Harmonizing Efficiency and Stability

An Improved Approach to Phosgene Reactor Energy and Stress Management

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Abstract

Energy costs related to utility usage in a chemical plant is a big slice of the yearly total operating costs. This thesis is part of an effort to improve the energy recovery system in the phosgene synthesis section in the COVESTRO’s site in Tarragona.

This study will explain how this task was approached and its discoveries. Due to restrictions in what can be and what cannot be done by an internship student, the project has been focused on solutions that do not involve any purchase, costs or changes in conditions that could affect the production or its quality.

Once an introduction to the nature of the process and their chemicals is made, a brief summary of the situation is discussed. Later on, the path followed is described as clearly as possible while censoring what could be sensitive data (by having empty axis in plots, talking in percentages, referencing documentation by their unofficial name, etc…). If there is any doubt regarding any of that data, more information can provided with prior authorization of COVESTRO.

Finally, conclusions and results could be catalogued in two different parts: troubleshooting and optimization. The troubleshooting part was discovered during the creation of this work and it does not fulfil the mentioned objective but prevents future problems and increase the reliability of the system. The optimization gives as a result a change of operational control (conditioned by process, economical or strategic reasons) that takes the form of an EXCEL® file that is being used by the control panellists.

The project has been considered an overall a success leading to important savings in operational costs, when the collected results are extrapolated to a year basis, reaching the six figures number.

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1. BACKGROUND AND OBJECTIVES

COVESTRO is a name composed of syllables from three words: **CO**llaboration, in**VEST**, **STRO**ng, which are the pillars of the company. This organization is formally young, as it was created in 2015, but with many years of history.

In 2004 the Bayer Group restructured the organization Bayer Polymers AG. This changes lead to the foundation of Bayer Material Science AG once completed. This Bayer MS AG announced the spinoff of the company and an IPO, later known as COVESTRO, in 2014. This transition was fully completed in 2015 with the headquarters placed in Leverkusen (Germany). This spin off "…produces precursors for polyurethane foams and the high-performance plastic polycarbonate as well as precursors for coatings, adhesives, sealants, and specialty products, including films." [1].

The objective of COVESTRO as a worldwide company is to replace conventional materials with more economical and ecologically friendly alternatives, promoting sustainability and innovation.

In order to achieve this goal, COVESTRO has around 50 sites around the world, that vary in size, providing products and services for regional or world-size markets.

1.1. Covestro Tarragona

COVESTRO owns a site in Tarragona, near Vila-Seca. One can think of this site like a synergy between various companies that coordinate in order to achieve a greater value than the sum of their constituents.

Focusing on the proprietary plants, COVESTRO has four plants running continuously. The first one generates Carbon Monoxide via combustion of coke that will later be used as a reactant. The second one is in charge of synthesising MDA (Methylenedianiline) later used as a reactant for the final product. The third one, entered in operation formally this year, produces caustic soda and chlorine that will be fully used in the fourth plant. Last but not least, the MDI production factory, in charge of generating phosgene with the Chlorine and Carbon Monoxide and combine the MDA with it to obtain the two final products: MDI (Methylene diphenyl diisocyanate) and Chloric Acid.

Due to the synergies before talked about, the product is transported via cargo ships and trucks. The main buyer of the isocyanate is another site of COVESTRO that will transform it into another final product.

1.2. Objectives

Energy efficiency has been on COVESTRO's scope since its creation. In the past months some changes have led different stakeholders to think that it could be a good moment for optimization in this regard.

The focus has been putted on the phosgene synthesis section, where a specialized reactor that has an energy recovery loop. This section is one of the most crucial ones, regarding safety and operationality, and thus, is one of the least optimized. This is mainly due to its robustness and low free variability of the process conditions. There is where this thesis is focused on. For now the objectives at the start of the study are general and ambiguous and will be concretized as the research is carried out. Those are:

- Improve the gross production of 20 bar Steam in this section of the plant.
- If this improvement comes with an associated cost in another equipment, the decision matrix to implement the changes will be determined by the stakeholders.
- Improve the reliability of the system and perform troubleshooting if necessary.
- Make a positive impact in the company both practically and professionally.

2. PHOSGENE

Phosgene ($COCl_2$; CAS Number: 75-44-5) is an inorganic [2] chemical compound that at normal conditions is a colourless gas that in low concentrations has a distinct sweet odour that some refer as fermented fruits or freshly cut grass [3]. Its basic chemistry characteristics can be seen in the figure and the table below.

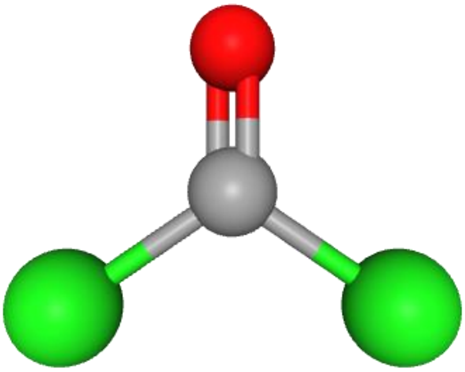


Figure 2.1 Phosgene Particle Structure [31]

Table 2.1 Chemical Data Summary of Phosgene [4]

Property	**Value**
Molecular Weight (g/mol)	98.92
Critical Temperature (ºC)	181.85
Critical Pressure (psia)	822.97
Critical Volume (cm^3/mol)	190
Normal Boiling Point (ºC)	8.3
Melting Point (ºC)	-118
Density at N.C. (kg/m^3)	4.25
Colour	Colourless
Note	In presence of humidity, water or ammonia, it may produce white clouds

2.1. Safety [5]

This compound is very toxic for humans and very dangerous due to its physical characteristics and no antidote, other than supportive medical care, has been found. The symptoms, as usual, can be categorized in short or long-term effects but is still important to keep in mind that the degree of exposure is key in the development of these signs.

2.1.1. Short-Term Effects

The immediate symptoms after exposure can be easily mistaken as they are usually developed by a grand group of household chemicals for example. Between these signs one can find:

- Coughing
- Burning / Watery Eyes
- Nausea

But a sudden exposure to a high concentration of phosgene will develop into a pulmonary enema in 4 hours approximately.

Some effects can prevail hidden for up to 48 hours after exposure even when the patient is feeling better than before. That’s why every person that has been in contact with this agent must be monitored for days so the following symptoms can be treated quickly if they appear:

- Difficulty breathing or coughing pinkish fluid
- Low blood pressure
- Organ Failure

2.1.2. Long-Term Effects

Usually, all the people exposed to this chemical may recover in long periods of time but there is a possibility of developing chronic bronchitis or emphysema as a result of that contact.

2.1.3. History [6]

This compound was first synthesized by John Davy (1790-1868) in 1812 by combining carbon monoxide and chlorine gas (the same reaction used by COVESTRO) under direct sunlight. The procedure gave name to this new discovered compound from Greek φῶς (**phos**, light) and γεννάω (**gennaō**, to give birth).

Figure 2.2 Picture of USA propaganda to inform the citizens how to detect phosgene. [32]

This chemical was further studied and some applications to phosgenite other chemicals where develop, but, as usual, it end up in the scope of the chemical warfare frame. By taking advantage of the already mentioned effects, phosgene was deployed with a mixture of chlorine gas at the battleground. It was first released on the WWI the 19th of December of 1915 injuring 1000 British soldiers and killing 120 [7]. By the end of the war 85% of the 91,000 gas related deaths were from pure or based phosgene weaponry. These events lead to phosgene to be included in the Schedule 3 of the *Chemical Weapons Convention* in order to supervise every site that manufactures more than 30 tonnes per year by the Organization for the Prohibition of Chemical Weapons (OPCW) [8].

COVESTRO is subject to this regulation that has been in place due to the potential phosgene has to create many important chemicals related to isocyanates, that are a pilar of our everyday life.

3. MDI PLANT

As it is understandable, the exact layout of any section of the plant is confidential and part of the know-how of Covestro. In order to explain the project, a block-diagram simplification is going to be used as a model explaining just the crucial elements and instrumentation that have a direct impact on the result

Before that, is important to understand the basic chemistry that supports that layout and the whole "why" of its existence. Starting with the overall reaction:

$$Cl_2 + CO \xleftrightarrow{Act.\ Carb.} COCl_2 \qquad (-107.6\ kJ/mol) \qquad \textbf{Equation 3.1}$$

3.1. Phosgene Reaction Synthesis

This reaction is historically carried out using light as energy source as explained before in the *2.1.3 History* section. Very few people in the company have access to the mechanism of the reaction or it's rate. In order to put into perspective the reaction, the light-based mechanism will be explained as its expected to not differ much from the activated-carbon-based one (in the basic principles, not in the catalyst or yield) [9].

The mechanism that considers the inhibiting action of oxygen is the following:

$$Cl_2 + light \leftrightarrow 2Cl \qquad \textbf{Equation 3.2}$$

$$CO + Cl \leftrightarrow COCl \qquad \textbf{Equation 3.3}$$

$$CO + Cl_2 + Cl_{(catalyst)} \leftrightarrow COCl_2 + Cl \qquad \textbf{Equation 3.4}$$

$$COCl + Cl \leftrightarrow CO + Cl_2 \qquad \textbf{Equation 3.5}$$

$$COCl + O_2 \leftrightarrow CO_2 + ClO \qquad \textbf{Equation 3.6}$$

$$Cl + CO \leftrightarrow CO_2 + Cl \qquad \textbf{Equation 3.7}$$

In this case the decomposed chlorine acts as the catalyst of the phosgene synthesis. The actual case in Covestro, the activated carbon is the catalyst basically eliminating the *Equation 3.2* and modifying obviously the *Equation 3.4* .

Overall the reaction rate is can be aproximated at relatively low temperatures to:

$$\frac{d(COCl_2)}{dt} = K_I^{\frac{1}{2}}(Cl_2)(CO)^{1/2} \qquad \textbf{Equation 3.8 Reaction Rate}$$

In Covestro this reaction is carried out at 2 bar (absolute) in gas phase with an excess around 8% of CO. The arguments behind this excess are:

- It is wanted to minimize Chlorine gas at the outlet of this section in order to avoid by-products in later stages of the process that can ruin equipment, products or endanger workers.
- From the economical point of view, chlorine feed stock is more expensive than CO, so the maximum efficiency of that reactant is wanted.

3.2. Block Diagram

The simplified block diagram of the plant section can be found below:

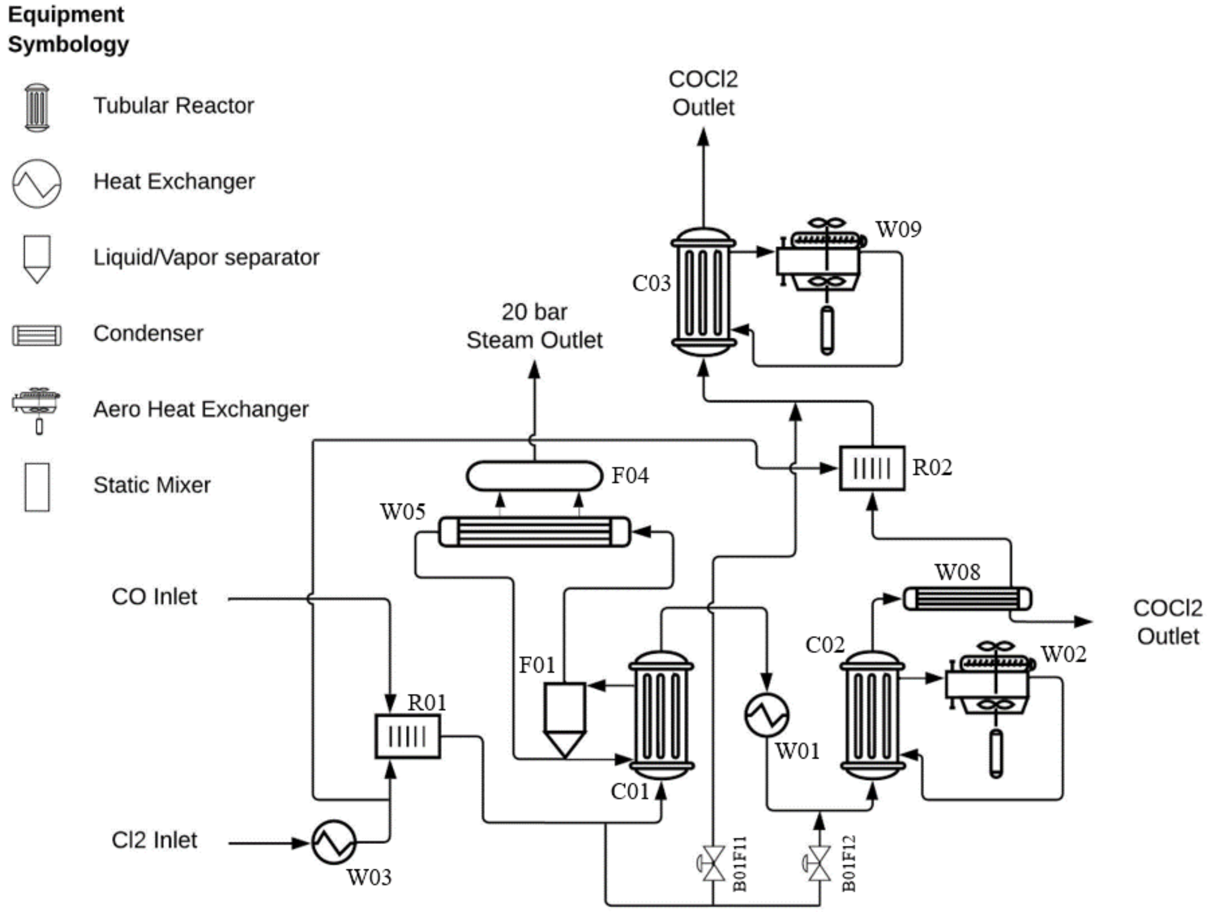


Figure 3.1 Block Diagram of the Plant Section of Phosgene Synthesis

3.3. Explanation

The process starts with two inlets: Carbon Monoxide (from CO plant) and Chlorine (from ELO plant).

The carbon monoxide coming via pipeline is ready to be used, so it is sent directly to the static gas mixer R01. In the order hand, chlorine must be heated (to ≈ 30ºC) in order to avoid condensation due to high pressures or low temperatures. This current, once treated, is divided into 2 streams: the principal is feed into the static mixer R01 and the other one to the second static mixer R02. Both inlets to the process are monitored closely searching for impurities like moisture, bromine (typical impurity of chlorine form electrolysis [10]), solids, etc…

From R01 the stream is sent directly to the first reactor C01 (also called HPG “Hot Phosgene Generator”). The geometry of this reactor can be summarized as: 2236 tubes of 4 meters of length, 30 mm of diameter and 2.6 mm of wall width. The goal of this first vessel is to withhold as much overall needed reaction as possible to recover part of the energy released in *Equation 3.1*. Heat is absorbed by an evaporating Decalin bath that is in the shell side of the tubular reactor. The vapour is separated from the possible dragged liquid in F01, the gaseous phase continues its way to the W05 Heat exchanger while the liquid part is returned to the reactor's bath.

In W05 an array of tubes exchanges the heat of the Decalin running inside them with a pool of condensate, that is evaporating in the shell side, in order to generate steam at 20 bar. That steam generation is the parameter is wanted to be optimized in this thesis. Once the Decalin has been cooled down and condensed, it is sent back to the original bath. The overall wet area of the tubes is around 410 m^2 and is distributed non symmetrically across the vertical plane. There is a gap between the tubes and the "ceiling" of the heat exchanger to prevent dragging of condensate to the outlet, that is connected to F04 right above. Similarly to F01, its goal is to clean the steam of undesired liquid.

The outlet product stream from C01 is mostly phosgene but has some unreacted chlorine and Carbon Monoxide. As explained in "3.1Phosgene Reaction Synthesis", one constrain is to not have any free chlorine downstream. To achieve this 100% conversion on this reactant now the stream is cooled down in W01 heat exchanger to 115 ºC approximately. Now it is ready to enter the second reactor C02 (also called PPR "Post Phosgene Reactor").

This second reactor is smaller than C01, in this case it has 571 tubes of 4 m with 60.3 mm of diameter and 4.5 mm of wall width. As the reaction is quite exothermic, by reducing the temperature the equilibrium point will move substantially towards phosgene, decreasing the quantity of Chlorine at the outlet of this vessel down to less than 50 ppm. The heat generated in this reactor is contained by a condensate circuit operating in vacuum (270 mbar abs.) refrigerated using an aero-exchanger (W02.1) or a shell-tube exchanger with process water. This cooling loop is similar to the one found in C01 where there is a liquid separator and the reactor's tubes are wetted in an evaporating liquid bath.

Now the main stream is brought to the W08 condenser. There, the phosgene is liquified with small traces of the other constituents and the gas phase is composed of mainly phosgene and carbon monoxide (the chlorine part is negligible). The liquid exists the equipment from below and the gas continues its way through the upper outlet to the final part of this section.

Here comes into play the before mentioned Cl_2 stream that will enter the static mixer R02. The gas phase from W08 and this chlorine are mixed in order to enter a final reactor (C03, also called PPG "Post Phosgene Generator"). The basic strategy behind this procedure is to again shift the equilibrium by removing the product and adding fresh chlorine that uses the excess CO from C01 and C02 (making the new CO excess in the inlet of C03 approximately 5%).

C03 and C02 are exactly the same reactors but with different inlet concentrations and a different temperature. C02 typically has an inlet temperature around 90ºC and CO3 of 34ºC (ensuring the best final conversion possible).

The main stream continues its way into the process but the section upstream is outside the scope of this thesis.

3.4. Management

As it could be expected, the management of this section of the plant is quite complicated and many process-flows are working simultaneously in equilibrium. The management that is going to be explained here is just the relative to the scope of the thesis and will be expanded in detail at section *6 Current Situation*.

There is a pipe circuit that interconnects these reactors in such way that they can be putted in 3 different arrays, that from now on they will be referred as: in series, semi-parallel or parallel. When they are in series the reactors are feed the outlet of the anterior one in numerical order following the TAGs. Parallel is when all reactors' inlet is totally or partially from fresh reactants (coming straight from the inlets). The final case, the semi-parallel, is when the in series position is in place but B01F11 or B01F12 are opened in order to fight against pressure drop, leading to just two of the three reactors' inlet is totally or partially from fresh reactants. As mentioned before there are many process-flows working at the same time and maybe those valves are a bit opened due to other reasons such as to avoid desorption of reactants in the catalyst.

The decision factors that adjust how the reactors layout is set up is the pressure drop. This pressure drop is directly correlated with the production of phosgene but is not the only factor. Many factors enter into play such as:

- Pressure of reactants from storage
- Power limitations of pumps (such as the condensate pump for W05)
- Outlet temperatures
- Composition of the outlets
- Catalyst health

These parameters are highly dependent on external factors such as atmospheric conditions, how old is the catalyst or when is scheduled to be changed, from which situation or production are you coming from, malfunctions, etc…

4. STUDENT'S ROLE IN THE COMPANY

Where does the student fit in the company, what is his role and the tasks that performed throughout his stay. The tasks related to the Deployment Engineer position are very diverse and situation related.

The first and more time-consuming task performed is the asset implementation in an internal software. The definition of an asset is an equipment (independently of its size) that is wanted to be monitored using data gathered directly or indirectly using continuous signals from instruments. An asset is deployed when it is incorporated in the PI AF system. The student's involvement in the PI AF system extends to the meticulous monitoring and regular updating of asset data. It must ensured that the system accurately reflects the current state of each asset, which requires a keen attention to detail and an understanding of the technical nuances of the equipment and its operation. This system is a centralized data base that stores signals in data banks related to the corresponding asset. It can be considered like a step to digitalization of the instruments into a virtual plant model that can be accessed from different software.

From a list of equipment, the student firstly examined if all the proposed equipment to be implemented satisfied the next conditions:

- The equipment type has a PI AF template
- The particular asset configuration was applicable for that template
- There is enough instrumentation/information for a useful deployment

If those conditions were met, the deployment began. Starting with situating the asset in the correct section of the distribution tree of the software and filling up the “Description” fields correctly. Once the bank for all the future stored data is created using support material (PIDs, Technical Data Sheets, Technical Drawings, etc…) a description of the involved variables is made. In some instances, a critical variable is not measured directly by an instrument and it is inferred from the surrounding equipment/conditions. When a case like this is found a “Soft Sensor or Instrument” must be created. The “Soft” adjective means that is not hardware, is a fake instrument created virtually in the program for calculation porpoises but with an individual tag.

The usual example easily found trough out the deployment is when the template demands the total inlet mass flow and the instrumentation measures 4 different inlets in volumetric units. The newly created sensor uses 4 volumetric flows and 4 densities as an input. Using the software code language, a set of equations and automatizations is done so the output value of that instrument is the desired total inlet flow.

To facilitate accurate soft sensor creation, the student must engage in regular consultations with the engineering team to understand the operational dynamics of the plant. They play a crucial role in translating complex engineering principles into practical software solutions that enhance the plant's operational efficiency.

Once the equipment is fully deployed and the program starts showing the data collected from the finalization moment there is one final step. In order to have a full picture of the asset is important to have historical data. The software can use a backfilling algorithm that takes the created structure and searches for past instrumentational data and perform the soft calculations. The user can specify how far into the past the equipment can search information for, but usually a 3-year period is standardised.

The student's task of integrating historical data is not just about data entry, but also about ensuring the reliability and consistency of this data. This may involve cross-referencing with legacy systems and resolving any discrepancies that arise, thus providing a dependable foundation for asset performance analysis.

One of the automatizations of the templates is to create links to internal web pages that act as a control dashboard for that specific equipment in a very user-friendly display. The final step is to doble check that all the results are coherent, and all links are created successfully.

In the context of asset implementation, the role of document management is multifaceted and crucial for the successful execution of the project. This responsibility includes the systematic handling of documents that encompass a wide range of information pertinent to the asset's operation. The student's document management responsibilities also encompass the creation and upkeep of a comprehensive knowledge base. This digital repository includes all the necessary documentation, guidelines, and protocols that can be readily accessed by the team, fostering an environment of knowledge sharing and collective learning.

One aspect of this documentation pertains to the comprehensive recording of the asset's implementation details. The precision and accuracy of this documentation are paramount as they serve as a reference for the project's standards, protocols, and guidelines, ensuring consistency and quality control throughout the implementation phase.

Within the scope of document management, a critical monthly task is the recording and analysis of specific energy consumption data related to the site and each individual plant. This process involves the diligent collection of energy usage figures, which are then meticulously categorized by source and location. The gathered data is scrutinized to identify patterns, trends, and opportunities for efficiency improvements. This analysis is not only fundamental for monitoring the energy footprint of each operation but also for formulating strategies to optimize energy use, thereby enhancing sustainability and cost-effectiveness across the site.

Additionally, there are miscellaneous documentation tasks that arise sporadically. These tasks, although seemingly random, are essential in supporting the broader goals of the company. They may involve updating records, collating data from different sources, or preparing reports for stakeholders. Collectively, these tasks contribute to the maintenance of a dynamic and up-to-date documentation system.

5. METHODOLOGY

The project at hand is quite extend and with many moving parts that work in perfect equilibrium. Finding a substantial improvement in a such complex machine is a challenge, and it must be faced as rigorous as possible. The methodology (theoretical and practical) sets the amount of rigor in every study. That’s the point that give porpoise to this section.

5.1. Theoretical Methodology

As this thesis is a product of a discovery journey where there was no concrete answer to seek for, a methodology according to this reality was selected. Such method is called “Zettelkasten”.

