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INNOVATION IN CONCEPTUAL DESIGN OF CHEMICAL PROCESSES

Presentata da: Eugenio Tacchini

Coordinatore Dottorato

Alessandro Tugnoli

Supervisore

Valerio Cozzani

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Table of content

Table of content 3
Abstract 7
Section 1: Introduction 8
Importance of Polyolefin production 8
Sustainability in process industry 9
Sustainability and circular economy 9
Plastic and Sustainability 10
Sustainability in Process Design 11
Management of change 13
Section 2: Proposed methodologies and tools 14
Sustainable Design Portfolio 14
Process Design Assessment Method (PDAM) 15
General Overview of the Method 15
Preliminary activities 16
Data gathering and process simulation 18
Primary process data collection 18
Background process data collection 20
Calculation of a set of Indicators 21
Calculation of environmental indicators 22
Classification 24
Characterization 24
Combination 25
Normalization 25
Calculation of exergy indicators 25
Calculation of economic indicators 26
Interpretation and sensitivity 27
Calculation support tool 27
Screening method for polyolefin technology comparison 28
Overview of the problem 28
Procedure outline 29
Definition of the reference 30
Data gathering 32
Assumptions 32
Indicators calculation 32

Environmental performance indicators 33
Excess of raw material (Hydrocarbons) 34
Exergy destruction and loss 34
Exergy Indicator: focus on calculation and interpretation 35
Specific provisions on step 1 and 2 of PDAM 35
Step 1. Definition of the reference scheme 35
Step 2.1 Data gathering 35
Step 2.2 Process simulation 36
Calculation of Exergy Indicator 36
Step 3.1 Application of the Exergy Balance 36
Reference environment 38
Step 3.2. Calculation of Exergy destruction and Exergy efficiency 39
Interpretation of Exergy Indicator results 40
Database of energy sources 40
General overview 40
Definition of the Reference 41
Indicators calculation 43
Environmental impacts indicators 43
Safety Indicator 43
Economic indicator 43
Data gathering 44
Results 44
Conclusions 47
Section 3: Case Studies 48
Case Study 1: Environmental impact evaluation of polypropylene production chain 49
Case-study description 49
Definition of the reference scheme 49
Definition of input data 50
Data gathering for Unit process within the Design Scope 50
Results from methodology application 53
Interpretation and sensitivity 54
Final remarks 56
Case study 2: Screening of principal polypropylene polymerization technologies 57
Overview of current propylene production technologies 57
Identification of reference schemes for technologies 63
Indicator results 71

Role of the context 76
Role of process improvement 77
Final remarks and results overview 79
Annex 1 – Emission factors for GWI computation 80
Annex 2 - Assumptions for the calculation of Ex,d 81
Case study 3: Comparison of polymerization processes based on reaction phases 82
Case-study description 82
Definition of the reference 82
Results 83
Final remarks 85
Case study 4: Exergy case study 86
Case-Study 4A: Application of PDAM to polymerization option with principal focalization on exergy analysis 87
Definition of the reference scheme 87
Data gathering e process simulation 90
Thermodynamic models 90
Assumptions 91
Exergy characterization of streams 92
Application of exergy balance 94
Computational of Exergy destruction and Exergy efficiency 94
Final remarks 95
Case-Study 4b: Analysis of potential polypropylene process improvements 97
Introduction of a heat exchanger (2) 97
Data gathering and assumptions 98
Definition of the optimal heat exchanger (1) outlet temperature 99
Definition of the exergy minimum condition 100
Results and discussion 103
Substitution of reactors' pumps and compressor with steam turbines 105
Definition of the reference schemes 105
Data gathering and simulations 105
Economic results 109
Exergetic results 111
Final Remarks 111
Introduction of a splitter unit 112
Definition of the reference scheme 112
Data gathering and process simulation 113

Environmental results 114
Exergetic results 115
Final Remarks 115
Conclusions 116
References 119
ANNEX A 126
Introduction 126
General description of the process 126
Typical alternative configurations 127

Abstract

Nowadays, the chemical industry has reached significant goals to produce essential components for human being. Multiple process options and alternatives are typically well defined and developed to produce a single product at industrial scale. The growing competitiveness of the market caused an important acceleration in R&D activities, introducing new opportunities and procedures for the definition of process improvement and optimization. In this dynamicity, sustainability is becoming one of the key aspects for the technological progress encompassing economic, environmental protection and safety aspects.

With respect to the conceptual definition of sustainability, the literature reports an extensive discussion of the strategies, as well as sets of specific principles and guidelines. However, literature procedures are not completely suitable and applicable to process design activities. Therefore, the development and introduction of sustainability-oriented methodologies is a necessary step to enhance process and plant design. The definition of key drivers as support system is a focal point for early process design decisions or implementation of process modifications. In this context, three different methodologies are developed to support design activities providing criteria and guidelines in a sustainable perspective. In this framework, a set of key Performance Indicators is selected and adopted to characterize the environmental, safety, economic and energetic aspects of a reference process. The methodologies are based on heat and material balances and the level of detailed for input data are compatible with available information of the specific application.

Multiple case-studies are defined to prove the effectiveness of the methodologies. The principal application is the polyolefin productive lifecycle chain with particular focus on polymerization technologies. In this context, different design phases are investigated spanning from early process feasibility study to operative and improvements assessment. This flexibility allows to apply the methodologies at any level of design, providing supporting guidelines for design activities, compare alternative solutions, monitor operating process and identify potential for improvements.

The work is divided in 3 main sections:

- **Section 1** provides an introduction to the approaches for the implementation of sustainability in design activities. Potential applications and expected results are briefly described.
- **Section 2** describes the portfolio of developed methodologies with particular focus on Goal and scope, required input and expected results.
- **Section 3** presents several case studies demonstrating the application and flexibility of the developed methodologies. The case studies concern the analysis of polypropylene productive chain, a comparison of different polymerization technologies and the identification of optimal configuration for process improvement.

Section 1: Introduction

Importance of Polyolefin production

During its history of only less than 80 years, plastics have emerged as the key material in a huge variety of applications regarding automotive, aerospace, packaging, etc. The global plastic market size was valued at USD 568.9 billion in 2019 [1] and is expected to grow at a compound annual growth rate (CAGR)of 3.2% from 2020 to 2027 as illustrated in Fig. 1.

