CIMAT

Centro de Investigación en Matemáticas, A.C.

METHODOLOGY TO ESTIMATE LIFE CYCLE INVENTORY FOR EARLY DESIGN OF A CHEMICAL PROCESS

T E S I N A

Que para obtener el grado de
Maestro en Modelación y Optimización de Procesos

Presenta
Moisés Cortés Jerónimo

Director de Tesina:
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For my parents.

Abstract

Currently there is a good deal of chemical process placed within the production value chain in the global economy. Enriching, expanding and designing not only products but also processes while following international environmental standards either by reducing environmental burdens connected with services, products and processes or by making industrial processes, services and practices chasing sustainability is a must-do activity. The life cycle assessment is a valuable tool that names all the direct and indirect environmental consequences or impacts caused by the industrial processes; if the energy inputs and outputs of such processes as well as their residual materials are identified many innovative practices can take place, for instance: planning strategies considering the environment, selecting more sustainable waste and residual policies, designing and improving products, making comparisons of similar products or processes as well as optional designs of processes aiming to lower environmental impacts. In order to apply the life cycle assessment and develop any of the previously mentioned innovations, scope and goals must be declared in doing so we will start to gather inventory data. Putting together characteristic inventory data (of energy and material flows) is essential and useful to create a proposal which will meet the expected project's goals. This is a key step within the LCA methodology because once this inventory data is gathered it will be evaluated and deciphered so that a decision according to the purposes of the study can be taken. However, many projects deal either with a shortage of information or with an inability to access the available information - many projects are restricted because of copyright status or the confidentiality of the companies which sponsored them. This work presents a methodology to estimate a life cycle inventory for early design of any chemical process. Even though this methodology can help any industrial chemical process it will be especially useful for projects focused on the chemical and chemical pharmacological sectors since most projects connected to such areas usually come across a lackness of data and this is a huge obstacle that most of them can not easily over-

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come. This work represents a priceless technical path due to the fact that helps to reduce the amount of time and effort invested in the search of industrial and academic projects. Another benefit of this methodology is that it predicts the inventory data for ranges different from those presented in any simulator software. By combining engineering and statistical tools and this work is able to obtain precise data that will facilitate the decision making process keeping in mind international environmental guidelines such as ISO 14040 either to improve, redesign or create new processes or policies. This decision making process is found within a case study. Such case study is basically an investigation which must have the following steps: defining goals and scopes, obtaining a life cycle inventory data, pointing an environmental assessment impact,interpreting the results of the environmental assessment impact, and finally taking a decision is the last step in this case study. This thesis creates through both the combination of linear regression and the simulation software Aspen a new framework able to work out the specific quantity of energy and material flows data needed to cover the life cycle inventory - which is the core of a life cycle assessment guideline. This present work displays a case study that presents the implementation of a process simulation and the usage of a statistical modeling and how through their application of these tools it is possible to overcome the lackness of available data inventory in a chemical processes and to carry out a reliable study of LCA before the process is scaled up.

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Introduction

Summary

In this section, a briefly introduction to the environmental problems presented in chemical industries and how to deal with is posed. The motivation, objectives, scopes, and a general overview of this work are presented.

1.1   Motivations

Pollution worldwide problem is growing everyday and according to Khoo *et al.* [2018], in many industries like chemical and pharmaceutical, the implementation of sustainable practices in their business operations to tackle pollution is a common task. Similarly, Righi *et al.* [2018] mentions that due to the main role that the chemical industry plays within the economy value chain, the design and creation of new sustainable products and processes with less environmental impacts has a key role.

Carrying out an early-stage analysis of the environmental impacts of any product allows having information to guide and support research and development that lead to reduce the generated emissions. Therefore, evaluating environmental impacts from the early stages of process design is essential to achieve adequate solutions in terms of eco-efficiency and sustainability.

Khoo *et al.* [2018] pointed out that although green chemistry and process intensification have become more relevant as frontier topics for research and development

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in the chemical and pharmaceutical industries, the application of effective environmental management tools to analyze the environmental performance of all kinds of products during their manufacture should not be left aside. Life cycle analysis (LCA) has positioned itself as the most widely used resource to assess the environmental performance of both petro-based and bio-based chemicals and solvents.

LCA, a globally recognized and wildly established tool for environmental sustainability, works as a guiding system provided by ISO14040 [2006], to oversee the lifespan of a product since the early stages of its creation, its path and life in the market, as well as previous stages in the production chains, until the very final stages: disposal and recycling. The intention is to grade consequences on the environment, once graded, those results are applied on eco-design by pointing out conflictive centers of activities and areas with low efficiency and delays within the production path as well as making comparisons of the material with products that are alike.

The top-specialized guiding method to apply an LCA technical framework involves four stages:

- defining goals and scope,

- analysing the input/output inventory,

- assessing environmental impacts

- interpreting results.

Khoo *et al.* [2018] mentions that inventory analysis is the core stage among all the phases but the required data for carrying out an LCA are neither directly obtainable nor measurable, furthermore collecting data is both a high-demanding activity and challenging for the development of the LCA.

The advantage of carrying an LCA study out at early research stage of a new product allowing a wide-range flexibility due to the fact that modifications can be easily-attained from both cost view and technical view. Even though using LCA at

the first-research phase has shown to be flaw, in terms of data availability. pioneer laboratory processes do not operate inside an optimized environment, and are not the best scenarios of real-efficiency results, Piccinno *et al.* [2018]. Therefore when doing a comparison with a competitor the second-research phase of LCA does not favor the new product on the contrary it undervalues this new product from any late capability than it may offer.

Righi *et al.* [2018] indicates that the scant information, which may be available, is usually obtained from laboratories, scientific literature and process' patents. Scant information later would be used for the preliminary energy and material process scale-up. Process scale-up is a complex activity due to the resources (time and financial resources) needed to pass from a laboratory scale to an industrial scale, because the technologies and performance (yield, energy demand, etc.) of single operations may change significantly.

The main research topic at this work is the inventory analysis, also called life cycle inventory (LCI). The intention is to make easier the process of gathering information, especially information related to early research stage. In an LCI, flows(raw material, energy, emissions) of the production process must be quantified. Using well-known input/output libraries allow to obtain high-quality data. Whenever brand new technologies emerges, they demand data. This may represent such a big challenge due to the fact that these technologies may be the first of its kind. The well performed development of LCA investigations relies on adequacy and quality of data that is obtained and used. This data-obtaining process can be arduous, and the data may be non-existing as in the bio-derived material niche because of commercial privacy.

1.2 Context of the Study

A gate-to-gate LCA study requires a LCI where the exact amount of each raw material, the detailed energy consuption as well as the specific waste and emissions generated by each unit process are know. As the boundaries are expanded, more data are going to be needed for LCI, as transportation mode, shipping distance of

routes and information on disposal management.

The central point of the work is to reduce the time that an engineer could spend obtaining the LCI in a research. It is proposed to use both simulating and statistics tools for modeling and inferring data needed. So, in future when an LCA will be carried out this methodology would permit to have access on an easier way to obtain the inventory of an industrial process, mainly for the chemical industry.

This work will provide a methodology that facilitates the LCI stage in an LCA study at early stages of a chemical process. In addition, a reliable data set about the production process of styrene as a study case, which will work as a sample, and that will show how this groundbreaking technique can be performed. Styrene process has been selected due to several authors have used it for analyzing in different researches, so it makes easier to obtain data for developing the methodology.

Styrene, an exudate produced in sapwood and bark of Liquidambar orientalis and L. styraciflua trees, was discovered in 1831 as result of the distillation of storax balsam. Styrene became relevant until World War II, when the United States began developing synthetic rubber. Since then, styrene is one of the most important chemical products and it is used in the manufacture of numerous products in addition to synthetic rubber. Nowadays, the packaging of several foodstuffs (sliced meat, fats, dairy products, etc.) is possible thanks to styrene-related polymers, Miller *et al.* [1994].

This methodology measures all the inputs and outputs on equipments (energy, material and emissions) used in any kind of production, this is possible due to the fact that the standard ISO 14040 sets guidelines,principles of practical mathematical equations and chemical engineering to achieve it.

Furthermore, the methodology involves specifically a simulating program called Aspen Plus, version 2006, which is especially used to model chemical processes and provide reliable data on how both supply as well as energy moves through any chem-

ical process. It also provides statistical modeling tools which are used to model and evaluate the data that is obtained.

1.3 Objectives

1.3.1 General objective

To propose a methodology that allows to identify the flows of material and energy most representative of a chemical process to create an LCI and then easily implement it into the early designing phase of LCA in an industrial scale.

1.3.2 Specific objectives

- To develop a reliable strategy that could be used in further researches in the chemical processes field.

- To apply the strategy firstly mentioned in a case study.

- To provide both a dataset and a tool for future researching in chemical processes.

1.4 Overview of the Thesis

The idea of this research is to use simulation software and statistic methods to facilitate the achievement of an LCI, in consequence making easier the LCA implementation. The research approach is focused on chemical process however the final product could be used in other fields.

The thesis outline can be summarized as is shown in the following points:

- Section 1 presents relevant literature about LCA, including LCA history, its evolution over time and LCA applications in different areas. The four LCA stages are reviewed with particular emphasis in the LCI stage. The principal

challenge to apply an LCA is described and a few options found in literature about how this issue has been handled are presented. In the end Aspen Plus and Statistical Modeling Tools, especially regression analysis, are introduced as potential medium to deal with the LCA challenge.

- Section 2 explains how the tools mention above were used to construct a methodology which allows obtaining inputs and outputs flows (materials, energy and emissions) in a chemical process, in other words for accomplish the LCI. The method consists of 5 steps, firstly the system analyzed must be understood thus, goals and scopes will be set. Secondly the simulation related to the system will be performed. As third step, the simulation must be verified and validated, this process need to be done through the construction of the simulation. After that, getting data for analyzing the behavior of an LCI will be required, for this reason a variation in the input parameters are applied and finally by using the data obtained above the statistical modeling tool is implemented.

- Section 3 illustrates the methodology developed with an application on the industrial production process of styrene. In the beginning chemical components, chemical reactions and flow sheet of the styrene are introduced.

  Then, using Aspen Plus the model starts to be made and a short description about how it was carried out is presented. Subsequently, when the simulation runs without errors, the parameters variation is made and statistical models are obtained.

  After all, plots of the data obtained and equations of modeling are reported.

- Section 4 summarizes the work and emphasizes its contributions. As well as suggestions and directions for further researches are given.

Chapter 2

Theoretical framework

Summary

This is the introduction to relevant literature about LCA, including LCA history, its evolution over time and LCA applications in different areas. The four LCA stages are reviewed with particular emphasis in the LCI stage because LCA represents the LCA core. The principal challenge in an LCA is and a few options found in literature about how this has been handled. In the end Aspen Plus and Statistical Modeling Tools, especially regression analysis, are introduced as potential medium to deal with the LCA challenge.

2.1   Life Cycle Assessment

2.1.1   Definition

According to Jiménez-González & Overcash [2014], LCA is a framework that allows to work out ecological stress coming from input and output of the supply chain. Therefore the input and output of energy needed will be both measured and studied in every single phase (raw material extraction, conversion, manufacturing, shipping).
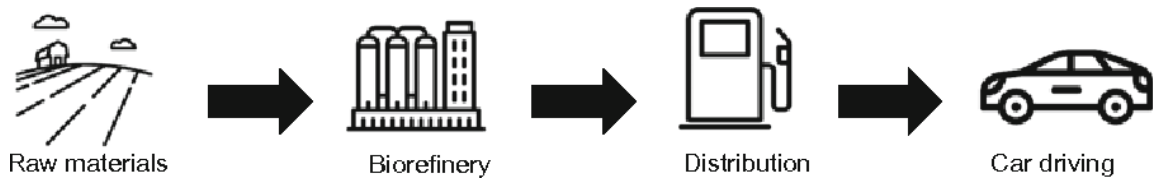
Figure 2.1: Lifespan and process of biofuels, Dijkman *et al.* [2018].

2.1.2 History

Regarding to Dijkman *et al.* [2018] by 1960 the concept of LCA has already been spreading as both environmental degradation and natural resources became a social concern. LCA was first used in packaging studies by analyzing energy use and only some emissions. These studies stimulated the development of a largely uncoordinated method in the United States and northern Europe.

Studies were mainly performed by companies, which kept them for internal usage and only rarely were they shared with stakeholders. Since 1970 there has been an increasing teamwork to share and develop among academic centers and the scientific society methodological development.

From 1997 to 2000 a structured way to perform LCAs was set in motion by the Organization for Standardization which was the first step into creating the standards ISO 1404,14041,14042 and 14043. In 2006 an update was made to the standards by merging them into the ISO 14040 and 14044.

Once seated the methodological basis, a significant growth in LCA applications was observed both in products and systems made by industries and by governments. The results achieved from these studies were increasingly accessible through academic papers or technical reports. Today, the scientific community worldwide continues to strengthen the LCA methodological framework to incorporate new technological developments in emission measurement and characterization, Dijkman *et al.* [2018].

2.1.3 Application areas

There are many commonly used references on LCA applications not only in the private sector but also in the public organizations. The following tools and method checklist were extracted from ISO14040 [2006] and and they can benefit from using an LCA methodology.

- Environmental Impact Assessment (EIA);

- Environmental Management Accounting (EMA);

- Assessment of policies (models for recycling, etc.);

- Product stewardship, supply chain management;

- Life Cycle Management (LCM);

- Life Cycle Costing (LCC).

Given the flexible nature of the LCA, it is not possible to determine which is the best way to implement it as part of the process of reflection for decision-making in an organization. Therefore, each organization has to solve and decide how to use the LCA on a case-by-case basis taking into account aspects such as the size and culture of the organization, its products, strategy, internal systems, tools and procedures, and external drivers, ISO14040 [2006].

2.1.4 Evolution

McManus & Taylor [2015] establish that the industry, policy makers and academia have embraced the use of LCA, making it a famous technical guideline. As climate and sustainability issues started to get attention so did LCA. It did so by using scientific research publications.

In a short time, the number of LCA-related publications has grown considerably. From 1961 to 1975 at least one publication per year was done but since 2008 the

number of new publication has increased rapidly. Figure 2.2 shows annual LCA related publications throughout 1991 to 2019.

Annual LCA related publications
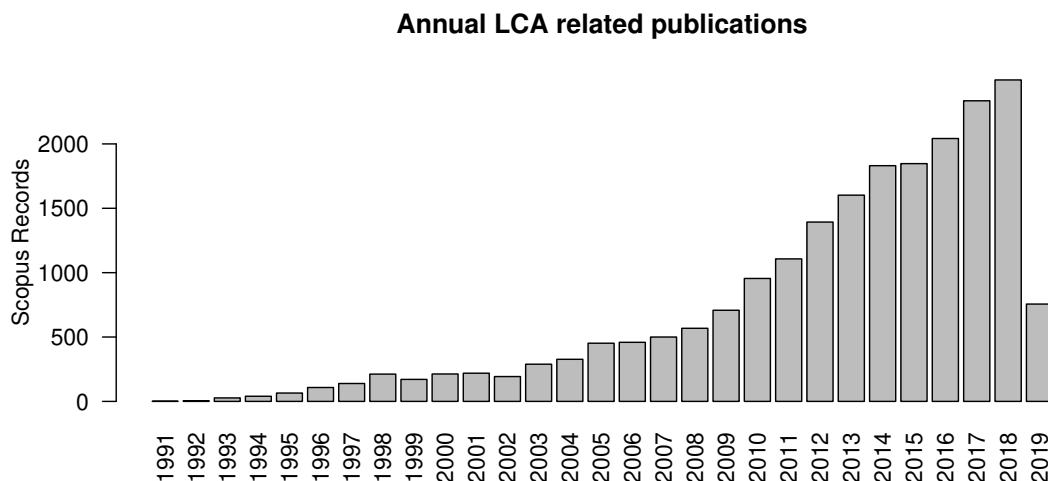
Figure 2.2: Evolution in the increasing numbers of articles and academic papers showing LCA's framework ("Life Cycle Assessment"), since 1991 to March 2019 according to the data on Scopus; this search was made on March 25th 2016.

Two periods are distinguished, in the first the moment in which the foundations of the technique begin to be established, so the number of publications is very small, while in the second period there is a strong expansion that reflects their recognition.

Table 2.1 shows crucial examples depicting how the LCA has evolved as a practical application tool. Here are some significant illustrations of this evolution in real-case scenarios:

- Boustead (1979).

  The pharmaceutical and chemical niche needed to make materials and chemicals-glass milk bottles; to obtain this they agreed to send their data production to an independent group. This date was later analyzed and its average showed the Gate to Gate's LCI in making a chemical component. This is a big-time

Table 2.1: Descriptive case studies of the historical progress of life cycle usages, Jiménez-González & Overcash [2014].

Year	Illustrative example
1969	Coca Cola (Type of packaging)
1962	REPA (Resource & environmental profile analysis) (Mobil/polystyrene tray)
1979	Boustead (Glass milk bottle)
1973	Germany (Degradable plastics)
1974	Initiation of public life cycle thinking (e.g., REPA, Plastics, Solid waste, Primitive impact assessment)
1975	U.S. Federal Energy Agency - Solid waste to energy.
1977	Switzerland - First accessible database - BUWAL
1987	Germany - Creation of economic equivalent of life cycle
1990s-present	Specific case studies - targeting a given plant, process, or product
1990	Paper versus plastic - public awareness
1990 - 1993	SETAC-Europe (Development of life cycle method)
1993	European Plastics Study - Aggregate Industrial Methodology
1995	Process or Design-based LCI
1998	Economic Input Output Life Cycle Inventory
1997 - 2006	ISO Standardization of life cycle assessment
2000spresent	Streamlined LCA tools

approach action, every single chemical would need between 6 months to 2 years to be totally developed. Furthermore deciding which suppositions should each contributor chose is a hard-task move due to the fact that they will chose the same. The plastic Europe 2005 data is a proved sample on how LCI usage evolved within LCA's framework.