Created by the sociologist Niklas Luhmann, the Zettelkasten Method, which translates to "note box" in German helps users and organizations get better insight generation and knowledge development.

"Zettels" or discrete notes that concentrate on a single idea, are at the heart of it. Each note is identified uniquely and connected to other notes to form a network. Notes are more easily categorized and found with tags. The approach stresses a perpetual archive where notes are never removed but instead connected and reconfigured, whether it be on actual index cards or digital technologies. It encourages iterative thinking and progressive improvement, assisting users in making connections between concepts and encouraging innovation.

The objective is a systematic, connected collection of notes for efficient knowledge organization, retrieval, and synthesis, whether using actual playing cards or digital apps. In the case of this thesis, it has been developed using OBSIDIAN®. This is an application that storages locally a set of “.txt” notes, pdfs and pictures that are accessed through a user interface. The network obtained can be found below. The interface and the resulting diagram can be found in *A.1 OBSIDIAN*.

5.2. Practical Methodology

Having the right tools for the right tasks is as important as having a clear vision or knowledge data base. Covestro knows this fact and is a company that is moving towards tool development and implementation for easy diagnosis, control and definition of its processes.

Two of those tools have been used in this thesis in order to optimize the plant section. Those tools are PI AF and SeeQ, and others that are not speciality software.

5.2.1. PI AF

The PI Asset Framework is an app part of the suit PI System. It is a hierarchical model of assets/equipment’s of a plant. Each level is separated by its dimension (Site, Team, Plant, Section, Equipment, Instrumentations, KPI, etc…). These assets are introduced, using templates already created by the Covestro Digital Team, in the correct placement of the hierarchical tree. Once created it must be filled with TAGs regarding the correspondent instrumentation attached to the equipment.

This is not an easy task as in many instances there is no direct measurement of a variable and it is inferred from others. So in order to have a reliable model it is imperative to do a rigorous job in this part. More concrete information and snapshots can be found in *A.A.2 PI AF SOFTWARE*.

5.2.2. SeeQ

SeeQ is a focused-on data displaying and monitoring program. This tool is used to automatically search past events or conditions, clean instrument data, make interpolations and calculations and predict behaviour using Artificial Intelligence.

As this tool is quite complex and requires extensive knowledge to extract the full potential, it has been used mainly to identify, qualify behaviours, extract data and monitor results. More concrete information and snapshots can be found in *A.A.3 SeeQ*.

5.2.3. Excel

EXCEL® will be used to analyse in more depth the historical data and make a dashboard that suits the needs of the workers in the control panel. The need of excel is due to the complexity of SeeQ and the amount of time required to learn the tool to a similar level that the student currently have in EXCEL.

5.2.4. Python

Finally, Python has been instrumental for performing specific calculations and generating plots. Utilizing its Matplotlib library, enabled to create detailed, informative visual representations of the data. Python's combination of powerful computing capabilities and extensive libraries like NumPy for numerical operations, made it an ideal choice for complex data analysis and mathematical modelling. Its application in this research was focused on conducting precise calculations and producing clear, concise visualizations to support the findings.

6. CURRENT SITUATION

These reactors have been used for many years without issues and under the focused supervision of professionals. Through “Know-How” and mentorship inside the workforce, an optimization has been done constantly having a much broader picture of the facilities that the one that can be obtained in only a few months.

To achieve an improvement and for the sake of clarity, a clear representation of past data that reflects the current strategy is necessary. As this is confidential and sensitive data, all the graphs will have the less quantitative information possible.

6.1. Material Balance

The best way to start wrapping the mind around the current management is understanding where the product is being generated. How much is each rector contributing to the overall production of the product. In the *Figure 6.1* we can see how the total output is distributed.

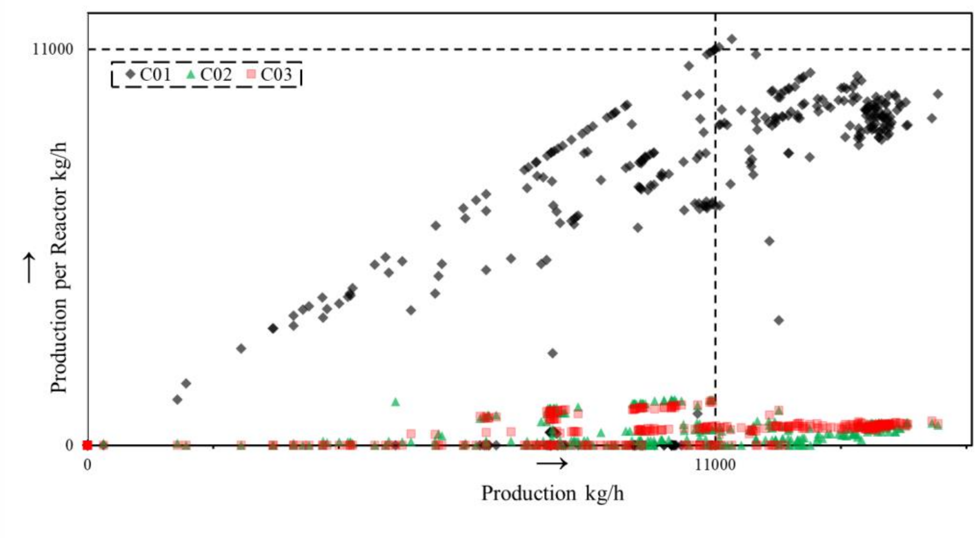


Figure 6.1 Daily average contribution of each reactor to the overall production of phosgene from 01/02/2023 until 01/08/2023

Form this graph one can see quite clearly that as expected C01 leads the total contribution of the production (as mentioned before, it is the biggest of the group). C02 and C03 act basically as support for that reactor to achieve the desired amount of product (and satisfy the constrains mentioned at *3.3 Explanation*).

But there is something off. Looking at the C01 tendency (that is quite linear) there is a maximum point. From there the reactor is slowly shut off and C02 and C03 start to increase production. This is not optimal in any case, if the first reactor has arrived at its full safe sustainable capacity, it should be kept there as much time as possible. That reactor is the only one that has energy recovery resources and by replacing it with energy inefficient reactors at large productions (the usual production rate in a plant) there can be a loss of profit.

The only relevant data has been plotted at the axis, and that is the position where the tendency changes. From the figure a clear change when C01 is in charge of the whole production at 11000kg/h. This is not always the case as some times the change is done earlier (all the black points below the upper linear tendency). This is surprising as the production cap of C01 is 12500 kg/h.

Leaving space not only for improvement in maintaining maximum productivity at large productions, but also setting a new point of change between in series/semi-parallel/parallel

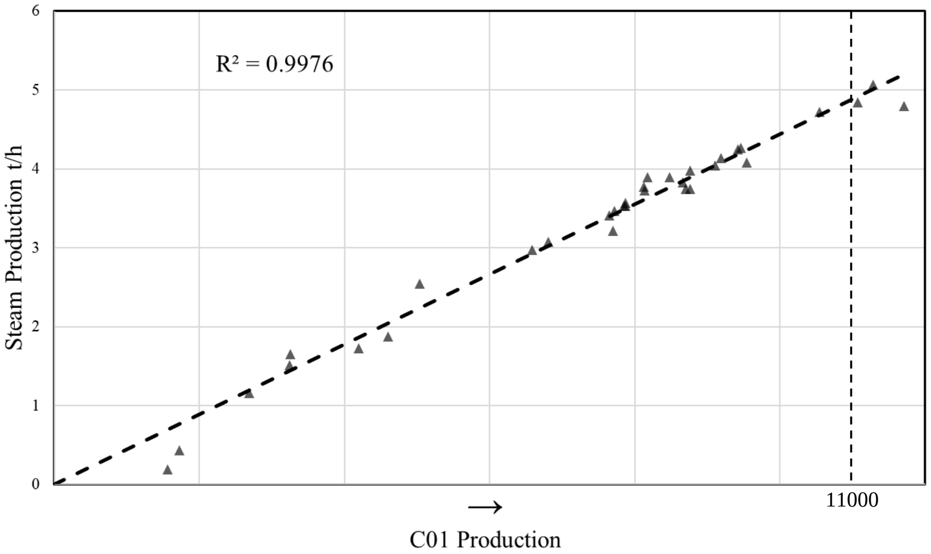


Figure 6.2 Daily average steam production from C01 at different production rates from 01/02/2023 until 01/08/2023 where B01F11 and B01F12 aperture are lower than 10%

In the figure above a quite good linear tendency between the generated steam and the production of the reactor can be seen. This represents the black points at the *Figure 6.2* but filtered, so only the points that represent “in series” case are plotted. It is not straight forward to define each scenario numerically as almost never B01F11 and B01F12 are closed (due to issues that will be explained at *8.3 Feedback Solutions*. To nuance the definition the “in series” case, it has been defined that when the aperture of those valves are both below 10%, as they are isopercentage.

6.2. ELO Plant

Another important angle of the current situation is the implementation of the Electrolysis Plant. This change in the chlorine inlet to the process, that was performed at the beginning of 2023, changed dramatically the phosgene reactors limitations due to pressure drop improvement and impurities control.

As the reactant, that was before purchased outside the facilities, now is done and controlled in-house, the tunning and optimization for COVESTRO’s needs has been possible.

In order to show the importance of this change, the following figure shows the comparison between both situations regarding the pressure differentials.

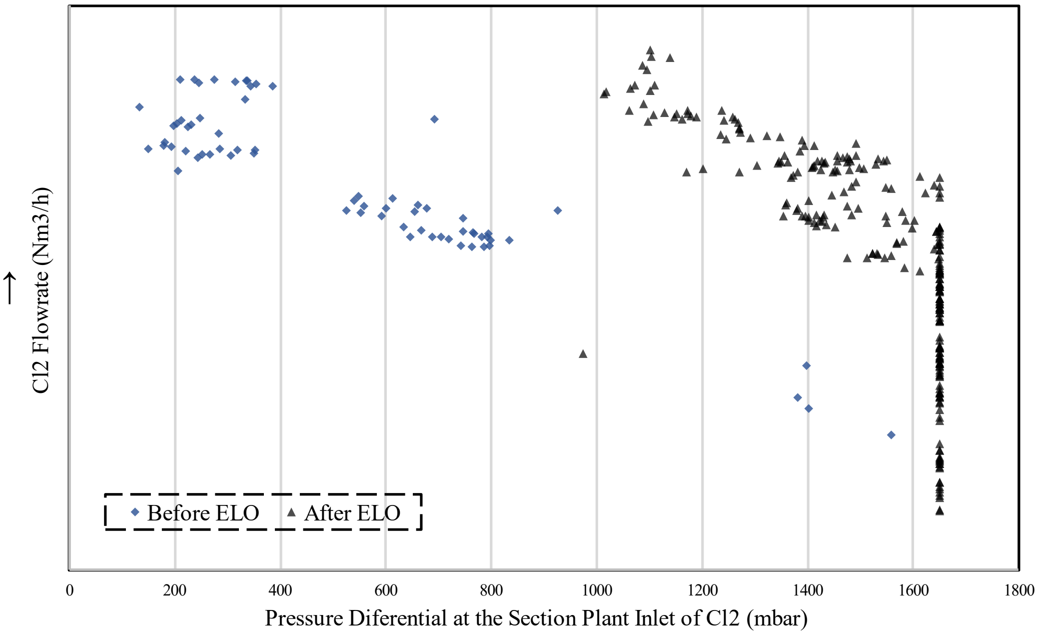


Figure 6.3 Comparison of Flowrates and Pressure Differentials between the outside provider and ELO's plant. The values are daily averages since 01/01/2023 excluding the non-productive days.

A clear area differentiation can be seen comparing the anterior provider with the in-house one. This change not only affected the supply pressure, but also the quality, impurities control and reliability. The past set up could lead to sudden changes of production due to external problems, intermediary or secondary characters and close future uncertainty. For now, the new plant hasn't been putted under full stress and both, workers from MDI and ELO, are still getting used to operate under such flexible conditions.

6.3. New Catalyst

The final key factor to understand the current situation of the plant would be the catalyst aging. The behaviour of the catalyst in its lifespan is very complex and difficult to predict at long time scales. As mentioned before, the reaction occurs thanks to this element and its health is critical to the production, scheduling and control of the plant section.

Generally speaking, there are two factors that determine the lifespan of the active carbon:

- Packaging procedure: The way the active carbon is lay down inside the tubes, and the rest of reacting areas, is critical for the wellbeing of the structure itself and the catalyst. This is such a critical step that there have been studies (comparing different plants around the world) to find the most efficient one.
- Operational conditions [11]: The type of catalyst always remains the same but, in some instances, the activated carbon brand makes an improvement on their product, or the facilities change the supplier. Usually, the changes can vary from particle size/shape to some protective coating or a change in its synthesis that increase the porosity/tortuosity/etc… For every type of "charge" there is a suitable and optimal range of operation. There is usually no reason for a reactor to work in a bad operational window, so the crucial moments are in its stop and start up cycles.

7. HEAT EXCHANGER

Once understood the current situation and all assets where correctly deployed in the PI AF software, the analysis began. The first intuitive move is to firstly analyse the responsible of the direct steam generation, the W05 Heat Exchanger.

7.1. Variable Analysis

In order to try some new approach, for example changing a given non critical variable, the theoretical back ground must be robust and secure. Next the variables will be listed and discussed on why they can be changed or not. In this analysis there is no mention on how that would be possible to do, because that would have been the next step in the case where the variable is suitable for a change.

7.1.1. Fluid Speed

The liquid within the tube is the only one that can be speeded up as the shell side fluid is in a pseudo-static bath, where the planar velocities are negligible compared to the vertical component (caused by the buoyancy of the steam bubbles).

By changing the tube fluid speed, the transfer coefficient at the heat exchanger will improve proportionally to the speed up. This will mean that the outlet will be slightly cooler meaning that the decalin inlet to the reactor will be cooler promoting more exothermic reaction. This will increase the vapour stream entering the heat exchanger which would mean that the outlet temperature now is higher as there is more mass to condense. This cycle will continue on and on in a harmonic behaviour that will lead to little to no improvement in the steam generation. Some other problems that could be found, is that the time it takes for a vapour particle to close the system loop would be decreased or increased leading to variations in the level of decalin in the reactor outer shell.

7.1.2. Condensate Temperature

The temperature at which the condensate enters the heat exchanger is another possible parameter that can be changed. Know exactly how this variable will affect the system is complicated in economic terms. If the temperature decreases the decalin will be cooler going back to the reactor making the decalin hot stream hotter (and faster) that has more energy to exchange. Which phenomena would prevail in that case is difficult to predict and will lead to some issues like the ones mentioned above. Maybe the energy saved by adding cooler inlets is more expensive that the lost steam production, but it is not the objective of this thesis.

7.1.3. Bath Level

The height of the condensate in the shell side has no effect in the efficiency of the heat exchanger and could potentially be diminishing the equipment potential.

If the tubes are submerged there is no improvement in the steam generation. In some cases, by design a heat exchanger could have a setting point of the level at the middle of the tube array. This is done because the equipment is oversized thinking in a future expansion, and as long as the material is rated to withstand the unwetted conditions, there should be no issues. This is not the case for W05 as it was set to use all the tubes and be filled at 80% at all times. The only improvement regarding this variable would be founding a miss selected set point (very unlikely as it is controlled by the computer plant program).

7.2. Unearthing Historical Data

Looking at the reasoning above, one could think there is little to no room of improvement by this approach of the problem. That fact didn’t mean to stop searching for a new approach. Instead of applying reasoning to a very complex system without any factual evidence of any situation, the next step is to look for the best case scenarios in the historical data.

By finding those cases and understanding why they happened and why aren’t they happening all the time continuously could make a difference. This approach also lead to no results, as there were non “good” or “bad” cases and all mathematically “better” scenarios could be attributed to ambient conditions or instrumentation margin of error.

The research was not for nothing, as the pattern seen in the figure below was found frequently.

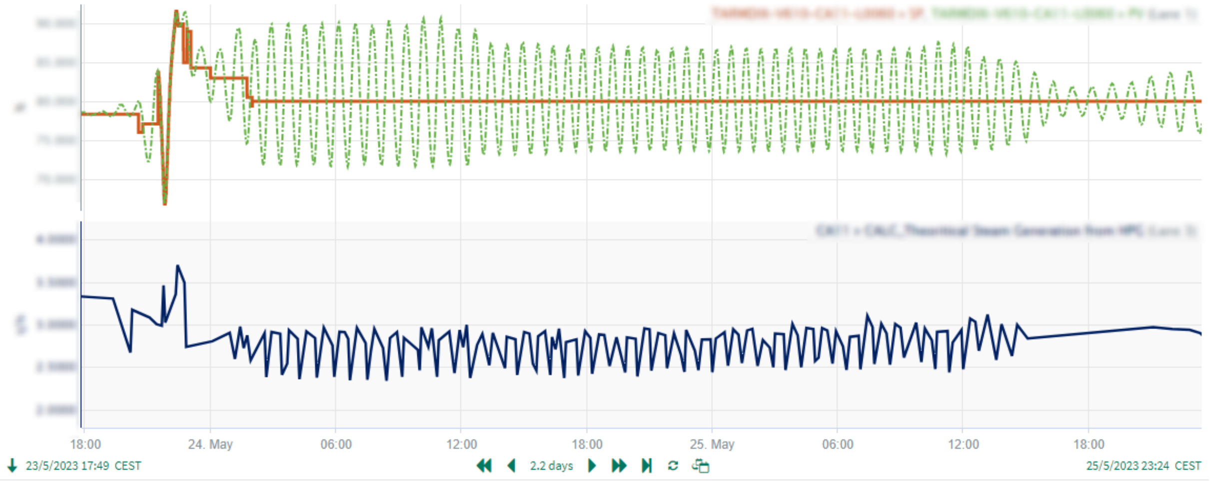


Figure 7.1 Harmonical pattern in the W05 Historical Data; Steam t/h (blue), Level Set Point (Orange), Level Value (Green)

This harmonical coupling between the level and the steam generation is found throughout whole periods of time in the historical data. It’s difficult to find the starting point of this behaviour as they vary in frequency, amplitude and duration. One common place to find this patterns is when the plant is moved from nominal conditions due to an operational procedure (sometimes this lead to harmonical decay in the level) or when for some reason the level control is putted in manual mode (the worker opens or closes the manual valve eye-balling the level from the control panel).

What is striking is that this behaviour is not expected to be correlated to those variables. For the reasons explained in the section *7.1.3 Bath Level* that variable coupling should not exist but the instrumentation and asset calculation showed something different. This led to think that some other phenomena were the responsible.

The first thoughts where focused on the hydrodynamic behaviour of the shell side. As can be seen in the figure below, the inlet of fluid is distributed on the bottom of the equipment.

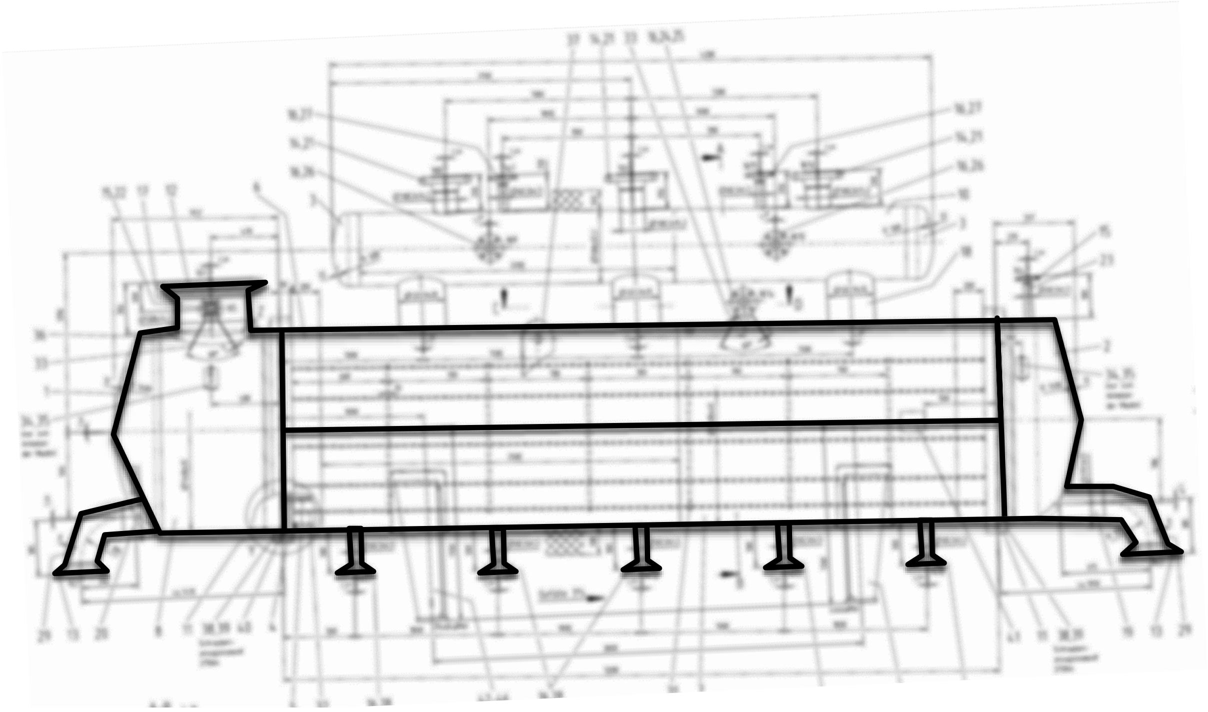


Figure 7.2 Blurred technical drawing of W05 with a simplification representation of the overall form of the Heat Exchanger.

In a normal operation, the level of that vessel must remain stable once the steady state has been reached. Maybe forming preferential paths for the water to move inside it, conforming a map of currents that may not be optimal or leave static spheres of water within the level.

One way to break that predefine path and assuring that the assumption of “completely mixed up” regarding the movement of all water particles is to change the inlet stream. As the level must be stable for the normal operation of the plant, the inlet must oscillate in order to keep an average level that approximates a constant level.

The amplitude of the change would set how much the preferential paths do change; the frequency will be capped by the valve operational procedures.

This hypothesis will account for the improvement (in average) on generation of steam during these scenarios compared to the stable ones but no for the sudden bursts of steam. That will not satisfy completely what the historical data shows, as in that case the steam generation graph should just increase and stabilize at a net upper value.

Further investigation with the instrumentation team and some workers revealed that at some point in time the level contraption suffered and issue. This event changed the calibration in the device. The initial configuration was defined so the 100% value meant the equipment is full of condensate and 80% is the threshold at which all the tubes are fully covered. The mistaken calibration moved the distance from 100% to 0% making the 100% value the new threshold at which all the tubes are fully covered.

At the moment there is no information about the incident, but the expected cause is human error. As this situation was not planned, all the controllers and working procedures kept being the same, so the level was still wanted to be at 80% (tube array partially submerged).

This could have easily been unnoticed for a long time as there are no apparent phenomena easy to detect in a daily plant operation. If so, the exposed tubes could have suffered TSC (Thermal Stress Cracking), crevice corrosion on baffles and secondary defects due to tube vibrations [12].

The exact mechanism for these defects is quite complex and are out of the scope of this thesis. Internal documentation agrees that one of the corrective actions to avoid these phenomena is to fully submerge the bundle and don't let the water level be at exactly the last row of tubes. Some years ago, there was issues with thermal stress failures in condensers in sites in Japan and Germany, incidents that led to serious modifications and studies on these equipment's [13].