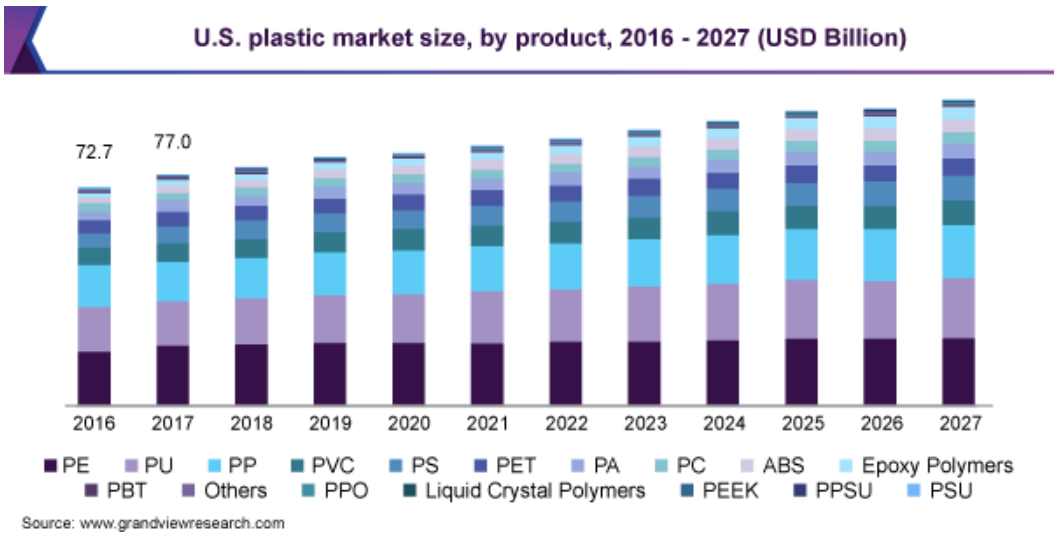


Figure 1: Annual US Plastic market size

During the last few decades, in terms of global per-capita [2], plastics clearly outperformed competing materials such as wood, metal, glass and ceramic as a material of construction. There is a continuing trend of the substitution of these competing materials by plastics in building, packaging, construction and medical devices. The principal reason behind this impressive market success of plastics is attributed to its unique functionality [3] and low cost [4]. On the other hand, Plastic pollution has gained viral attention in recent decade, mainly focusing on the waste disposal problem. The ever-increasing demand for plastic products has led to an inevitable increase in plastic waste and consumption of oil-based raw materials. In this framework, the management of plastic waste fraction has become one of the most debated issues during the discussion on the integrated municipal solid waste systems. Several technologies are well-known and implemented for energy and material recovery. While new unconventional processes are studied to reach higher sustainability targets and reduce the carbon footprint of plastic disposal. A schematic overview of plastic waste management is exhibited in Fig. 2 derived from literature [5].

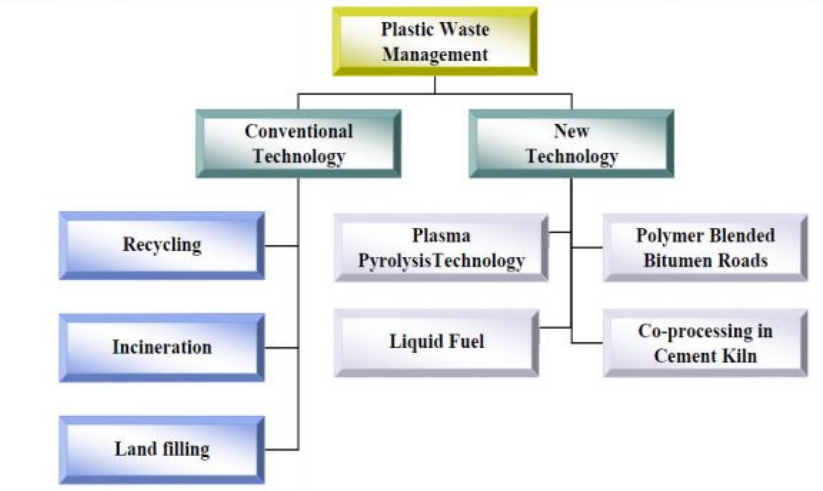


Figure 2: Plastic waste management scheme

In this thesis a particular focus is given to Polypropylene as one of the major plastic products all over the world. Polypropylene (PP) is a thermoplastic polymer that finds a wide number of applications in packaging, textiles, stationery, containers, and components in the manufactory industry. Polypropylene production is a well-established industrial process, whose history dates back to 1954 with the development of a stereoregular polymer by Giulio Natta and Karl Ziegler [6]. Nowadays about 130 Mt of polypropylene is produced every year all over the world with a growth forecast of up to 192 Mt/y by 2030 [7]. New plants are continuously built to full fill the ever-increasing plastic demand. In spite of the fossil origin of the feedstocks currently used in production of PP, outlooks of the future of the market agree on the expectation that production will increase, and new plants will be built in the future [8].

Sustainability in process industry

Sustainability and circular economy

Sustainability is a complex and nonlinear concept. There is no universally agreed definition of sustainability. In fact, there are several viewpoints of the concept with different approaches and targets. Etymologically, the word *sustainability* is formed by the coupling of sustainable + ity. Moreover, *sustainable* is a composition of sustain + able which means “give support to”, “to hold up” or “to bear”. Applied to the human sphere, sustainability aims to a balanced and respectful way to conduct our activities which can be improved or at least maintained indefinitely. Sustainability encourages businesses to frame decisions in terms of environmental, social, human and reputation impact for both long-term and short-term decisions. In this framework, it’s popular to define not the sustainability itself, but the collection of dynamic processes and approaches that evolve in accordance with sustainability aspects. This concept defines the *sustainability development.* The idea of *sustainability development* was first widely articulated in the World Commission on Environment and Development [9]. The “Brundtland definition” of this concept was framed as “the development that meets the needs of the present without compromising the ability of future generations to meet their own needs". This definition posits that the right sustainable form of process matches simultaneously aspects of economy, environment and social and their connections.
Earth’s natural resources are inevitably limited in quantity and, once depleted, have their personal and specific regeneration rates. This qualitative observation is at the base to a development model that interfaces human activities with the Earth in a sustainable way, in order to allow long-term

coexistence and prosperity. In this framework, the Triple Bottom Line (TBL) theory is developed to achieve new sustainability targets. This methodology believes that companies should commit to focusing as much on social and environmental concerns as they do on their own profits. TBL posits that instead of one bottom line, there should be three main concepts: Profit, People and Planet. A TBL seeks to gauge a corporation's level of commitment to corporate social responsibility and its impact on the environment over time. This approach is based on guidelines introduced by the sustainability development concept and could face the challenge of a sustainability progress. Fig reports the definitions and the interlinking of the three major aspects of the theory.