- SETAC-Europe.

  This company's contribution to LCA was defining how obtaining data is the most important stage to develop any LCA.

- Specific case studies.

  This means that isolated cases, measuring sources, cannot be entirely reliable for LCA's usage because different companies can set different criteria to measure and limit the data used. This makes impossible to integrate different studies not only because they did use use the same boundaries but also because these researches were almost never shared to the public.

- Economic input-output (EIO). EIO use national economic data obtained from critical national policy needs as a framework to assess environmental impacts. The indirect/overhead and the direct use of energy and chemicals applied in any manufacturing process are estimated from the economic connection between industral sectors.

- Process or design-based LCI.

  When working on one of the several chemical manufacturing processes of the life cycle of any chemical, it is common to take as a guide already-created patterns, can be either industrial designs or engineering designed formulas or equations. Both engineering and chemical principles are available for all the academic sector,public and scientific community and thus they can be used to create process data as LCI in any other field and theoretical project. It has been proved that generally this implementation faces approximately with a 10 percentage to 30 percentage range variability.

- ISO Standards.

  ISO standards has made it possible to set boundaries on the guidelines for the LCA methodology and to lead while using its LCA's standards.

  The International Standardization Organization has worked to achieve standardized technical methods to develop LCA's ideas, including Environmental Product Declarations and establishing the Product Category Rules.

The shown cases indicate how crucial it is to get the LCI, and therefore it represents such a big challenge for an LCA.

2.1.5 Phases

LCA indicates and involves potential and non-potential environmental outcomes in every phase of the LCA starting at the acquisitions of raw materials and then in the production phase, usage, end-of-life handling, recycling and final disposal just as ISO14040 [2006] points. The standards of ISO 14040 (2006) describes only 4 stages for a complete LCA study.

- **The goal and scope definition phase**, an LCA study will always be defined according to the subject it is aiming to work on, this subject will help to define the limits and how well detailed it should be. the dimension of LCA studies will always change because each one of them always has unique and specific LAC goals.

- **The inventory analysis phase**, it is a huge data storage of energy and materials that flow in and out of the selected area by the study. This phase fullfills the goals, of the previously defined study, by gathering any data that might be required in order to use it in the LCA.

- **The impact assessment phase.** The target of Life Cycle Impact Assessment (LCIA) is to improve formerly used information from previous phases in order to escalate how well the results are being valued, this represents reckoning and identifying the environmental impacts and their importance.

- **The interpretation phase** the closure stage of any LCA application, outlines and values the outcomes of any LCI and LCA that might have been done, so that leads for conclusions can be obtained always meeting previously defined targets.

Figure 2.3 summarizes the four stages of an LCA previously described.
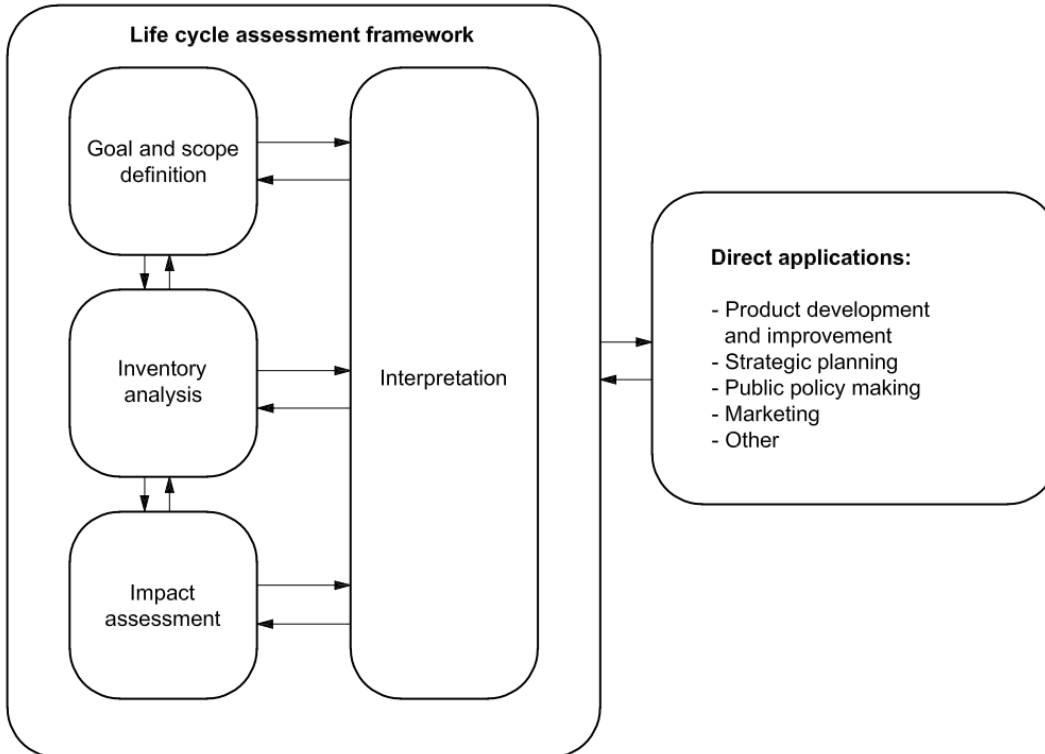
Figure 2.3: Stages of an LCA.

2.1.6 Scopes

It is common to find different scopes in the development of an LCA, as reported by Haya [2016]. The most frequent are the following:

- **Gate to gate scope:** for studies that exclusively apply LCA guidelines in the production processes.

- **Cradle to gate scope:** this is an LCA highlighting the data involving the material's extraction until it is about to be transformed by industrial processes.

- **Gate to grave** considers the production process of the company and covers until the stage of waste management to which the product gives rise.

- **Cradle to grave scope:** studies that work LCA standardization policies from the extraction to the pre-process stages, production process, the management of waste,which might be created during the production, until the disposal or the recycling of the product.

Figure 2.4 set five main stages of the product lifetime, starting with the row material and distribution, and finishing with disposal and recycling stage. Each scope is illustrated including its stages covered.
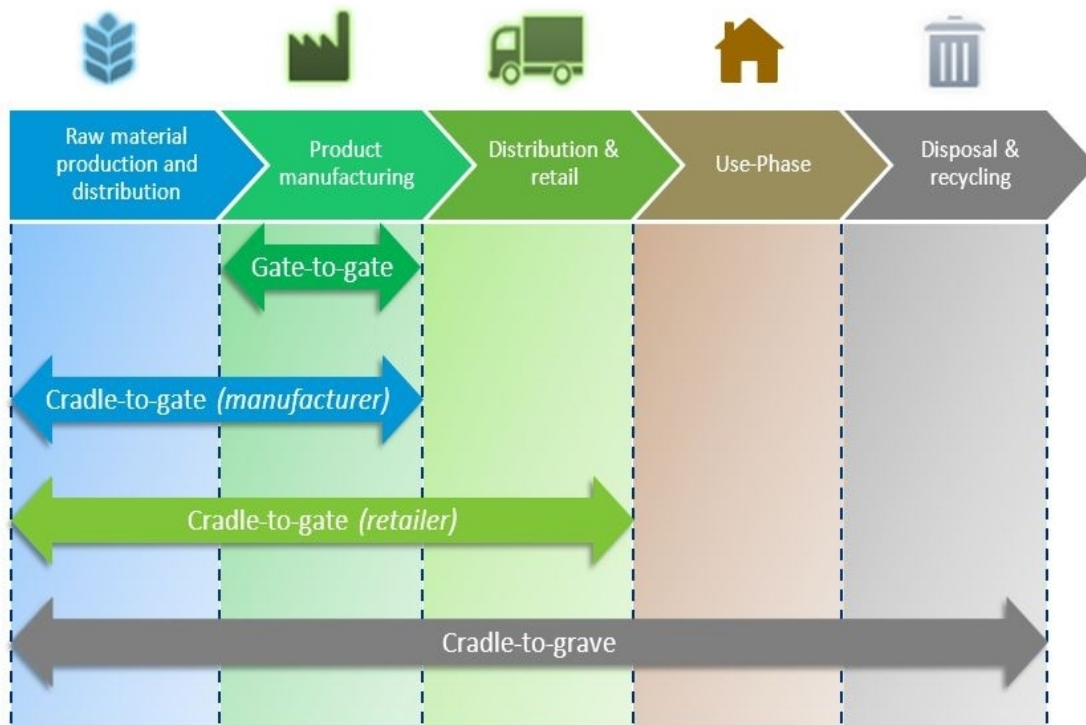
Figure 2.4: LCA scopes, SlydePlayer [2016].

2.2 Challenge

2.2.1 Obtaining appropriate data

There is a significant absence of most of the raw materials data ,which is essential to design and create new products. To overcome this lackness of data there are 3 leading schools which approach this problem differently. It is important to point that all of them have both inconveniences and benefits.

i) **Life cycle thinking**- the pre-evaluation and the evaluation, either on drugs or other chemicals, make changes by evaluating connections within the product's process. By pointing out how several nods of a system modify the environment they are linked to we can make changes into the links of the process. (There is a need to constantly know how a product's system damages the environment).

   The stored information required to summarize this stage is both barely existing and less specific, because of this qualitative data or standard-like LCA tools will be used to obtain an early sight of the impacts. As life cycle thinking has a qualitative nature, it is handy to use it to measuring environmental impacts.

ii) **Current commercial software and databases and streamlined tools** - many software have been created to process LCA's guidelines. They are easy-to use, some of the well-known are SimaPro, Ecoinvent and Boustead. there are streamlined tools that come in handy either; GlaxoSmithKline (GSK), one of many software companies, has created tools to work in LCI and LCIA. Recognized Academic entities using these software and streamlined tools are the American Chemical Society of Green Chemistry Institute Pharmaceutical Roundtable, the UNEPs LCA Initiative, Lyfe Cycle Regional Networks, ACLCA, Calcas, CCaLC and ETH.

   The downside of studies, which cannot access to real data and thus are using software and streamlined tools, is that these software and tools will give them acceptable quantitative values but barely-reliable qualitative values.

   Many process trying to cope with data lackness by using software and streamlined tools have proved that the information obtained by using them is smoky

gate-to-gate data. This non-transparent data often includes a variety of allocation systems, whose data cannot be universally applied. Another of the drawbacks of using software and streamlined tools to generate data is that they use data which cannot be tracked (because the data might be patented).

iii) **Engineering-based life cycle assessments** - using established manufacturing process principles to supply gate-to-gate analysis is another approach to supply data for an LCI. This approach is wildly respected, as a source, because of the forward steps that science is constantly taking; this data is not only reliable but also transparent (about the engineering calculations, assumptions used in the unit operations of chemical engineering). Another benefit of this approach comes from how easy it summarizes the production data and by doing that it provides legitimacy.

The unit process analysis is a long-time consuming task, this is consider a disadvantage. Despite this it offers a couple of benefits: the first is a whole comprehension of the main factors that an LCI faces. The second is that by the time that we comprehend those given factors we can start to create streamlined tools to tackle them, ultimately this will help in the final-decision process.

2.3   Life cycle inventory analysis (LCI)

ISO 14040-2006 sets that the inventory analysis process will require data collection and procedures assessment to summarize inputs and outputs linked to a product system. Performing an inventory analysis is an iterative procedure. The more data on inputs and outputs of a product system is stored, the more easily the process is understood by the researchers, since data are steadily gained more command about the case study will be held. Constrictions could emerge in this iterative process, this can be an opportunity-scenario because we can increase the whole factors that impact an LCI process. Probably, this will modify the data collection procedures in order to meet either the scope of our project or its targets.

2.3.1   Data collection

According to ISO14040 [2006], data can be broken down under the following categories:

- energy inputs, raw material inputs, ancillary inputs, other physical inputs,

- products, co-products and waste,

- emissions to air, discharges to water and soil, and

- other environmental aspects.

ISO14040 [2006] highlight that collecting data is such an important process which demands a lot of resources. Similar and practical databases should be considered. It should always kept in mind that the studied data comes from an environment that may have special constraints, they should be considered taking into consideration the target study, else the data can not fully help our LCA's study.

2.3.2   Functional Unit

The main goal of a functional unit is to highlight a quantitative reference on the links of the inputs and outputs which are used in the manufacturing process of any product. Such quantitative data reference is key to guarantee doing an LCA-result comparison. Evaluating the LCA results, on different systems, can only be possible if such process grades them taking as reference a principle that both of them share.

Defining the input and output linked to the manufacturing flow will determine the amount of supply required to both evaluate and develop the functional unit process.

For example, in the function of baking bread by using ovens, both a gas oven and an electric oven will be analyzed. The selected functional unit may be determined by 1 kilogram of bread. It will be feasible to obtain an inventory of inputs and outputs for both systems on the basis of the reference flow. In the case of generating 1 kg of

bread in a gas-based oven, this would be reflected on the volume of gas consumed to generate a kilogram of bread. And in the case of the electric oven it will be projected on the amount of electricity needed to generate one kilogram of bread.

2.3.3 Data calculation

After collecting data, the next phase is calculation procedures. This phase involves:

- validating the collected data,

- linking the data to the unit processes, and

- understanding and connecting the information to the reference flow of the functional unit, this will be required to create the results of the inventory in every single unit process with a defined system and, so, the defined functional unit of the product system will be modeled later, ISO14040 [2006]

The computation of energy flows has to consider the various fuels and electricity sources demanded by the process, how the energy distribution processes flow -and how efficient their conversion is, in addition to the inputs and outputs connected with the generation and usage of the energy flow.

2.3.4 Data sources

The data can be obtained from different types of origins, which can be sorted as the table 2.2 describes.

If applying data from and electronic base, specialized literature or any other academic publications, it is needed making sure that such databases are both reliable sources and relatable. Those databases should meet and relate with the target objective and the system scope formerly established, Sonnemann & Schuhmacher [2004].

Unreported data sources and technical computational sources are useful for collecting technical knowledge since data collection can display significant variations on how available the input and output data are. Input documentation is easily obtainable for both energy and raw material usage because they are commonly recorded

Table 2.2: Data source, Sonnemann & Schuhmacher [2004].

Source	Description
Digital databases sources	There are many LCA databases available to study they can be fed though Internet sources and public and commercial software
Specialized literature sources	Academic papers and projects on already created LCA studies
Unreported data sources	This kind of data can be extracted from research academic centers, leading authorities on a scientific field, laboratories, etc.
Technical computations sources	Obtained by using manufacturing engineering principles.

by the industry. There are companies which have steady production outlines, in those cases the energy usage per product can be obtained from the total numbers of consumed energy. For non-steady outlines, energy consumption will be obtained by calculating the usage of energy demanded by every single process. Output data on the one hand are easy to find when it is about the main products and its subproducts, on the other hand they are difficult to adquire for other processes. This lackness of data is caused by both the shortage of control records of all releases, and the inability to find already-existing data to the individual product. This industrial trait depends on how big the studied company is. However, this output data availability issue can be evaded in some cases by performing mass and energy balanced using a few of the inputs to calculate output data. Addressing the lackness of data with this technique can be more precise than usign data from direct measurements of both process emissions and releases.

Using simulations is another path to come across LCI. For instance, Schultmann *et al.* [2004], Spatari *et al.* [2009] or Sajid *et al.* [2016] focus on chemical process and they all have used Aspen Hysys or Aspen plus software to simulate the production process and to obtain input/outputs of energy and materials.

2.3.5   Aspen Plus

Aspen Plus, a modeling tool able to figure out crucial engineering and operational obstacles, can supply a substantial assets database, as in the cases of physiochemical properties and property methods. This software is also capable of testing and figuring out problems within a unit process. When working with integrated and complex process, the use of Aspen Plus is a reliable way to set and highlight unit operations.

Chemical processes simulation has already been performed using Aspen Plus, for example, methanol synthesis in Petersen *et al.* [2015], the combustion process in Hu *et al.* [2018], carbonating process in Rupesh *et al.* [2016], combined heat and power process in Ong'iro *et al.* [1996], cement plant processes in Meunier *et al.* [2014]. Aspen Plus can help obtaining a simulated process performance by taking into account mass and energy balance, chemical and phase equilibrium, thermodynamic properties and reaction kinetics.

Industrial problems are usually arduous and therefore hard to solve by hand due to both their time consumption and human error. It is more reliable to use Simulator programs to foretell process behaviors within an industrial environment. Aspen Plus is a well-known software to solve these situations especially when calculating thermodynamic modeling, such as heat capacity, density, thermal conductivity, surface tension, diffusion coefficient, and viscosity. This software solves engineering process by offering psycho-chemical traits, industrially-focused templates, sensitivity analysis, scientific designs of unit operations.

Another usage of Aspen Plus comes when working with oil and gas production, chemical processing, coal gasification, environmental case studies, hydrocarbon combustion, and power generation systems. Some of the former processes features unit processes perform mixing, heating, and cooling tasks of components. When transporting components throughout the unit processes it normally requires knowing not only how a process streams work but also if it embodies material streams or energy streams. The first will be referenced by the volume flow rate, from which three categories are derived mixed, solid and non-conventional, the mass and mole. And the

second, energy streams will be symbolized by heat flow rate and work units.

Aspen Plus contain other engineering-solving tasks, as estimation of physical properties, optimization of processes, creation of custom graphical output results, obtention of data inventory, and generating sensitivity analysis. In order to have a whole picture of the principles of chemical engineering providing reliable data on process parameters will be an obligation. Aspen Plus's users have to know how unit processes flow and their functions within the production process. Finally it is important to bring up that experimental data results are vital to legitimate the process performance.

Today, the Aspen Plus software (developed by AspenTech©) is a leader in the field of modeling technological processes of various industries.

2.4   Statistical modeling: regression analysis

Regression analysis is a statistical modeling technique which points the links and relationships among variables. Samples of applications of regression analysis can be found into many academic fields such as biology, chemistry, physics, economics, engineering, etc. This well known acceptance has turned regression analysis into a trusted statistical technique.