7.3. Thermal Stress [14] [15]

Once the real problem has been identified and successfully solved, the next step is to analyse the quantitative aspect of this phenomena. In this section the thermal stress depending on the submersion time and the fatigue on the material would be calculated. To achieve this objective is necessary to set a proper model that resembles the reality. Starting by staying the approximations and simplifications necessary so it doesn't depend on complex software simulations, excessive computational time or excessive dedication outside the scope and objectives of the thesis.

Approximations and simplifications [16] [17] [18]:

1. The only stress existing on the tube is the axial thermal stress as it is the prevalent axis. The other stresses that play when submerging a hot tube in cold liquid (hydrostatic pressure stress, temperature gradient stress, vibrations, etc…) are not calculated.
2. The tube is approximate to be infinitely thin, so the temperature is uniform radially.
3. The study is done in the worst-case scenario (between the inlet of the hot fluid and the inlet of the cold fluid).
4. There is a uniform change in temperature in all the structure.
5. The material is assumed to behave elastically returning into its original form after the deformation.
6. The material is perfectly homogeneous in all directions.
7. There is no crack formation between cycles.
8. The thermal expansion coefficient is temperature independent.
9. There is no free expansion or contraction (fully constrain material)
10. Plane Sections Remain Plane (PSRP condition) after deformation. Therefore, the inner and outer surfaces that were flat at the beginning continue being flat on its respective reference after the deformation.

Some of these simplifications come from historically made approximations that ease the calculations while not sacrificing accuracy in the results, others are sacrifice the fidelity to reality to analyse just a facet of the phenomena while the others come from resources limitations. Is important to keep in mind the scope of the project and allocate the efforts accordingly.

7.3.1. Mathematical Model

For the sake of transparency in this section the selected model and the rigorous model will be explained. The rigorous model, not calculated due to the computational reasons, would also need experimental data beyond what is generally available.

Rigorous Model [19]

In the next figure a pipe with moving fluid inside and an applied heat flux to the outside can be seen.

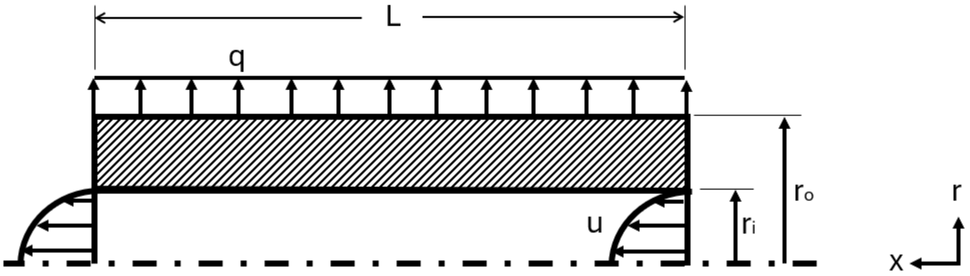


Figure 7.3 Schematic Diagram of the model of the Rigorous Model

The rigorous model is also evaluated in the worst-case scenario (the inlet of the hot fluid). The temperature of the inlet tube is assumed to vary along the axial axis (as the worst-case scenario is that the fluid is overheated). There is no moving fluid at the outer side and it’s at saturation temperature so there the cooling is represented just by a heat flux.

Governing Formulae

For a turbulent flow in the inner side of the tube the heat conduction equation for a steady state would be:

$$\frac{1}{r}\frac{d}{dr}\left(r\frac{dT}{dr}\right)+\frac{d^2T}{dx^2}=0$$ **Equation 7.1**

The relationship between thermal stress and strain follows the thermoelastic equations [20]. Where “ε” is strain in the “θ” tangential, “r” radial or “x” axial axis, “v” is Poisson’s ratio, “E” is the modulus of elasticity, “α” is the coefficient of thermal expansion and “σ” the thermal stress in the subscripted axis:

$$\epsilon_x=\frac{1}{E}[\sigma_x-\nu(\sigma_r+\sigma_\theta)]+\alpha T$$ **Equation 7.2**

$$\epsilon_r = \frac{1}{E}[\sigma_r - \nu(\sigma_x + \sigma_\theta)] + \alpha T$$ **Equation 7.3**

$$\epsilon_\theta = \frac{1}{E}[\sigma_\theta - \nu(\sigma_x + \sigma_r)] + \alpha T$$ **Equation 7.4**

By modifying these general equations for a hollow tube [21], the results are:

$$\sigma_x = \frac{E\alpha}{1-\nu}\left[\frac{2}{r_o^2 - r_i^2}\int_{r_i}^{r_o} \mathrm{Tr}\,dr - T\right]$$ **Equation 7.5**

$$\sigma_r = \frac{E\alpha}{(1-\nu)r^2}\left[\frac{r^2 + r_i^2}{r_o^2 - r_i^2}\int_{r_i}^{r_o} \mathrm{Tr}\,dr - \int_{r_i}^{r} \mathrm{Tr}\,dr\right]$$ **Equation 7.6**

$$\sigma_\theta = \frac{E\alpha}{(1-\nu)r^2}\left[\frac{r^2 + r_i^2}{r_o^2 - r_i^2}\int_{r_i}^{r_o} \mathrm{Tr}\,dr + \int_{r_i}^{r} \mathrm{Tr}\,dr - Tr^2\right]$$ **Equation 7.7**

The effective stress following the Von-Mises Theory [22] would be:

$$\sigma_{eff} = \left[\sigma_x^2 + \sigma_r^2 + \sigma_\theta^2 - (\sigma_x\sigma_r + \sigma_r\sigma_\theta + \sigma_x\sigma_\theta)\right]^{\frac{1}{2}}$$ **Equation 7.8**

The equations responsible for characterizing the flow are simplified using Boussinesq [23] approximations, leaving in polar coordinates these 3 formulae:

$$\frac{du}{dx} + \frac{1}{r}\frac{d}{dr}(vr) = 0$$ **Equation 7.9**

$$\frac{1}{r}\frac{d}{dr}(rvu\rho) + \frac{d}{dx}(\rho u^2) = -\frac{dp}{dx} + \frac{1}{r}\frac{d}{dr}\left[r(\mu + \mu_t)\frac{du}{dr}\right]$$ **Equation 7.10**

$$\frac{1}{r}\frac{d}{dr}(rvT\rho) + \frac{d}{dx}(\rho uT) = \frac{1}{r}\frac{d}{dr}\left[r\left(\frac{\mu}{Pr} + \frac{\mu_t}{Pr_t}\right)\frac{dT}{dr}\right]$$ **Equation 7.11**

The viscosity “μ” and the Prandtl Number (“Pr” bulk and “Pr_t” turbulent) the k-ε model is advised.

Boundary Conditions

- Axis: The radial gradients of the velocity fields and radial velocity are set to zero.

$$\frac{du}{dr}(x,0) = \frac{dT}{dr}(x,0) = v(x,0) = 0$$ **Equation 7.12**

- No-slip conditions {u [axial velocity] and v [radial velocity]}.

$$u(x, r_i) = v(x, r_i) = 0$$ **Equation 7.13**

- Homogeneous and constant properties, where ψ is any property of the materials and η is any arbitrary direction.

$$\frac{d\psi}{d\eta} = 0$$ **Equation 7.14**

- Interfaces

$$T_solid(x, r_i) = T_fluid(x, r_i)$$ **Equation 7.15**

$$T_{solid}(x, r_o) = T_{fluid}(x, r_o)$$ **Equation 7.16**

$$\frac{dT_{solid}}{dr} k_{solid} = \frac{dT_{fluid}}{dr} k_{fluid}$$ **Equation 7.17**

- Homogeneous Inlet Conditions.

$$\frac{dT}{dr}(0, r, t) = \frac{du}{dr}(0, r, t) = 0$$ **Equation 7.18**

Solver

Generally speaking, a numerical method is going to be used to obtain the solution. The set of differential equations from Equation 7.5 to Equation 7.8 must be discretized into algebraic equations using approximative operators (FDA “Forward Difference Approximation”, BDA “Backward Difference Approximation”, Second Derivative Approximation, etc…)

Once this has been performed and the differential terms are now algebraic, and iterative solver should be used. For example, historically this kind of problems have been solved using the Finite Volume Method [24] to perform calculations into a mesh of controlled volumes.

Selected Model

The only workflow that didn’t implied using simulation or complex numerical methods (by hand or with computing power) was trough pseudo-experimental correlations. The main idea is to calculate the worst-case scenario with those correlations for the case at hand and get conclusions from those results comparing it with the factual facts.

The pseudo-experimental correlations are from The Babcock & Wilcox Company. That business was founded in 1867 being the pioneers in water-tube boilers and, over time, became an industry standard for designing heat exchangers. Resulting from becoming a reference in the industry, B&W edited a handbook on heat exchangers called “Steam: Its Generation and Use”. The 41st edition of that manual is the basis of this model [15].

Governing Formulae

The stress developed, on a body restricted in one direction, is calculated using the next expression:

$$\sigma = \pm E \cdot \alpha \cdot \Delta T$$ **Equation 7.19**

The sign in this case defines if the stress is due to tension or compression. This equation is not suitable for this case as a tube in a heat exchanger is considered to be restricted in three directions (fully restricted). For that case the modified equations are:

$$\sigma_r = \frac{\alpha E}{(1-\mu)r^2}\left[\frac{r^2 - IR^2}{OR^2 - IR^2}\int_{IR}^{OR} Tr\ dr - \int_{IR}^{r} Tr\ dr\right]$$ **Equation 7.20**

$$\sigma_\theta = \frac{\alpha E}{(1-\mu)r^2}\left[\frac{r^2 + IR^2}{OR^2 - IR^2}\int_{IR}^{OR} Tr\ dr + \int_{IR}^{r} Tr\ dr - Tr^2\right]$$ **Equation 7.21**

$$\sigma_x = \frac{\alpha E}{(1-\mu)}\left[\frac{2}{OR^2 - IR^2}\int_{IR}^{OR} Tr\ dr - T\right]$$ **Equation 7.22**

These are the general expressions for the depicted scenario where the variables and axis have already been defined in the “Rigorous Model” except for “OR” and “IR” that refer to the outer and inner radius. To further focus the equations for a cylindrically shape object where the heat is just flowing radially, there are another set of equations. From that set, the maximum thermal stress is found in the tangential axis governed by these two expressions:

$$\sigma_\theta(\text{inner side}) = \frac{\alpha E T_{IR}}{2(1-\mu)\ln\left(\frac{OR}{IR}\right)}\left[1 - \frac{2OR^2}{OR^2 - IR^2}\ln\left(\frac{OR}{IR}\right)\right]$$ **Equation 7.23**

$$\sigma_\theta(\text{outer side}) = \frac{\alpha E T_{IR}}{2(1-\mu)\ln\left(\frac{OR}{IR}\right)}\left[1 - \frac{2IR^2}{OR^2 - IR^2}\ln\left(\frac{OR}{IR}\right)\right]$$ **Equation 7.24**

From these equations, an approximation can be done so the temperature gradient is quite large per unit length, meaning a thin tube. By doing so the resulting equations are:

$$\sigma_\theta(\text{inner side}) = \frac{-\alpha E \Delta T}{2(1-\mu)}$$ **Equation 7.25**

$$\sigma_\theta(\text{outer side}) = \frac{\alpha E \Delta T}{2(1-\mu)}$$ **Equation 7.26**

The Equation 7.25 and Equation 7.26 are the ones that will be used in the mathematical model to calculate the maximum thermal stress suffered at various temperature differentials. By looking at those equations one can see that the thermal stress is arithmetically dependent on the temperature, but the temperature is time dependent also.

Calculating rigorously the temperature change is outside the scope of this thesis, so a general equation for tendency analysis would be enough. This generalization is based on the Newton's Law of Cooling [25]. In order to be applicable, the case must satisfy three conditions:

- Small temperature difference.
- The mechanism of heat transferring, and the properties of the objects can be approximated to be temperature independent in the scenario's range.
- The object is a thermally thin substance, meaning that it's Biot Number [26] is lower than 0.1 [27].

The first condition is satisfied as in nominal operation the difference of temperature between each side of the tubes is 6 ºC. The second one is also satisfied as usually the thermal conductivity of non-exotic materials is weakly temperature dependent, so the heat transfer coefficient is generally considered constant.

For the third condition to be true, the Biot Number must be calculated for the tube present in the heat exchanger. These tubes have 5 meters of length, an inner radius of 25 mm and a wall thickness of 2.6 mm. So the Biot number, following the original formulation, would be:

$$Bi = \frac{h\frac{V_{tube}}{A_{tube}}}{k}$$ **Equation 7.27**

For the case at hand, the heat transfer coefficient is set to 6000 W/(m2 K) [26], which is the highest tabulated value for a condenser scenario, that will lead to the highest Biot Number. The thermal conductivity of the steel has been set to 40 W/(m K) [26]. The resulting Biot Number is:

$$Bi = \frac{6000\frac{\pi \cdot L \cdot (0.0026)^2}{2\pi \cdot L \cdot 0.0276}}{40} = 0.018 < 0.1$$ **Equation 7.28**

So the third and final condition is also satisfied.

Having proved the applicable use of this law, the form of "*First-order transient response of lumped-capacitance objects*" would be applied. The mathematical procedure would be found in *A.A.4 First-order transient response of lumped-capacitance objects* leading to this final formulation:

$$T(t) = T_{water} + [T(0) - T_{water}]^{-t/\tau}$$ **Equation 7.29**

$$\tau = \frac{Cp \cdot m}{h \cdot A_{tube}}$$ **Equation 7.30**

The specific heat capacity for steel 490 J/(kgºC) [28] and its density is approximately 8000kg/m^3, meaning that each tube weights 0.85 kg. Meaning that the "τ" time constant has a value of 0.08.

The final aspect of the mathematical model is how to calculate the number of cycles necessary for a rupture in the tubes. Currently the most common method for determining these values is done through computational simulations for exotic materials or researching applications or trough experimentally obtained coefficients. These take into account many primary deformations and secondary such multiaxis thermal stress, vibrations, momentums, etc… That level of study is outside the scope of this thesis, so a more old, general and simplified model was selected. Specifically, the Basquin's [29] model was selected as it is a well-studied method with rather available data and coefficients.

This model is based on exponential equation with two experimental parameters "A" and "B":

$$\sigma = A \cdot N^{-B}$$

Equation 7.31

Many authors suggest that the approximations done to use this formula are generally representative of the truth. This is mainly due to the equality of errors. The error in this formula regarding the number of cycles is neglected as is similar to the error inputted by just the specific grains, heterogeneity and nanoscopic cracks of a daily material. Of course, this is only true in uncontrolled environments, in researching facilities where the production of the probes is heavily supervised, that statement is false. The main reference used on this section states that a representative value of "A" and "B" are 841 MPa and 0.1 respectively [30].

Solver

To obtain a solution for this model two Python codes were used. These Python codes were synthesised using PyCharm® as the user interface. The first code will calculate the thermal stress at different temperature differentials, the cooling of the outer surface of the tube and how the stress changes (from Equation 7.19 until Equation 7.26). The second one will contain the rest of the model: S-N curve. This one has some loops that allows the user to plot a stress line on the S-N curve, returns the calculated number of cycles and asks the user if he would like to plot another stress line. When doing so the lines already drawn are stored in the memory of the computer and plotted at the same time in the same figure.

7.3.2. Results

The python codes from where these figures are obtained can be found with a comprehensive explanation in *A.A.5 Python Coding*

The first code called "*Thermal_Stress.py*" delivers this graph:

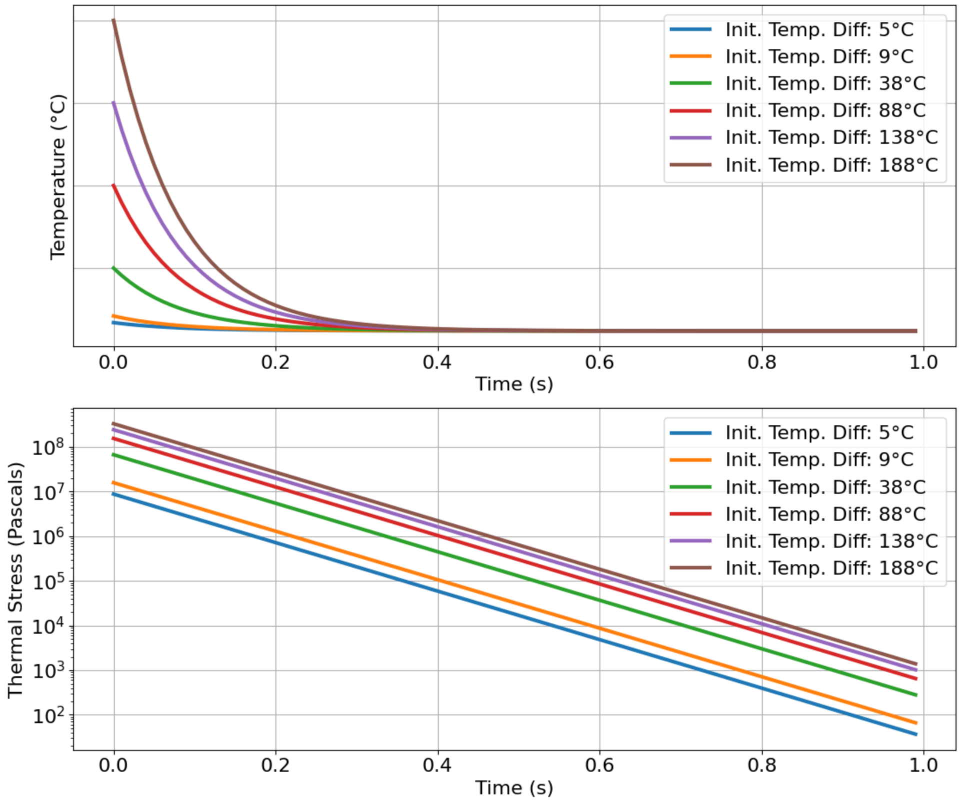


Figure 7.4 Temperature of the outer surface (ºC) (upper plot) and Thermal Stress (logarithm scale) at the outer surface (Pascals) (lower plot). Both plots depending on time and at different temperature differentials (T_{tube}-T_{water})

The case of suddenly wet tubes in nominal conditions is the case with 5ºC difference. All the above cases are related to start ups of the equipment, depending on how cold the condensate feed during that period is. These are quite important to consider as it is proven that these non-nominal moments are one of the main mechanisms for crack formation and deterioration of the materials.

Looking the plot at the top of the Figure 7.4 one can see that the change in temperature is very abrupt needing just 0.5 second approximately to equal the temperature of the water outside the tube. In the extreme cases will for sure create imperfections and cracks in the weld or surfaces. These would affect the immediate integrity of the structure or will over time. As this phenomenon, and others, are not identified by the proposed model, the exact impact of those cannot be predicted.

If those values are plotted in the S-N curve resulting from the second python code, the next figure is obtained:

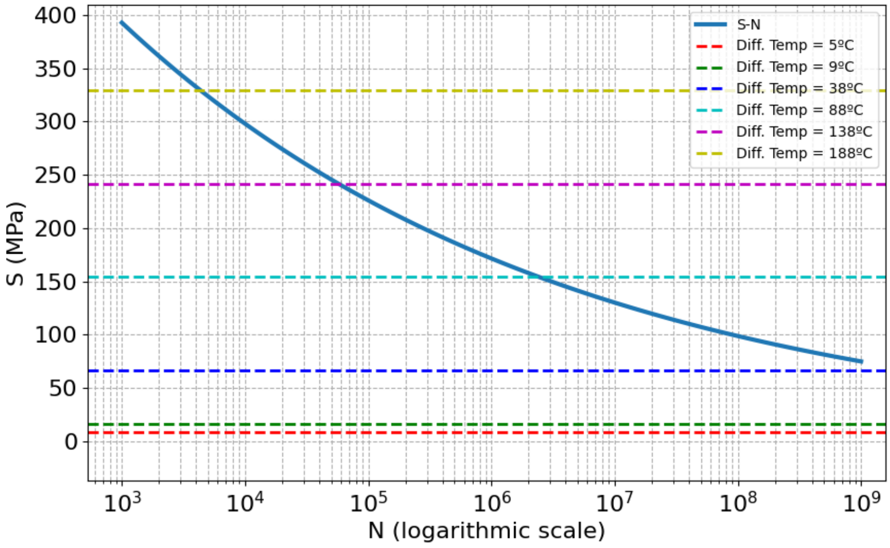


Figure 7.5 S-N Curve relating the stress (S) and the number of cycles to have a failure (N) at different temperature differentials.

From this plot one can see that there is no real danger putting more emphasis on the cases with low differentials. These are well above the 1.000.000 cycles, amount that will never be surpassed needing or a very quick frequency of wetting and drying off or a low frequency with prolonged time (>10 years).

Moving on to the lower plot, all the thermal stress calculated are in the order of the 10 to 100Mpa. The exact values for each case can be seen below:

Table 7.1 Thermal Stress for the different scenarios

Temperature Differential (ºC)	Max. Thermal Stress (MPa)	Cycles to Failure
5	8.75	$5.86\cdot10^{16}$
9	15.75	$4.38\cdot10^{14}$
38	66.5	$2.68\cdot10^{9}$
88	154.4	$2.39\cdot10^{6}$
138	241.5	57000
188	329	4300

8. REACTORS OPERATIONAL OPTIMIZATION

In the *Section 6. Current Situation*, the room for improvement has already been stablished and the possible faces of that improvement are starting to emerge. In this section the strategy is going to be stablished. To do so, the software stated in the methodology will be used constantly to gather historical data that will be the base of all the calculations.

The new strategy must use the current equipment and don't change any other section of the process. Meaning that neither conditions, production or quality can be affected by the approach selected, any part of the plant must not feel any perturbation when the project is deployed.

Having this reasonable restrictions, selected approach for this problem is:

"Improve the energy recovery system by modifying just the aperture of valves"

The valves that will be analysed would be B01F11 and B01F12, the ones responsible for the direct inlets at C02 and C03 reactors. These two variables do not change directly any condition of the process outside this section and have much influence to the ones inside this section as they control: pressure drop, reactors' temperature, catalyst usage, utilities usage by other equipment, etc…

8.1. Calculations

The main pilar of any process is its production, and as so that variable is going to be the independent variable. It's wanted to have a plan for every production case to always have the optimal scenario.

The reaction mechanism and rates are not available to study in order to correlate the inlets with the outlet of every reactor with precision. In case that information was available, in those equations, a new variable should be added. That new variable would account for the physical elements in the process, mechanism almost impossible to simulate and has to be obtained experimentally.

A way to get around this problem for all variables is to take historical data, that is experimentally obtained, and trough regressions and tendencies, gather equations that approximate the reality quite good.

From now on, all the historical data would be from the 1st of February of 2023 until 1st of August of 2023 and representing the daily average of the variable from 00:00 to 23:59. The starting date was selected as it is when ELO plant was firstly started up with a stable MDI plant, so it is considered nominal operation. The ending date is when this part of the thesis kicked off.

8.1.1. Inlet and production

Starting with the relationship between the two reactants (Carbon Monoxide and Chlorine) and the phosgene produced at C01. The information available in the instrumentation is the amount of reactant that enters the whole section (Nm^3/h) and the amount of product that is generated in each rector.