Figure 3: Sustainability ad a combination of different aspects

Plastic and Sustainability

Plastic is not only a versatile material allowing it to be used for a huge variety of uses but it also has benefits in terms of sustainability. Recent studies demonstrate that the environmental cost to replacing plastic with alternatives materials would be nearly 4 times greater [10]. Principal sustainability characteristics of plastic are:

- *Lightweight*: The low density on this material allows to save around 3000 litres of fuel over the lifetime of an average car
- *Durability*: Plastic has a high durability against environmental agents. Typical piping applications prove that plastic pipes are designed to last for more than 100 years and they can reduce the overall failure rate [11].
- *Water saving*: Processes for plastic production are usually more eco-friendly. For example, processes required for the production of a plastic bags reduce the consumption of water and energy required compared to paper bag's processes [12]
- *Bio-inhert*: Plastics is the principal material uses for food-contact application. It's able to preserve specific atmosphere for food-packaging extending their shelf-life and preventing waste generation.

- *Formability*: Plastics can be simply processed in multiple shape with low energy technologies as injection moulding or blow moulding. Formability can also allow the recyclability at low-cost.

Furthermore, plastic waste represents one of the great environmental challenges of our time. Plastic waste is widely recognized as a major environmental issue because most plastics do not biodegrade, and they are estimated to persist for centuries to millennia into the environment [13]. In this framework, the most impactful class is represented by single-use plastic products (SUPs) which are used once or for a short period of time before being thrown away. Single-use plastic products are more likely to end up in our seas than reusable options. The 10 most commonly found single-use plastic items on European beaches, alongside fishing gear, represent 70% of all marine litter in the EU [14].

Recently, a promising new technique has been developed, which converts waste plastics into petrochemical feedstock by injecting them into a gas-fluidised bed of heated particles. Heat transferred to the plastic cracks long-chain molecules into shorter hydrocarbons which are extracted from the system and refined into valuable petrochemical products.

Despite demonstrating considerable potential, there remain significant impediments to the development, upscaling, and widespread adoption of this technology; the proposed project directly addresses these issues, helping to bring fluidised-bed-based waste-plastic recycling from a promising and potentially transformative nascent technology to a scalable, adaptable and commercially-viable reality.

Sustainability in Process Design

The theoretical principles of sustainability reported in the previous sections point out the role of the design phase in defining the sustainability of the process. In particular, early design steps of a process (e.g feasibility study, conceptual design) show a great potential for the implementation of sustainability, since they define some core elements for the impact of a product all over its lifecycle.

The principles of sustainability provide theoretical support and inspiration, but do not help an effective implementation of sustainability criteria during design activities. In this scenario, practical tool and procedures are required for the quantification of sustainability index and performance of a reference system. These strategies should be flexible and applicable with the available level of design information. Although many significant efforts were made in this direction, the availability of widely accepted quantitative assessment tools suitable for supporting process design activities is still limited.

Some Authors [15] [16] identified sustainability indicators in the evaluation of a critical parameters directly related to the process (non-renewable energy consumption, consumption of non-renewable raw materials, waste production, water use, CO_2 emission, yield, value creation, etc.). Other literature assessment are tailored to the consumption of raw material and energy for process optimization [17]. Though these parameters define the sustainability profile of the reference system, the connection between their value and the impact of the process is not straightforward. Thus, the size of positive effects on sustainability of marginal improvements on some of those parameters is difficult to recognize.

Sustainable indicators and criteria for the assessment and characterization of process profile are usually calculated elaborating raw process data. Several approaches were proposed in the literature

to assess sustainability aspects of projects [18] ,industrial layout [19] or multiple process options [20]. Results are typically proposed through midpoint environmental indicators [21] [22] or endpoint criteria [23] [24].

However, they are not completely suitable to support early process design activities and be adopted as driver for conceptual design of chemical plant. The current presented methodologies are tailored to the chemical industrial sphere, with particularly focus on early design operations. In general, the following methodologies are intended to identify critical issues within a reference scheme, compare the obtained Key Performance Indicators with benchmark results, propose new alternative solutions to optimize the system and quantify potential improvements impacts from sustainability standpoint. In this framework, iterative approaches will be introduced through the application of developed methodologies to support early process design decisions. Process Design of polyolefin project is the principal scope of the assessment which includes conceptual design and the know-how proprietary bases. This function is involved in the conceptual design phase of new licensed plants for different polymeric pellet production (e.g., PP, PE, PB). Conceptual design phase is characterized by low costs for process changings and high degrees of freedom. In this framework, the presented methodologies can support the design of new plant during their early design activities by monitoring their sustainability performances, defining critical issues and comparing alternative solutions. Output of these methodologies can be helpful for equipment or unitary operation choices and definition of optimal thermodynamic conditions with low computational time and costs for process changes. Furthermore, improvement assessment projects are suitable applications for the developed methodologies. The current presented methodologies can support decision making also for these activities, defining strength and weaknesses of already implemented schemes and proposing the optimal working conditions for specific equipment. In these cases, sustainability benefits are compared with potential costs changing from current configuration.

The developed methodologies are flexible and suitable for multiple process design phases. The following Tab. 1 briefly highlights the involved design phases, the principal targets for the application of methodologies and the description of the application.

Table 1: Sequential process design phases and description of methodologies' application

Process design phases	Description of application
Feasibility Study	Support early characterization of a process
Conceptual design	Provide guidelines to support early process design activities
Basic design	Define more specific Sustainability profile based on vendors' reports
Detailed design	Characterize reference process based on detailed information
Construction	Methodologies are not applicable to this phase
Operation	Monitor the performance of operating process
Process Changing	Provide strategies for alternative comparisons
Decommissioning	Methodologies are not applicable to this phase

Management of change

Operating processes are continuously monitored and under specific assessment to determinate potential improvements or technologies modifications. In this context, when a modification is required, for process, safety or manufacturing reason, a proper Management of Change procedure is required. Generally, it is defined by HSE department providing criteria and guidelines to finalize the project. Scopes of this procedure are “manufacturing” and “Research and Development” activities. In this framework, industrial procedure schedules the required steps to carry out a process changing and is finalized to ensure that there is no repercussion on Health, Environmental and Safety aspects related to the modification. The presented methodologies provide criteria and drivers for the quantification of Sustainability aspects of a project. In this direction, the developed procedures can give integrity and support industrial Management of Change quantifying the potential impacts and performances of a process modification.

Section 2: Proposed methodologies and tools

Sustainable Design Portfolio

This section briefly introduces the developed methods in terms of Involved design lifecycle phase, Goal, Scope, principal Input and Output. Methodologies are based on simple and practice tools to support early process design activities of new processes, identify critical issues and compare alternatives solutions. Methods are versatile and can be applied to any level of available information during early design activities or operative phases. In this context, the presented methods are intended to introduce new sustainability concepts as supportive guidelines for design procedure. Principal output of the methodologies are Key Performance Indicators (KPI) which intends to characterize environmental footprint, energetic performance, safety and economic aspects of a reference scheme.