The case described below is an example of regression analysis: many different computer systems data performance have been obtained in order to compare their performance while all of them use a standard benchmark program. That information is pointed in the table 2.3. Details of every system are represented in a single row. As n systems are being evaluated, there will be needed n rows within the table.

The first column describes the index numbers from 1 to n which were randomly assigned to each of the systems. Columns 2 to 4 represent the input parameters also known as independent variables. The given values of the input parameters were assigned either by the system configuration or by the researcher who determined the measurements. By doing this we will have the values of the inputs (clock ,

Table 2.3: An example of computer system performance data.

System	Inputs			Output
	Clock (MHz)	Cache (kB)	Transistors(M)	Performance
1	1500	64	2	98
2	2000	128	2.5	134
...	...	...	...	
i	...	...	...	...
...	...	...	...	...
n	1750	32	4.5	113

Cache,and transistors) but the output performance will not always be obtained this can be easily resolved by using a regression analysis. The first given example has processors clocks of 1500 MHz, a cache size of 64 kbytes and the processor contained 2 million transistors.the performance of the studied system is represented in the last column while it executed a standard benchmark program. This value is known as output of the system or as the dependent variable.

By using regression modeling we can set a mathematical function, $f()$, this mathematical function will use the independent measurements n to represent the connection among input parameters and the output, this is a regression model:

$$performance = f(Clock, Cache, Transistors) \qquad (2.1)$$

Finally there is a general regression model ($y = X\beta + \varepsilon$) which fits any linear relationship in the unknown parameters β. This also covers the important class of polynomial regression models.

2.4.1 Polynomial Models in One Variable

When working with polynomial regression models with one variable we will set

$$y = \beta_0 + \beta_1 x + \beta_2 x^2 + \varepsilon \qquad (2.2)$$

The previous model, called quadratic model, represents a second-order model in

single variable. The expected value of y is

$$E(y) = \beta_0 + \beta_1 x + \beta_2 x^2 \tag{2.3}$$

From equation 2.3, the linear effect parameter is expressess by β_1 while the quadratic effect parameter is contained at β_2. When $x = 0$, the parameter β_0 represents the average value of y. β_0 takes no physical interpretation if the range of x do not includes 0. The representation of the kth-order polynomial model in one variable is:

$$y = \beta_0 + \beta_1 x + \beta_2 x^2 + ... + \beta_k x^k + \varepsilon \tag{2.4}$$

Polynomials models are particularly handy for analysts in study cases in which they know that curvilinear effects wil be reflected in true response functions. Polynomial models are also an important mathematical tool when working with approximating functions to unknown and complex nonlinear relationships. This use of the model is commonly used in practice.

Chapter 3

Methodology

Summary

Steps of the methodology developed are discussed. There are 5 steps but basically they are grouped into three stages. Firstly a simulation is performed which help us to obtain the LCI that is the main challenge in an LCA. Secondly a variation over the simulation is done, so, data for analyzing the behavior of the LCI in different functional units of the process is gotten. Finally using the data obtained above the statistic modeling is applied.

3.1 Step 1: Set goals and understand the system.

Setting the case goal and scope, as it was already defined, will include the system boundaries and how further it will be studied.

Having selected a goal the second stage will be understanding how this system works. This thesis will only work on the gate to gate goal, therefore only chemical production process data must be collected.

For understand a chemical production process is needed:

- to register the components implicated in the chemical process

- to establish the chemical reactions involved in the process

- to obtain reaction rates and power law kinetics for them

- to research for the equipment needed in the industrial process for carrying out the production process

- to choose the equipment for accomplishing the production process

- to calculate parameters of the process such as flow rates, temperature, pressure, molar compositions, etc.

- to make a flow sheet for the production process. This point is appropriate to establish a functional unit due to this is the benchmark for estimating the emissions.

Once all information has been gotten we can continue selecting the software to make the simulation. In this case Aspen Plus is the software selected. More about this software is mentioned in the next step.

3.2   Step 2: Simulation

When all the information is already gathered for carrying out the simulation, second step is applied. This is for selecting the most convenient simulator and because of the system studied is a chemical process where flow rates, compositions, temperatures, pressure, among other operating conditions need to be examined, a simulator for chemical process is preferred.

The software selected for developing the simulation is Aspen Plus 2006. As was discussed in chapter 2, Aspen plus is a simulator for chemical processes able to help if working with engineering and process operation problems,and in evaluating the whole process performance. In other words with Aspen Plus is possible to develop the process design and to obtain inputs/outputs of it.

Basically the steps for performing any simulation in Aspen Plus are:

- registration of components

- selection of thermodynamic model

- insertion of reaction stoichiometry

- introduction of reactor parameters, separation units or recycle systems included in the process

To have a good model it is vital to have an adequate design of the process for modeling, this comes remarkable benefits as developing the model in a reasonable time and avoiding the programming hazards.

While a simulation is developed is required to verify the simulation, and in the end of it, is appropriate to validate the model, that is why the next step of this methodology discuss more about it.

3.3   Step 3: Verification and validation

As Robinson [1997] mentions, two important concepts verification and Validation. When doing verification it requires to make sure that the conceptual model has accurately been transformed into a computer model; however, verification will only represents that a model has the right elements as accurate as possible but this may not represent that the model should be capable to obtain the purpose we might be working on. While validation is a procedure which guarantees that the model is accurately fit to work a scenario always fulfilling the purpose of the model on which it will be assigned upon-this means making the right model. How accurate a model is will depend on how close it is to meet the purpose it was built for. The purpose or objectives of a model have to be established earlier so that the model will be properly validated. Such purpose may have been established at the beginning of the simulation study as it was made in this very work.

Figure 3.1 shows altogether several types of both validation and verification within the modeling process. First the different types of validation are going to be described:

- Conceptual model validation: when the degree of detail for both scope and level of the suggested model is not only enough to reach the purpose we are looking forward to obtaining but also once all assumptions are correct. By doing this the model will tell if all the goals of the study are satisfied by the conceptual model.

- Data validation: this concept describes that all the data used to make a model building validation and experimentation are accurate enough to be used and therefore they will help to reach data projections close to real example.

- White-box validation: this is step that will always hold as a priority including every single part of the model resembles as accurately as their real world counterparts.

- Black-box validation: this is a type of validation which verifies the general model operation by testing both if the overall model depicts with precision and whether or not the overall model supplies a faithful concept of the real world system.
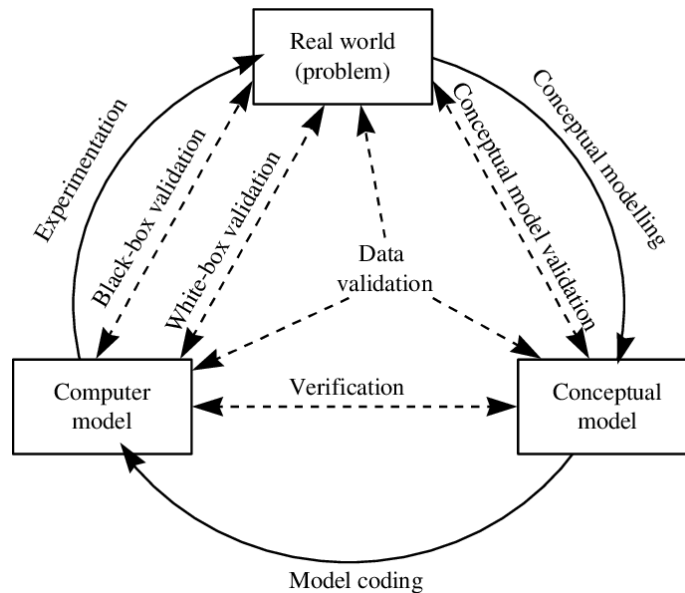
Figure 3.1: Representation of the validation and verification model process, Robinson [1997].

Verifying and validating is a continuous improvement loop made during all of the simulation study. However, this can not be fully reliable if the validation and verification are done once the complete model has been finished. By constantly checking the model we prove both its accurate design and its usefulness into reaching the goal we are looking.

On the one hand verification and white-box validation have natures, on the other hand they both are essential checking methods while doing the model coding. As verification makes sure that the model is faithful to the conceptual model, white-box validation will focus on guarantee that the core substance of the model is accurate to the real world.

Robinson [1997] sets three methods on verification and white-box validation.

- Checking the code

  There are some ways by which you can check your model in order to test and approve both its data and logic. A first useful idea is to have a modeling specialist to analyze the code. In case that none reaching one was not an option there is a second way to go, this will be using a simulation software offered by most software vendors. Finally by expressing in a non-technical style the code, a non-expert might verify the data and logic. This is a helpful way to get feedback from those expert with specific knowledge of the modelled system.

- Visual Checks

  The visual expression of the model has demostrated being a powerful aid for verify and validate. Both the logic of the model and its behaivor against the real world can be test by running the model and monitoring the behavior of the elements of the process under analysis.

  Showing the model will be a useful mechanism to observe the way every single unit forming the system works and interacts into the system. Several ideas help to point this:

  - double checking the examined model one event at the time

- stopping the model while creating a prediction, and then compile the model once again and checking whether our prediction happened or not.

- setting up conditions and have them happen at the user's will

- being able to run the model without some of its areas making it able to run faster the verification and validation stages.

- being able to run the model without some of its areas making it able to run faster the verification and validation stages.

- tracking the path of an item while it advances through the model

Watching a model running for a certain period of time enables to learn about the performance of the model. Exhibiting, formally and informally, the model to expert of the system permit them identify any weakness in the model but also increase the credibility of the work by involving them.

- Inspecting Output Reports

By double checking the model reports of a simulation run we can easily compare the obtained results with the expected ones.

Another widely used tool to improve our simulation model is a blow-by-blow history. This tool record every single step made while the model was being run. Reviewing this report can be an way to diagnose and delete flaws in the design of the model.

Since it is not possible to ensure that the model is one hundred percent accurate, the verification and validation stage allows for sufficient confidence about the acceptance of the results.

A model verification and validation will aim to gather confidence in the results given by a model. This will be obtained by testing the model looking to prove it wrong. The more a model is proved not to be incorrect, the more confidence on the model will be obtained.

3.4   Step 4: Run and experimenting

As soon as the model is completely finished, the simulation is run. Aspen Plus will generate chart describing the inputs and outputs involved in the process that was studied. The figure 3.2 details this

Heat and Material Balance Table					
Stream ID		FEED	W-FEED	PRODUC	BEN-TOL
Temperature	C	220.0	25.0	120.8	81.0
Pressure	bar	4.000	1.013	0.505	1.200
Vapor Frac		1.000	0.000	0.000	0.000
Mole Flow	kmol/hr	152.600	3400.000	116.188	23.542
Mass Flow	kg/hr	16188.302	61251.952	12101.741	1999.142
Volume Flow	cum/hr	1446.381	61.624	14.920	2.465
Enthalpy	MMkcal/hr	2.260	-232.000	3.376	0.209
Mole Flow	kmol/hr				
EB		152.142		0.291	0.008
B		0.458			11.465
S				115.897	trace
H					
E					0.028
T				trace	11.930
M				trace	trace
W			3400.000		0.082
CO					
CO2				trace	0.029
Mole Frac					
EB		0.997		0.003	325 PPM
B		0.003			0.487
S				0.997	28 PPB
H					
E					0.001
T				trace	0.507
M				trace	trace
W			1.000		0.003
CO					
CO2				trace	0.001

Figure 3.2: Simulation results.

The first column contains the operating conditions and main input/output flows of the process, also called variables. Second column shows the unit type of each variable in the process; for example: pressure's unit value is bar and temperature's unit used will be Celsius degrees. The following column describes the parameter values and the amount of energy for both input and output flow within the process.

In addition, a functional unit is established for the entire analysis in order to relate all the process flows. Due to statistical modeling, data from several simulated

scenarios are demanded. The scenarios will be created by varying the functional unit respecting the limits of technical capacity of the modeled chemical process.

3.5   Step 5: Statistical modeling

The number of simulations depend on the type of statistical tool used, in this time 45 simulation were done. Based on these data, the statistical modeling is carried out. The statistic modeling purpose is to observe the LCI behavior depending on the feeds or the functional unit in the process studied. Figure 3.3 represents this idea.
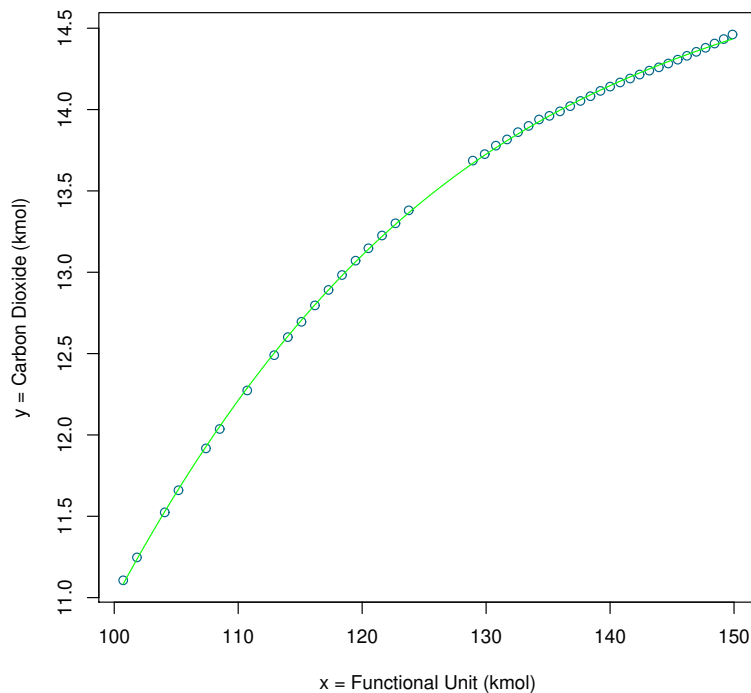
Figure 3.3: Simulation results.

Every point seen in the plot represents a simulated scenario using a specific input and obtaining a specific output. The x-axis and y-axis represents the functional unit

and the amount of a specific emission generated at the process respectively. Observing the trend shown in the graph, we proceed to estimate a mathematical model that represents this behavior.

Polynomial regression will be used. As it was seen in section 2.4, this statistical tool helps to create a mathematical function which relates variables, in this case there are two variables which should be related, on the one hand is the functional unit (FU) and on the other hand is the emission of a pollutant.

Chapter 4

Case Study and Results

Summary

This section illustrates the methodology developed with an application on the production process of styrene. In the beginning chemical components, chemical reactions and flow sheet of the process are introduced. Then, the model starts to get built using Aspen Plus and a short description about how it was carried out is presented. Subsequently, when the simulation runs without errors, the parameters variation is made and statistical models are obtained. After all, plots of the data obtained and equations are reported.

4.1 Setting goals and Understanding the System

Due to this is only a demonstration about how the methodology must be applied, the goal selected is gate to gate, and the scope for this is an analysis only related to the production process which covers activities of the industry where the manufacturing process is carried out. Figure 4.1 illustrates the conditions chosen.

The process selected for researching is the styrene production because of several authors have used it for analyzing in different researches, Luyben [2011]. Styrene is a chemical component used to manufacture polystyrene, it is better known for being used in packaging and for being a widely used to produce insulating Styrofoam

cups. The chemical process involving styrene requires the dehydrogenation of ethylbenzene. The resulting reaction will be endothermic, nonequimolar and reversible; this can only be obtained using high temperatures together with low pressures are conducted to a high conversion inside the adiabatic vapor-phase reactors. Steam is combined with ethylbenzene (EB) increasing the conversion. There are many other sub reactions which produce unwelcome byproducts such as benzene, toluene, ethylene and carbon dioxide. These byproducts have reaction rates which get bigger with both partial pressures and temperature.

Figure 4.1: LCA goal and scope selected, SlydePlayer [2016].

4.1.1 Chemical reactions

- Styrene Reaction:

$$C_6H_5CH_2CH_3 \Longleftrightarrow C_6H_5CHCH_2 + H_2 \qquad (4.1)$$

- Other side reactions occur that consume ethylbenzene and produce unwelcome by-products.

    - Benzene/Ethylene Reaction:

$$C_6H_5CH_2CH_3 \longrightarrow C_6H_6 + C_2H_4 \qquad (4.2)$$

- Toluene/Methane Reaction:

$$C_6H_5CH_2CH_3 + H_2 \longrightarrow C_6H_5CH_3 + CH_4 \qquad (4.3)$$
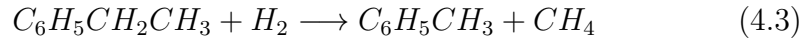
- Carbon Monoxide Reactions:

$$2H_2O + C_2H_4 \longrightarrow 2CO + 4H_2 \qquad (4.4)$$

$$H_2O + CH_4 \longrightarrow CO + 3H_2 \qquad (4.5)$$
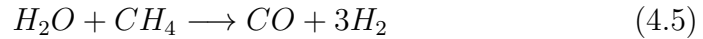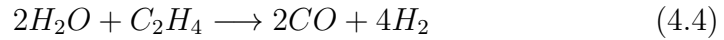
- Carbon Dioxide Reaction:

$$H_2O + CO \longrightarrow CO_2 + H_2 \qquad (4.6)$$
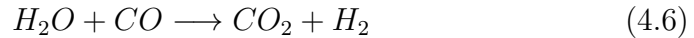
4.1.2 Components and reaction rates

Table 4.1 summarizes the components and gives, standard names, chemical formula and also there are special IDs for referring the substances in the flow sheet.

Table 4.1: Chemical components.