To have a good relationship the data collected is filtered out so only in series data is used following the already stated: "*To differentiate the (in series) case, it has been defined as when the aperture of those valves are both below 10% as they are isopercentage.*"

By doing so, the following plot has been obtained:

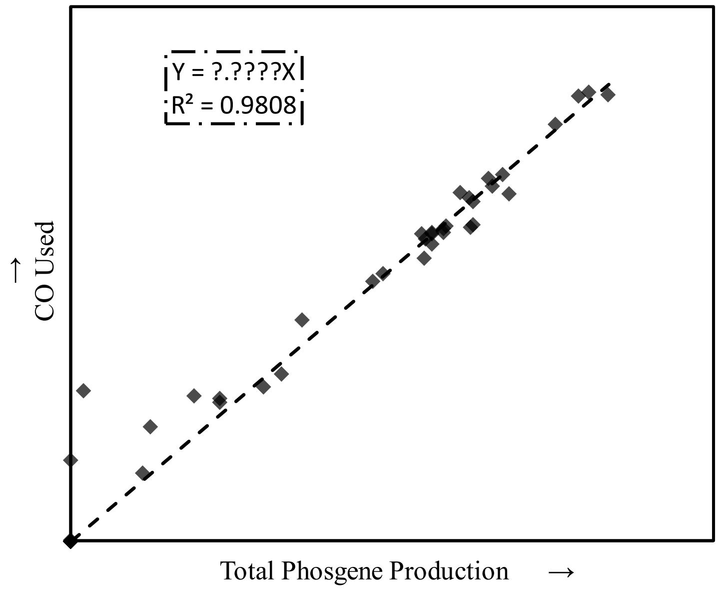


Figure 8.1 Relationship between CO and Production Rate.

Of course, all the data has been censored, as well as the regression ship equation (this practice will be throughout all this section). Not visualizing the numbers is not critical to understand the procurement. The tendency is quite clearly linear (as expected) with some outliers at the lower end of the plot.

No reason for this average data being so off has been found, but could correlate with instrument malfunction or maintenance run on the pipes that lead to a miss lecture of the variable (mainly because it is occurring at zero or almost zero production). Of course, the equation just have a pendent parameter as the pivot point is the axis intersection.

Continuing doing the same with the Chlorine inlet:

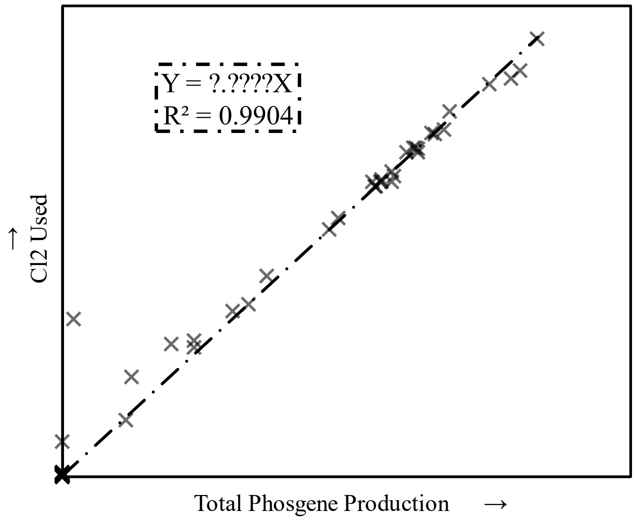


Figure 8.2 Relationship between Cl_2 and Production Rate

The conclusions are the same as before for the *Figure 8.1 Relationship between CO and Production Rate*. One could expect looking at the *Equation 3.1* that the linearity of both reactants should be more or less the same following the same tendency, but that's not the case. In order to show the difference visually the next plot has been done putting together both figures:

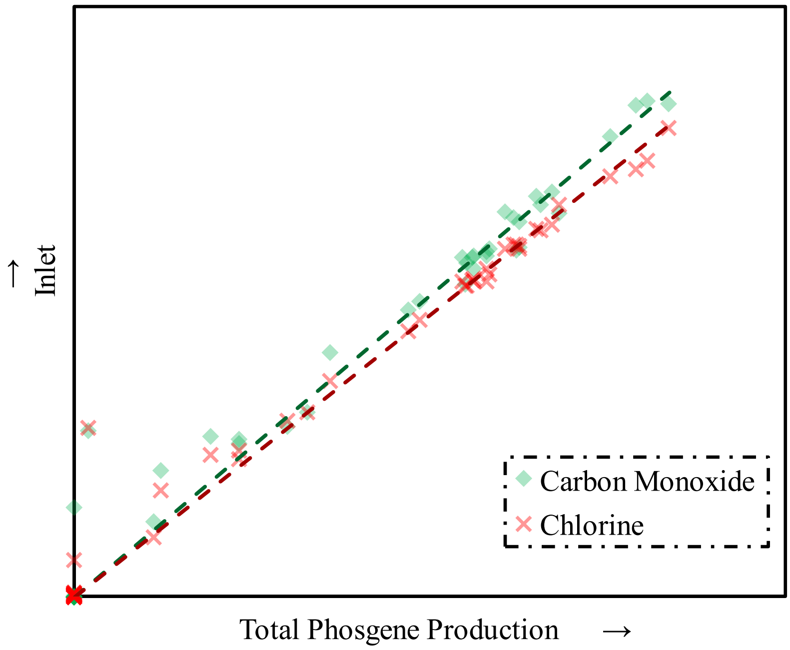


Figure 8.3 Comparison of Inlet Tendencies between CO and Cl_2 Depending on Production

From the *Figure 8.3* one can see quite clearly the difference between the inlets of both reactants. This is due to excess of carbon monoxide used to react all the chlorine in this section of the plant. This regression reflects the strategy followed by the panellists at different production rates. No changes regarding this aspect are wanted, so take it into account from now on is essential. With this regression one can calculate the amount of reactant necessary with the current CO excess strategy to achieve a higher production at the first rector. More specifically, increase the production until 12000 kg/h (number agreed with the company mentor of this thesis).

8.1.2. Pressure

Now that the expected amount of production is set and the mechanics of the material balance are understood, the next step is to validate if that scenario is possible. This validation is necessary because the current narrative between workers is that the reactor can not be more optimized due to pressure differentials in this section. Gathered information from the different stakeholders revealed four important points of interest that must be taken into account in order to consider correct the new approach. Those variables are:

- Pressure differential at the Carbon Monoxide inlet to the section (B01P02)
- Pressure differential at the Chlorine inlet to the section (B01P09)
- Pressure differential at the outlet of C03 (B01P41)
- Pressure at the outlet of C03 (B01P40)

Besides these, also common sense must prevail. If to achieve the desired production a result has no meaning (105% valve aperture for example) the approach must be reconsidered. Carbon Monoxide case will be firstly analysed. The validation has been also done with the same filters for the data as explained before.

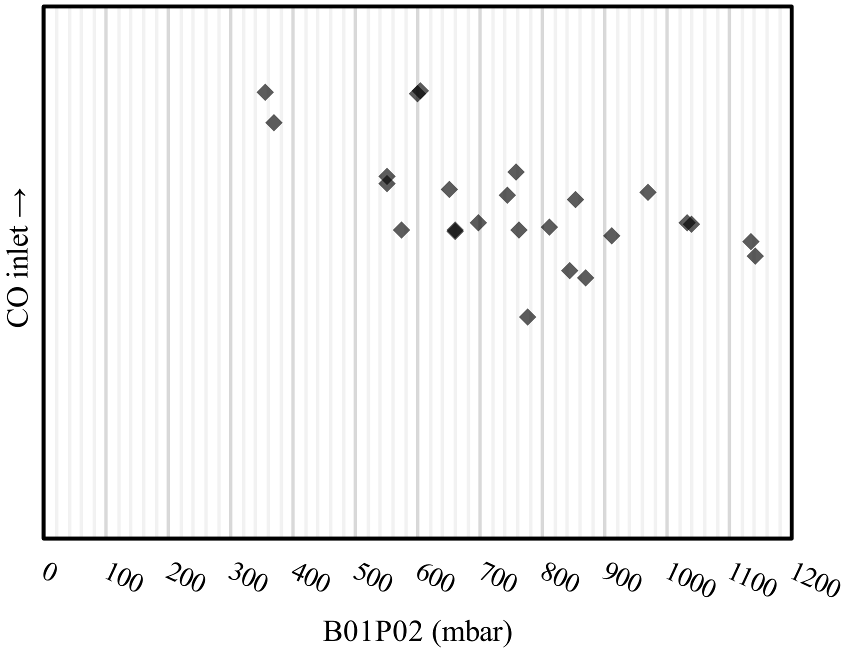


Figure 8.4 B01P02 Pressure Differential relationship with the CO inlet in series reactor configuration

No data about the amount of carbon monoxide is given as these are daily averages and directly correlate to the site's production. One thing that can be said, is that the data points that are found around 350 mbar are almost the desired amount of inlet for the new approach. For the sake of transparency, those points represent approximately the 95% of the necessary inlet.

The boundary set by the experts in production for these differentials is 50 mbar and the historical data suggests that the constrain would be satisfied comfortably in this case.

$$\mathrm{B01P02} \mid \mathrm{B01P09} \mid \mathrm{B01P41} \geq 50\ \mathrm{mbar}$$ **Equation 8.1**

Maybe the cap in this case is not found in the differential pressures, but in the valve itself, but as can be seen below, it is not the case.

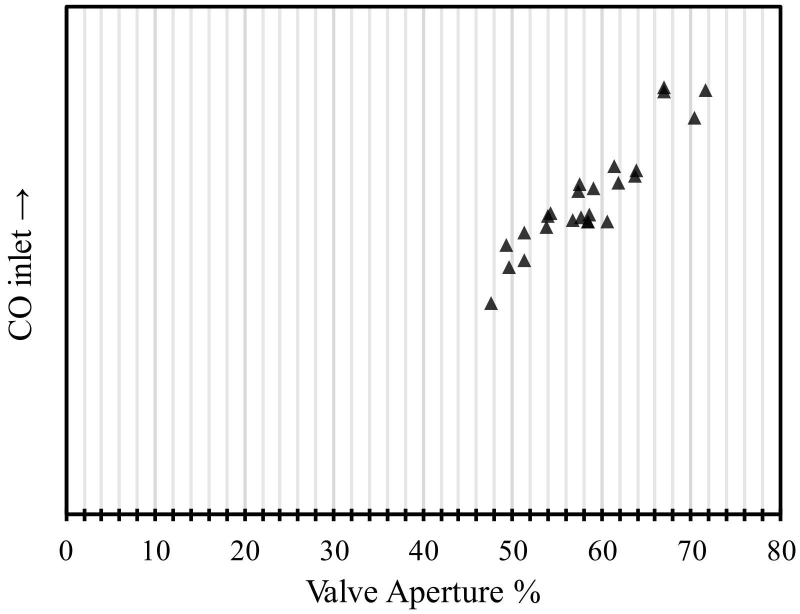


Figure 8.5 Valve Aperture B01P02 at the inlet relationship with the CO inlet in series reactor configuration

There is enough space to get the desired scenario without putting the installation at risk or squeezing the margins.

This same reasoning must be done with the chlorine inlet and this exact figures regarding that species are found below.

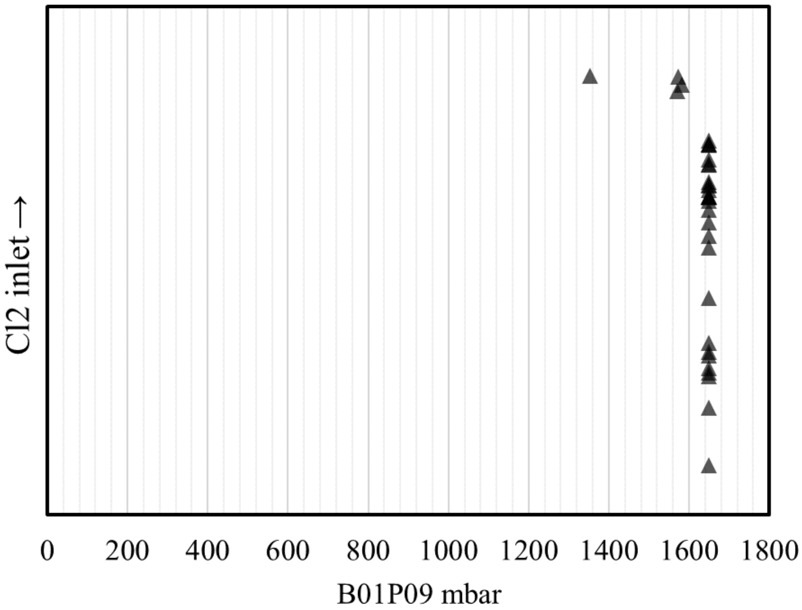


Figure 8.6 B01P09 Pressure Differential relationship with the Cl_2 inlet in series reactor configuration

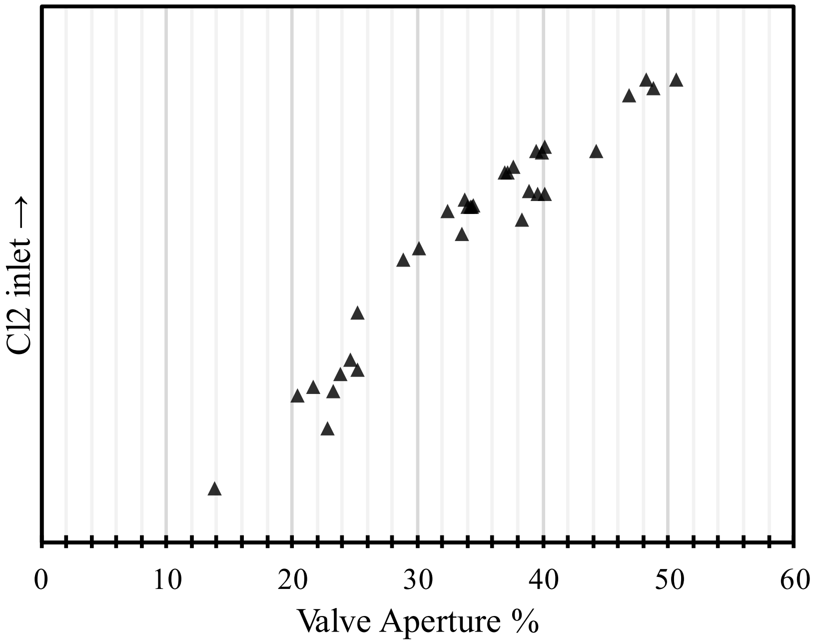


Figure 8.7 Valve Aperture at the inlet relationship with the Cl_2 inlet in series reactor configuration

In these two figures (Figure 8.6 and Figure 8.7) there is also no data relating the amount of chlorine for each data point to protect the internal information of the company. What can be said is that the points in the first figure that yield the most flow represent approximately the 92% of the necessary inlet for the new approach. These are found well above the minimum constrain of 50 mbar so there is confidence that the system will for sure be reliable (mainly due to the ELO plant).

Regarding the second plot, only 50% of the total valve passage section is being used for that 92% input. This leads to think that there will also be no problem with the pipes and valves in both cases (CO and Cl_2)

The two final constrains in this section are the pressure differential at the outlet of CO3 and the outlet absolute pressure.

This absolute pressure is quite important as when it decreases below 0.7 bar the operating costs down the lane (other plant sections) increase significantly. So the condition for this variable is:

$$1.1\ \text{bar} \geq \text{B01P40} \geq 0.7\ \text{bar}$$

Equation 8.2

The plot of these two variables can be found below depending on the production rate.

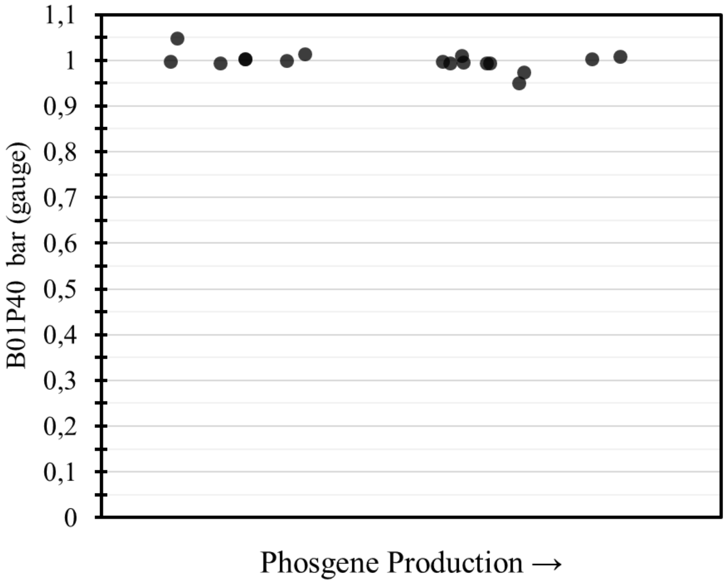


Figure 8.8 B01P40 Pressure relationship with Phosgene Production in series reactor configuration

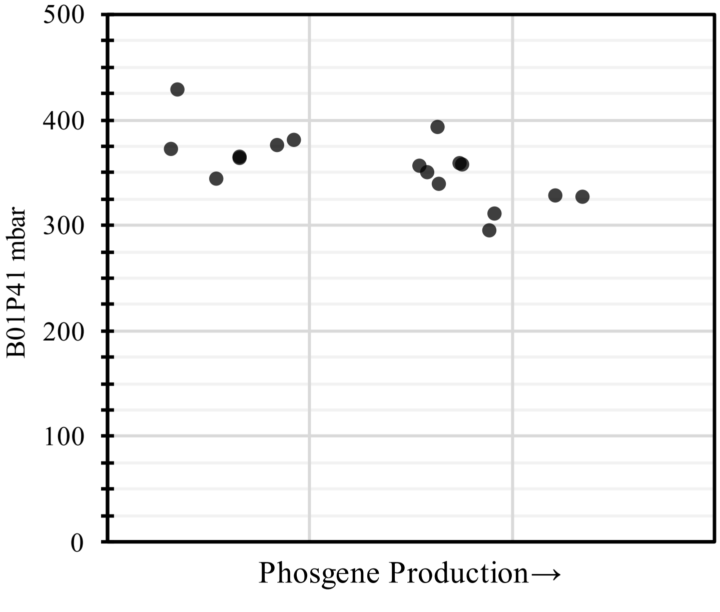


Figure 8.9 B01P41 Pressure Differential relationship with the Cl_2 inlet in series reactor configuration

Without showing the internal information one thing that can be assured is that the points with maximum production rate are quite near the objective of the new approach and far away from the constrains already set.

These four variables would need to suffer a sudden change in tendency in a very abrupt way to be a problem for the new strategy. No data studied has shown any evidence of that necessary change so there is trust in the changes.

8.2. Product Development

The direction is already set and the improvement can be glimpsed on paper. The product of this work is an improvement that is not selfsustained, meaning it requires workers to keep using the new approach in the less intrusive and time-consuming way possible with their daily work.

The desired agreed link is an EXCEL® file that will be opened in the control panel so the operators can easily check if everything is as it should be. This file must satisfy some design criteria:

- The layout must be self-explanatory so there is no room for misinterpretation.
- No worker intervention must be needed.
- It should contemplate different scenarios.
- The limitations of the program must be explicitly shown and monitored in a visual way.
- It must warn the worker if there is any issue in real time.

The first step on the development of this file is to set the independent variable from which everything would be calculated. To isolate the section from the overall plant that follows a more complex scenario and can be disturbed by other phenomena, the independent variable selected is the chlorine supplied. Being it the limiting reactant it is the variable used to set a production rate.

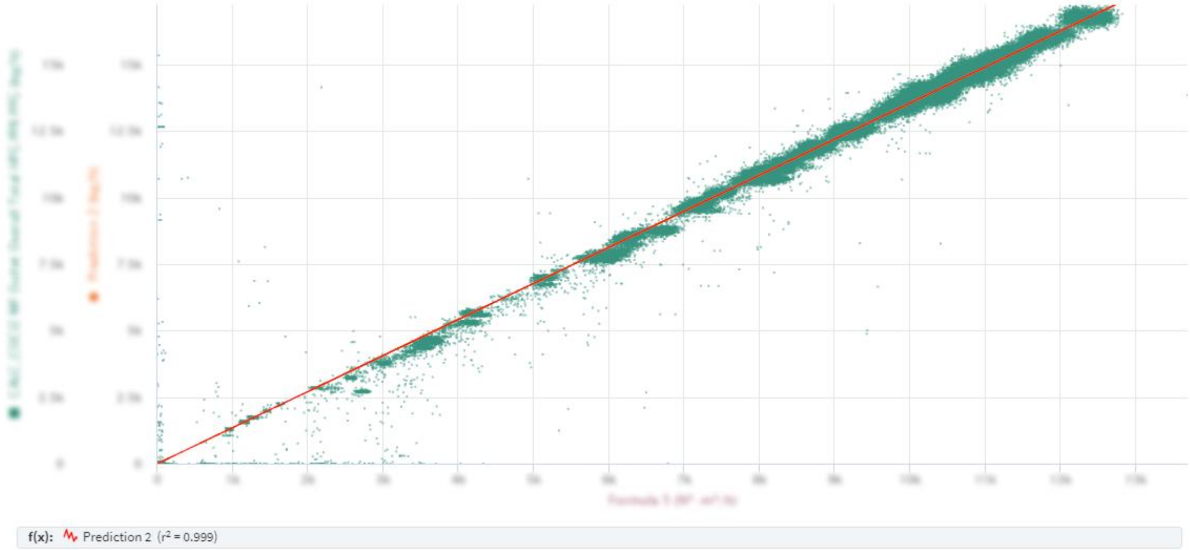


Figure 8.10 Production Rate of Phosgene depending (Y axis) on Chlorine inlet (X axis) with a regression of the data (red) using SeeQ

That regression has been done with a linear regression using five and a half months as training window, with Ordinary Least Squares (OLS) as regression method with a variable selection of data with p-values less than 0.05, forcing the result to go through the (0,0) point.

Now the production can be calculated more or less accurately. And set an strategy for each scenario. The next step would be to calculate the amount of total material needed for each production so it can be split in half and feed into C02 and C03 once C01 has reached it's full capacity.

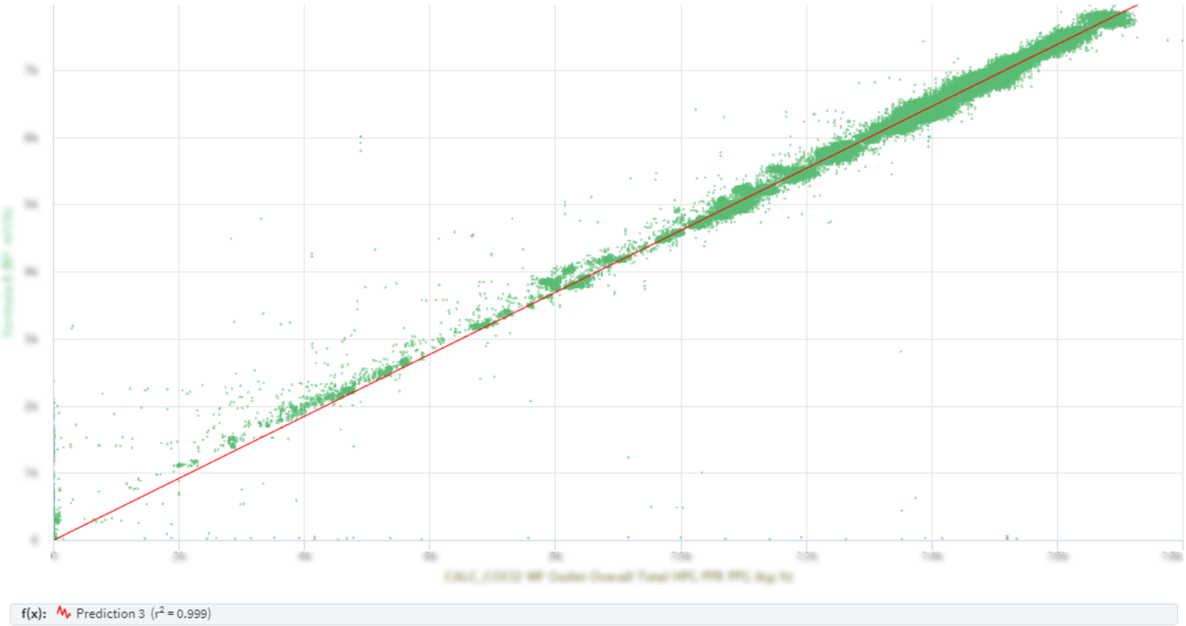


Figure 8.11 Raw materials used depending (Y axis) on Desired Production Rate of Phosgene (X axis) with a regression of the data (red) using SeeQ

That regression has been done with a linear regression using five and a half months as training window, with Ordinary Least Squares (OLS) as regression method with a variable selection of data with p-values less than 0.05, forcing the result to go through the (0,0) point.