Direct application of the methodologies is the polyolefin production sphere, regarding specific polymerization technologies, monomer production unit and material and energy supply processes. However, new targets can be selected in accordance with the scope of the methodology. The following Tab. 2 reports a schematization of the methodologies.

Table 2: Brief introduction of the developed methodologies

Methodology	Involved phase in design lifecycle	Goal	Scope	Main input data required	Principal Results
PDAM: Process design assessment method	1) design phases (e.g., feasibility, conceptual) 2) Operative phase	1) Identify process inefficiencies 2) Support design choices improvement opportunities 3) Define criteria for process comparison	1) Overall productive chain 2) Specific Plant framework	1) Process scheme 2) Energy and material balances (design scope process, auxiliary options)	1) KPIs regarding Sustainability sphere: Environmental, Economic and Exergetic aspects 2) Design support guidelines
Screening method for polyolefin technology comparison	Operating Plants	Compare the alternative processes technologies within the polyolefin industry sector	Alternative polymerization technologies	Overall material and energy consumptions	1) Environmental and exergetic efficiency 2) Identification of best option for specific contexts of application
Database of Energy Sources	1) Feasibility study 2) Operative phase	Provide baseline information on sustainability profile of energy sources (enabling application of other methods)	Electric power generation technologies	1) Specific site location 2) Energy and material balances	I/O data and indicators regarding Energetic, Environmental, Safety and Economic impacts and performances

Process Design Assessment Method (PDAM)

General Overview of the Method

In this section a new sustainability assessment method is presented. The developed methodology is specifically aimed at the quantification of environmental impacts and energy efficiency indicators to be used for supporting FEED design activities of chemical industries, with particular attention to polyolefin polymerization processes. In particular the method supports the evaluation of the sustainability profile of a process scheme, the identification of critical points of improvement, the screening design of alternatives and the prediction of the operative impacts. The approach implements the concept of Life Cycle Thinking at different levels to compute indicators as a function of chemical processes input and output. This study was developed in the context of the process design. Therefore, the methodology is focused on the polymerization technologies and all the auxiliary processes for supplying of raw materials and utilities, disposal of waste and by-products treatment. In detail, the process object of the design is assumed as Primary process of the assessment (e.g polymerization process). Auxiliary technologies (Background processes) are required for raw material and energy supply: these are generally out of the scope of design, but must be included in the analysis as they affect the overall environmental performance of the system (i.e. Lifecyle perspective). A certain level of detail (compatible with the information available in the FEED design phase) is required to characterize energy and material consumption of the Primary process. Background processes are instead out of the control of designer, and generic datasets that measure the average technologies performances can be used. Background datasets can characterize specific site-location technology or average performances. The manipulation of background processes allows to define multiple process schemes carrying out specific assessment based on polymer type, polymerization configuration and geographical location. In this perspective, this method allows to generate quantitative impacts and performances measuring the interactions between primary and background processes of a reference layout.

This procedure is totally versatile and applicable to every chemical process. Multiple scenarios can be generated to measure the effectiveness of different supply technologies out of the primary process scope (e.g renewable technology for electric power generation) or define the repercussion of design decisions (e.g introduction of new equipment). Principal result obtained is represented by a set of Key Performance Indicators (KPI) aimed at supporting sustainability-oriented activities. Secondary results characterize specific information about equipment and facilities within the reference scheme. The adopted set of indicators plan to quantify the impact associated to resources exploitation, emissions of toxic or pollutant substances and the quality of energy conservation. Indicators are in accordance with the set reported in literature polymer sustainability report (i.e PlasticsEurope,..) and new index are introduced matching the data usually available in the early stages of process design (feasibility study, Conceptual design). In this direction, the application of the method in the early design phases of new plants (e.g Conceptual design) allows to drive design decisions and support technologies analysis. Furthermore, the methodology is also suitable to perform sustainability assessment of preliminary technologies inventories (e.g Feasibility study) or currently operating plants. In this direction, KPI are intended to support technologies selection, monitor benchmark conditions and detect potential improvements.

The method is developed in accordance with Lifecycle thinking approach and exergy analysis and consists of four main steps (fig):

1. Preliminary activities (Goal and Scope, system of interest/definition of process options, site-location, reference unit and system boundary)
2. Data gathering and process simulation
3. Calculation of indicators
4. Interpretation and sensitivity

In the following, the detail of each step of the procedure is described. The procedure is demonstrated by the application to several case-studies in section 3. Results are intended to be sustainability drivers for polyolefin design activities. Furthermore, the repetitive application of the methodology to several case studies allows to generate an internal database evaluating the company state-of-the-art regarding specific operating plants, capacity dependence study and technological improvements analysis. This database can be constantly updated with new case study and offers the opportunity to monitor and compare different sustainability profiles.

Preliminary activities

The starting point of the procedure is the definition of Goal and Scope of the assessment. Goal is intended to be the reason for carrying out the analysis, the audience and whether the expected results are intended to be used. The Scope should be sufficiently well defined to ensure that all details of the study are compatible and sufficient to address the stated goal. Assumptions and limitations are required to be defined in this preliminary phase. In this perspective, it's essential to identify a reference scheme with particular attention to the definition of chemical processes material and energy interactions. In this context, a *Primary process* is defined to be the main process object of the assessment (e.g polymerization technology). Auxiliary technologies (*Background processes*) are required for raw material and energy supply: these are generally out of the scope of design, but must be included in the analysis as they affect the overall environmental performance of the system (i.e. Lifecyle perspective).

Subsequently to the clarification of the reference scheme, it's mandatory to specify the *reference unit* and *system boundaries* adopted in the assessment. The *reference unit* is the analogous of the functional unit of an LCA [25]. However, for the current goals, the identification of the reference unit is generally more straightforward than in the typical life cycle analysis, since in the chemical industry it may be easily identified in the flow-rate of a key stream leaving (i.e final product) or entering (i.e raw material) the process. In cases where the presented method is used as support strategies for comparative assessment, the reference unit must be the same for all the alternatives to simplify the interpretation of results.

This method is implemented by defining product systems as models that describe the key elements of physical systems. In this perspective, the *system boundary* defines the process to be included in the system. The choice of elements (i.e chemical process) of the physical system to be modelled and include in the framework depends on the goal and scope of the specific study and its intended applications and audience. Given the complexity of interactions between primary and background processes a certain flexibility is allowed in the definition of units within the boundaries. Furthermore, it's possible to define and adopt different levels of system boundaries performing impact analysis of multiple frameworks. Fig. 4 briefly illustrates possible boundaries and interaction between processes.