Number	Standard name	Formula	Symbol in the flowsheet
1	Ethylbenzene	$C_6H_5CH_2CH_3$	EB
2	Styrene	$C_6H_5CHCH_2$	S
3	Hydrogen	H_2	H$_2$
4	Benzene	C_6H_6	B
5	Ethylene	C_2H_4	E
6	Toluene	$C_6H_5CH_3$	T
7	Methane	CH_4	M
8	Water	H_2O	W
9	Carbon monoxide	CO	CO

Table 4.2 highlights the kinetic boundaries that were used in this sample study. Simple power law kinetics, equations 4,7 to 4,13, are being used for all the reactions

every single overall rate is expressed using $kmol \cdot s^{-1} \cdot m^{-3}$. Concentration units are proportional to partial pressures and these are expressed in Pascals.

Table 4.2: Reactions Kinetics^a.

	k	$E(kJ/kmol)$	concentration (Pascals)
reaction 1 forward	0.044	90981	P_{EB}
reaction 1 reverse	6×10^{-8}	61127	$P_S P_H$
reaction 2	27100	207989	P_{EB}
reaction 3	6.484×10^{-7}	91515	$P_{EB} P_H$
reaction 4	4.487×10^{-7}	103997	$(P_W)^2 P_E$
reaction 5	2.564×10^{-6}	6723	$P_W P_M$
reaction 6	1779	73638	$P_W P_{CO}$

^{a} Overall reaction rates have units of $kmol \cdot s^{-1} \cdot m^{-3}$

$$\mathscr{R}_{1F} = p_{EB} k_{1F} e^{-E_{1F}/RT} \tag{4.7}$$

$$\mathscr{R}_{1R} = p_S p_W k_{1R} k_{1R} e^{-E_{1R}/RT} \tag{4.8}$$

$$\mathscr{R}_2 = p_{EB} k_2 e^{-E_2/RT} \tag{4.9}$$

$$\mathscr{R}_3 = p_{EB} p_H k_3 e^{-E_3/RT} \tag{4.10}$$

$$\mathscr{R}_4 = p_W (p_E)^{0.5} k_4 e^{-E_4/RT} \tag{4.11}$$

$$\mathscr{R}_5 = p_W p_M k_5 e^{-E_5/RT} \tag{4.12}$$

$$\mathscr{R}_6 = p_W p_{CO} k_6 e^{-E_6/RT} \tag{4.13}$$

The chemical transformation of the process shows that high temperatures are

key to obtain the first reaction since the activation energy of the following reaction is bigger than the activation energy of the reverse reaction as this is a endothermic reaction. The kinetics reactions can also describe that both high ethylbenzene concentrations and low pressure will aid in the manufacture process of Styrene. Nevertheless, other reactions have distinct reaction measures which will grow with the temperature.

4.1.3 Styrene Flowsheet

Next diagram, figure 4.2, was obtained from Luyben [2011], which is a styrene production process researching. It is possible to see that there are process parameters for the unit operations, in that case when the simulation is carried out those parameters are used. They are related to temperature, pressure, components, input and outputs flows among others.

The styrene production process has a the ethylbenzene feed of $152.6kmol/h$ and the functional unit is $115.6kmol/hr$ of Styrene. The fresh feed of ethylbenzene is consolidated with $74.6kmol/h$ of recycle stream (mostly ethylbenzene) and $612kmol/h$ of low pressure steam. The stream will be heated using a feed-effluent heat exchanger (E2), this requires the hot reactor effluent to heat the supplied stream to $487°C$. Furthermore low pressure process steam $2788kmol/h$ is being heated using a furnace (E1) until reaching $777°C$ and is combined with the stream from (E2) to accomplish a reactor inlet temperature of $650°C$. The heat duty in the furnace is $16.9MW$ the total process steam will be $3400kmol/h$.

- Reactors. This process uses two gas-phase adiabatic reactors in series. Every one of them with the following measures: $3.3m$ diameter, a catalyst loading of $35,700kg$ and a length of $3.5m$. The exit temperature of the first reactor is $588°C$ caused by the endothermic reaction. A furnace heats this stream to a temperature of $650°C$ just before it moves to the second reactor. The furnace heat duty is $3.5MW$. The total EB entering the first reactor R1 is $225.1kmol/h$. The ethylbenzene leaving the second reactor has a molar flow rate of $80.9kmol/h$, so the per-pass conversion of EB in the two reactors is 64%.

There is a molar flow rate of styrene of $119 kmol/h$ which is generated in the second reactor. Should all the ethylbenzene in the fresh feed be transformed into styrene, this would represent $152.6 kmol/h$ of manufactured styrene. It is easily observed that there is a large quantity of ethylbenzene being discarded in making sub products. There are more losses of ethylbenzene and styrene in the two streams leaving the process. The production measurement of styrene which leaves the process from the bottom of the first distillation column is $115.6 kmol/h$ that provides a styrene production of 76%.
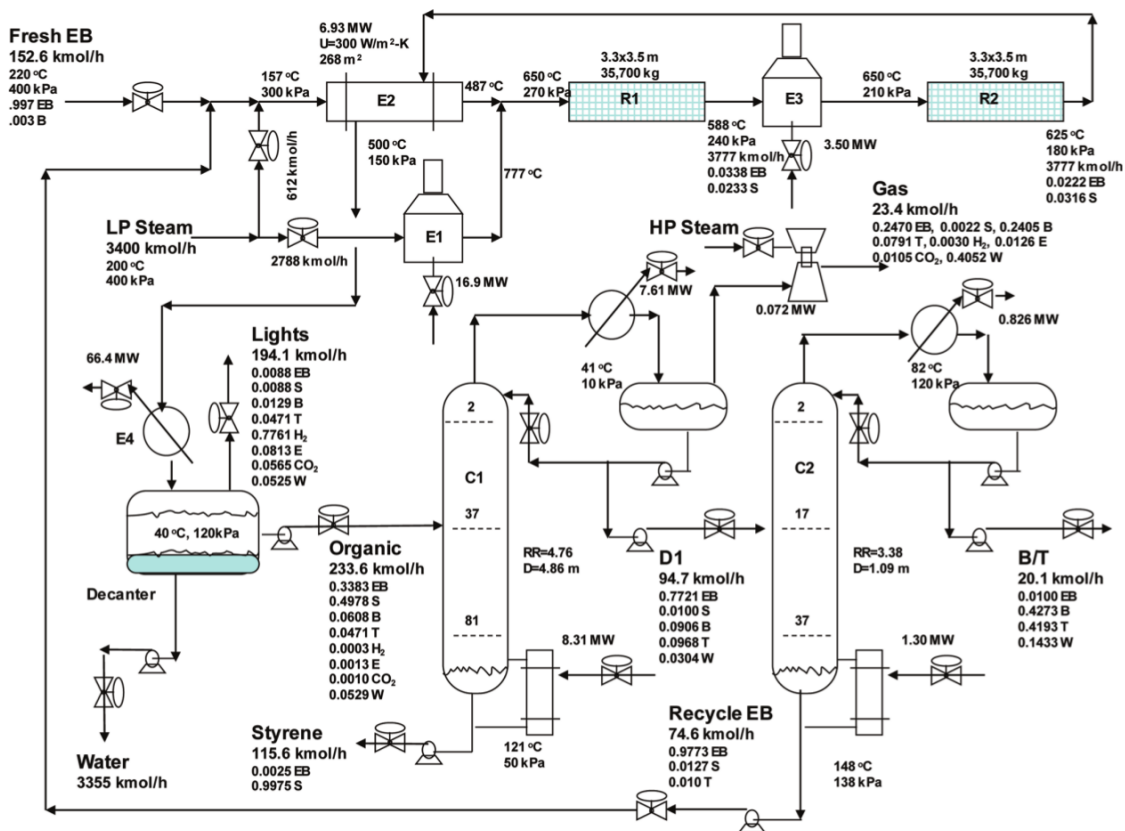
Figure 4.2: Styrene production process flowsheet, Luyben [2011].

- Condenser and Decanter. Once cooled in E2 and partially condensed in heat exchanger E4 applying cooling water, the process stream goes to a decanter

which is operating at $4040°C$ and $120kPa$. The dimension that the decanter needs are $2.8m$ meters of diameter and a length of $5.6m$. The water will be drained from the bottom of the container at a rate of $3355kmol/h$. The gas phase, also known as "Lights",that leave the top of the decanter at a flow rate of $194.1kmol/h$also carries the hydrogen produced in the basic reaction, it might also contain other elements. The ethylbenzene that is lost is $1.71kmol/h$ and the styrene that is lost is 1.71 $kmol/h$.

- Product Column C1. The organic phase has to be fed into the first distillation column at a flow rate of $233.6kmol/h$ and it this must have a composition of $33.83mol\%$ of ethylbenzene, $49.78mol\%$ of styrene, $6.08mol\%$ of benzene, $4.71mol\%$of toluene, and $5.29mol\%$ of water, and a little amount of the light components. The 82-step column is made under vacuum with a reflux-drum pressure of 10kPa. The assumed decline pressure per plate is $0.5kPa$. The diameter of the column is $4.86m$, and the reboiled duty that is being provided by low pressure steam is $8.31MW$. The reflux ratio is 4.76. The feed is fed on stage 37, which minimizes reboiler duty. Both design specifications for the column are a bottoms purity of $99.75mol\%$ styrene and a distillate impurity of $1mol\%$ styrene.

- Recycle Column C2. The bottoms from column C1 are provided to stage 17 of a 38-stage distillation column whose function is to collect ethylbenzene in order to use it in another cycle. The specs for both designs have a bottom impurity of $1mol\%$ toluene and a distillate impurity of $1mol\%$ of ethylbenzene. Such distillate is chiefly benzene and toluene with some water. The bottoms are recycled back into the reaction. The column works at $120kPa$, and its designed with a diameter of $1.09m$, and it needs a reflux ratio of 3.38. The reboiler duty is $1.3MW$. The total expenses for obtaining the fresh feed of ethylbenzene, the process steam and the energy that will be used in the furnaces and the distillation columns is $174,400,000 per year. A big portion of such expense will be used to acquire raw material. To create $115.6kmol/h$ of styrene, the fresh feed of ethylbenzene is $152.6kmol/h$. In the suggested design described in the previous segment, an equal amount of styrene is made from less ethylbenzene

fresh feed ($132.8 kmol/h$).

4.2 Simulation of Styrene Process

At this point, the information required for modeling the system studied is already gathered. So, next step must be the construction of the model in Aspen Plus; when the simulation will be finished, it will be run. Basically the software includes a user interface where the user adds the initial conditions included in the process for obtaining results related to the final conditions of the process. Next points show a briefly summary of the main steps made in the development of the simulation.

- Firstly, Aspen Plus is open and there will appear a window as figure 4.3. The equipment used in chemical processes are shown in the bottom, and bars with options that will help us to construct the model are in the top of the window.
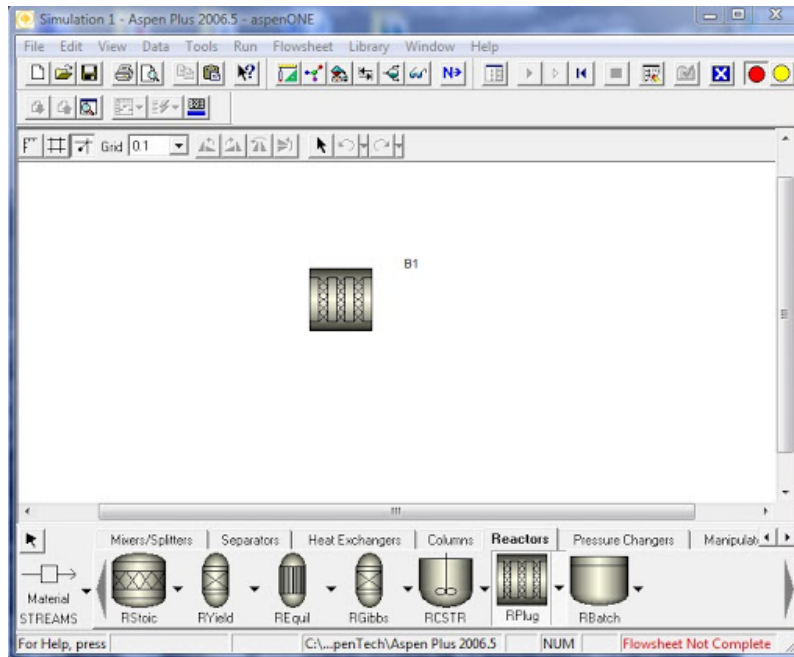
Figure 4.3: Principal Aspen Plus window.

- Then, the chemical components of the process are entered in the model. Figure

4.4 shows the window where the components are specified.
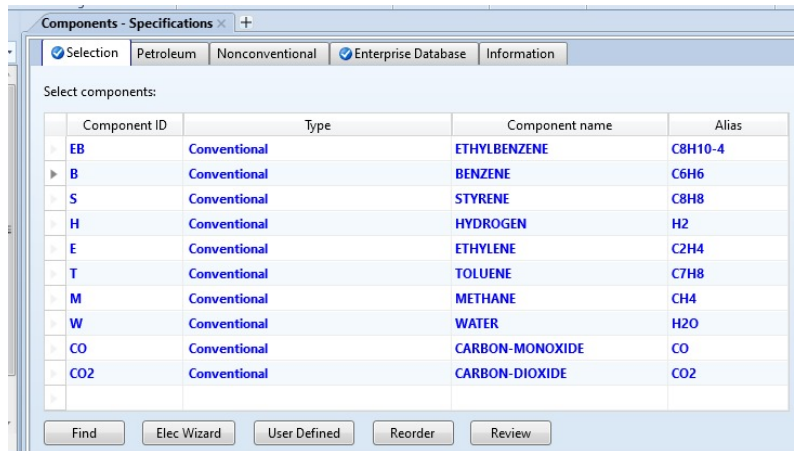
Figure 4.4: Chemical components insertion.

- From the equipment section in Aspen, the equipment required is introduced. Notice that this selection is based on the equipment seen in the flow sheet of the process. Once they are in the model, they must be connected following the sequence of the flow sheet. After verifying that they are properly connected, the parameters of each component are entered. Figure 4.5 is presented as an example of the window where the pressure and temperature of a heater are inserted.

Figure 4.5: Parameters insertion.

When the conditions are already set in every equipment the styrene process simulation model is ready to be run. The resulting model must be validated with one or more options mentioned above. Figures 4.6 and 4.7 illustrate the windows where chemical reactions and their reaction rates are indicated.
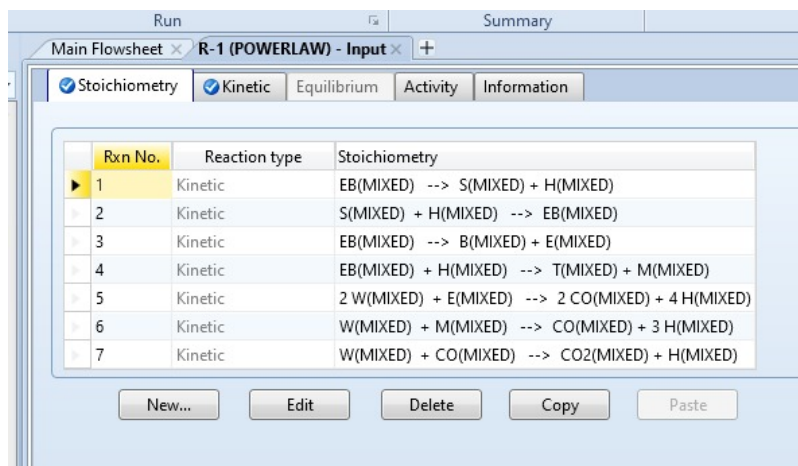
Figure 4.6: Reactor window for providing the stoichiometry.
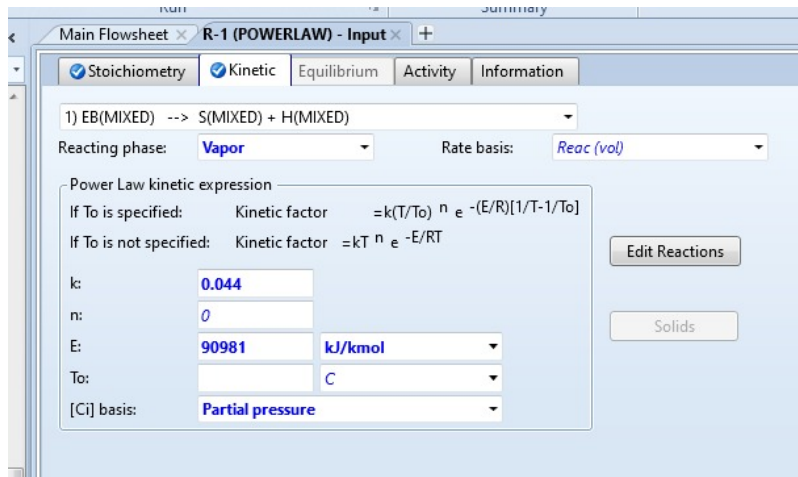
Figure 4.7: Reactor window for inserting reaction rates.

- In the moment when each equipment and parameters are already inserted, and the model running does not have error then, we can start to experiment on it. Figure 4.8 shows the final model.

Figure 4.8: Full Styrene production process model constructed in Aspen Plus.

4.3 Experimentation

Once the simulation has been run, a variation in the input quantities are made, so different results in outputs are obtained. Those data (input/output) will be intentionally managed to help to describe the behavior of pollutant emissions.

Every result of each simulation running is taken as a sample of the statistical modeling. Forty six simulation runs were done, they were generated only changing randomly the input flow parameter into the simulation, so a scenario was done for each change. See appendix A for visualizing the data calculated in this work. There are four tables, first one has the total streams required, second one has the total energy used, third one has the emissions to water and the last one has emissions to air. All them are related to the Styrene process seen above.

4.4 Statistical modeling

Polynomial regression technique is used to obtain the mathematical equations that model the behavior of emissions depending on the functional unit. For carrying out this statistic analysis R Studio software was used. This is a statistical software with quite a few libraries which help to model data. In this case it helped to find the mathematical model which best fit to the data obtained in experimentation. It is necessary to say that for knowing which model best fits the data, various polynomial regressions were assessed, as a result the polynomial degree that best represents their behavior was gotten. For this data a third degree polynomial curve was the one that best fits. For this reason all emissions reported have a corresponding polynomial model equations with those features.