The split in half of the raw material between the auxiliary reactors is done to distribute the punishment between both catalyst charges as the usual case while leaving some margin of disbalance if necessary. Both reactors have the same geometry, catalyst charge, tubes and refrigeration so there should be no issue whatsoever.

The next plots model the behaviour of B01F11 and B01F12 valves depending on the amount of fluid that is passing through.

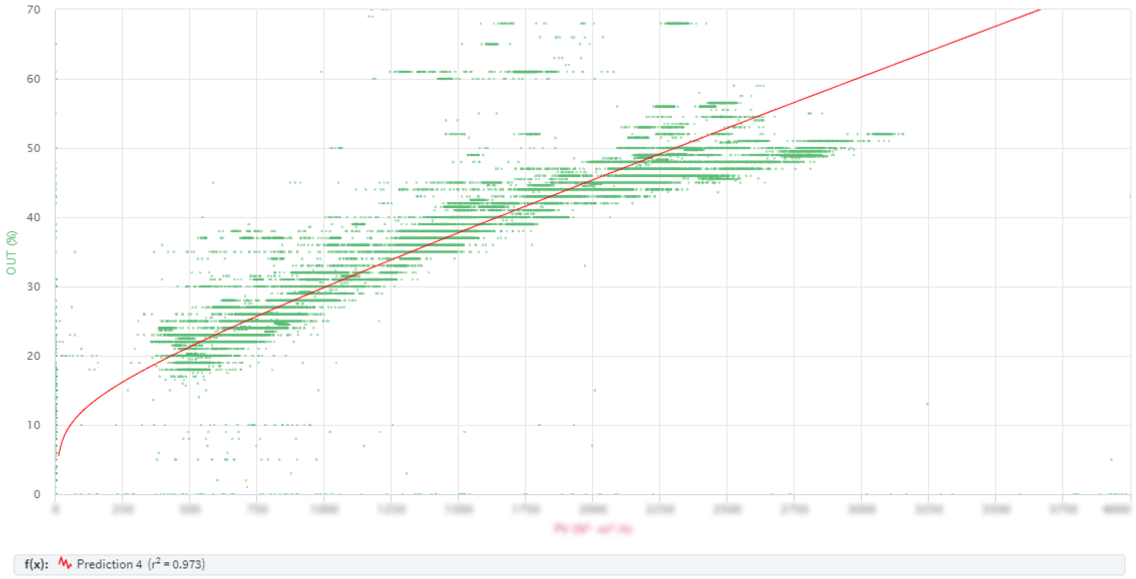


Figure 8.12 B01F11 valves opening depending on the flowrate passing through with a logarithmic regression (red)

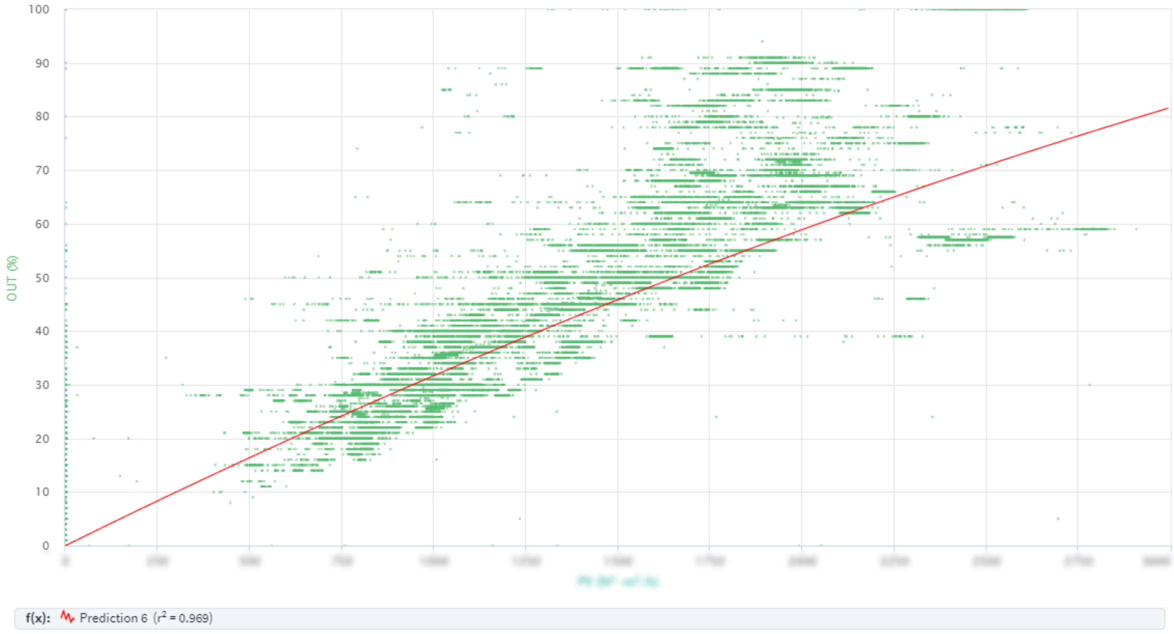


Figure 8.13 B01F12 valves opening depending on the flowrate passing through with a logarithmic regression (red)

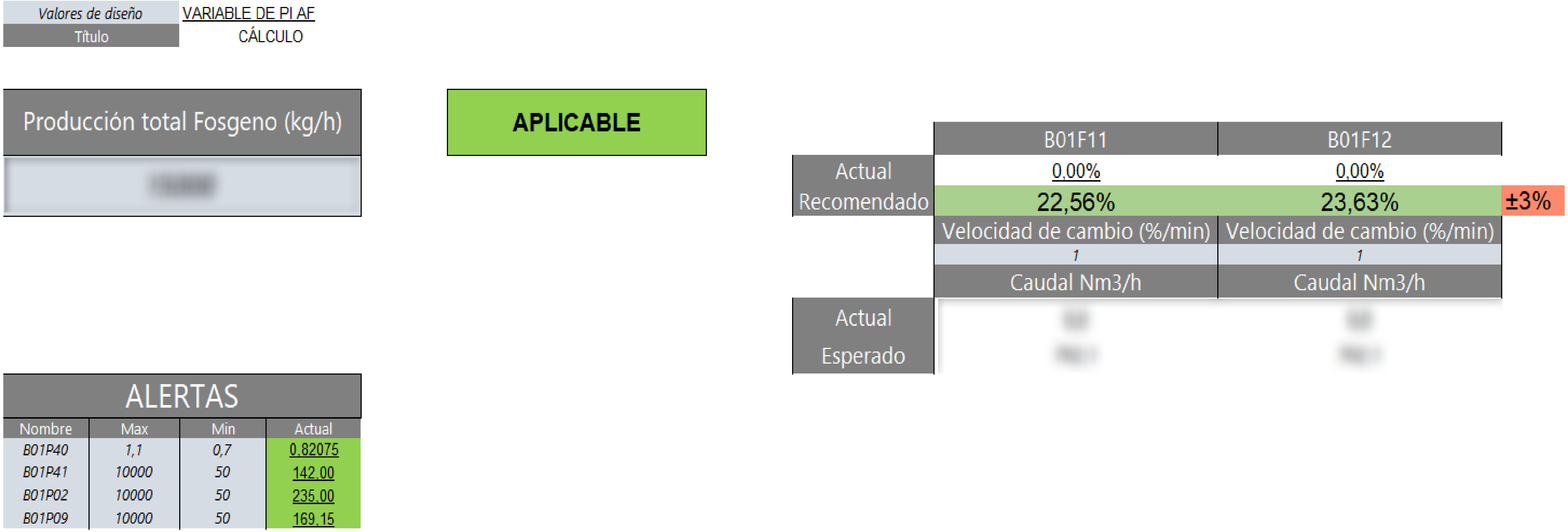
The regressions of B01F11 and B01F12 are both done following the regression parameters already explained in the figures before but the a logarithmic form for B01F11 and second order polynomial for B01F12.

The fitting for the isopercentage valves in the *Figure 8.12* is quite optimal deviating a bit at high flowrates (that will not be reached in normal operation), but the one found in the *Figure 8.13* have a lot of error. This, apparently, erroneous behaviour is under investigation at the moment and the regression will be taken as a good approximation by now as it seams that by analysing this week's data is describing the current reality quite accurately.

In order to put together the whole picture of the product, the approach can be summarized as:

- The valves B01F11 and B01F12 will be closed as long as the production of phosgene is below the C01 new set maximum capacity (sightly below the operational limit). The *Figure 8.11* will be the one followed.
- Once that capacity has been reached, the excess raw materials necessary to keep the production will be calculated using also the *Figure 8.11*.
- That amount will be distributed to C02 and C03 reactors equally by calculating the necessary aperture for each valve.
- This workflow will only be applicable when the plant is at steady state and all the constrains of design are satisfied.
- All the data will be updated each 5 seconds using the PI Datalink Add-On that reads the instrumentation signals directly

The final file can be seen below with an explanation of its use. Of course the exact formulas with the "if" and the regressions can not be shown as they contain the censored data form the graphs above.



Valores de diseño	VARIABLE DE PI AF
Título	CÁLCULO

Producción total Fosgeno (kg/h)
[redacted]

APLICABLE

	B01F11	B01F12	
Actual	0,00%	0,00%	
Recomendado	22,56%	23,63%	±3%
	Velocidad de cambio (%/min)	Velocidad de cambio (%/min)	
	1	*1*	
	Caudal Nm3/h	Caudal Nm3/h	
Actual	[redacted]	[redacted]	
Esperado	[redacted]	[redacted]	

ALERTAS

Nombre	Max	Min	Actual
B01P40	*1,1*	*0,7*	0,82075
B01P41	*10000*	*50*	142,00
B01P02	*10000*	*50*	235,00
B01P09	*10000*	*50*	169,15

Figure 8.14 EXCEL® File developed for the Control Panel to set correctly B01F11 and B01F12 valves.

The file was implemented the 19th of September of 2023 at approximately 11:00 AM, when Marc Bové send an email to all the related personnel communicating the changes and stating the new procedure. It was used for approximately three weeks until the 6th of October, when it was stopped indefinitely.

All the data captured that period was satisfactory and will be explained and showed in the *9.Results*.

The file was retired from service due to an unexpected problem with the condensate system. The file was creating so much steam that the pumps feeding water to W05 were over-stressed and some alarms for high usage were flagged. This collides head-on with the objective of this thesis. Problems with those over-stressed pumps have been seen in the past, before this thesis even started.

That is why the decision of change one of the pumps with a new one, capable of supporting, the system was made. Of course, while the purchase was taking place, the supplier was shipping the pump and the equipment was set up, the thesis project was stopped.

While the file was being used, another issue emerged. Some shifts shared that some evidence of catalyst desorption was being produced in C02 (feedback based in a mixture of data gathering and Know-How). This issue was occurring due to C01 being now the main or the only phosgene producer in series.

The activated carbon inside the reactors has a radial gradient of reactants and product in it’s nominal state and it’s kept quite constant throughout production. What was happening now is that as the outlet of C01 is forced to go trough C02 by design, to used as much of $Cl2$ as possible as explained before, now there was just only or manly phosgene in the mixture. This was kept for long periods of time and that phosgene stream was replacing the chlorine encapsulated in the catalyst. When the production rate needed C02 and C03 and the direct inlets were opened the catalyst was not ready to operate as now the reactant needed to fully wet the interior of the particles again, leading to an outlet rich in chlorine (which is not wanted).

Having seen this issues that were never in the scope of the limits a communication channel was opened with the workers in order to receive feedback of cases that were not contemplated. From these communications two final worries were sent. The first one was regarding the outlet temperature of C01, some workers find it quite high and some alarms were fired due to that issue. The second one was regarding the data updating period as in some cases no update was happening for hours.

8.3. Feedback Solutions

The solutions found for the three issues communicated are:

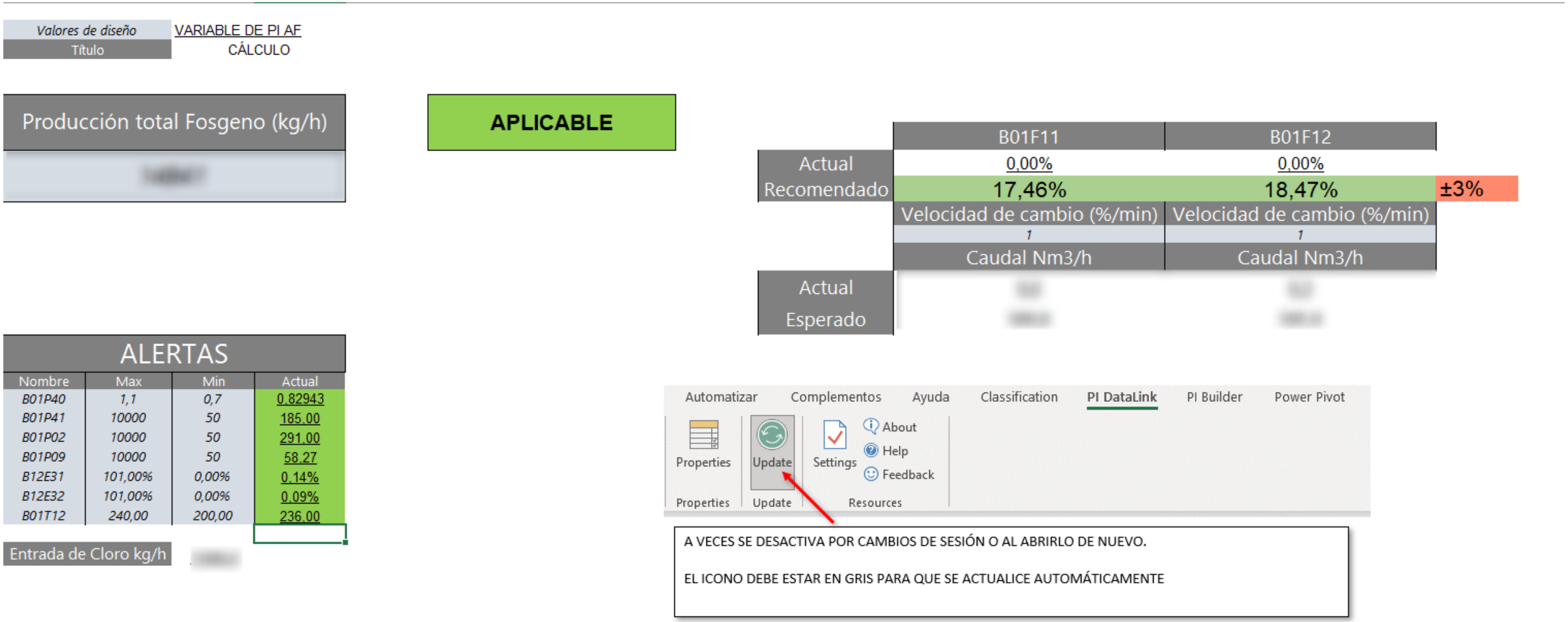
- New alarm system: As can be seen in the *Figure 8.14* there is a panel with some alarms and constrain conditions that show the applicability of the file in each case. Three new parameters were added to the panel: B12E31, B12E32 and B01T12. The first two (E31 and E32) are the power requirements of the two redundant pumps of the condensate system. These are displayed as a percentage, being 0% no power usage and 100% maximum nominal power usage. B01T12 is the temperature of the outlet of C01.

- Minimum Apertures: A minimum aperture has been added to just C02 to prevent desorption in the catalyst. This change has only been applied on this reactor as in C03 there is always a bit of reaction from the pure chlorine addition to the excess carbon monoxide. This minimum aperture has been set to 12.5% due to the isoporcentuallity of the valve B01F12.
- Alarm changes: The higher temperature at the outlet of C01 is expected, as an increase in total product generation coming from an exothermic reaction increases that variable substantially. Historically there were problems regarding this aspect because it could punish excessively the catalyst particles reducing the useful life of the reactor. As mentioned before, there is a new catalyst charge in that reactor that is also manufactured differently so it can withstand higher temperatures, but the set point of that alarm was still programmed as it was the past catalyst. Once talked to the corresponding people, a change on that value was effectuated and communicated to the panellists.
- Update Enabler Reminder: Finally, regarding the updating data, the issue has been found to be related to the add-on and the panellists workflow. When there is a shift change or a changer in the user in the control panel, sometimes the “update” button is deactivated. As a corrective action a remainder and explanation has been added so the workers can check if the data is being updated correctly.

By applying the mentioned changes, a second iteration was made through October along with some overall improvements. These improvements are related to the correlations of expected aperture/flowrate and the margins of error. The most notorious and important is the manual override of the calculations. Once implemented the system was more relax than the expected, leading the team to think that there was more room of improvement that was not considered in this thesis. That’s why a manual override over the calculations has been done. This change is agreed to subtract a 4% to the calculated valve aperture.

This will be the first approximation in order to tune the behaviour, the idea is to find the optimal behaviour trough experimental approaches to model indirectly the complexity of the system.

The resulting EXCEL file can be seen below following the same structure as the previous one:



Valores de diseño	VARIABLE DE PI AF
Título	CÁLCULO

Producción total Fosgeno (kg/h)
[redacted]

APLICABLE

	B01F11	B01F12	
Actual	0,00%	0,00%	
Recomendado	17,46%	18,47%	±3%
	Velocidad de cambio (%/min)	Velocidad de cambio (%/min)	
	1	1	
	Caudal Nm3/h	Caudal Nm3/h	
Actual	[redacted]	[redacted]	
Esperado	[redacted]	[redacted]	

ALERTAS

Nombre	Max	Min	Actual
B01P40	1,1	0,7	0,82943
B01P41	10000	50	185,00
B01P02	10000	50	291,00
B01P09	10000	50	58,27
B12E31	101,00%	0,00%	0,14%
B12E32	101,00%	0,00%	0,09%
B01T12	240,00	200,00	236,00

Entrada de Cloro kg/h [redacted]

A VECES SE DESACTIVA POR CAMBIOS DE SESIÓN O AL ABRIRLO DE NUEVO.

EL ICONO DEBE ESTAR EN GRIS PARA QUE SE ACTUALICE AUTOMÁTICAMENTE

Figure 8.15 Second iteration of the EXCEL® File developed for the Control Panel to set correctly B01F11 and B01F12 valves.

Following the schedule of the plant, this file would only be used for a week. That’s the period between the pump implementation and the planned stop for this year. Due to external issues this iteration was never used and has been archived to be used from the next start up.

The expected results are quite difficult to predict as here two phenomena are fighting in different directions. In one hand an expected decrease in efficiency is expected as now the base case is not full in series but is semi-parallel with the changes from the feedback. In the other hand an override of 4% will stress more the system leading to more steam generation. Which phenomena will surpass the other and in which conditions is the key, but it will be reviled in some months.

9. RESULTS

Having showed all the relevant step by step development of the new approach, in this section the obtained results will be discussed. The improvement can be seen from different points of view and throughout many variables/conditions/plots, but for the sake of simplicity and clarity, the ones that will be represented is the one considered to be more visual and intuitive.

Apart from the economical results, the impact of the implementation has been denoted in other aspects of the company, that will be now discussed, as reactor generation distribution, steam production predictivity, steam quality, etc…

9.1. Savings

As steam production can be easily correlated to overall production of phosgene and thus, to the overall production of the site, the improvement will be only showed in percentage. To do so, some cases must be taken as "old base cases" in order to compare the new approach. The dates and names of those cases can be seen in the next table:

Table 9.1 Base Cases for Comparison

Low Production Rate		**Medium/High Production Rate**		**High Production Rate**	
Start Date	*Finish Date*	*Start Date*	*Finish Date*	*Start Date*	*Finish Date*
07/06/2023	12/06/2023	11/09/2023	12/09/2023	14/09/2023	15/09/2023

These dates and productions have been chosen looking the production rates found throughout the three-week implementation. The medium and high production rate cases are chosen as close as possible to the implementation week, so the plant section is as similar as possible operationally. The low production rate is not the nominal production rate so the date is further from the implantation one, and as in that production is when the biggest improvement is found, for the sake of consistency and transparency, a longer period has been selected.

The workflow to gather data has been ensuring, as far as possible, a good EXCEL file implementation throughout the day. The next morning at 8:00 PM the data was collected from the last 24 hours and added to an internal dataset. If for any issues the last 24 hours were no suitable to be compared, that day was never recorded in the dataset.

From the 17 days of implementation, only 13 were suitable for being entered into the databanks. This are showed in the figure below

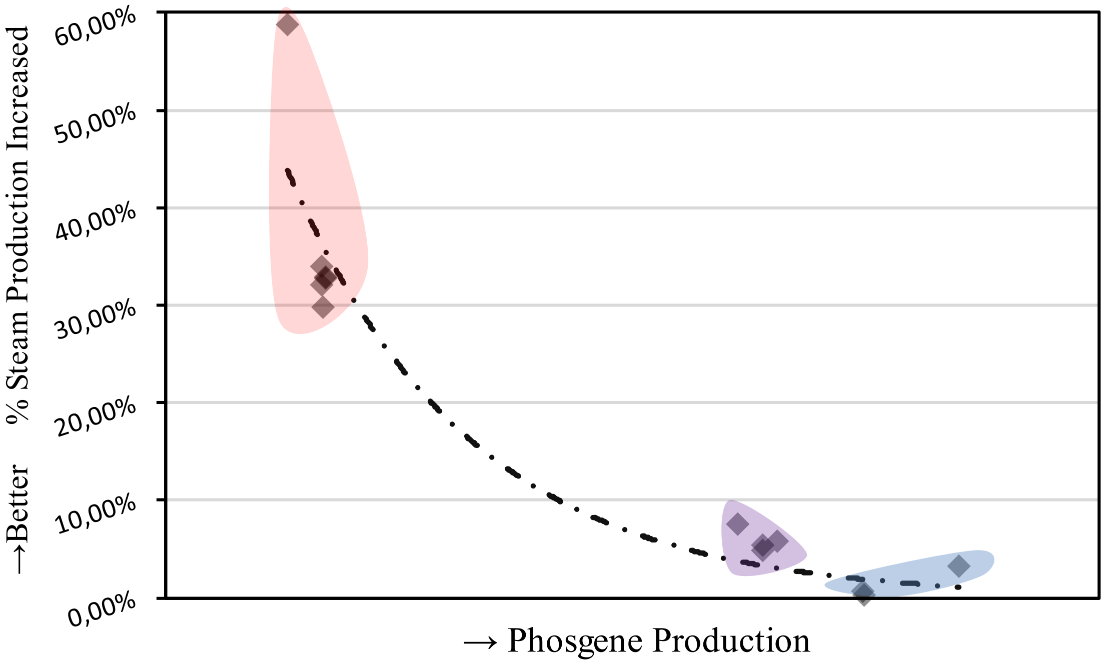


Figure 9.1 Steam Production Increase depending on Phosgene Production Rate with a exponential regression curve with three areas of production: Low (red), Medium/High (purple) and High (blue).