This versatility allows to monitor performances at different process level generating case-specific results.

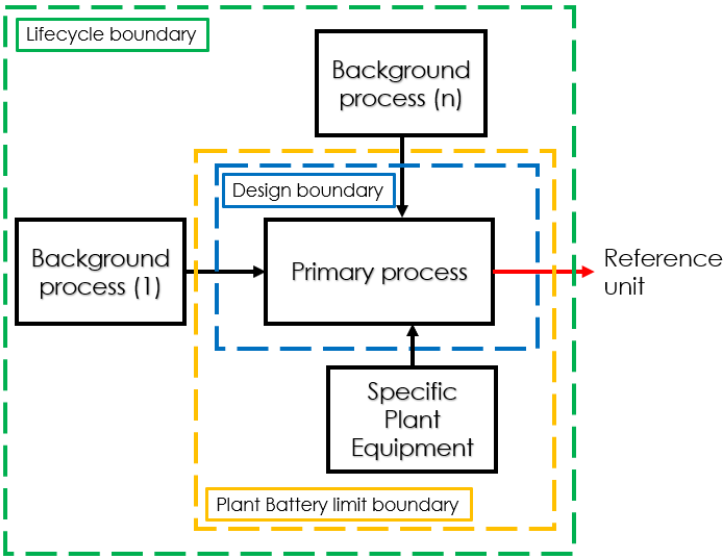


Figure 4: Conceptual definition of scope and boundaries in the application of the proposed method

The design boundary is comprehensive of primary process activities which typically represent the main scope of the assessment. Therefore, a certain level of detail it's recommended to respect in material and energy input and output characterization. Clearly, approximations are allowed and suggested in case of lack of process data. However, the adopted level of detail for primary process characterization determines the reliability of results. The computational of background processes impacts is based on primary process input and output (e.g waste treatment). More than one Design boundary could be introduced in the analysis in order to distinguish and separate specific primary process facilities or operations (e.g optional or plant specific equipment). In addition, another level of analysis is reached by the definition of Plant Battery limit boundary which includes all the activities and operations involved in the reference plant. Usually, operating plants includes facilities that are not designed during early process conceptual design but are required to guarantee the operability and integrity of the plant (e.g. off gas boilers, purge compressor). The last and more extended framework is the Lifecycle boundary which is comprehensive of the primary process and all the required background processes. These boundaries include auxiliary supporting operations which are essential to perform primary process activities (e.g electric power generation). The introduction of these boundaries allows to monitor and predict impacts of more complete systems including all the activities required to support primary process (e.g supply of raw material, waste disposal). Furthermore, the application of the presented methodology to Lifecycle boundary allows to define the specific contribution to the energy and environmental impacts of each operation. This configuration highlights criticises and potential improvements of the primary process lifecycle chain in a sustainability perspective. This flexibility allows to monitor specific interaction between processes within the reference scheme and perform comparative assessment (e.g identify strength and weaknesses of the adoption of renewable resources rather than conventional one).

Moreover, another key aspect to be defined in this preliminary phase is the site-location of the reference processes. Results could be affected by the specific geographical location of primary and background processes (e.g different electricity grid mix). In cases where this information is not available, average information could be adopted for the analysis.

Data gathering and process simulation

Given the definition of system boundaries, different strategies for data collection are proposed for each one of the reference frameworks, matching the level of knowledge required and data availability. Several sources can be used in order to support the collection of input data and the definition of the inputs and outputs (i.e. Life Cycle inventories) of chemical processes. Therefore, the proposed methodology is of general applicability and the procedure does not pose restrictions in the approach used to obtain the required input data. Obviously, the choice of input data affects the quality of final results (e.g. Environmental KPI).

Primary process data collection

The methodology requires to characterize the primary process. In this perspective, two approaches can be followed:

- Primary process can be considered as a black box and only input and output material and energy streams are evaluated. This configuration doesn't allow to distinguish the different repercussion to the results of each primary operations. However, this approach is extremely functional for the early design activities (e.g Feasibility study, conceptual design) where primary process is under development and data are approximated and not completely available. In this perspective, results obtained can support the design of new primary processes and drew up sustainability guidelines to enhance primary operations in a sustainability perspective. The iterative application of the methodology during this preliminary phase can quantify the environmental and energy benefits of different design configurations.
- Otherwise, the Primary process can be divided into its specific operations. This approach requires to define the desired spanning level in accordance with the goal and scope (e.g division of a chemical plant into its principal unitary operations or at equipment level). In this direction, more complete results could be obtained in accordance with the data reliability. This configuration requires to characterize material and energy streams of the primary process operations in accordance with the desired level of detail (e.g electrical consumption of different unitary operation of the primary process). This approach is tailored to the specific case when a relevant set of data is available (e.g Analysis of chemical plant operative phase). Results can highlight source of inefficiencies and potential for improvements regarding internal primary process operations.

Once it's defined the reference adopted approach for primary process characterization, multiple sources can be adopted for data gathering matching data availability and reliability. In particular, given the direct application of the methodology to the polyolefin industrial sphere, the following principal sources are typically used:

- Feasibility study: results derived by preliminary material and energy balances can be utilized as input for the methodology. In this perspective, preliminary technology evaluation can be placed side by sustainability guidelines.
- Process Design Package (PDP): the adoption of material and energy input and output data for PDP allows to apply the methodology at the conceptual design level. In this phase, the

analyzed technology is already defined and a good set of data is available, even with approximation.

- Basic Design Package (BDP): data derived by BDP are more accurate but not always available in the early design phase. The adoption of BDP can data increase the accuracy of results due to the adoption of more realistic data (e.g electric power consumption of equipment for vendor proposal)
- Benchmark: data derived by operative phase are typically more accurate and representative of specific plant performances.

The versatility of the methodology allows to use every source of data derived by material and energy balances as input for the assessment. Even more detailed approach can be adopted derived by process simulation. In this perspective, primary process data collection is intended to be the sequential activity of a stream characterization phase of a design or operative procedure. A focal point in the definition of primary data source is that the level of detail adopted for data collection strongly influences the entire assessment. Primary process data are typically available or derived by calculation, so a certain level of accuracy is suggested. This methodology is tailored to polymerization technologies analysis, therefore expected primary data are typically in the polyolefin framework. However, the methodology is completely versatile and does not impose any limitations, new information can be introduced to characterize specific case study applications. Tab. 3 and 4 present the list of default input and output for the primary process characterization comprehensive of raw material and energy consumptions, process purges, off-gas and waste.