4.4.1 Modeling Emissions to Water

Next graph provides information about ethylbenzene emissions into water in the Styrene process. Below there are the statistical model and statistical parameters which help to know if the model is good or not.
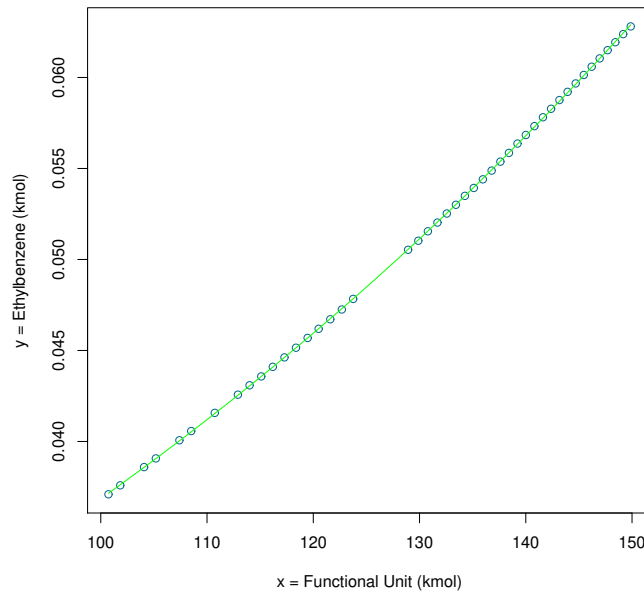
Figure 4.9: Ethylbenzene Water Emissions

The model resulted of the polynomial regression for ethylbenzene water emissions is shown at equation 4.14.

$$y = 0.05121 + 0.0515x + 0.0028x^2 + 0.0001x^3 \qquad (4.14)$$

Next figure contains the parameters of the model, firstly there is the `Residual` section, it is important that these values are near zero because it means the error in the model is minimum. The parameter estimations and their standard errors are pointed in the second and third columns of the `Coefficient` section. This figure also shows that the t statistics and the $p - values$, which are related to the t tests, are represented in the columns four and five. As the $p - values$ outcome data is less than 0.05 gives us enough proof to conclude that there is a solid evidence proving that these parameters $\beta \neq 0$, $\beta^2 \neq 0$ and $\beta^3 \neq 0$, and so the statistical significant linear relationship between the the functional unit and the Ethylbenzene emissions is shown. In the last section is the `Multiple R-squared` and the `Adjusted R-squared`,

high values of them indicate that the odel fits well very well. Taking into account all the previous information it is statistically correct to set the model as one able to foresee the emissions using the functional unit.

```
Residuals:
      Min         1Q     Median         3Q        Max
-9.276e-05 -2.592e-05  1.998e-06  3.418e-05  6.320e-05

Coefficients:
             Estimate Std. Error  t value Pr(>|t|)
(Intercept) 5.121e-02  5.608e-06 9131.951   <2e-16 ***
poly(q, 3)1 5.152e-02  3.762e-05 1369.349   <2e-16 ***
poly(q, 3)2 2.848e-03  3.762e-05   75.708   <2e-16 ***
poly(q, 3)3 1.090e-04  3.762e-05    2.898    0.006 **
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Residual standard error: 3.762e-05 on 41 degrees of freedom
Multiple R-squared:      1,     Adjusted R-squared:      1
F-statistic: 6.27e+05 on 3 and 41 DF,  p-value: < 2.2e-16
```

In figure 4.9 is observed a line which means the model equation outcome, it gives informations about the relationship between both variables ethylbenzene and the functional unit. The graphic reveals that the relationship between ethylbenzene and the functional unit is linear upward trend.

The data and model shown a proportional rise in emissions and quantity of product generated. In other words, if there is a higher production of Styrene, there will be a higher emission of Ethylbenzene to the water. Notice that both variables have *kmol* units. The range analyzed of the functional unit is approximately between $100kmol$ (10441.8kg) and $150kmol$ (15662.7kg).

Next graphics shown the result of the others emissions, basically the process generates two kind of emissions, to water and to air. There are an analysis of the total flows outputs and an analysis about the energy consumption. Those results only differing to this first in the model parameters and type of emission analyzed (y). Contrary to figure 4.9, figure 4.10 reveals that the emission of Benzene decreases when the functional unit grows. That means while the amount of styrene demand

increases, Benzene emission decreases.
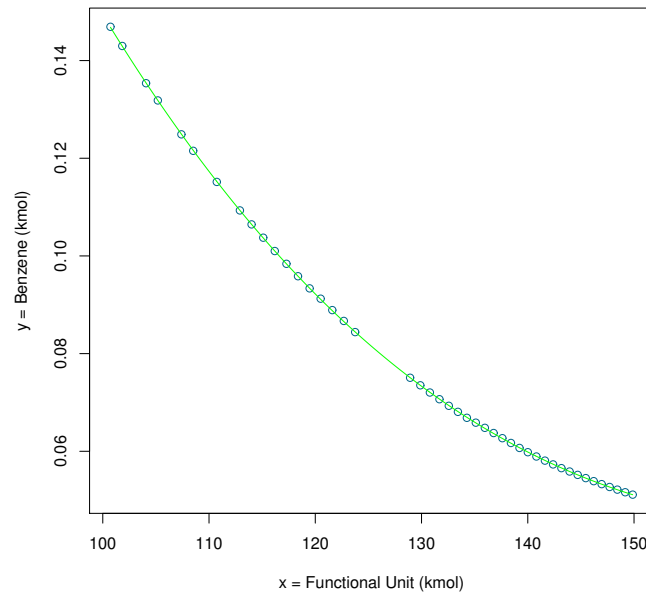
Figure 4.10: Benzene Water Emissions

$$y = 0.0805 - 0.1806x + 0.0354x^2 - 0.0021x^3 \tag{4.15}$$

```
Call:
lm(formula = y ~ poly(q, 3))

Residuals:
      Min         1Q     Median         3Q        Max
-1.018e-04  -4.180e-05  -7.832e-06  2.127e-05  1.256e-04

Coefficients:
              Estimate Std. Error  t value Pr(>|t|)
(Intercept)  8.053e-02  9.082e-06  8867.50   <2e-16 ***
poly(q, 3)1 -1.807e-01  6.092e-05 -2965.94   <2e-16 ***
poly(q, 3)2  3.544e-02  6.092e-05   581.70   <2e-16 ***
poly(q, 3)3 -2.176e-03  6.092e-05   -35.71   <2e-16 ***
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Residual standard error: 6.092e-05 on 41 degrees of freedom
Multiple R-squared:      1,     Adjusted R-squared:      1
F-statistic: 3.045e+06 on 3 and 41 DF,  p-value: < 2.2e-16
```

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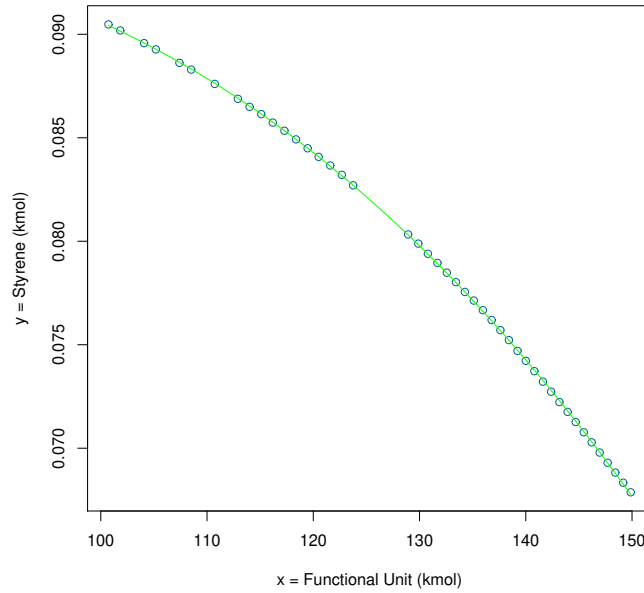
Figure 4.11: Styrene Water Emissions

$$y = 0.0791 - 0.0458x - 0.0059x^2 - 0.0002x^3 \qquad (4.16)$$

```
Call:
lm(formula = y ~ poly(q, 3))

Residuals:
       Min          1Q      Median          3Q         Max
-7.096e-05  -3.075e-05  -3.194e-06   3.173e-05   1.037e-04

Coefficients:
              Estimate Std. Error    t value Pr(>|t|)
(Intercept)  7.912e-02  6.060e-06 13055.057  < 2e-16 ***
poly(q, 3)1 -4.584e-02  4.065e-05 -1127.523  < 2e-16 ***
poly(q, 3)2 -5.998e-03  4.065e-05  -147.534  < 2e-16 ***
poly(q, 3)3 -2.124e-04  4.065e-05    -5.225 5.42e-06 ***
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Residual standard error: 4.065e-05 on 41 degrees of freedom
Multiple R-squared:     1,     Adjusted R-squared:     1
F-statistic: 4.31e+05 on 3 and 41 DF,  p-value: < 2.2e-16
```
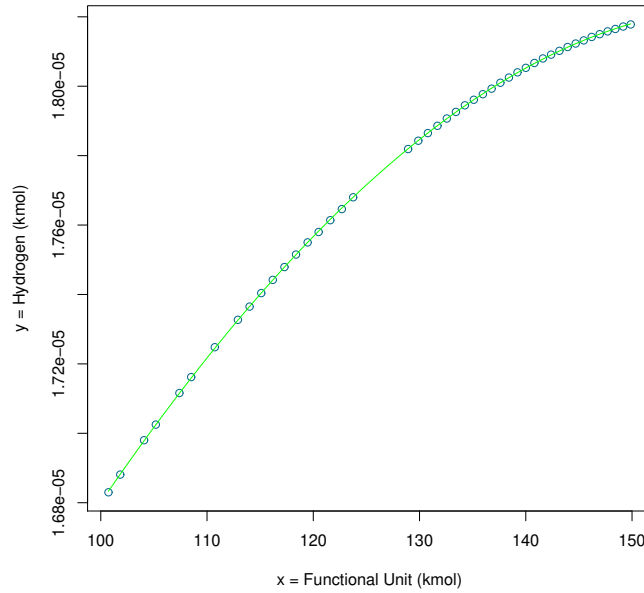
Figure 4.12: Hydrogen Water Emissions

$$y = 1.775 \times 10^{-5} + 2.6051 \times 10^{-6}x - 4.4621 \times 10^{-7}x^2 - 1.0132 \times 10^{-8}x^3 \quad (4.17)$$

```
Call:
lm(formula = y ~ poly(q, 3))

Residuals:
       Min         1Q     Median         3Q        Max
-3.223e-09 -6.645e-10  3.620e-11  6.875e-10  3.080e-09

Coefficients:
              Estimate Std. Error   t value Pr(>|t|)
(Intercept)  1.775e-05  2.038e-10 87091.661  < 2e-16 ***
poly(q, 3)1  2.605e-06  1.367e-09  1905.474  < 2e-16 ***
poly(q, 3)2 -4.462e-07  1.367e-09  -326.364  < 2e-16 ***
poly(q, 3)3 -1.013e-08  1.367e-09    -7.411 4.36e-09 ***
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Residual standard error: 1.367e-09 on 41 degrees of freedom
Multiple R-squared:      1,     Adjusted R-squared:      1
F-statistic: 1.246e+06 on 3 and 41 DF,  p-value: < 2.2e-16
```

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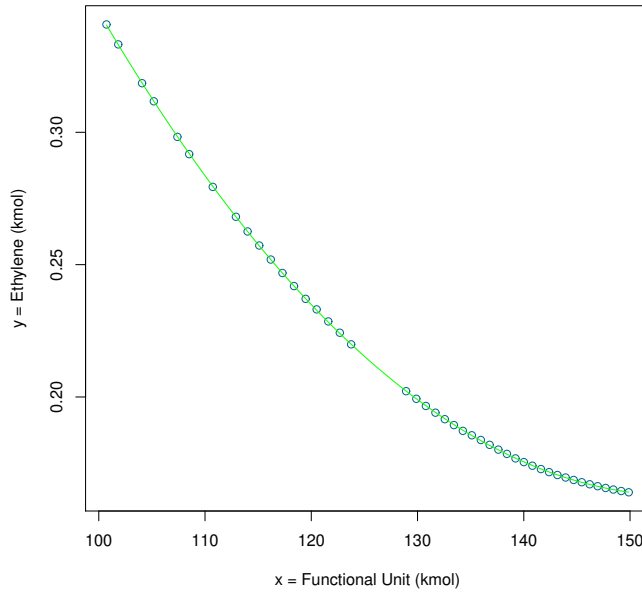
Figure 4.13: Hydrogen Water Emissions

$$y = 0.2145 - 0.3347x + 0.0775x^2 - 0.0011x^3 \qquad (4.18)$$

```
Call:
lm(formula = y ~ poly(q, 3))

Residuals:
      Min         1Q      Median         3Q        Max
-2.747e-04 -7.915e-05 -1.369e-05  5.852e-05  3.174e-04

Coefficients:
              Estimate Std. Error   t value Pr(>|t|)
(Intercept)  2.146e-01  2.025e-05 10596.027  < 2e-16 ***
poly(q, 3)1 -3.348e-01  1.358e-04 -2464.748  < 2e-16 ***
poly(q, 3)2  7.755e-02  1.358e-04   570.968  < 2e-16 ***
poly(q, 3)3 -1.117e-03  1.358e-04    -8.221  3.3e-10 ***
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Residual standard error: 0.0001358 on 41 degrees of freedom
Multiple R-squared:      1,     Adjusted R-squared:      1
F-statistic: 2.134e+06 on 3 and 41 DF,  p-value: < 2.2e-16
```
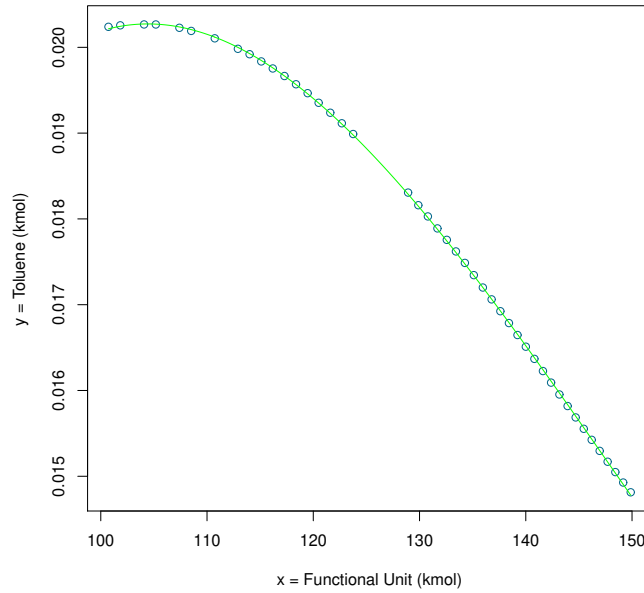
Figure 4.14: Toluene Water Emissions

$$y = 0.0178 - 0.0119x - 0.0025x^2 + 0.0005x^3 \tag{4.19}$$

```
Call:
lm(formula = y ~ poly(q, 3))

Residuals:
      Min        1Q     Median        3Q       Max
-1.734e-05 -1.013e-05 -2.812e-06  1.128e-05  3.350e-05

Coefficients:
             Estimate Std. Error t value Pr(>|t|)
(Intercept)  1.783e-02  1.954e-06 9127.39   <2e-16 ***
poly(q, 3)1 -1.195e-02  1.311e-05 -911.63   <2e-16 ***
poly(q, 3)2 -2.558e-03  1.311e-05 -195.14   <2e-16 ***
poly(q, 3)3  5.154e-04  1.311e-05   39.32   <2e-16 ***
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Residual standard error: 1.311e-05 on 41 degrees of freedom
Multiple R-squared:      1,     Adjusted R-squared:  0.9999
F-statistic: 2.902e+05 on 3 and 41 DF,  p-value: < 2.2e-16
```

The behavior of CO_2 emission shows that between the range examined is a point where high CO_2 emission is reached, it is when the functional unit is around $120 kmol$. Then the emission plunges until reach the lowest level into the range.
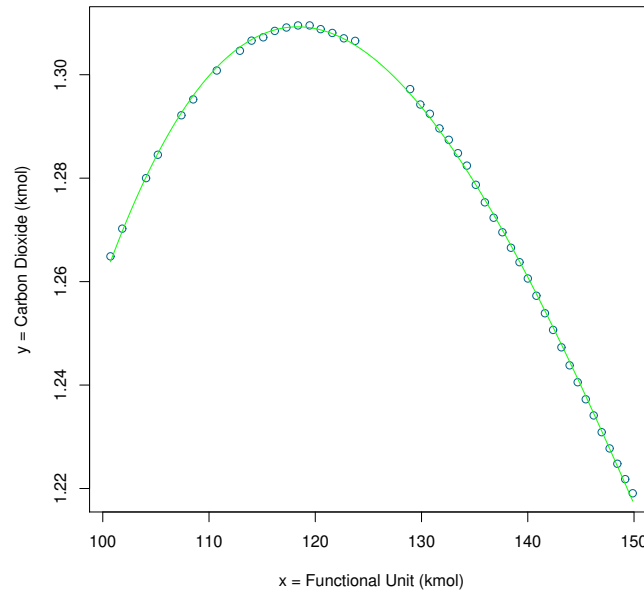
Figure 4.15: Carbon Dioxide Water Emissions

$$y = 1.2750 - 0.1394x - 0.1257x^2 + 0.0184x^3 \qquad (4.20)$$

```
Call:
lm(formula = y ~ poly(q, 3))

Residuals:
      Min         1Q     Median        3Q        Max
-0.0007329 -0.0004745 -0.0001951  0.0004352  0.0015028

Coefficients:
              Estimate Std. Error  t value Pr(>|t|)
(Intercept)  1.2750580  0.0000904 14104.03   <2e-16 ***
poly(q, 3)1 -0.1394508  0.0006065  -229.95   <2e-16 ***
poly(q, 3)2 -0.1257981  0.0006065  -207.44   <2e-16 ***
poly(q, 3)3  0.0184616  0.0006065    30.44   <2e-16 ***
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Residual standard error: 0.0006064 on 41 degrees of freedom
Multiple R-squared:  0.9996,    Adjusted R-squared:  0.9995
F-statistic: 3.228e+04 on 3 and 41 DF,  p-value: < 2.2e-16
```