Looking at Figure 9.1 an improvement throughout all production rates can be easily seen. The exponential regression is the best fitting expression studied but, in order to ensure that behavior, some data points would be wanted at a Medium and Medium/Low productions. The most improvement ratio can be found in low productions. This is mainly due to the change in management (not only valve aperture) at that production, by pushing higher the in series roof further into the production planning. The average improvement can be seen in the next table.

Table 9.2 Average Increase in Steam Production at different Production Rates

Production rate	Low	Medium/High	High
Average % Steam Production Increased	36.73	5.87	1.38

In order to quantify the savings produced during that three-week period and extrapolate that to a whole year, is necessary to know the price of each kilogram of steam. The actual value and calculation has already been performed in house, but is sensitive information. In order to show the full picture a value has been calculated using open correlations [31].

$$\frac{€}{kg\ Steam} = (A \cdot\ CE\ PCI\ + B \cdot C)\ \cdot\ 0.91 \frac{€}{\$} \qquad \textbf{Equation 9.1}$$

$$A = 2.7 \cdot 10^{-5} \cdot m^{-0.9} \qquad \textbf{Equation 9.2}$$

$$B = 0.0034 \cdot p^{0.05} \qquad \textbf{Equation 9.3}$$

This set of equations is only valid for pressures (p) between 1 and 46 bar and for mass flowrates (m) between 0.06 and 40 kg/s, the process satisfies both conditions. The C parameter is the fuel price used in $ (US)/ GJ and the CE PCI is the parameter that accounts for inflation for USA projects that has a value of 293.7 (April, 2023). This leads to a result of 52€/ton of steam, result that is a good representation and approximation of the actual inhouse price. On the other hand the efficiency in the form of kg Steam/Kg Phosgene has increased a 14% comparing the implantation weeks to the average in 2022. Knowing the production of 2022 which was approximately 94,000 tones of phosgene one can calculate that the expected savings extrapolating the results would be of approximately **200,000 €/year**.

9.2. Reactor Generation Ratio

The Figure 6.1 shows very clearly how the ratio between the reactor production depending on the overall production rate of phosgene. One interesting view is comparing that plot to the new data gathered, and that is what can be seen in the figure below.

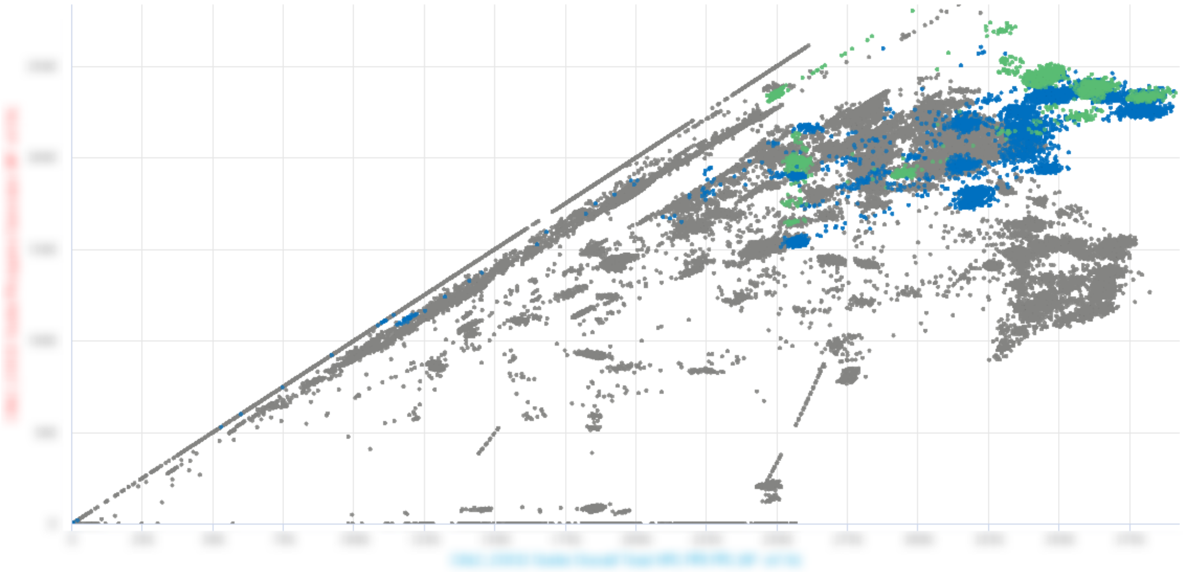


Figure 9.2 C01 Production (Y axis) Depending on Overall Production Rate (X axis) with a three color scheme: Historical (grey), Implementation Weeks (green) and weeks before and after Implementation Weeks (blue).

The perfectly diagonal lane in this plot do not represent the reality of the “in series” configuration as all those data points are from when the catalyst was brand new and the efficiency was perfect. The lane representing the normal operation is it’s parallel one that is thicker and more deviated.

The “cloud at the end” represents the semi-parallel and parallel configurations at different scenarios of the plant.

Looking at the diagonal lane, some green points can be seen extending longer in the trend revealing that indeed the maximum production for C01 has been raised. Focusing on the cloud on the left one can see that overall the green points are above or on top of the blue ones and notoriously above the grey ones. The exact mechanisms of the whole plant are more complex and constantly changing that’s why there are points below or at the same heigh as blue or grey.

Another key aspect is that this program does not differentiate normal operation from production changes, maneuvers and instrumentational malfunctions.

9.3. Steam Predictivity

Another point of view of the improvement is the ability to predict the amount of steam that will be generated at each production rate. This is not the most accurate predictive model due to lack of data, but with more implementation time, about 3 months, the model will be quite robust and the regressions will fill the regression more smoothly.

In the next figure the intentionality of the model can be glimpsed compared to historical data from dates surrounding the implementation and in red the compared dates from Table 9.1.

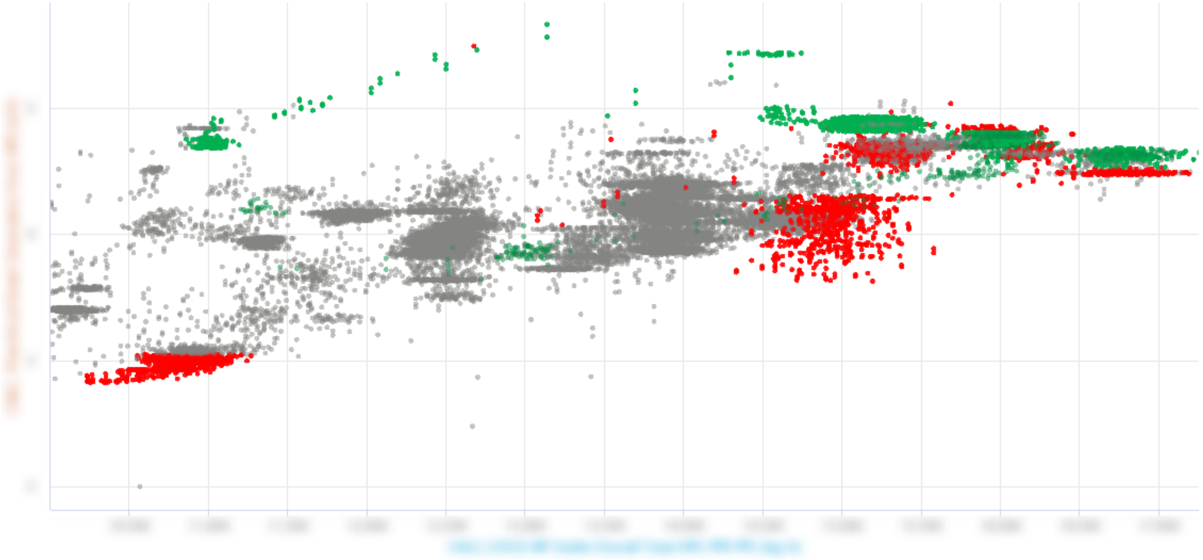


Figure 9.3 Steam Generation at different Production Rates comparing different groups: Historical data (Grey), Implementation Weeks (Green) and Data from Dates from Table 9.1 (Red)

Generally speaking, the green data points form a dome in top of all the rest of the points. With some more data it is expect form a less pronounce “dome-shape” and more like a polynomial/exponential that will be flattish at the early/middle and decay quicker as the production increases. By opposition the red and grey dots follow a more dispersed pattern for every production, being hard to predict. It is though that this is mainly do the “know-how” and manners of procurement that each shift has and the situation that they feel comfortable with.

9.4. Steam Productivity

In addition to the already shown point of views, the productivity associated with each kilogram of steam that is generated with each kilogram of phosgene produced is another key aspect of the improvement. This is also seen depending on the production rate and with the same groups of comparison as the Figure 9.3.

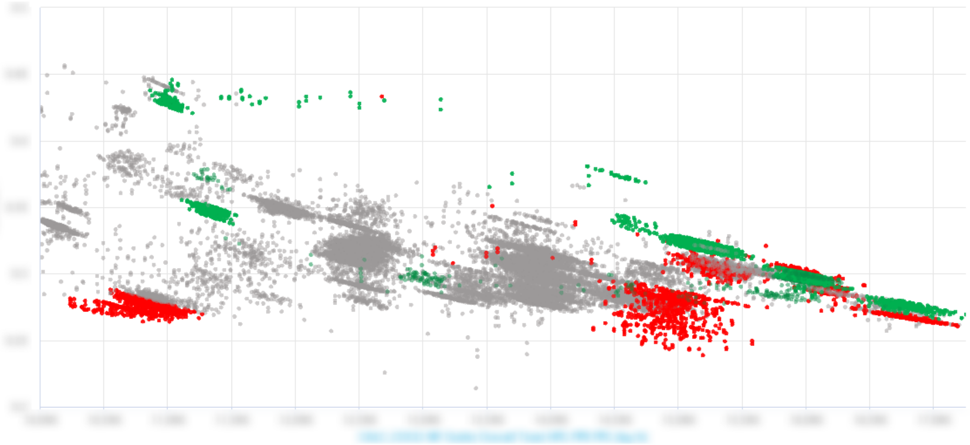


Figure 9.4 Steam Productivity (kg Steam/kg Phosgene) at different Production Rates comparing different groups: Historical data (Grey), Implementation Weeks (Green) and Data from Dates from Table 9.1 (Red)

In this figure the same characteristics as in Figure 9.3 can be seen. The green data points are above the rest, mainly, and can be glimpsed a tendency, that could be modeled with more time of implementation trough more production ranges. The green data clusters that are between or below the historical data correspond to some days denominated es “relaxed” where the panelists implemented the EXCEL file but at the worst-case scenario for energy recovery inside the range given. That range is quite big and it has been done so the workers can feel comfortable with the approach and could be tighten up as the shifts get used to this workflow and more data is gathered.

9.5. Steam Quality

To finalize, if the steam production is increased but the system is not reliable or that steam has not the wanted quality, the improvement is compromised and its usefulness is null. One of many ways to check the quality and consistency of the generated steam is trough the pressure created at the outlet of W05. It should be time-independent and as close as possible to the nominal steam pressure of 20 bar.

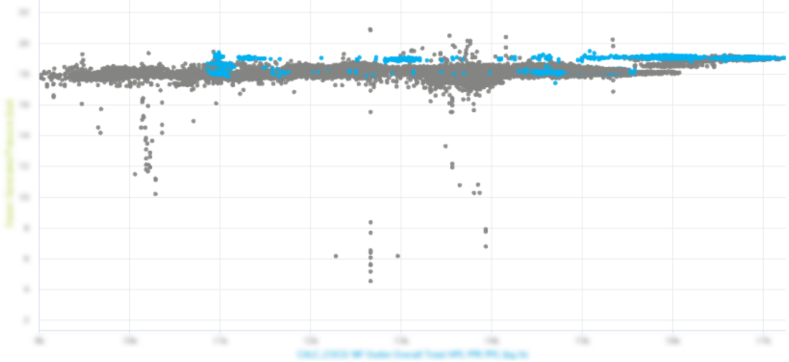


Figure 9.5 Steam Pressure at different Production Rates Comparing the Historical data (grey) with the Implementation Weeks Data (blue)

Looking at the plot above one can se that the implementation kept the pressure over time and production ensuring a constant quality and, in some cases, improve it.

10. CONCLUSIONS

This thesis culminates in this section that synthesizes the extensive research and analysis conducted throughout. This section is pivotal in drawing together the key findings and insights, highlighting the original contributions made to COVESTRO’s phosgene synthesis plant, and considering the wider implications and potential for future research.

Next, significant conclusions are enumerated, offering a concise summary of each. These conclusions serve to underscore the research's value, the new perspectives it provides, and the avenues it opens for further inquiry. The aim is to provide a comprehensive understanding of the research achievements, their relevance, and how they contribute to the broader context of the work done. These are:

- The mathematical model used to predict the failure of the tubes in W05 do not reflect the reality seen in the case studies. The model is correct and backed up by numerous papers and studies referenced in that section but, do not contemplate the mechanism that made the real scenarios fail. The answer to this issue relies, possibly, in the assumptions set in the models or phenomena not contemplated in the first place. Examples of phenomena that might contribute significantly to the failure of the structure could be:
    - Tangential or radial thermal stresses
    - Vibrations
    - Initial cracks of the non-homogeneous metal and crack propagation
    - Corrosion
    - Failure started in joints and unions
- Neither this study nor the internal documentation denies or affirms that the issue of the failure is in the nominal stress. The discussions made in-house and the results obtained from the heat exchanger may indicate that the main issue could be at the start up process where the temperature differential is at its highest. This could create a crack that progresses trough nominal operation.
- More instrumentation or a lab size equipment would be needed to get enough data for an experimental model backed up by mathematical expressions.
- The study may be conducted using software like COMSOL but making a long enough time-dependent simulation where each cycle is slightly different than the previous and can deform the mesh used (that should be incredibly thin) according to the deformation is a very difficult task. That exercise is impossible to be done by a normal computer with reasonable computational times.

- The new approach improving the energy recovery system of the phosgene system has been only possible recently. The point of improvement has not been overlooked for years, its been glimpsed as a result of the new ELO plant as chlorine quality has been the bottleneck for years.
- There results obtained in the first iteration satisfy every constrain and the improvement is measurable (approximately 200,000€ per year).
- The operation has not been altered in any way or manner by the implementation.
- There is more room for improvement that will be seen in the second iteration. This improvement doesn't necessarily has the form on more direct economical impact, it is expected to be reliability and plant comfort. A third iteration is advisable to convert the current overdrive value of 4% into an equation that changes the override value depending on the plant situation.
- The bottlenecks that are or will be found in as more energy recovery is wanted will be basically two.
    - The pump of condensate in the W05 circuit is currently insufficient and can not feed enough water to be evaporated in that heat exchanger. This is an important operational problem as this pump not only is the supplier for this equipment but also for many others. The replacement with a new pump oversized to be used in the future with possible productions expansions is advised.
    - The reactors geometry is currently setting a cap for the amount of phosgene that can be produced in there quite low but reasonable. In the case of a wanted increased total capacity it would be wise to not change C02 and C03 if possible and invest on a bigger C01 reactor with the same energy recovery capabilities.

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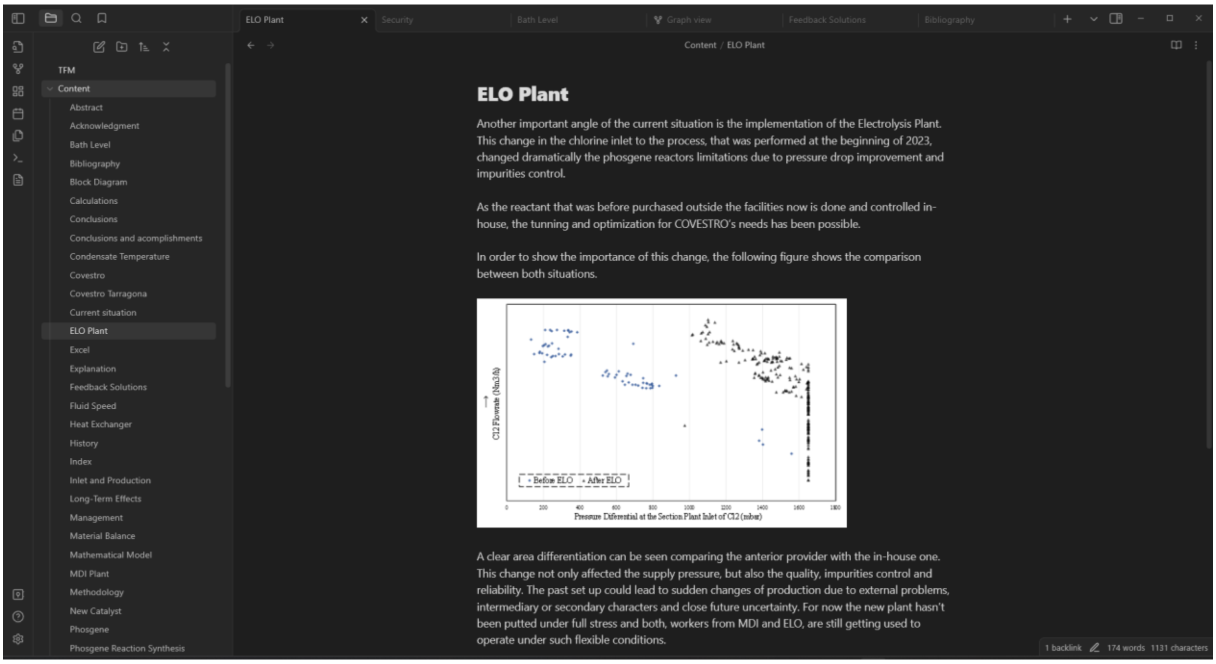
A. ANNEXES

A.1. OBSIDIAN



ELO Plant

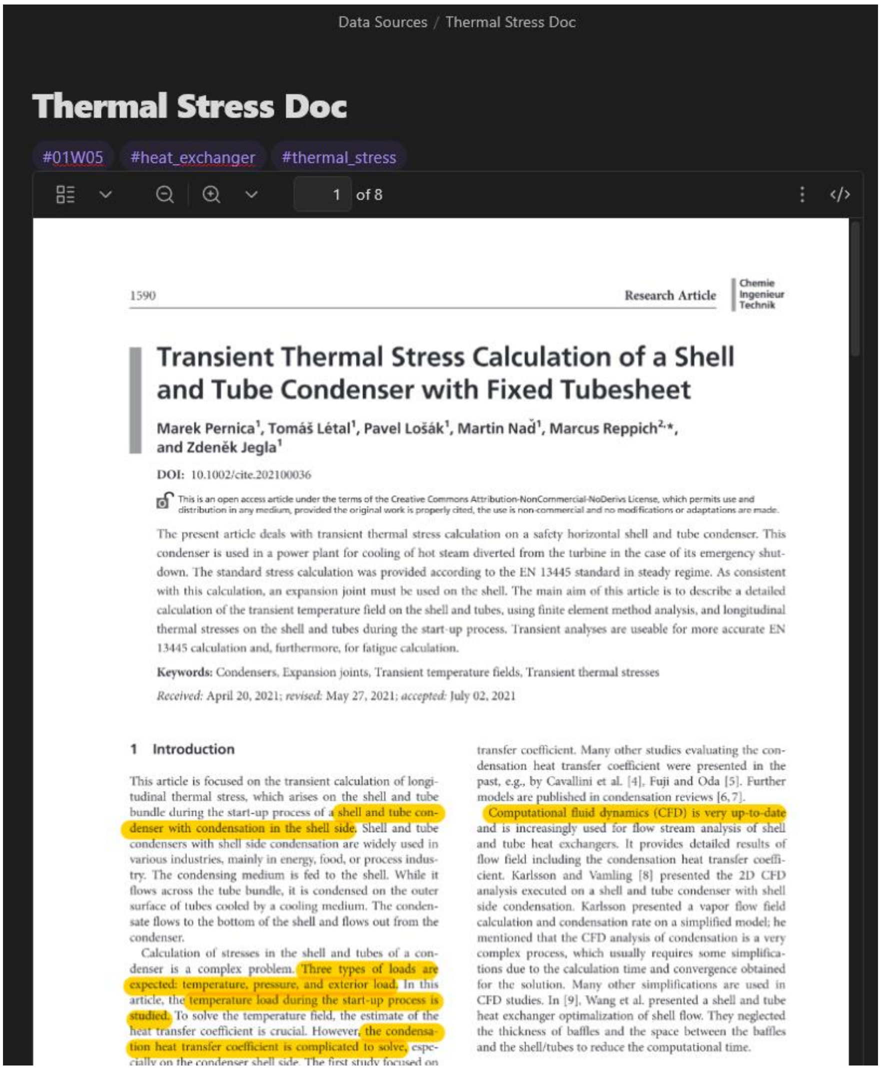
Another important angle of the current situation is the implementation of the Electrolysis Plant. This change in the chlorine inlet to the process, that was performed at the beginning of 2023, changed dramatically the phosgene reactors limitations due to pressure drop improvement and impurities control.

As the reactant that was before purchased outside the facilities now is done and controlled in-house, the tunning and optimization for COVESTRO's needs has been possible.

In order to show the importance of this change, the following figure shows the comparison between both situations.

A clear area differentiation can be seen comparing the anterior provider with the in-house one. This change not only affected the supply pressure, but also the quality, impurities control and reliability. The past set up could lead to sudden changes of production due to external problems, intermediary or secondary characters and close future uncertainty. For now the new plant hasn't been putted under full stress and both, workers from MDI and ELO, are still getting used to operate under such flexible conditions.

Figure 11.1 User interface of OBSIDIAN® with the table of contents and a file opened



1590 **Research Article**

Transient Thermal Stress Calculation of a Shell and Tube Condenser with Fixed Tubesheet

Marek Pernica[1], Tomáš Létal[1], Pavel Lošák[1], Martin Nad̆[1], Marcus Reppich[2,*], and Zdeněk Jegla[1]

DOI: 10.1002/cite.202100036

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The present article deals with transient thermal stress calculation on a safety horizontal shell and tube condenser. This condenser is used in a power plant for cooling of hot steam diverted from the turbine in the case of its emergency shutdown. The standard stress calculation was provided according to the EN 13445 standard in steady regime. As consistent with this calculation, an expansion joint must be used on the shell. The main aim of this article is to describe a detailed calculation of the transient temperature field on the shell and tubes, using finite element method analysis, and longitudinal thermal stresses on the shell and tubes during the start-up process. Transient analyses are useable for more accurate EN 13445 calculation and, furthermore, for fatigue calculation.

Keywords: Condensers, Expansion joints, Transient temperature fields, Transient thermal stresses

Received: April 20, 2021; *revised:* May 27, 2021; *accepted:* July 02, 2021

1 Introduction

This article is focused on the transient calculation of longitudinal thermal stress, which arises on the shell and tube bundle during the start-up process of a shell and tube condenser with condensation in the shell side. Shell and tube condensers with shell side condensation are widely used in various industries, mainly in energy, food, or process industry. The condensing medium is fed to the shell. While it flows across the tube bundle, it is condensed on the outer surface of tubes cooled by a cooling medium. The condensate flows to the bottom of the shell and flows out from the condenser.

Calculation of stresses in the shell and tubes of a condenser is a complex problem. Three types of loads are expected: temperature, pressure, and exterior load. In this article, the temperature load during the start-up process is studied. To solve the temperature field, the estimate of the heat transfer coefficient is crucial. However, the condensation heat transfer coefficient is complicated to solve, especially on the condenser shell side. The first study focused on

transfer coefficient. Many other studies evaluating the condensation heat transfer coefficient were presented in the past, e.g., by Cavallini et al. [4], Fuji and Oda [5]. Further models are published in condensation reviews [6,7].