Table 3: List of required input for the Design Scope

Input	Source
Monomers and Reactants	
Propylene	PDP
Ethylene	PDP
Butene	PDP
Hexene	PDP
Octene	PDP
Vinyl-Acetate	PDP
Hydrogen	PDP
Inert	
Propane	PDP
Ethane	PDP
Hexane	PDP
Nitrogen	PDP
Catalyst, Co-Catalyst and other components	
Catalyst	PDP
Co-Catalyst 1	PDP
Co-Catalyst 2	PDP
Oil/Grease	PDP
Antistatic Agent	PDP
Additives	PDP
Utilities	
Water	PDP
Steam	PDP
Electricity	PDP / Basic Design Package

Table 4: List of output from the Design Scope

Output	Source
Direct Emissions	
Vent to atmosphere	PDP / Integrated Environmental Authorization
Liquid waste/by-products	PDP / Integrated Environmental Authorization
Solid waste	PDP / Integrated Environmental Authorization
Purges	
Off-gas	PDP
Liquid purges	PDP
Other output	
Oil/Oligomers	PDP
Wastewater	PDP

Other process options and relative input and output can be included tailored to the specific application. Typically, during early process conceptual design some facilities are not completely designed and are mentioned as packages which will be characterized by the specific selected vendors during detailed design subsequent activities. In this phase, packages can be characterized by available options (e.g. Literature datasets, other conceptual design information).

Background process data collection

The characterization of background processes requires alternative approach. Background processes are out of the primary process scope and activities; therefore, a suitable set of data is typically not available. In this direction, the methodology is completely versatile and imposes no limitations for background processes characterization. Methodology requires to define principal material and energy input and output from background processes. In order to facilitate the applicability of the methodology and offer the opportunity to generate multiple scenarios, the methodology is comprehensive of a database developed from literature. Due to the direct application of the polyolefin sphere, the database reports a set of material and energy balances of the principal chemical processes that are usually required to support polymerization activities (e.g electric power generation, monomer production, steam production). In addition, based on the specific assessment it is possible to select appropriate auxiliary technology (e.g electricity from natural gas, fuel oil, photovoltaic) and the productive country. This flexibility allows to generate specific case-study scenario offering the opportunity to evaluate optimal configurations and critical issues inside the product lifecycle chain (e.g polymer). Moreover, it's possible to insert specific background datasets as support or as substitute of preexisting database. This allows to introduce specific case-study data or simply update the database with future technologies.

The list of default background processes inventories is presented in Table 5.

Table 5: List of units process within the LCA boundary and the Specific design scope

Units Process	System boundary
Crude Oil extraction	Lifecycle boundary
Reforming (Naphtha)	Lifecycle boundary
Steam Cracker (Propylene)	Lifecycle boundary
Steam Cracker (Ethylene)	Lifecycle boundary
1-Butene production	Lifecycle boundary
1-Hexene production	Lifecycle boundary
Octene production	Lifecycle boundary
Vinyl-acetate production	Lifecycle boundary
Reforming (Hydrogen)	Lifecycle boundary
Propane Dehydrogenation, PDH (Propylene)	Lifecycle boundary
Oil / Oligomers treatment	Lifecycle boundary
Solid (fine) treatment	Lifecycle boundary
Wastewater treatment	Lifecycle boundary
Catalyst production	Lifecycle boundary
Co-Catalyst 1 production	Lifecycle boundary
Co-Catalyst 2 production	Lifecycle boundary
OIL production	Lifecycle boundary
Grease Production	Lifecycle boundary
Killer agent production	Lifecycle boundary
Additives production	Lifecycle boundary
External flare	Lifecycle boundary
Air compressor	Lifecycle boundary
Nitrogen production	Lifecycle boundary
Steam production	Lifecycle boundary
Electricity production	Lifecycle boundary
Regenerative thermal oxidizer, RTO	Design boundary
Dedicated Boiler for off gas	Design boundary
Dedicated nitrogen compressor	Design boundary
Splitter	Design boundary
Pre-heater	Design boundary
Dedicated flare	Design boundary
Dedicated wastewater treatment	Design boundary

Calculation of a set of Indicators

This section presents the strategy adopted to characterize the reference scheme. A set of Key Performance Indicators (KPI) is introduced as metric for monitoring the environmental and energy performances of the assessment scheme. In accordance with the goal of the application, specific KPI can be selected to define a tailored set of indicators. In addiction, KPI can be defined at each boundary level to characterize environmental and energy performance at different framework.

This approach allows to carry out specific analysis inside the polymer production chain, supporting the evaluation of sustainability profile of a process scheme. In this direction, KPIs are adopted for the identification of critical issues and potential for improvement, the screening design of alternatives and the prediction of operative benchmark impacts. These parameters must be the core issues in

affecting the sustainability performance of future plants, operating process or technological improvements analysis.

The methodology for the calculation of indicators is based on the LCA technique [25]. It must be remarked that the set of indicators is comprehensive of environmental impacts and energy management indicators, therefore different procedures are adopted for the computation.

Calculation of environmental indicators

The basic set of environmental indicators to be used in the method is proposed in Tab. 6. These derive from midpoint indicators typically adopted in LCA studies. The basic set of environmental indicators can be adapted in accordance with the specific goal of the application. Air, water and solid can be selected as target for environmental analysis. The defined method plans to consider 5 KPI for resources' exploitation and 10 for the emissions in air, water and soil. The definition is based on literature available information [26] [27]. Clearly enough, the set is open to the addiction of further indicators in the context of a specific assessments, regarding for example new environmental problematics or changing inside the reference production chain.

Table 6: List of environmental KPIs adopted in the presented methodologies.