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4.4.2   Modeling Emissions to Air

As the emissions of Ethylbenzene to the water, the trend of the emissions of Ethylbenzene to the air raises if the Styrene production increases.
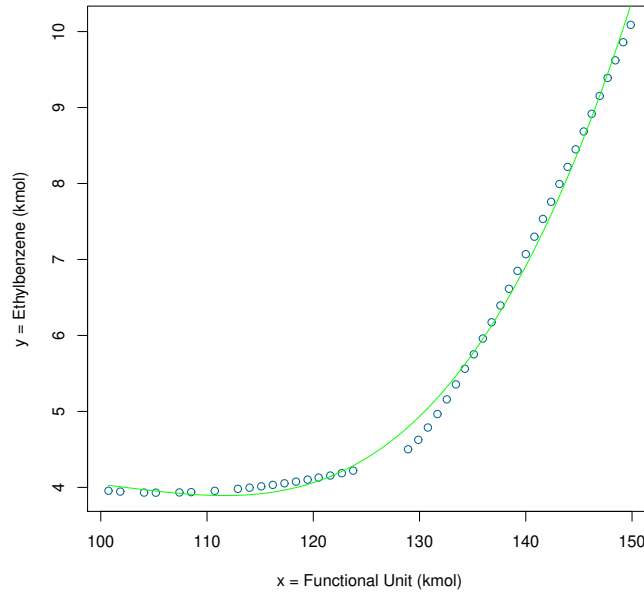
Figure 4.16: Ethylbenzene Air Emissions

$$y = 5.8949 + 12.1661x + 5.8270x^2 + 1.1115x^3 \qquad (4.21)$$

```
Call:
lm(formula = y ~ poly(q, 3))

Residuals:
     Min       1Q    Median       3Q       Max
-0.29324 -0.06380   0.02874   0.09234   0.16976

Coefficients:
             Estimate Std. Error t value Pr(>|t|)
(Intercept)   5.89495    0.01985 296.917  < 2e-16 ***
poly(q, 3)1  12.16617    0.13318  91.349  < 2e-16 ***
poly(q, 3)2   5.82706    0.13318  43.752  < 2e-16 ***
poly(q, 3)3   1.11160    0.13318   8.346 2.23e-10 ***
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Residual standard error: 0.1332 on 41 degrees of freedom
Multiple R-squared:  0.996,      Adjusted R-squared:  0.9958
F-statistic:  3443 on 3 and 41 DF,  p-value: < 2.2e-16
```
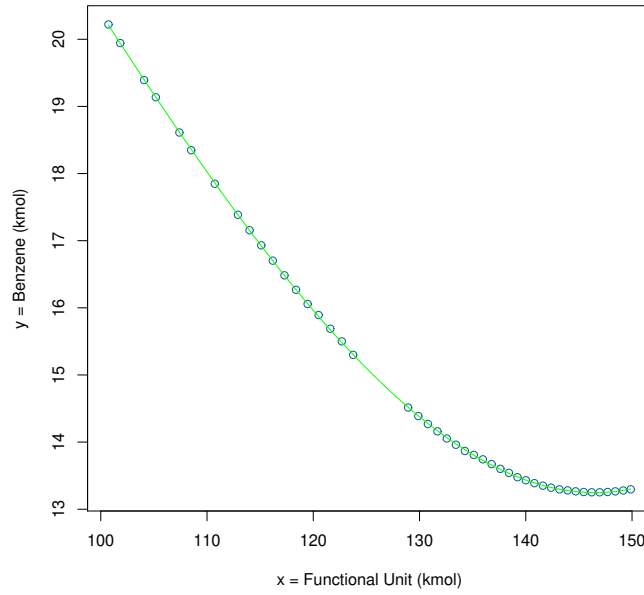
Figure 4.17: Benzene Air Emissions

$$y = 15.1136 - 13.6884x + 3.5479x^2 + 0.4719x^3 \qquad (4.22)$$

```
Call:
lm(formula = y ~ poly(q, 3))

Residuals:
      Min         1Q      Median         3Q         Max
-0.0184184 -0.0045990 -0.0006615  0.0037021  0.0214660

Coefficients:
              Estimate Std. Error  t value Pr(>|t|)
(Intercept)  15.113633   0.001340 11281.87   <2e-16 ***
poly(q, 3)1 -13.688421   0.008987 -1523.21   <2e-16 ***
poly(q, 3)2   3.547963   0.008987   394.81   <2e-16 ***
poly(q, 3)3   0.471980   0.008987    52.52   <2e-16 ***
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Residual standard error: 0.008987 on 41 degrees of freedom
Multiple R-squared:      1,     Adjusted R-squared:      1
F-statistic: 8.263e+05 on 3 and 41 DF,  p-value: < 2.2e-16
```

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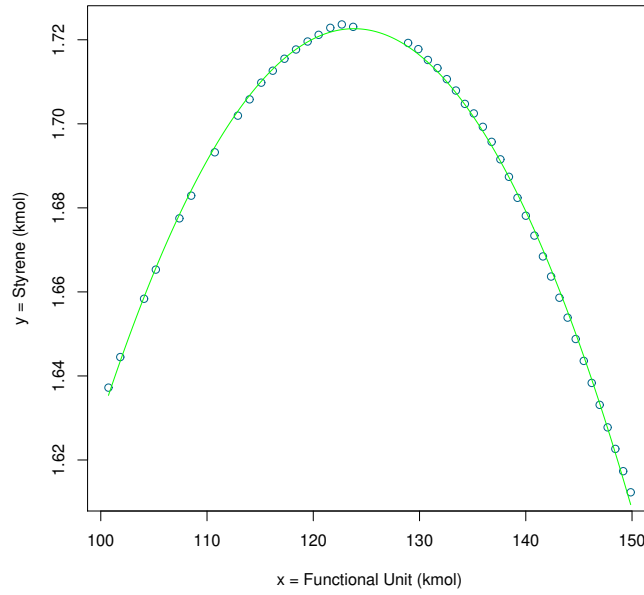
Figure 4.18: Styrene Air Emissions

$$y = 1.6826 - 0.0879x - 0.2044x^2 - 0.0012x^3 \qquad (4.23)$$

```
Call:
lm(formula = y ~ poly(q, 3))

Residuals:
      Min         1Q     Median         3Q        Max
-1.790e-03 -9.349e-04  8.345e-05  9.022e-04  2.959e-03

Coefficients:
              Estimate Std. Error   t value Pr(>|t|)
(Intercept)  1.6826722  0.0001677 10031.024   <2e-16 ***
poly(q, 3)1 -0.0879287  0.0011253   -78.139   <2e-16 ***
poly(q, 3)2 -0.2044737  0.0011253  -181.709   <2e-16 ***
poly(q, 3)3 -0.0012402  0.0011253    -1.102    0.277
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Residual standard error: 0.001125 on 41 degrees of freedom
Multiple R-squared:  0.999,     Adjusted R-squared:  0.9989
F-statistic: 1.304e+04 on 3 and 41 DF,  p-value: < 2.2e-16
```
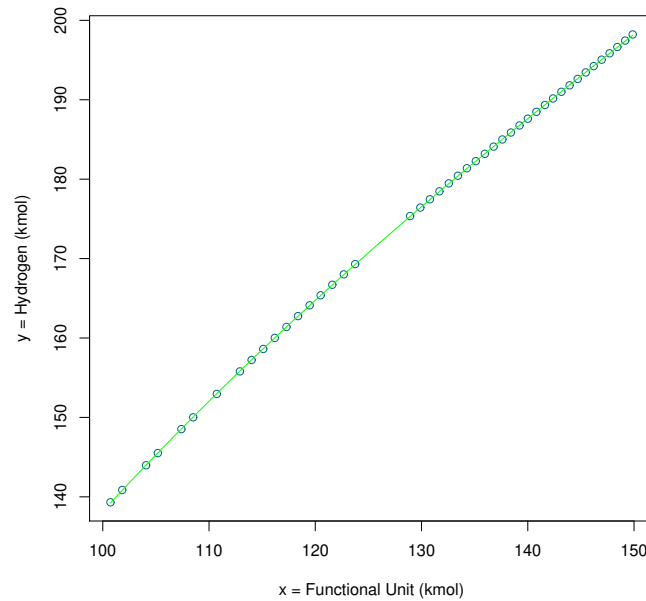
Figure 4.19: Hydrogen Air Emissions

$$y = 174.8571 + 115.2609x - 4.8257x^2 + 0.6333x^3 \qquad (4.24)$$

```
Call:
lm(formula = y ~ poly(q, 3))

Residuals:
    Min      1Q   Median      3Q      Max
-0.05035 -0.02898 -0.01122  0.02721  0.09001

Coefficients:
             Estimate Std. Error t value Pr(>|t|)
(Intercept) 174.857195   0.005458 32035.7   <2e-16 ***
poly(q, 3)1 115.260967   0.036615  3147.9   <2e-16 ***
poly(q, 3)2  -4.825728   0.036615  -131.8   <2e-16 ***
poly(q, 3)3   0.633373   0.036615    17.3   <2e-16 ***
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Residual standard error: 0.03661 on 41 degrees of freedom
Multiple R-squared:      1,     Adjusted R-squared:      1
F-statistic: 3.309e+06 on 3 and 41 DF,  p-value: < 2.2e-16
```
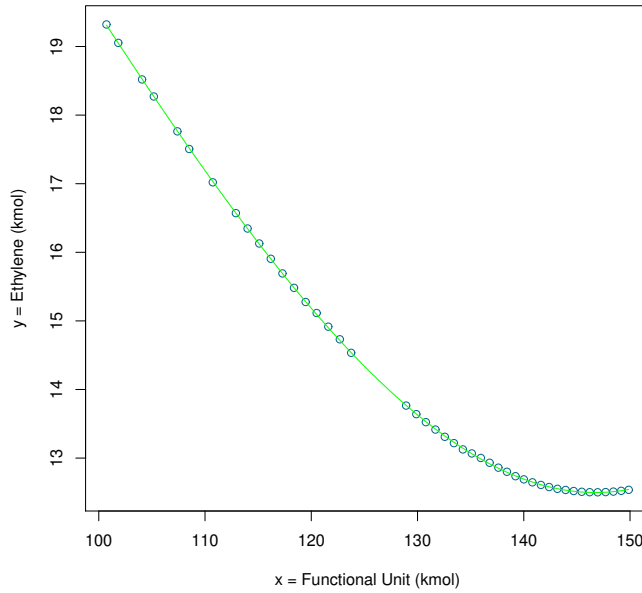
Figure 4.20: Hydrogen Air Emissions

$$y = 14.3393 - 13.4288x + 3.4054x^2 + 0.4667x^3 \qquad (4.25)$$

```
Call:
lm(formula = y ~ poly(q, 3))

Residuals:
      Min         1Q      Median         3Q        Max
-0.0181297 -0.0041681 -0.0009458  0.0034832  0.0208449

Coefficients:
             Estimate Std. Error  t value Pr(>|t|)
(Intercept)  14.339339   0.001301 11020.16   <2e-16 ***
poly(q, 3)1 -13.428877   0.008729 -1538.48   <2e-16 ***
poly(q, 3)2   3.405483   0.008729   390.15   <2e-16 ***
poly(q, 3)3   0.466764   0.008729    53.48   <2e-16 ***
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Residual standard error: 0.008729 on 41 degrees of freedom
Multiple R-squared:      1,     Adjusted R-squared:      1
F-statistic: 8.407e+05 on 3 and 41 DF,  p-value: < 2.2e-16
```

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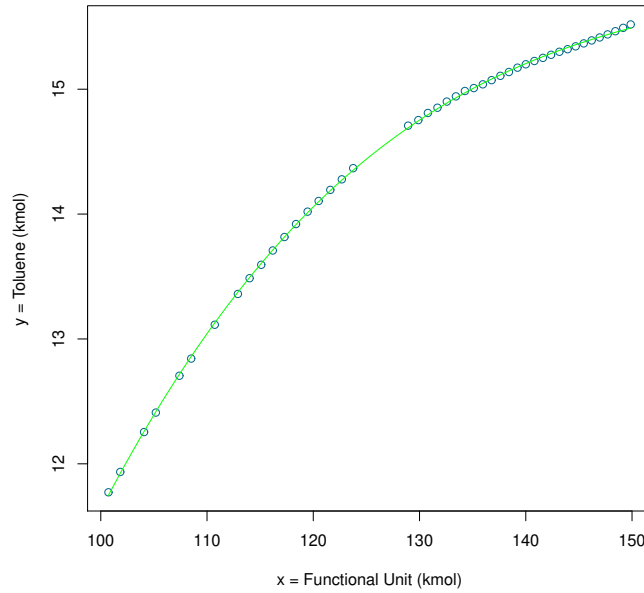
Figure 4.21: Toluene Air Emissions

$$y = 14.4305 + 6.8382x - 1.6909x^2 + 0.2132x^3 \qquad (4.26)$$

```
Call:
lm(formula = y ~ poly(q, 3))

Residuals:
     Min        1Q    Median        3Q       Max
-0.016544 -0.009190 -0.003821  0.007960  0.028755

Coefficients:
             Estimate Std. Error t value Pr(>|t|)
(Intercept) 14.430535   0.001773 8140.26   <2e-16 ***
poly(q, 3)1  6.838257   0.011892  575.04   <2e-16 ***
poly(q, 3)2 -1.690907   0.011892 -142.19   <2e-16 ***
poly(q, 3)3  0.213214   0.011892   17.93   <2e-16 ***
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Residual standard error: 0.01189 on 41 degrees of freedom
Multiple R-squared:  0.9999,    Adjusted R-squared:  0.9999
F-statistic: 1.171e+05 on 3 and 41 DF,  p-value: < 2.2e-16
```
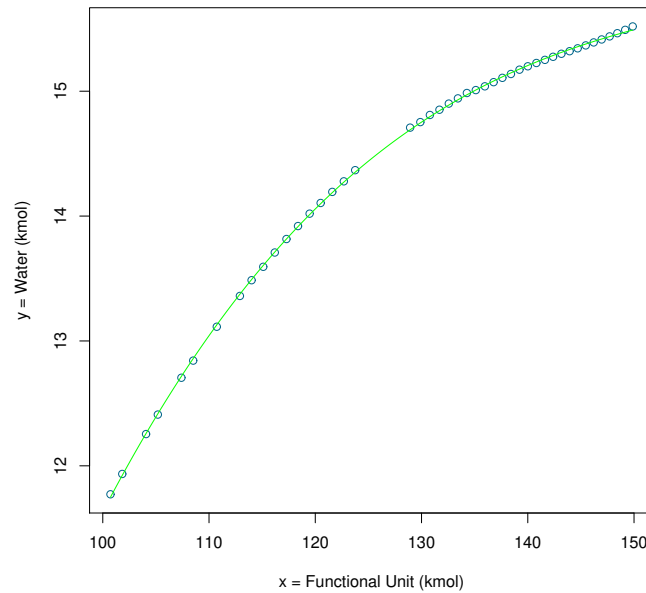
Figure 4.22: Water Air Emissions

$$y = 14.4305 + 6.8382x - 1.6909x^2 + 0.2132x^3 \qquad (4.27)$$

```
Call:
lm(formula = y ~ poly(q, 3))

Residuals:
     Min        1Q     Median        3Q        Max
-0.016544 -0.009190 -0.003821   0.007960   0.028755

Coefficients:
             Estimate Std. Error t value Pr(>|t|)
(Intercept) 14.430535    0.001773 8140.26   <2e-16 ***
poly(q, 3)1  6.838257    0.011892  575.04   <2e-16 ***
poly(q, 3)2 -1.690907    0.011892 -142.19   <2e-16 ***
poly(q, 3)3  0.213214    0.011892   17.93   <2e-16 ***
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Residual standard error: 0.01189 on 41 degrees of freedom
Multiple R-squared:  0.9999,   Adjusted R-squared:  0.9999
F-statistic: 1.171e+05 on 3 and 41 DF,  p-value: < 2.2e-16
```

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Figure 4.23: Carbon Dioxide Air Emissions

$$y = 13.4543 + 6.1394x - 1.4123x^2 + 0.1929x^3 \qquad (4.28)$$

```
Call:
lm(formula = y ~ poly(q, 3))

Residuals:
     Min        1Q    Median        3Q       Max
-0.015877 -0.008445 -0.003518  0.007620  0.027391

Coefficients:
             Estimate Std. Error t value Pr(>|t|)
(Intercept) 13.454319   0.001683 7992.98   <2e-16 ***
poly(q, 3)1  6.139498   0.011292  543.72   <2e-16 ***
poly(q, 3)2 -1.412351   0.011292 -125.08   <2e-16 ***
poly(q, 3)3  0.192948   0.011292   17.09   <2e-16 ***
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Residual standard error: 0.01129 on 41 degrees of freedom
Multiple R-squared:  0.9999,    Adjusted R-squared:  0.9999
F-statistic: 1.039e+05 on 3 and 41 DF,  p-value: < 2.2e-16
```