Computational fluid dynamics (CFD) is very up-to-date and is increasingly used for flow stream analysis of shell and tube heat exchangers. It provides detailed results of flow field including the condensation heat transfer coefficient. Karlsson and Vamling [8] presented the 2D CFD analysis executed on a shell and tube condenser with shell side condensation. Karlsson presented a vapor flow field calculation and condensation rate on a simplified model; he mentioned that the CFD analysis of condensation is a very complex process, which usually requires some simplifications due to the calculation time and convergence obtained for the solution. Many other simplifications are used in CFD studies. In [9], Wang et al. presented a shell and tube heat exchanger optimalization of shell flow. They neglected the thickness of baffles and the space between the baffles and the shell/tubes to reduce the computational time.

Figure 11.2 Example of a PDF source imported in obsidian linked to some note files

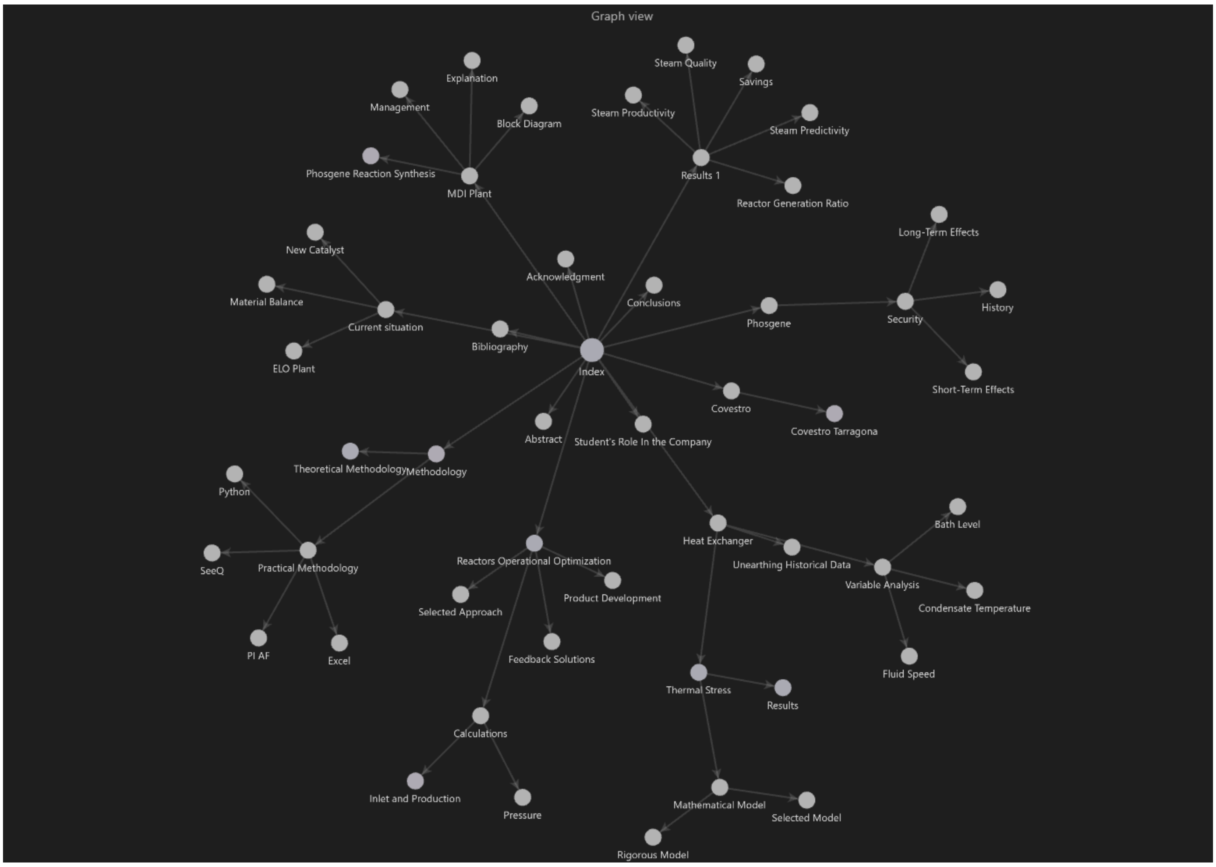


Figure 11.3 Resulting diagram of the nodes related to the thesis

A.2.PI AF SOFTWARE

This section is a brief description of the PI AF software used in this work. To describe the software with just a phrase, it would be:

> *"Data gathering structure that organises it at different levels of complexity with an intuitive tree-like format."*

In the figure below that has been blurred to protect sensitive data the main search menu can be seen.

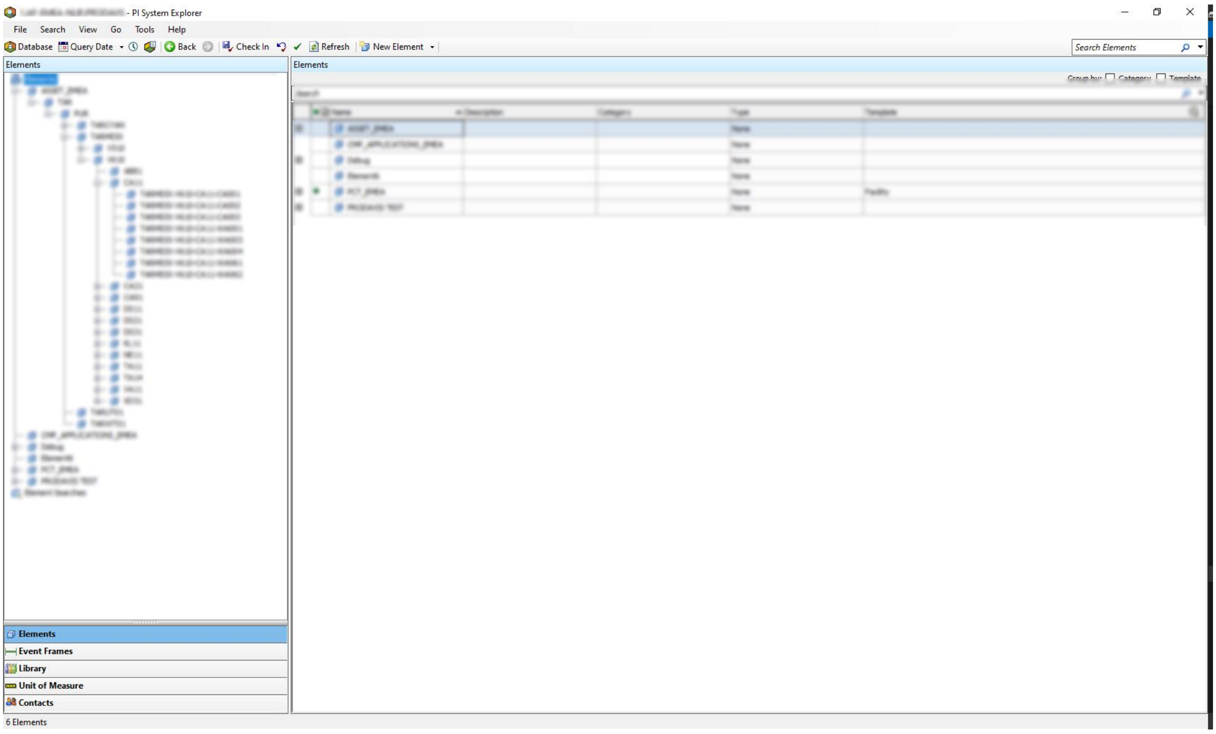


Figure 11.4 PI AF Screeshot Num. 1

The tree structure is seen on the left side window called “Elements”, using it is how the assets can be searched at different plant organization levels. At the left a more detailed information of the selected level is shown following a table format.

Once an asset has been selected and opened or newly created, the first window that appears is shown in the next figure.

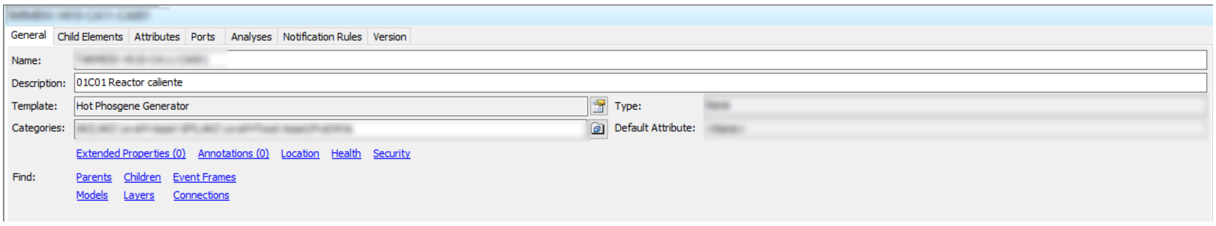
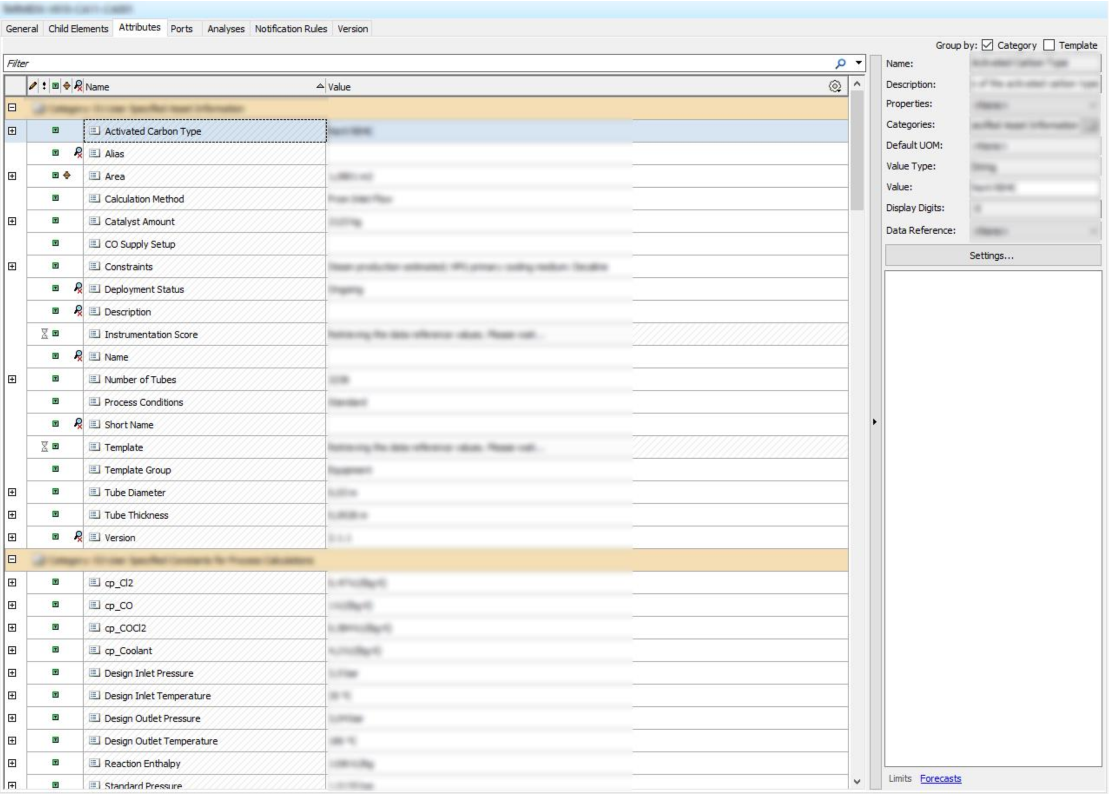

Description: 01C01 Reactor caliente
Template: Hot Phosgene Generator

Figure 11.5 PI AF Screenshot Num. 2

Here the identity of the asset is showed very summarized. As part of the COVESTRO’s workflow, the name field is a set of numbers and letters that gives the ID to that equipment. The description is the site where natural language is used to put a common name to the asset. More information that is showed here is the templated from Digital Services used, the type of asset, the category of the equipment and if it has any default attributes.

From the part below this fields, an array of hyperlinks can be used to navigate trough the different menus of this asset. The menu that is used 95% of the time as it is the base of the data gathering is the “Attributes” and a screenshot can be seen below.

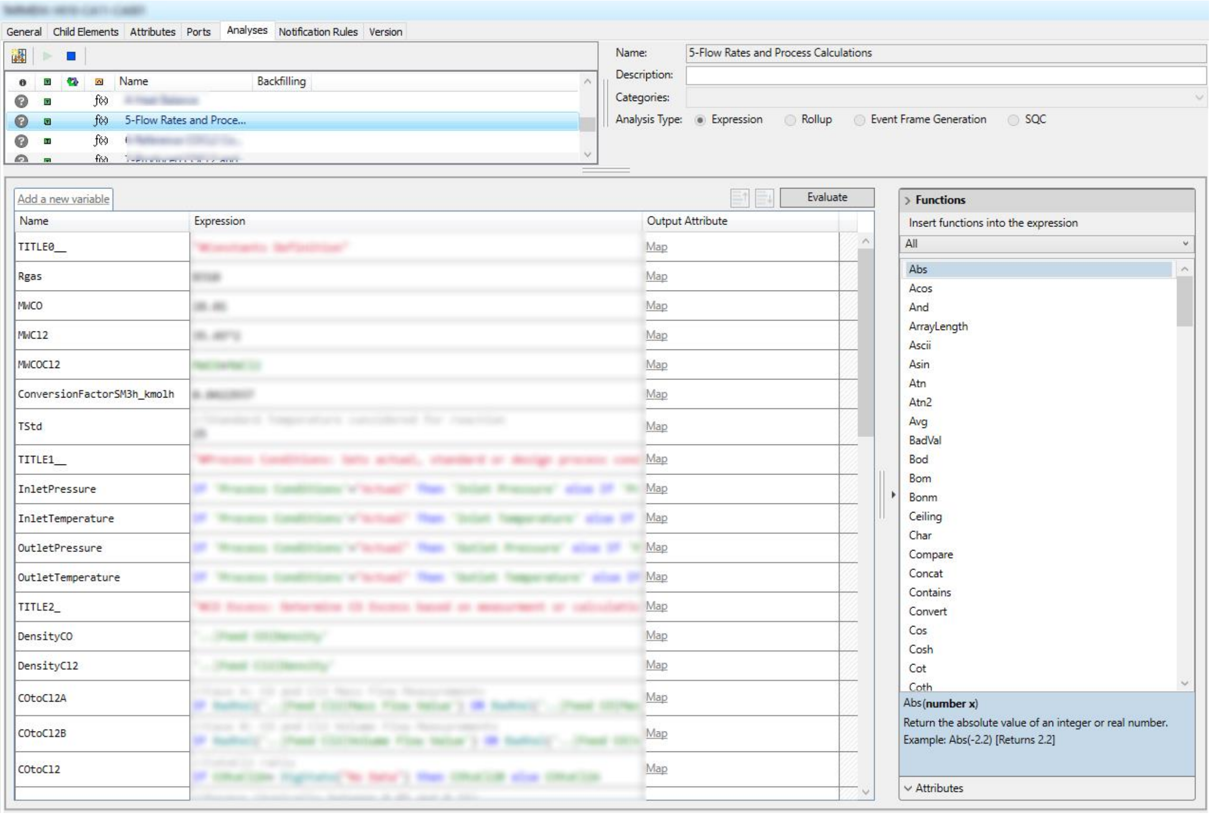


Activated Carbon Type
Alias
Area
Calculation Method
Catalyst Amount
CO Supply Setup
Constraints
Deployment Status
Description
Instrumentation Score
Name
Number of Tubes
Process Conditions
Short Name
Template
Template Group
Tube Diameter
Tube Thickness
Version
cp_Cl2
cp_CO
cp_COCl2
cp_Coolant
Design Inlet Pressure
Design Inlet Temperature
Design Outlet Pressure
Design Outlet Temperature
Reaction Enthalpy
Standard Pressure

Figure 11.6 PI AF Screenshot Num. 3

Here EXCEL-like window is used to define the asset. This amount of cells just represent an small percentage of the total necessary information. These can vary from: number of tubes of a Heat Exchanger, instrumentation TAGs, specific heat of the mixture, design pressure of the pipes, etc…

The value written in the cells can be an string (word or sentence), a number, a variable or a function. The most time consuming case is when a function is used, as it must be define in another window called “Analyses” as can be seen below.



Name: 5-Flow Rates and Process Calculations
Description:
Categories:
Analysis Type: ● Expression ○ Rollup ○ Event Frame Generation ○ SQC

Name	Output Attribute
TITLE0__	Map
Rgas	Map
MWCO	Map
MWCl2	Map
MWCOCl2	Map
ConversionFactorSM3h_kmolh	Map
TStd	Map
TITLE1__	Map
InletPressure	Map
InletTemperature	Map
OutletPressure	Map
OutletTemperature	Map
TITLE2_	Map
DensityCO	Map
DensityCl2	Map
COtoCl2A	Map
COtoCl2B	Map
COtoCl2	Map

Abs(**number x**)
Return the absolute value of an integer or real number.
Example: Abs(-2.2) [Returns 2.2]

Figure 11.7 PI AF Screenshot Num. 4

Here a computer program is written so the calculations can be performed. In the top left corner, one can see what is being calculated in that “sheet” of calculation. Once the analysis has been coded, it all summarizes in a function name that is putted directly in the Attributes window.

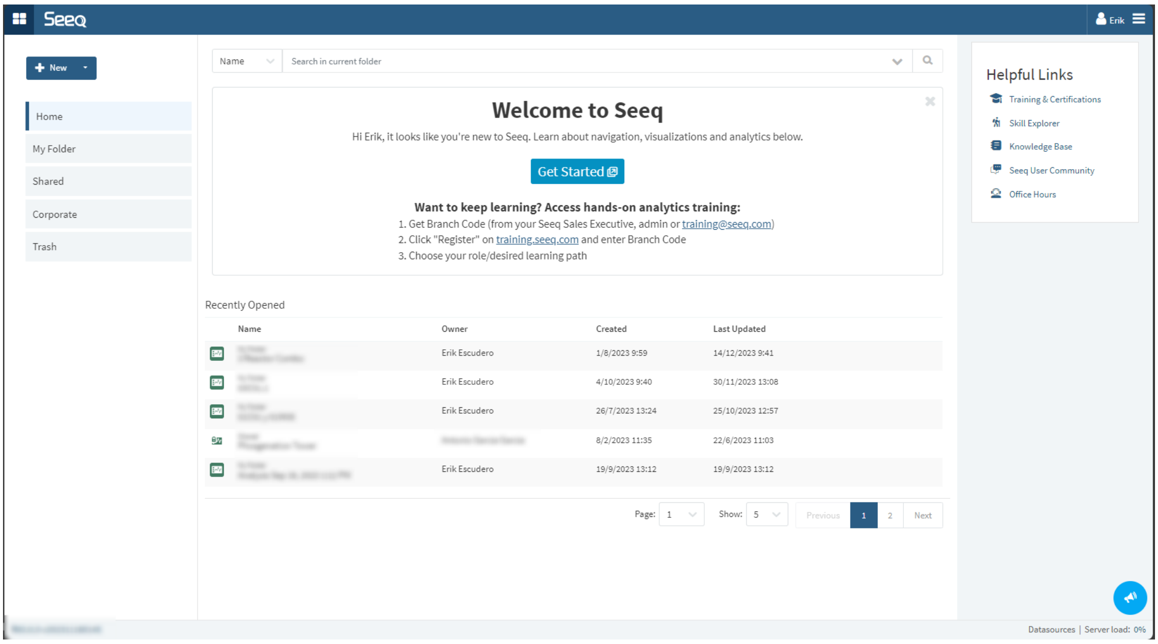
A.3.SEEQ

This section is a brief description of the PI AF software used in this work. To describe the software with just a phrase, it would be:

“Calculation software build to visualize historical data and extrapolate it to the future or extract conclusions from the past.”

To begin, the software is a web application that doesn’t need to be downloaded or updated, but requires specific software and ID authorization provided by VPNs and protection of the computer in order to access it.

Once accessed the first window that appears can be seen below:



Name | Search in current folder

Welcome to Seeq

Hi Erik, it looks like you're new to Seeq. Learn about navigation, visualizations and analytics below.

Get Started

Want to keep learning? Access hands-on analytics training:

1. Get Branch Code (from your Seeq Sales Executive, admin or training@seeq.com)
2. Click "Register" on training.seeq.com and enter Branch Code
3. Choose your role/desired learning path

Recently Opened

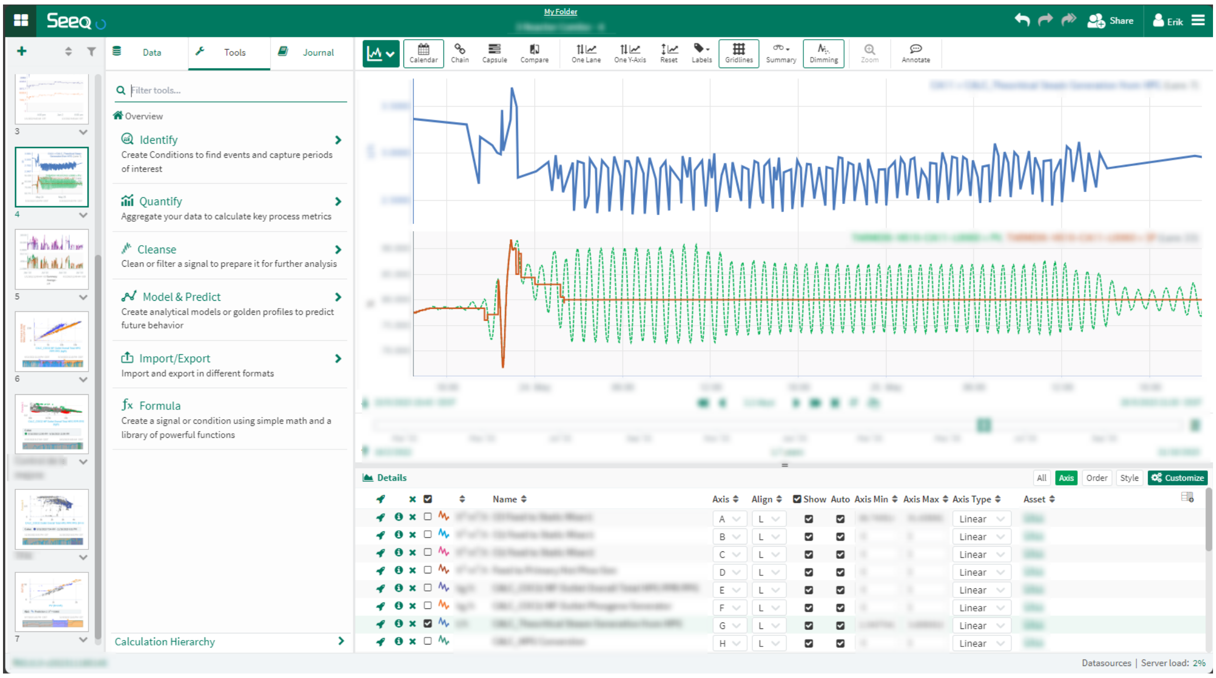
Name	Owner	Created	Last Updated
[redacted]	Erik Escudero	1/8/2023 9:59	14/12/2023 9:41
[redacted]	Erik Escudero	4/10/2023 9:40	30/11/2023 13:08
[redacted]	Erik Escudero	26/7/2023 13:24	25/10/2023 12:57
[redacted]	[redacted]	8/2/2023 11:35	22/6/2023 11:03
[redacted]	Erik Escudero	19/9/2023 13:12	19/9/2023 13:12

Page: 1 Show: 5 Previous 1 2 Next

Figure 11.8 SeeQ Screenshot Num. 1

Here the used can see the recently opened files, all the files or the ones that are shared with him. This shared mode is quite important to the efficiency of the workflow. The share process is done using the email address of the people that is wanted. Tailor access can be give as the user can say if the file can be modified, just seen, just seen in a limited time frame, just some variables, etc… Another important aspect is the history section of the file as one can set a heir of the template in case his activity of the company is ceased or access removed.