Indicator ID [I_j]	Indicator name	Description	Example of substances (*reference)	Unit of measure
ADI,e	Abiotic Depletion Indicator (elements)	Exploitation of mineral sources. The depletion mechanism is based on the quantity of required materials, their concentration reserves and the rate of deaccumulation.	Sb*, Al, Pb, Ti, Na	[kgSb,eq/ref. unit.]
ADI,f	Abiotic Depletion Indicator (fossil fuels)	Inlet Energy amount derived by Non-renewable fuel sources.	Fossil fuel*, natural gas, coal, oil crude	[MJ/ref. unit.]
RnW,e	Renewable Resources (Energy)	Inlet Energy amount derived by Renewable sources.	Photovoltaic, Geothermal, Wind Power	[MJ/ref. unit.]
RnW,f	Renewable Resources (Feedstock)	Raw material quantity produced by renewable feedstock (e.g. Biomass). Currently is not implemented in the calculation tool.		[kg/ref. unit.]
WC	Water consumption	Dissipated water that during the process changed its physical-chemical state (e.g evaporation for steam production).	H_2O*	[kg/ref. unit.]
GWI	Global Warming Indicator	Emission into atmosphere of Greenhouse gasses (GHGs). The Global Warming Indicator is computed by considering the released mass of GHGs, their persistence and their predicted radiative forcing. These factors measure the mass of carbon dioxide equivalent for a time horizon of 100 years. The consequence directly connected to this problematic is the increase of the atmosphere temperature, but in a longer time view this affects human health and ecosystem.	CO_2*, CH_4	[kg CO_2,eq/ref. unit.]
AI	Acidification Indicator	Quantity (mass) of acids emitted into the environment. Acids are responsible for local pH decreasing which can be harmful for native flora and fauna. Another possible scenario is the formation of Acid Rain.	SO_x, (SO_2)*, NO_x, NH_3, HF	[kg SO_2,eq/ref. unit.]
EI	Eutrophication Indicator	Mass of components, typically containing Phosphorus or Nitrogen, which over-fertilize local water and soil ecosystem. Nutrient enrichment may cause an undesirable biomass over-production with an effect of competition for oxygen towards native Flora and Fauna. In addiction, the excess of chemicals can make the water undrinkable.	PO_4^{3-} *, NO_x, NH_3	[kg PO_4^{3-},eq/ref. unit.]
POCI	Photochemical Ozone Creation Indicator	Mass of gasses realised, typically Volatile Organic Compounds, that act as catalyst for radical reactions of Tropospheric Ozone formation. Ozone in the first layer of the atmosphere is an harmful gas for human health (lung diseases, asthma,..).	C_2H_4 *, VOCs, NO_x	[kgEthylene,eq/ref. unit.]
HTI	Human Toxicity Indicator	Mass of toxic components for human being emitted.	1,4 – Dichlorobenzene*, Benzene, Acrylonitrile, Arsenic	[kg 1,4 – Dichlorobenzene,eq/ref. unit.]
FETI	Freshwater Ecotoxicity Indicator	Mass of toxic components for freshwater emitted.	1,4 – Dichlorobenzene*, Benzene, Acrylonitrile, Arsenic	[kg 1,4 – Dichlorobenzene,eq/ref. unit.]
MAETI	Marine Aquatic Ecotoxicity Indicator	Mass of toxic components for Marine ecosystems emitted.	1,4 – Dichlorobenzene*, Benzene, Acrylonitrile, Arsenic	[kg 1,4 – Dichlorobenzene,eq/ref. unit.]
TETI	Terrestrial Ecotoxicity Indicator	Mass of toxic components for earth emitted.	1,4 – Dichlorobenzene*, Benzene, Acrylonitrile, Arsenic	[kg 1,4 – Dichlorobenzene,eq/ref. unit.]
Dust / PM	Dust and Particulate matter Indicator	Mass of Dust, Particulate matter and Low dimensions substances emitted. The principal target is the human's health and respiratory system.	PM10*, NO_x, SO_x, NMVOCs, NH_3	[kg PM10,eq/ref. unit.]

Reference substances are adopted to characterize environmental results in accordance with LCA technique [25] . Literature average datasets are used to simulate background processes. Characterization factors (CF_i) from the CML-2002 method [28] [29] are introduced to convert specific emissions into their reference substance as shown in Eq. (1).

The following flow chart summarises the procedure for indicators' calculation.

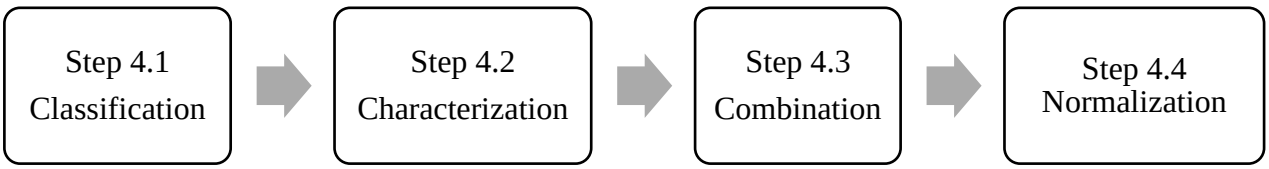


Figure 5: Flow chart of principal steps for indicators' computation

Classification

First, it's essential to classify all the emitted or consumed substances in the related impact categories. Each impact category generates at least one indicator. Some substances are related to more than one impact category, as Methane or NOx.

Characterization

Each substance within the impact categories is converted to the reference one by its characterization factors [29]. The calculation procedure is represented by Eq. (1) and (2).

$$I_{j,UP} = \sum_{s=1}^{n} (CF_{s,j}) \cdot m_s \qquad (1)$$

$$m_s = \frac{\dot{m}}{P} \qquad (2)$$

- j: Impact category
- UP: Unit Process
- s: Substance (Resource exploited or Component emitted)
- $\dot{m}$: mass (or energy) flow rate of the substance s [kg_s/ h]
- P: plant's potentiality $\left[kg_{fu}/\text{h}\right]$
- m_s: mass of the substance per mass of the reference unit $\left[kg_s/kg_{fu}\right]$
- $CF_{s,j}$: Characterization factor of the substance s for the impact category j $\left[kg_{eq}/kg_s\right]$

The output of this step is a table of partial indicators which relates impact indicators with the numerical results of each unit process.

Combination

Subsequently partial indicators are combined to compute the impact indicators at each boundary level. Eq. (3) reports the formula.

$$I_j = \sum_{UP=1}^{z} I_{j,UP} \qquad (3)$$

This approach allows to evaluate the environmental impact at different level. It's possible to quantify the environmental footprint of specific unit process, at boundary level or the entire polymer's production chain.

Normalization

The last step is optional. Impact indicators could be normalized by reference information to carry out specific comparative analysis, Eq. (4) reports the formula:

$$I_{j,norm} = \frac{I_j}{I_{j,REF}} \qquad (4)$$

- $I_{j,norm}$: normalized indicator
- $I_{j,REF}$: reference information $\left[kg_{eq}/kg_{fu}\right]$

Calculation of exergy indicators

The exergy of a system is defined as the maximum shaft work that can be done by the composite of the system and a specified reference environment [30]. More simply exergy can represent the available energy quantity of a system before it reaches the equilibrium with the environment. Exergy of a system (e.g. process stream) is assumed equal to zero at environmental equilibrium (dead state). Exergy analysis is based on the simultaneous application of the First and the Second Thermodynamic Laws. It is able to assess the way energy is used in operations, overcoming the limitation of energy balances based on the First Thermodynamic Law, that do not provide information about the degradation of energy or material sources during a process use.

Due to the entropic component, exergy is always destroyed when a process is irreversible. More in detailed, the Exergy destruction indicator (Ex,d) is defined as the quantity of exergy lost due to irreversibility of chemical and physical transformations inside a system. It allows to identify specific points of inefficiency in the reference process. As a consequence, the quantification of exergy destruction term is a key concept for the definition of process sustainability and definition of source of inefficacy.