4.4.3   Modeling Energy Consumption
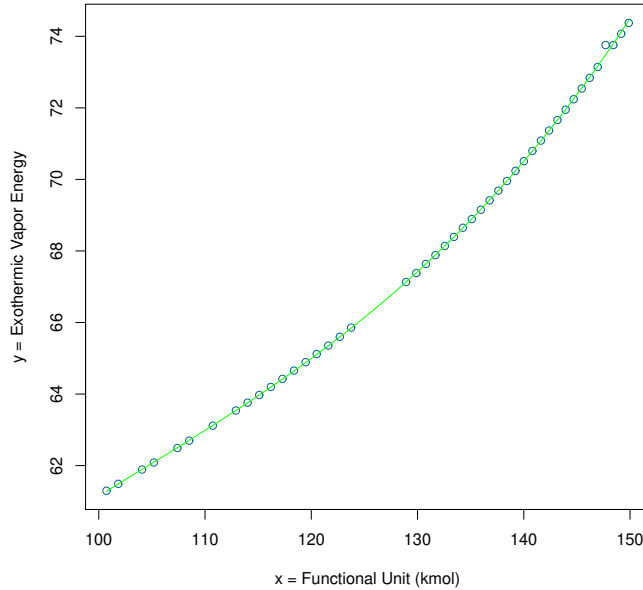
Figure 4.24: Exothermic Vapor Energy

$$y = 67.84 + 25.88x + 3.46x^2 + 0.67x^3 \qquad (4.29)$$

```
Call:
lm(formula = y ~ poly(q, 3))

Residuals:
      Min        1Q     Median        3Q       Max
-0.065341 -0.010555 -0.000819  0.003407  0.269583

Coefficients:
             Estimate Std. Error t value Pr(>|t|)
(Intercept) 67.846124   0.006795 9984.81   <2e-16 ***
poly(q, 3)1 25.885316   0.045582  567.89   <2e-16 ***
poly(q, 3)2  3.460367   0.045582   75.92   <2e-16 ***
poly(q, 3)3  0.676889   0.045582   14.85   <2e-16 ***
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Residual standard error: 0.04558 on 41 degrees of freedom
Multiple R-squared:  0.9999,    Adjusted R-squared:  0.9999
F-statistic: 1.095e+05 on 3 and 41 DF,  p-value: < 2.2e-16
```
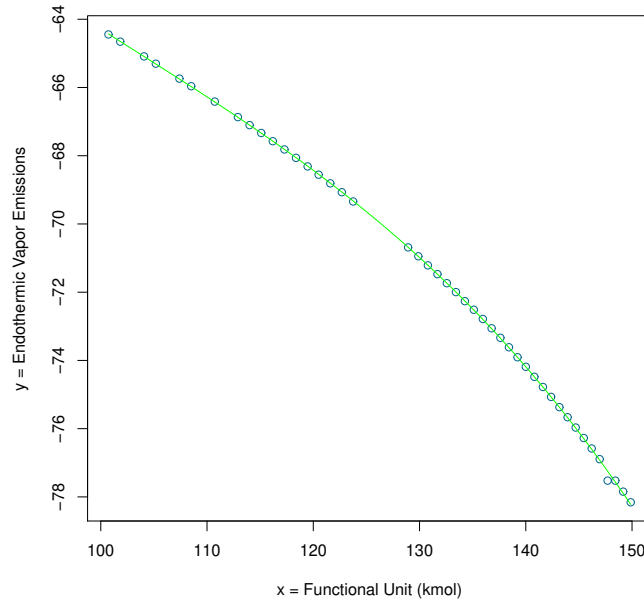
Figure 4.25: Exothermic Vapor Energy

$$y = -71.38 - 27.13x - 3.38x^2 - 0.67x^3 \qquad (4.30)$$

```
Call:
lm(formula = y ~ poly(q, 3))

Residuals:
     Min        1Q    Median        3Q       Max
-0.278015 -0.004608  0.001735  0.011894  0.061362

Coefficients:
             Estimate Std. Error   t value Pr(>|t|)
(Intercept) -71.38452    0.00697 -10242.40   <2e-16 ***
poly(q, 3)1 -27.13335    0.04675   -580.36   <2e-16 ***
poly(q, 3)2  -3.38088    0.04675    -72.31   <2e-16 ***
poly(q, 3)3  -0.67279    0.04675    -14.39   <2e-16 ***
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Residual standard error: 0.04675 on 41 degrees of freedom
Multiple R-squared:  0.9999,    Adjusted R-squared:  0.9999
F-statistic: 1.141e+05 on 3 and 41 DF,  p-value: < 2.2e-16
```

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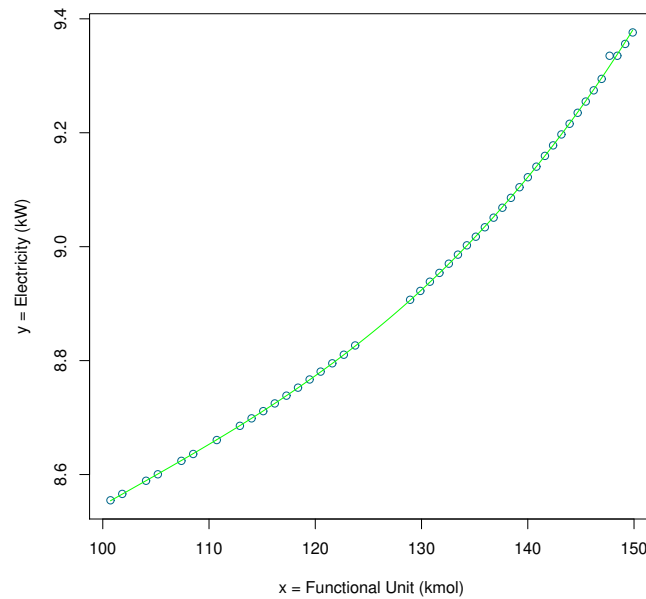
Figure 4.26: Electricity

$$y = 8.95 + 1.62x + 0.24x^2 + 0.046x^3 \tag{4.31}$$

```
Call:
lm(formula = y ~ poly(q, 3))

Residuals:
      Min          1Q      Median          3Q         Max
-0.0040406  -0.0007508  -0.0001328   0.0002990   0.0179915

Coefficients:
             Estimate Std. Error  t value Pr(>|t|)
(Intercept) 8.9563663  0.0004525 19792.47   <2e-16 ***
poly(q, 3)1 1.6258499  0.0030356   535.60   <2e-16 ***
poly(q, 3)2 0.2488676  0.0030356    81.98   <2e-16 ***
poly(q, 3)3 0.0466945  0.0030356    15.38   <2e-16 ***
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Residual standard error: 0.003036 on 41 degrees of freedom
Multiple R-squared:  0.9999,    Adjusted R-squared:  0.9999
F-statistic: 9.794e+04 on 3 and 41 DF,  p-value: < 2.2e-16
```

4.4.4 Modeling Total Emissions
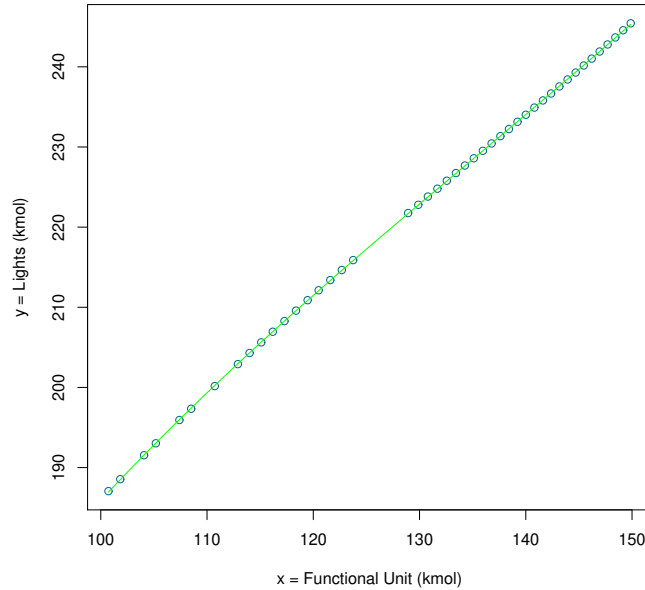
Figure 4.27: Total Light Gas Emissions

$$y = 221.6234 + 113.5849x - 2.7933x^2 + 1.3945x^3 \qquad (4.32)$$

```
Call:
lm(formula = y ~ poly(q, 3))

Residuals:
    Min       1Q    Median       3Q      Max
-0.08519 -0.03590 -0.01220  0.03510  0.12024

Coefficients:
              Estimate Std. Error  t value Pr(>|t|)
(Intercept) 221.623420   0.007629 29051.55   <2e-16 ***
poly(q, 3)1 113.584948   0.051174  2219.57   <2e-16 ***
poly(q, 3)2  -2.793373   0.051174   -54.59   <2e-16 ***
poly(q, 3)3   1.394592   0.051174    27.25   <2e-16 ***
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Residual standard error: 0.05117 on 41 degrees of freedom
Multiple R-squared:      1,      Adjusted R-squared:      1
F-statistic: 1.643e+06 on 3 and 41 DF,  p-value: < 2.2e-16
```

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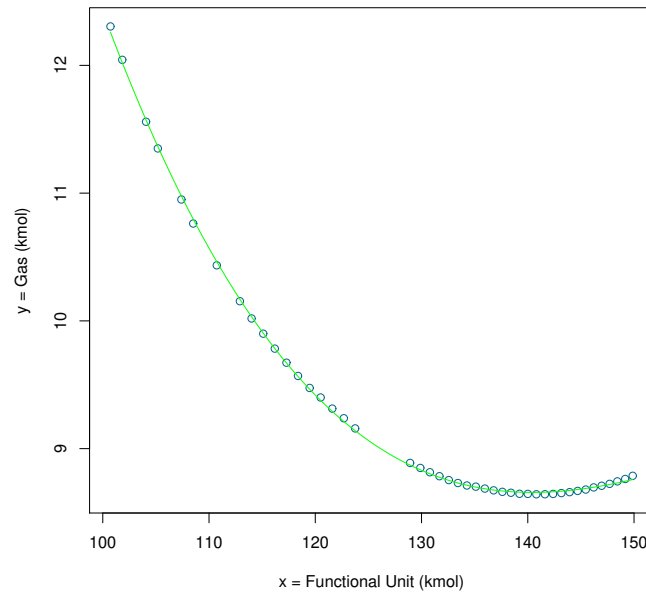
Figure 4.28: Total Gas Emissions

$$y = 9.3400 - 5.8923x + 2.9357x^2 - 0.3957x^3 \tag{4.33}$$

```
Call:
lm(formula = y ~ poly(q, 3))

Residuals:
      Min        1Q    Median        3Q       Max
-0.034782 -0.013413 -0.001165  0.011931  0.044893

Coefficients:
             Estimate Std. Error t value Pr(>|t|)
(Intercept)  9.340077   0.002557 3653.45   <2e-16 ***
poly(q, 3)1 -5.892382   0.017150 -343.59   <2e-16 ***
poly(q, 3)2  2.935715   0.017150  171.18   <2e-16 ***
poly(q, 3)3 -0.395762   0.017150  -23.08   <2e-16 ***
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Residual standard error: 0.01715 on 41 degrees of freedom
Multiple R-squared:  0.9997,     Adjusted R-squared:  0.9997
F-statistic: 4.93e+04 on 3 and 41 DF,  p-value: < 2.2e-16
```
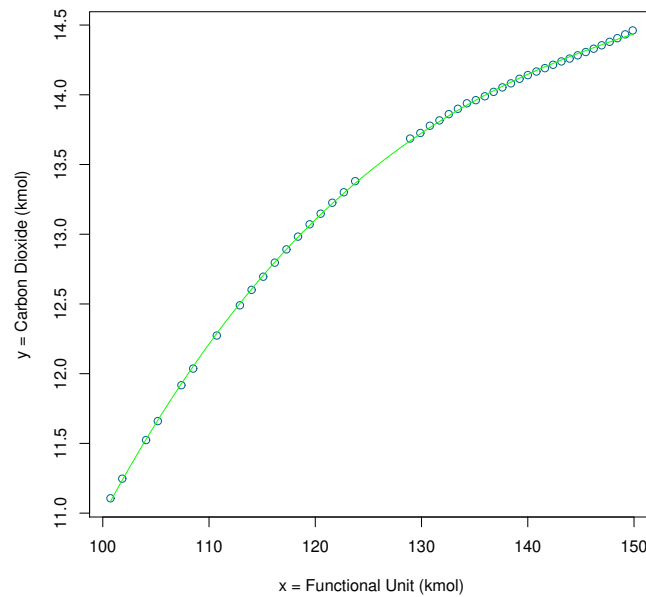
67
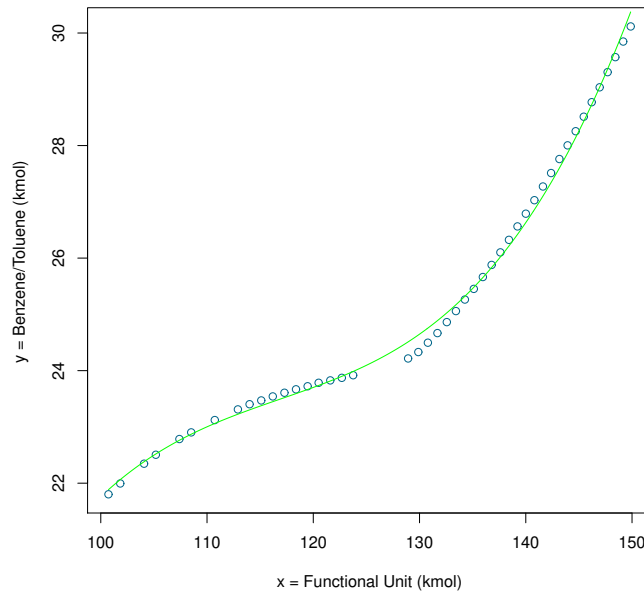
Figure 4.29: Total Benzene/Toluene Emissions

$$y = 25.4276 + 14.7979x + 4.4060x^2 + 2.1939x^3 \qquad (4.34)$$

```
Call:
lm(formula = y ~ poly(q, 3))

Residuals:
     Min       1Q    Median        3Q       Max
-0.30284 -0.06726   0.03252   0.09320   0.17137

Coefficients:
             Estimate Std. Error t value Pr(>|t|)
(Intercept) 25.42760    0.02017 1260.54   <2e-16 ***
poly(q, 3)1 14.79792    0.13532  109.36   <2e-16 ***
poly(q, 3)2  4.40607    0.13532   32.56   <2e-16 ***
poly(q, 3)3  2.19390    0.13532   16.21   <2e-16 ***
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Residual standard error: 0.1353 on 41 degrees of freedom
Multiple R-squared:  0.9969,    Adjusted R-squared:  0.9967
F-statistic:  4427 on 3 and 41 DF,  p-value: < 2.2e-16
```
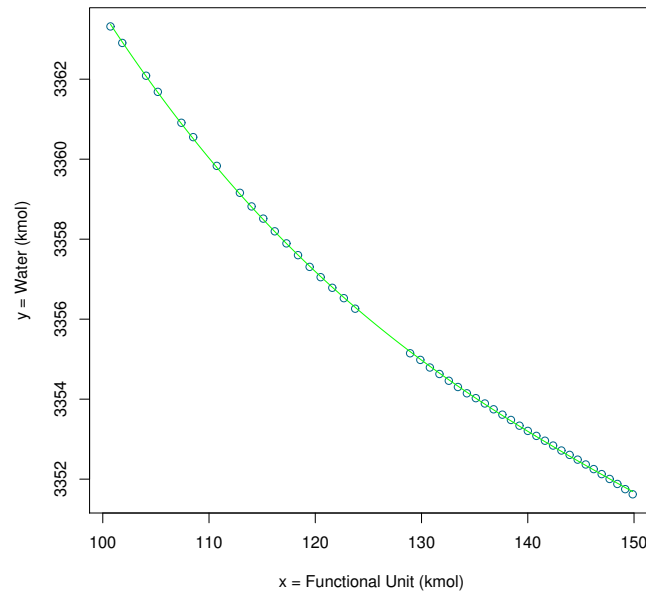
Figure 4.30: Total Water Emissions

$$y = 3355.6412 - 21.9550x + 3.1575x^2 - 0.5117x^3 \tag{4.35}$$

```
Call:
lm(formula = y ~ poly(q, 3))

Residuals:
      Min        1Q     Median        3Q       Max
-0.065814 -0.019424  0.007299  0.021516  0.037448

Coefficients:
              Estimate Std. Error   t value Pr(>|t|)
(Intercept)  3.356e+03  3.989e-03 841300.71   <2e-16 ***
poly(q, 3)1 -2.196e+01  2.676e-02   -820.55   <2e-16 ***
poly(q, 3)2  3.158e+00  2.676e-02    118.01   <2e-16 ***
poly(q, 3)3 -5.118e-01  2.676e-02    -19.13   <2e-16 ***
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Residual standard error: 0.02676 on 41 degrees of freedom
Multiple R-squared:  0.9999,    Adjusted R-squared:  0.9999
F-statistic: 2.292e+05 on 3 and 41 DF,  p-value: < 2.2e-16
```

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Chapter 5

Conclusions

This work represents a priceless technical path due to the fact that helps to reduce the amount of time and effort invested in the search of industrial and academic projects. Besides it has developed a methodology which reveals the importance of jointly applying tools for both process simulation and statistical modeling to facilitate the process of carrying out the LCI in early stage of a chemical process. All the steps of the methodology have been presented and they were emphasized through a case study about the styrene production process.

The case study described in this research highlighted how important is the use of process simulation and statistics modeling for achieving and quantifying the energy and raw material and emissions for overcoming the lack of available data to establish a reliable LCI. Not only a process already developed but also a process in early in early stage can be analyzed using a chemical process simulation software,this will be outlining the information about the industrial scale process with an appropriate level of detail fulfilling the purpose of the LCA of the project. Also statistical tools help to obtain equations that allow predicting the emissions generated for a specific functional unit. These equations can be used to determine the appropriate amount of styrene to attain a suitable level of generation of polluting emissions. Certainly, some experimental data are necessary to construct the simulation model and obtain the emission profile associated to the process. In this work, some available data reported in the literature have been used to test the proposed methodology.

