on markets fluctuations, natural events, political tensions, wars, technological progression, and supply and demand law could bring to different results in the trends analysis.

Further evaluations could be done using different approaches from predictive conceptual design, for example using financial indexes like the payback period, the net present value (NPV) or the internal rate of return (IRR). These indicators are different from the economic potential because they are based on a financial analysis and take into account the interest taxes of the investment.

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Appendix A

Cost estimation rules

As explained in 2.2.2 investment costs (CAPEXs) are calculated with Guthrie's formulae. Marshall & Swift index adopted is updated to 2010, because no more recent indexes are available for free. This index is equal to 1457.4. This appendix have the purpose to examine in dept the capital cost of each unit operation.

Factors

Each factor is different for every formula, but take into consideration the same parameter as specified as follow:

F_m = Material Variation

F_p = Pressure Variation

F_d = Design Variation

F_t = Mechanical Refrigeration Factor

F_s = Tray Spacing

F_c = Correlation Factor

Process Furnaces

$$C_{Furnaces}[USD] = \left(\frac{M\&S}{280} \right) \cdot (5.52 \cdot 10^3) \cdot Q^{0.85} \cdot (1.27 + F_c)$$
$$F_c = F_d + F_m + F_p$$

where Q = adsorbed duty, [MBtu/h] and $20 < Q < 300$

Heat Exchangers

$$C_{HeatExchangers}[USD] = \left(\frac{M\&S}{280} \right) \cdot 101.3 \cdot A^{0.65} \cdot (2.29 + F_c)$$
$$F_c = (F_d + F_p) \cdot F_m$$

where A = area ft^2 and $200 < A < 5000$

Gas Compressors

$$C_{Compressors}[USD] = \left(\frac{M\&S}{280} \right) \cdot 517.15 \cdot bhp^{0.82} \cdot (2.11 + F_c)$$
$$F_c = F_d$$

where bhp = brake horsepower and $300 < \text{bhp} < 10,000$

Pressure Vessels, Columns, Reactors

This formula is used for the reactors vessel, for the decanter and for the columns vessel. In the case of the columns and of the decanter, has been used a sizing utility already implemented in UniSim to evaluate diameter and height of the vessel. In the case of the columns an additional 15% has been added to the height to include the skirt and the head of the column (Price (2003)).

$$C_{Vessel}[USD] = \left(\frac{M\&S}{280} \right) \cdot 101.9 \cdot D^{1.066} \cdot H^{0.802} \cdot (2.18 + F_c)$$

$$F_c = F_m \cdot F_p$$

where H = height in ft

D = diameter in ft

Distillation Columns Trays

$$C_{Tray}[USD] = \left(\frac{M\&S}{280} \right) \cdot 4.7 \cdot D^{1.55} \cdot H \cdot F_c$$

$$F_c = F_s + F_t + F_m$$

where H = tray stack height, ft (24-in. spacing)

D = diameter, ft

Distillation Columns Internals

For the filling of the columns C-1 and C-3 has been assumed a fixed cost of 1000 USD/ m^3 and the volume of the filling has been estimated from the diameter and the height given by UniSim sizing utility.

Appendix B

Matlab-Unisim link

This appendix contains a little part of the MATLAB's code written to create a link with UniSim Design. Each part of the code has a specific aim, as it is explained in the green commentaries. UniSim's pieces of equipment names are in purple and the unit measure for the imported variable is written immediately after.

It must be noticed that MATLAB is case-sensitive, which means that a particular attention has to be paid to capital letters and spaces.

```
%% Open Unisim

Server = actxserver('UniSimDesign.Application');    %Open "Unisim Design"
StyrenePlant = Server.SimulationCases.Open('C:\Styrene_Plant.usc'); %Open file
StyrenePlant.Activate;

%% Shortcut for Operation, MateriaFlux, EnergyFlux

LPSteam_Unisim=StyrenePlant.Flowsheet.MaterialStream.Item('LPSteam');
Temp50_Unisim=StyrenePlant.Flowsheet.MaterialStream.Item('50');
R1TubeLength_Unisim=StyrenePlant.Flowsheet.Operations.Item('R1');
SplittingFactor_Uni=StyrenePlant.Flowsheet.Operations.Item('SplittingFactor');
Recycle1=StyrenePlant.Flowsheet.Operations.Item('RCY-1');
StyrenePlant.Solver.CanSolve = 0;                %Stop Solver
Recycle1.IsIgnored=1;                            % Ignore recycle 1
StyrenePlant.Flowsheet.Operations.Item('C3').IsIgnored=1; % Ignore Column C3
LPSteam_Unisim.MolarFlowValue=LPSteam/3600;     %[kmol/h]
Temp50_Unisim.TemperatureValue=Temp50;          %[degree C]
R1TubeLength_Unisim.TubeLengthValue=R1TubeLength; %[m]
SplittingFactor_Uni.Cell('A1').CellValue=SplittingFactor; %[-] Splitting Factor
StyrenePlant.Solver.CanSolve = 1;                %Start Solver
Ricircolol.IsIgnored=0;                          % Don't Ignore recycle1
StyrenePlant.Flowsheet.Operations.Item('C3').IsIgnored=0;% Don't Ignore C3

%% Read data of Interest

DiameterR1= StyrenePlant.Flowsheet.Operations.Item('R1').TubeDiameterValue;%[m]
DiameterR2= StyrenePlant.Flowsheet.Operations.Item('R2').TubeDiameterValue;%[m]
DutyE1= StyrenePlant.Flowsheet.EnergyStream.Item('DutyE1').HeatFlowValue; %[kW]
DutyE3= StyrenePlant.Flowsheet.EnergyStream.Item('DutyE3').HeatFlowValue; %[kW]
UA_E2=StyrenePlant.Flowsheet.Operations.Item('E2').UAValue;    %[kW/ C ]
UA_E4=StyrenePlant.Flowsheet.Operations.Item('E4').UAValue;    %[kW/ C ]
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