Now opening a file the next window can be seen blow:



Filter tools...

Overview

Identify: Create Conditions to find events and capture periods of interest

Quantify: Aggregate your data to calculate key process metrics

Cleanse: Clean or filter a signal to prepare it for further analysis

Model & Predict: Create analytical models or golden profiles to predict future behavior

Import/Export: Import and export in different formats

Formula: Create a signal or condition using simple math and a library of powerful functions

Figure 11.9 SeeQ Screenshot Num. 2

The SeeQ software have more possible aspects and applications, for the sake of simplicity only the historical data gathering part will be explained. At the left site some windows with created sheets can be seen. To its right the main many is displayed, there is where the data is selected, modified or saved. The amount of possible transformations by default is quite overwhelming but increases exponentially when one arrives at the "Formula" section. There, there is the possibility to write tailor-made data transformation algorithms quite easily as the default process are encoded in formulas.

At the far right the plot displayer is set and can be modified using the list blow it. Where from the imported variables a group can be selected to be plotted. The aspect of the plot or the variables can be also changed using this panel.

A.4.FIRST-ORDER TRANSIENT RESPONSE OF LUMPED-CAPACITANCE OBJECTS

The mathematical procurement can be deduced by the definition of this body. I is the define as a body with an uniform internal temperature [T(t)], so it's just time dependent being space independent inside the geometry of the body.

Knowing that the specific heat relation to the internal energy and temperature is as follows:

$$\frac{dU}{dT} = C \quad \leftrightarrow \quad \Delta U = C \cdot \Delta T$$ **Equation 11.1**

This can be differentiated with respect to time so:

$$\frac{dU}{dt} = C\,\frac{dT}{dt}$$ **Equation 11.2**

By applying the first law of thermodynamics and assuming no losses to work transference the next equation is obtained:

$$\frac{\mathrm{dT}}{\mathrm{dt}} = -\frac{\mathrm{hA}}{\mathrm{C}}\,(\,\mathrm{T(t)} - \mathrm{T}_{ext}\,) = -\frac{1}{\tau}\,\Delta\,\mathrm{T(t)}$$ **Equation 11.3**

The equations *Equation 7.29* and *Equation 7.30* are the result of the integration of this final equation.

A.5.PYTHON CODING

In this section the python codes will be showed and explained in detailed after being presented.

The student has wanted to follow the good practices of the coding standards and structure for explanation purposes. The codes could be reproduced in any computed with python capabilities installing the plugins shown in the upper part of the codes.

File - C:\Users\Asus\PycharmProjects\pythonProject1\Thermal_Stress_Final.py

```python
import matplotlib.pyplot as plt
import numpy as np
from functools import wraps
from typing import Callable, List, Tuple

# Define classes
class ThermalCalculator:
    def __init__(self, alpha: float, E: float):
        self.alpha = alpha
        self.E = E

    def calculate_stress(self, delta_T: float) -> float:
        numerator = self.alpha * self.E * delta_T
        denominator = 2*(1 - 0.28)
        stress = numerator / denominator
        return stress

class SteelCoolingSimulatorModified:
    def __init__(self, initial_temp: float, total_time: float, dt: float, tau: float, water_temp: float, calculator: ThermalCalculator):
        self.initial_temp = initial_temp
        self.total_time = total_time
        self.dt = dt
        self.tau = tau
        self.water_temp = water_temp
        self.calculator = calculator

    def simulate(self) -> Tuple[List[float], List[float]]:
        times = np.arange(0, self.total_time, self.dt)
        temperatures = self.water_temp + (self.initial_temp - self.water_temp) * np.exp(-times / self.tau)
        stresses = [self.calculator.calculate_stress(temp - self.water_temp) for temp in temperatures]

        return temperatures.tolist(), stresses

# Redefining the logger decorator
def logger(func: Callable) -> Callable:
    @wraps(func)
    def wrapper(*args, **kwargs):
        result = func(*args, **kwargs)
        print(f"Function {func.__name__} executed")
        return result
    return wrapper

# Applying the logger decorator to the plot function
@logger
def plot_results_with_initial_temp_diff(time_points, temperature_profiles, stress_profiles, initial_temperatures, water_temperature, subsampling_rate):
    fig, (ax1, ax2) = plt.subplots(nrows=2, figsize=(12, 15))

    for init_temp in initial_temperatures:
        subsampled_temperatures = temperature_profiles[init_temp][::subsampling_rate]
        subsampled_stresses = stress_profiles[init_temp][::subsampling_rate]
        temp_diff = init_temp - water_temperature
        ax1.plot(time_points[:len(subsampled_temperatures)], subsampled_temperatures, linewidth=3.0, label=f'Init. Temp. Diff: {temp_diff}°C')
        ax2.plot(time_points[:len(subsampled_stresses)], subsampled_stresses, linewidth=3.0, label=f'Init. Temp. Diff: {temp_diff}°C')

    ax1.set_ylabel('Steel Temperature (°C)', fontsize=16)
```

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Figure 11.10 Thermal Stress Calculation Python Code Part 1

File - C:\Users\Asus\PycharmProjects\pythonProject1\Thermal_Stress_Final.py

```
    ax1.set_xlabel('Time (s)', fontsize=16)
    ax1.legend(fontsize=16)
    ax1.grid(True)
    ax1.tick_params(axis='both', which='major', labelsize=16)



    ax2.set_ylabel('Thermal Stress (Pascals)', fontsize=16)
    ax2.set_xlabel('Time (s)', fontsize=16)
    ax2.legend(fontsize=16)
    ax2.grid(True)
    ax2.set_yscale('log')
    ax2.tick_params(axis='both', which='major', labelsize=16)

    for init_temp, stresses in stress_profiles.items():
        print(f"Initial Temperature: {init_temp}°C, First Stress Value: {stresses[0]} Pascals")

    fig.tight_layout()
    plt.show()

# Initialize parameters
alpha_steel = 12e-6  # Coefficient of thermal expansion in 1/°C
E_steel = 210e9  # Young's modulus in Pascals
original_water_temperature = 212  # Original water temperature in °C
k = 0.01  # Cooling constant
dt = 0.01  # Time step
total_time = 1  # Total simulation time
initial_temperatures = [217, 221, 250, 300, 350, 400]
tau = 0.08  # Time constant for the cooling process

# Create calculator and simulator instances
calculator = ThermalCalculator(alpha_steel, E_steel)
simulators_modified = [SteelCoolingSimulatorModified(init_temp, total_time, dt, tau, original_water_temperature, calculator) for init_temp in initial_temperatures]

# Running simulations with the new model and storing results
temperature_profiles_modified = {}
stress_profiles_modified = {}

for simulator in simulators_modified:
    temperatures, stresses = simulator.simulate()
    temperature_profiles_modified[simulator.initial_temp] = temperatures
    stress_profiles_modified[simulator.initial_temp] = stresses

# Calculating time points for plotting
subsampling_rate = int(0.01/ dt)  # Sampling every 0.01 seconds
time_points = list(np.arange(0, total_time, 0.01))  # Creating time points every 0.01 seconds

# Plotting the results with the modified model
plot_results_with_initial_temp_diff(time_points, temperature_profiles_modified, stress_profiles_modified, initial_temperatures, original_water_temperature, subsampling_rate)

```

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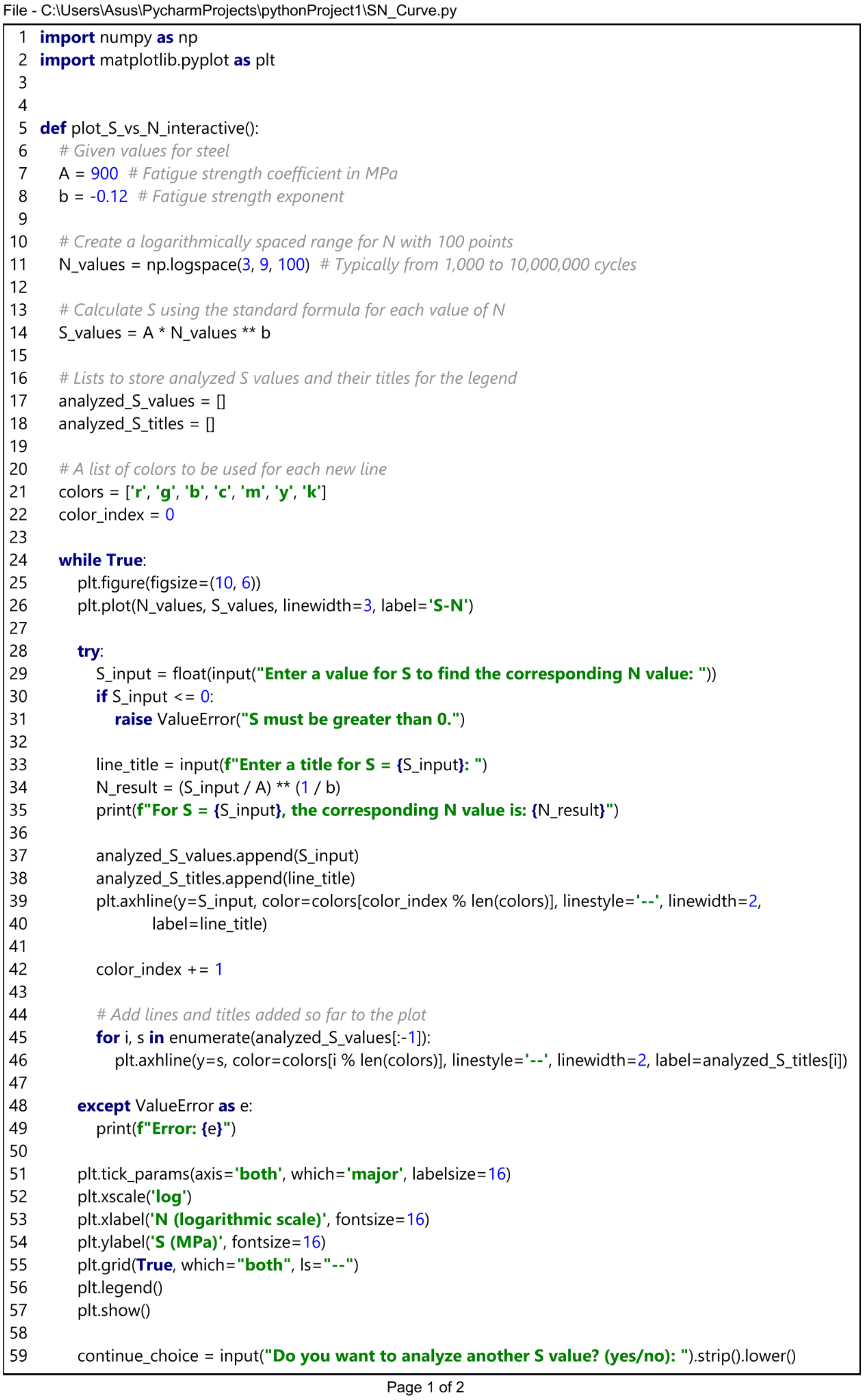
Figure 11.11 Thermal Stress Calculation Python Code Part 2



File - C:\Users\Asus\PycharmProjects\pythonProject1\SN_Curve.py

```python
import numpy as np
import matplotlib.pyplot as plt


def plot_S_vs_N_interactive():
    # Given values for steel
    A = 900  # Fatigue strength coefficient in MPa
    b = -0.12  # Fatigue strength exponent

    # Create a logarithmically spaced range for N with 100 points
    N_values = np.logspace(3, 9, 100)  # Typically from 1,000 to 10,000,000 cycles

    # Calculate S using the standard formula for each value of N
    S_values = A * N_values ** b

    # Lists to store analyzed S values and their titles for the legend
    analyzed_S_values = []
    analyzed_S_titles = []

    # A list of colors to be used for each new line
    colors = ['r', 'g', 'b', 'c', 'm', 'y', 'k']
    color_index = 0

    while True:
        plt.figure(figsize=(10, 6))
        plt.plot(N_values, S_values, linewidth=3, label='S-N')

        try:
            S_input = float(input("Enter a value for S to find the corresponding N value: "))
            if S_input <= 0:
                raise ValueError("S must be greater than 0.")

            line_title = input(f"Enter a title for S = {S_input}: ")
            N_result = (S_input / A) ** (1 / b)
            print(f"For S = {S_input}, the corresponding N value is: {N_result}")

            analyzed_S_values.append(S_input)
            analyzed_S_titles.append(line_title)
            plt.axhline(y=S_input, color=colors[color_index % len(colors)], linestyle='--', linewidth=2,
                        label=line_title)

            color_index += 1

            # Add lines and titles added so far to the plot
            for i, s in enumerate(analyzed_S_values[:-1]):
                plt.axhline(y=s, color=colors[i % len(colors)], linestyle='--', linewidth=2, label=analyzed_S_titles[i])

        except ValueError as e:
            print(f"Error: {e}")

        plt.tick_params(axis='both', which='major', labelsize=16)
        plt.xscale('log')
        plt.xlabel('N (logarithmic scale)', fontsize=16)
        plt.ylabel('S (MPa)', fontsize=16)
        plt.grid(True, which="both", ls="--")
        plt.legend()
        plt.show()

        continue_choice = input("Do you want to analyze another S value? (yes/no): ").strip().lower()
```

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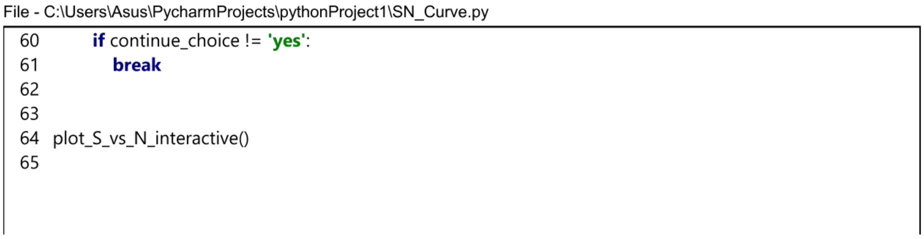
Figure 11.12 S-N Curve Calculation Python Code Part 1



File - C:\Users\Asus\PycharmProjects\pythonProject1\SN_Curve.py

```
        if continue_choice != 'yes':
            break


plot_S_vs_N_interactive()

```

Figure 11.13 S-N Curve Calculation Python Code Part 2

A.5.1. Thermal Stress

This script is design to plot and analyse the stress generated in the mathematical model explained in the thesis. The script uses four add-ons: Matplotlib.pyplot, Numpy, Functools.wraps and Typing.

Matplotlib is used to display the data calculated using Numpy capabilities. Functools is used as a decorator utility for preserving data of the wrapped functions and Typing provide support for type hints.

A part from that two classes have been defined:

1. ThermalCalculator: in charge of calculating the thermal stress
2. SteelCoolingSimulatorModified: in charge of calculating the temperature at different time values.

The only function defined as so is “plot_results_with_initial_temp_diff” that gives the final result of the program.

Inside these three blocks using the typical language form python and it’s four add-ons the mathematical model can be easily visualized if one goes step by step.

A.5.2. S-N Curve Calculation

This script is design to plot and analyse the S-N curve relationship in fatigue analysis. The script uses two add-ons that are imported like: “numpy as np” and “matplotlib.pyplot as plt”. The first one us used for numerical operations and the second one for plotting the results.

In all the plot there is just one function created called “plot_S_vs_N_interactive()” and it’s objective is encapsulate the script functionality.

Inside this function these steps are done iteratively:

1. Properties definition in “A” and “B” coefficients.
2. Generation of the cycle values in “N” using a logarithmic spacer
3. Calculation of the stress values in “S”.
4. Plot initialization entering the “while true” loop
5. User interface asking the desired “S” value and calculation the corresponding “N” and plotting it correctly
6. Error handling with the “ValueError” function
7. Plot customization and display
8. Continuation loop choice

B. SELF-EVALUATION QUESTIONNAIRE

a) Evaluate the acquired **competences** according to the **tasks** you have carried out.

Degree Competences		**Task in which you have observed the competence**	**Self-evaluation [Rank 1 to 10]**	**Aspects to be improved**
SPECIFIC COMPETENCES				
A1.1	Effectively apply knowledge of basic, scientific and technological materials pertaining to engineering.	Definition of the problem and approach to it	9	Better analysis of causes regarding the Heat Exchanger Analysis
A1.2	Design, execute and analyze experiments related to engineering	Implementation weeks	10	
A1.3	Be able to analyze and synthesize the continuous progress of products, processes, systems and services, whilst applying criteria of safety, economic viability, quality and environmental management. (G6)	Designing the new approach to the reactors operation	9	Take into account the secondary events possible. This would have prevented the second iteration to be made.
A1.4	Know how to establish and develop mathematical models by using the appropriate software in order to provide the scientific and technological basis for the design of new products, processes, systems and services and for the optimization of existing ones. (G5)	Using the new tools provided by the company like SeeQ, Pi AF and Pi vision	9	Use examples to familiarize with the software
A2.1	Be able to apply the scientific method and the principles of engineering and economics to formulate and solve complex problems that arise in processes, equipment, installations and services, in which the material undergoes changes to its composition, state or energy content, these changes being characteristic of industrial chemistry and other related sectors such as pharmacology, biotechnology, materials sciences, energy, food and the environment. (G1)	Definition of the methodology and the approach agreed with the supervisors	10	
A2.2	Conceive, project, calculate and design processes, equipment, industrial installations and services in the field of chemical engineering and related industrial sectors in terms of quality, safety,	Design of the operational procedure of the reactors	8	Take into account the secondary events possible. This would have prevented the second iteration to be made.

	economics, the rational and efficient use of natural resources and the conservation of the environment. (G2)			
A2.3	Lead and technically and economically manage projects, installations, plants, companies and technological centres in the ambit of chemical engineering and related industrial sectors. (G3)	Being highly independent engaging in an active way with coworkers and stakeholders	10	
A3.1	Apply knowledge of mathematics, physics, chemistry, biology and other natural sciences by means of study, experience, practice and critical reasoning in order to establish economically viable solutions for technical problems (I1).	Finding the points of improvement in Seeq	9	Slightly expand the scope of the analyzed equipment
A3.2	Design and optimize products, processes, systems and services for the chemical industry on the basis of various areas of chemical engineering, including processes, transport, separation operations, and chemical, nuclear, elctrochemical and biochemical reactions engineering (I2).	Design of the new approach	8	Take into account the secondary events possible. This would have prevented the second iteration to be made.
A3.3	Conceptualize engineering models and apply innovative problems solving methods and appropriate IT applications to the design, simulation, optimization and control of processes and systems (I3).	Using innovative ways with python and SeeQ to solve the problem	10	
A3.4	Be able to solve unfamiliar and ill-defined problems by taking into account all possible solutions and selecting the most innovative. (I4)	Solving the problem related to the steam production with very limited information due to lack of data	9	Using a more sophisticated method to the approach
A3.5	Lead and supervise all types of installation, process, system and service in the different industrial areas related to chemical engineering (I5).	Constantly checking on the progress in the implementation weeks	10	
A3.6	Design, construct and implement methods, processes and installations for the integrated management of waste, solids, liquids and gases, whilst also taking into account the impacts and risks of these products (I6).	Design of the new approach to the steam generation	9	More iterations would be needed to fully expand the possibilities of the improvement but another window of implementation could not be found

A4.1	Lead and organize companies and production and service systems by applying knowledge and abilities regarding industrial organization, commercial strategy, planning and logistics, mercantile and labour legislation, and financial and costs accounting (P1).	Organize the different shifts into the new strategy trough the implementation weeks	9	Emphasize more that the feedback from the coworkers is needed and important
A4.2	Lead and manage the organization of work and human resources by applying criteria regarding industrial safety, quality management, occupation risk prevention, sustainability and environmental management (P2).	Organize the different shifts into the new strategy trough the implementation weeks	9	Emphasize more that the feedback from the coworkers is needed and important
A4.3	Manage research, development and technological innovation whilst ensuring the transfer of technology and taking into account property and patent rights (P3).	Having a properly documented progress backed up as ordered	10	
A4.4	Adapt to structural changes in society caused by economic, energy or natural factors so as to be able to solve any resulting problems and to contribute technological solutions with a high commitment to sustainability (P4).	The core objective of the thesis is moved by those economic changes regarding energy costs	10	
A4.5	Lead and monitor the control of installations, processes, products, certification, auditing, verification, testing and reports (P5).	Reporting daily during the implementation week and monitoring all related variables	9	Automatize the process flow so is less time consuming
A5.1	Carry out, present and defend (once all the curriculum credits have been obtained) an original individually produced piece of work before a university panel. The work will consist of a professional integrated Chemical Engineering project that synthesizes (TFM1)	Presentation of the work to many juries outside the university with highly positive feedback	10	
TRANSVERSAL COMPETENCES				
B1.1	Communicate and discuss proposals and conclusions in a clear and unambiguous manner in specialized and non-specialized multilingual forums (G9).	The consultors for all used software were non-Spanish speakers	10	
B1.2	Adapt to changes and be able to apply new and advanced technologies and other important developments with initiative	Solving the problems found in the feedback during the implementation	9	Try to propose new solutions although the problems seem non-

	and entrepreneurial spirit. (G10)	week		related to the student
B2.1	Lead and define multidisciplinary teams that are able to make technical changes and address management needs in national and international contexts. (G8)	Being highly independent engaging in an active way with coworkers and stakeholders	10	
B3.1	Work in a team with responsibilities shared among multidisciplinary, multilingual and multicultural teams	During the whole stay at Covestro	10	
B4.1	Be able to learn autonomously in order to maintain and improve the competences pertaining to chemical engineering that enable continuous professional development. (G11)	Being highly independent engaging in an active way with coworkers and stakeholders	10	
B5.1	Carry out and lead the appropriate research, design and development of engineering solutions in new or little understood areas, whilst applying criteria of creativity, originality, innovation and technology transfer. (G4)	Research regarding the unexpected discoveries in the heat exchanger	10	
B5.2	Bring together knowledge, make judgements and take decisions on the basis of incomplete or limited knowledge whilst taking into account the social and ethical responsibilities of professional practice. (G7)	Defining how to stress-test the system during the implementation weeks	9	Some non-expected issues emerged that could have been seen with more bibliographic research in similar fields
NUCLEAR COMPETENCES				
C1.1	Have an intermediate mastery of a foreign language, preferably English	The use of English and German was daily due to the documentation format	10	
C1.2	Be advanced users of the information and communication technologies	Communication has been a key factor during the stay at Covestro	10	
C1.3	Be able to manage information and knowledge	Using the correct theorical methodology	10	
C1.4	Be able to express themselves correctly both orally and in writing in one of the two official languages of the URV	In the writing of this thesis and on the presentation regarding it	10	

C2.1	Be committed to ethics and social responsibility as citizens and professionals	During the whole duration of the internship	10	
C2.2	Be able to define and develop their academic and professional project	Full freedom to develop the thesis in the shape and form that the student wanted	10	

Key steps	**Evaluation [Mark 1 to 10]**	**Improvement proposed**
Selection/assignment of the project (dissemination, communication, assignment requirements...)	8	A more defined schedule
Stay (welcome, length, relationship, follow-up made by the company...)	10	
Follow-up made by URV tutor	8	A more defined schedule
Other aspects to be considered (which ones...)		