The methodology considers not only the main energy and material flow which are essential for the industrial process but also their importance within the process. Moreover it permits to develop an LCA which will be made of simulated data entirely. The main benefit of the integration of statistical modeling in the LCI stage is its wide-range capability to analyze data obtained through the simulation, this will make possible to do an analysis of sensitivity on the environmental factors as well as their connections with the process conditions and the selected design choices. For instance,in this case study nineteen mathematical functions were obtained, and these helped to study the effect of a different functional unit in the styrene plant, in some cases the wastes increased or decreased on the environmental burdens.

The case study chiefly highlighted that a real LCA would always require wide-ranging research efforts. Whereas the proposed simplified approach for process design is a suitable framework able to review the scopes belonging to exploratory LCA studies scenarios for chemical processes whose databases are neither widely available in usual or easily accessible databases nor existing in record. In addition it was generated a dataset that can be used to help to develop an LCA related to the styrene process. It must be mention that for new products which the chemical parameters are not available it will be needed to research about it until getting the parameters needed for carrying out the simulation. As future work this methodology will be applied in other case where other methodology has been applied for obtaining the LCA, so we could compare both methods and observing differences in their results. As well as future work, free simulation software will be used.

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Appendix A

Simulation results

Table A.1: Total Streams.

Observation	UF	Lights	Gas	Benzene/Toluene	Water Waste
1	135.108	228.59	8.702	25.453	3354.025
2	144.695	239.287	8.669	28.255	3352.488
3	140.004	234.02	8.646	26.789	3353.207
4	114.004	204.296	10.019	23.403	3358.819
5	149.876	245.43	8.787	30.117	3351.621
6	120.504	212.122	9.4	23.784	3357.05
7	112.905	202.904	10.154	23.311	3359.159
8	101.835	188.55	12.043	21.995	3362.907
9	119.468	210.884	9.475	23.722	3357.307
10	129.887	222.786	8.849	24.33	3354.982
11	104.075	191.539	11.559	22.346	3362.087
12	136.784	230.441	8.673	25.879	3353.747
13	121.602	213.392	9.313	23.827	3356.785
14	145.456	240.164	8.68	28.513	3352.367
15	146.204	241.027	8.696	28.771	3352.251
16	141.615	235.805	8.643	27.272	3352.961
17	132.567	225.789	8.754	24.862	3354.46
18	138.414	232.239	8.655	26.324	3353.48
19	105.182	193.03	11.35	22.505	3361.684
20	135.959	229.521	8.687	25.664	3353.892
21	140.811	234.916	8.643	27.029	3353.082
22	123.754	215.885	9.158	23.918	3356.262
23	133.425	226.744	8.731	25.059	3354.304
24	118.375	209.582	9.569	23.668	3357.6
25	115.104	205.62	9.9	23.47	3358.514
26	108.511	197.338	10.762	22.903	3360.551
27	117.287	208.277	9.673	23.607	3357.895
28	131.685	224.798	8.784	24.667	3354.629
29	100.723	187.059	12.305	21.803	3363.319
30	148.43	243.666	8.744	29.571	3351.88
31	137.609	231.348	8.662	26.102	3353.613
32	147.702	242.792	8.724	29.304	3352.005
33	128.926	221.754	8.888	24.216	3355.147
34	122.686	214.648	9.238	23.872	3356.525
35	107.4	195.935	10.95	22.785	3360.91
36	146.954	241.91	8.709	29.035	3352.126
37	130.785	223.814	8.815	24.497	3354.791
38	143.165	237.555	8.652	27.76	3352.716
39	142.382	236.671	8.646	27.512	3352.84
40	149.169	244.563	8.762	29.848	3351.75
41	134.269	227.686	8.711	25.263	3354.147
42	116.188	206.949	9.783	23.542	3358.196
43	110.729	200.166	10.435	23.122	3359.833
44	139.22	233.142	8.647	26.563	3353.337
45	143.937	238.42	8.659	28.004	3352.607

Table A.2: Total Energy Flows.

Observation	UF	Exothermic Vapor Energy	Endothermic Vapor Energy	Electricity
1	145.456	72.54	-76.274	9.255
2	135.959	69.152	-72.785	9.034
3	115.104	63.973	-67.334	8.711
4	149.876	74.374	-78.158	9.376
5	120.504	65.117	-68.556	8.781
6	139.22	70.239	-73.907	9.104
7	146.954	73.143	-76.894	9.295
8	149.169	74.071	-77.846	9.356
9	128.926	67.133	-70.687	8.907
10	123.754	65.858	-69.341	8.827
11	122.686	65.601	-69.07	8.81
12	119.468	64.891	-68.314	8.767
13	143.165	71.66	-75.37	9.197
14	136.784	69.415	-73.058	9.051
15	101.835	61.491	-64.657	8.566
16	116.188	64.197	-67.574	8.725
17	143.937	71.947	-75.665	9.216
18	118.375	64.655	-68.063	8.753
19	135.108	68.891	-72.515	9.017
20	141.615	71.085	-74.778	9.159
21	133.425	68.392	-71.997	8.986
22	117.287	64.424	-67.816	8.738
23	132.567	68.14	-71.736	8.97
24	137.609	69.686	-73.337	9.068
25	131.685	67.884	-71.471	8.954
26	134.269	68.648	-72.263	9.002
27	129.887	67.382	-70.948	8.922
28	140.004	70.51	-74.186	9.122
29	146.204	72.839	-76.581	9.274
30	148.43	73.756	-77.523	9.335
31	142.382	71.367	-75.069	9.178
32	100.723	61.296	-64.445	8.555
33	147.702	73.756	-77.523	9.335
34	140.811	70.795	-74.48	9.14
35	138.414	69.955	-73.614	9.086
36	104.075	61.889	-65.088	8.589
37	107.4	62.491	-65.74	8.624
38	130.785	67.637	-71.213	8.939
39	114.004	63.758	-67.103	8.699
40	105.182	62.086	-65.302	8.6
41	121.602	65.356	-68.81	8.795
42	112.905	63.538	-66.868	8.686
43	110.729	63.116	-66.413	8.661
44	144.695	72.24	-75.967	9.235
45	108.511	62.698	-65.963	8.636

Table A.3: Emissions to Water.

Observation	UF	EB	B	S	H	E	T	W	CO2
1	135.108	0.054	0.066	0.077	0	0.186	0.017	3352.347	1.279
2	144.695	0.06	0.055	0.071	0	0.169	0.016	3350.877	1.241
3	140.004	0.057	0.06	0.074	0	0.175	0.017	3351.563	1.261
4	114.004	0.043	0.106	0.086	0	0.263	0.02	3356.994	1.307
5	149.876	0.063	0.051	0.068	0	0.164	0.015	3350.042	1.219
6	120.504	0.046	0.091	0.084	0	0.233	0.019	3355.267	1.309
7	112.905	0.043	0.109	0.087	0	0.268	0.02	3357.328	1.305
8	101.835	0.038	0.143	0.09	0	0.333	0.02	3361.012	1.27
9	119.468	0.046	0.093	0.084	0	0.237	0.019	3355.518	1.31
10	129.887	0.051	0.074	0.08	0	0.199	0.018	3353.265	1.294
11	104.075	0.039	0.135	0.09	0	0.319	0.02	3360.204	1.28
12	136.784	0.055	0.064	0.076	0	0.182	0.017	3352.08	1.272
13	121.602	0.047	0.089	0.084	0	0.229	0.019	3355.01	1.308
14	145.456	0.06	0.055	0.071	0	0.168	0.016	3350.761	1.237
15	146.204	0.061	0.054	0.07	0	0.167	0.015	3350.65	1.234
16	141.615	0.058	0.058	0.073	0	0.173	0.016	3351.329	1.254
17	132.567	0.053	0.069	0.078	0	0.192	0.018	3352.763	1.287
18	138.414	0.056	0.062	0.075	0	0.178	0.017	3351.826	1.267
19	105.182	0.039	0.132	0.089	0	0.312	0.02	3359.807	1.285
20	135.959	0.054	0.065	0.077	0	0.184	0.017	3352.219	1.275
21	140.811	0.057	0.059	0.074	0	0.174	0.016	3351.444	1.257
22	123.754	0.048	0.084	0.083	0	0.22	0.019	3354.501	1.307
23	133.425	0.053	0.068	0.078	0	0.189	0.018	3352.613	1.285
24	118.375	0.045	0.096	0.085	0	0.242	0.02	3355.803	1.31
25	115.104	0.044	0.104	0.086	0	0.257	0.02	3356.696	1.307
26	108.511	0.041	0.122	0.088	0	0.292	0.02	3358.694	1.295
27	117.287	0.045	0.098	0.085	0	0.247	0.02	3356.091	1.309
28	131.685	0.052	0.071	0.079	0	0.194	0.018	3352.926	1.29
29	100.723	0.037	0.147	0.09	0	0.341	0.02	3361.418	1.265
30	148.43	0.062	0.052	0.069	0	0.165	0.015	3350.292	1.225
31	137.609	0.055	0.063	0.076	0	0.18	0.017	3351.952	1.27
32	147.702	0.062	0.053	0.069	0	0.166	0.015	3350.413	1.228
33	128.926	0.051	0.075	0.08	0	0.202	0.018	3353.424	1.297
34	122.686	0.047	0.087	0.083	0	0.224	0.019	3354.758	1.307
35	107.4	0.04	0.125	0.089	0	0.298	0.02	3359.046	1.292
36	146.954	0.061	0.053	0.07	0	0.166	0.015	3350.529	1.231
37	130.785	0.052	0.072	0.079	0	0.197	0.018	3353.081	1.292
38	143.165	0.059	0.057	0.072	0	0.171	0.016	3351.095	1.247
39	142.382	0.058	0.057	0.073	0	0.172	0.016	3351.213	1.251
40	149.169	0.062	0.052	0.068	0	0.164	0.015	3350.166	1.222
41	134.269	0.053	0.067	0.078	0	0.187	0.017	3352.461	1.282
42	116.188	0.044	0.101	0.086	0	0.252	0.02	3356.385	1.308
43	110.729	0.042	0.115	0.088	0	0.279	0.02	3357.988	1.301
44	139.22	0.056	0.061	0.075	0	0.177	0.017	3351.688	1.264
45	143.937	0.059	0.056	0.072	0	0.17	0.016	3350.991	1.244

Table A.4: Emissions to Air.

Observation	UF	EB	B	S	H	E	T	W	CO2
1	135.108	5.752	13.809	1.702	182.268	13.068	15.009	17.175	13.961
2	144.695	8.45	13.266	1.649	192.624	12.52	15.343	18.076	14.283
3	140.004	7.07	13.431	1.678	187.613	12.69	15.2	17.632	14.141
4	114.004	3.996	17.155	1.706	157.234	16.347	13.486	15.191	12.601
5	149.876	10.089	13.296	1.612	198.223	12.538	15.519	18.597	14.461
6	120.504	4.129	15.892	1.721	165.377	15.115	14.105	15.821	13.147
7	112.905	3.981	17.386	1.702	155.796	16.571	13.36	15.083	12.49
8	101.835	3.945	19.943	1.644	140.864	19.053	11.935	13.956	11.247
9	119.468	4.102	16.057	1.72	164.115	15.276	14.02	15.721	13.071
10	129.887	4.626	14.388	1.718	176.422	13.641	14.753	16.693	13.726
11	104.075	3.932	19.393	1.658	143.974	18.52	12.254	14.189	11.524
12	136.784	6.173	13.672	1.696	184.098	12.932	15.072	17.329	14.021
13	121.602	4.156	15.689	1.723	166.706	14.916	14.194	15.923	13.226
14	145.456	8.685	13.256	1.644	193.44	12.509	15.367	18.15	14.307
15	146.204	8.918	13.252	1.638	194.237	12.503	15.391	18.225	14.33
16	141.615	7.533	13.351	1.668	189.336	12.609	15.251	17.781	14.191
17	132.567	5.159	14.053	1.711	179.47	13.31	14.901	16.94	13.861
18	138.414	6.614	13.541	1.687	185.874	12.801	15.138	17.48	14.082
19	105.182	3.93	19.136	1.665	145.506	18.271	12.41	14.305	11.66
20	135.959	5.96	13.743	1.699	183.188	13.002	15.039	17.252	13.989
21	140.811	7.3	13.388	1.673	188.479	12.647	15.226	17.706	14.167
22	123.754	4.221	15.299	1.723	169.311	14.534	14.368	16.126	13.381
23	133.425	5.356	13.96	1.708	180.43	13.218	14.943	17.019	13.9
24	118.375	4.076	16.269	1.718	162.757	15.482	13.92	15.615	12.983
25	115.104	4.013	16.931	1.71	158.621	16.128	13.594	15.298	12.695
26	108.511	3.937	18.348	1.683	150.007	17.506	12.843	14.643	12.037
27	117.287	4.053	16.484	1.715	161.395	15.692	13.816	15.51	12.891
28	131.685	4.965	14.16	1.713	178.468	13.416	14.852	16.859	13.816
29	100.723	3.955	20.221	1.637	139.312	19.322	11.772	13.84	11.106
30	148.43	9.621	13.266	1.623	196.642	12.512	15.465	18.446	14.406
31	137.609	6.395	13.601	1.692	184.999	12.861	15.107	17.404	14.053
32	147.702	9.389	13.257	1.628	195.852	12.504	15.439	18.372	14.38
33	128.926	4.502	14.515	1.719	175.355	13.765	14.708	16.607	13.686
34	122.686	4.187	15.5	1.724	168.012	14.732	14.278	16.025	13.301
35	107.4	3.933	18.612	1.678	148.529	17.763	12.705	14.533	11.917
36	146.954	9.153	13.252	1.633	195.047	12.501	15.414	18.299	14.355
37	130.785	4.788	14.269	1.715	177.464	13.524	14.81	16.778	13.778
38	143.165	7.994	13.296	1.659	190.999	12.552	15.3	17.93	14.239
39	142.382	7.759	13.321	1.664	190.161	12.578	15.276	17.854	14.215
40	149.169	9.86	13.279	1.617	197.449	12.523	15.491	18.522	14.433
41	134.269	5.562	13.868	1.705	181.378	13.126	14.986	17.098	13.939
42	116.188	4.033	16.703	1.713	160.01	15.906	13.708	15.405	12.796
43	110.729	3.955	17.848	1.693	152.954	17.02	13.114	14.866	12.274
44	139.22	6.85	13.477	1.682	186.764	12.736	15.173	17.556	14.115
45	143.937	8.219	13.281	1.654	191.813	12.535	15.32	18.002	14.26

Appendix B

Recognitions

ITAM
INSTITUTO TECNOLÓGICO AUTÓNOMO DE MÉXICO

SMIO
SOCIEDAD MEXICANA DE
INVESTIGACIÓN DE OPERACIONES

Certificado de Participación

O T O R G A D O A :

Moisés Cortés Jerónimo

por su activa e invaluable participación como Autor en el

VIII Congreso de la Sociedad Mexicana de Investigación de Operaciones (CSMIO2019)

con el trabajo titulado *"Aplicación de la técnica TOPSIS para priorizar la introducción al mercado de productos a base de malanga"*

que se realizó del 16 al 18 de octubre de 2019 en el Instituto Tecnológico Autónomo de México.

DR. DAVID MUÑOZ
JEFE DEL DEPARTAMENTO DE INGENIERÍA
INDUSTRIAL Y OPERACIONES ITAM

DR. LUIS A. MONCAYO MARTÍNEZ
PRESIDENTE COMITÉ ORGANIZADOR DEL
CSMIO2019

Je confirme par la présente que je souhaite accueillir au sein Département Procédés et Systèmes Industriels du Laboratoire de Génie Chimique, **Moises Cortés Jerónimo** étudiant en Master en Modelacion y Optimizacion de Procesos au Centro de Investigación en Matemáticas, A.C., pour y effectuer un stage Master Recherche du 1 Julliet au 31 Août (2 mois), sous ma responsabilité scientifique, sous réserve de la gratification de stage versée par l'organisme CONACYT.

Le sujet portera sur l'Analyse du Cycle de Vie de Batteries, notamment lithium-ion (Li-ion).

Fait pour valoir ce que de droit,
Toulouse, le 6 avril 2018

Catherine Azzaro-Pantel
Professeur INP ENSIACET

Prof. Catherine AZZARO-PANTEL
Directrice
Ecole Doctorale MEGeP
Université de Toulouse

Campus Institut National Polytechnique　　**Campus Université Paul Sabatier**　　www.lgc.cnrs.fr

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Université de Toulouse

Toulouse, Francia, 31 de Agosto de 2018
ASUNTO: Carta de liberación de estancia

Sergio Martín Nava Muñoz
Coordinador de la Maestría en Modelación y Optimización de Procesos
PRESENTE

Por medio de este conducto, hago constar que el (la) C. **Moisés Cortés Jerónimo**, estudiante de la **Maestría en Modelación y Optimización de Procesos** del Centro de Investigación en Matemáticas, A.C., realizó una estancia en nuestra empresa **(LABORATOIRE DE GENIE CHIMIQUE)** en el periodo del día 01 de julio de 2018 hasta el día 31 de agosto de 2018, generando los siguientes productos:

-   Reporte técnico con al menos una introducción, un marco teórico, resultados y discusiones, conclusiones y referencias.
-   Una presentación que sintetice el trabajo que se realizó.

Doy fe de la realización y buena entrega de los productos mencionados.

Sin otro asunto de momento y agradeciendo de antemano la atención que se sirva brindar a la presente, quedo de usted.

Responsable/Facilitador en la Empresa

Prof. Catherine AZZARO-PANTEL
Directrice
Ecole Doctorale MEGeP
Université de Toulouse

Catherine AZZARO-PANTEL

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