Detailed equations are presented in the following chapter. The application of Exergy balance is limited to the design boundary which represent the principal focus of the assessment. Results obtained are able to define critical issues related to primary process activities and offers a design metric to compare process alternatives.

Calculation of economic indicators

Economy is one of the three major classes of sustainability sphere. As a consequence, preliminary considerations about economic efficiency of the reference scheme can be delineated. Literature indicators are selected and adopted in the presented methodology. In particular the following indices can be utilized in the assessment:

- Costs NPV (Net present value of the costs NPV_c) which allows to incorporate CAPEX and OPEX of the reference process defining the attractiveness of a design solution. This indicator is particularly effective for comparison of technology alternatives and presented by Eq (5):

$$NPV_c = \sum_{i=0}^{m+n} \frac{A_{cf,i}}{(1+i_r)^i} \qquad (5)$$

  Cash flows ($A_{cf,i}$) are representative of CAPEX for the first m years of construction and OPEX for the subsequent n years of operability. i_r indicates the discount rate. NPV_c evaluates only the costs related to the reference process, in this framework the most attractive alternatives are the one that reduces the indicator.
- Investment NPV (Net present value of the investment NPV_I) which is characterized by the same Eq (5) where $A_{cf,i}$ are now representative of Net Cash inflow-outflow. This indicator includes also proceeds from products sale. In this context, NPV_I is suitable to characterize assessment that includes an entire plant as reference process and not only specific part. Regarding this indicator, the most attractive options are the one that has higher NPV_I.

Raw material and energy costs can be derived from literature [31], [32] [33][34][35]. Average values adopted in the present work are reported in Tab. 7.

Table 7: Example of raw materials and energetic costs of principal polymerization input, West Europe 3H2018

Costs of Raw materials and Energy				
	$/ton	$/Nm3	$/MWh	$/ton PP
HP Steam	14,3			
MP Steam	12,7			
LP Steam	12,5			
Electricity			51,6	
Nitrogen		0,08		
CW	0,03			
Hydrogen	4530			
Propylene	1150			
Polypropylene	1500			
Catalyst & Chemicals				12
Extruder Additives				9

Interpretation and sensitivity

The final step of the method consists of KPI analysis (interpretation and sensitivity) to define strength and weaknesses of the reference scheme. KPIs are obviously influenced by characterization factors and specific unit inventories. Since these parameters refer to policy considerations that are inevitably affected by significant uncertainties, their value should be considered as reliable than other parameters evaluated in the assessment. Thus, a sensitivity analysis is worth to check the influence of variation in the background process technologies on the final results. Of course, because of the mathematical structure of the procedure, a variation in the background inventories will change the numerical value of the KPIs. However, in many practical applications it is not the absolute values of the indicators that is of interest, but the relative performance from alternative options.

The first step toward a sensitivity analysis is to quantify the percentage of contribution of each background process to the final KPIs. In this direction, some technologies are more impactful in the reference lifecycle scenario (e.g Cracker for monomer production). It could be helpful to define a confidence interval of variation for background performances. This will derive by an evaluation of the uncertainty of the data sources.

Calculation support tool

Calculation tool is developed with and excel sheets to facilitate the applicability of the procedure, save the results and collect them in an internal database for future comparisons. PDAM-on-Excel sheets are:

- INPUT: where the input for the Design Scope are assigned
- OUTPUT: definition of output streams from Design Scope
- Unit Process: The first table allows to select each available unit process. The following tables are the inventories for each unit process where are reported energy and material consumptions and air and water emissions
- Emissions&Consumption: This sheet is a table that shows the mass or energy flow rate of each substance (emitted or consumed) by each unit process
- CF_Convertion: based on the Table reported in the previous sheet, each mass or energy flow rate are classified in their impact category and converted to the reference substance by its characterization factor. Then they are divided by the plant's potentiality
- Partial Indicators: reports the list of indicators and the numerical result for each unit process
- Indicator Results: presents the results, the numerical list of impact indicators at each boundary level. In addiction, it's possible to normalize each indicator for specific analysis.
- Characterization Factors: is the database of the characterization factors

The Input sheet is proposed in Fig. 6.

Figure 6: Input sheet of the Tool

	Design Scope																		
	Electrical feed	Steam	N2	Propylene	Propane	Ethylene	Butene	Hexene	Octene	Vinyl-Acetate	H2	Antistatic	Catalyst	Co-Cat 1	Co-Cat 2	Oil/Grease	Killer agent	Water	Additives
Area	[kW] Required	[kg/h]	[Nm3/h]	[kg/h]	[kg/h]	[kg/h]	[kg/h]	[kg/h]	[kg/h]	[kg/h]	[kg/h]	[kg/h]	[kg/h]	[kg/h]	[kg/h]	[kg/h]	[kg/h]	[kg/h]	[kg/h]
A																			
B																			
C																			
D																			
E																			
F																			
G																			
H																			
I																			
Overall																			

Screening method for polyolefin technology comparison

Overview of the problem

Nowadays, several technological procedures for polymer production are well known and implemented at chemical plant level. These options are the result of an evolution mostly driven in the past by economic and market considerations. As research in the field moves towards the definition of more and more efficient system, it became more and more evident in the last decades the synergy of economic and environmental protection goals: higher overall yields, reduced energy demand, efficient recovery of by-products clearly share benefits in both domains. Technology developments continue to redefine state-of-the-art products and processes in the polyolefins industry. In this dynamic evolution it is essential to monitor the environmental performance of production technologies, allowing comparative analysis and pinpointing strength and weaknesses of available options.

Early process design is a key phase in the adoption of the sustainability perspective, as higher degrees of freedoms for change are possible at low marginal costs [36][37]. The development of quantitative tools for the sustainability analysis of process schemes received significant attention in the last two decades. Metrics based on material and energy flow analysis [38], exergy balances [39][40] [41][42], midpoint environmental indicators [43][44][45] [46], endpoint environmental indicators[47], ecological indexes[48][49], and combinations of indicators[50][51] were proposed. These metrics found application in the assessment of several kind of chemical and petrochemical processes and technologies, including polymerization technologies[52] [53]. For example, Vink and Davies[54] studied the environmental eco-profile of production of Ingeo polylactides biopolymers, proposing a set of impact indicators regarding resources exploitation and pollutant emissions issues. Tabone et al. [55] introduced a matrix to compare packaging polymers based on Green chemistry and Green Engineering concepts.

However the environmental and exergetic impacts of alternative technologies in polypropylene production remains unexplored, as current literature on process analysis focuses mainly on technical and efficiency issues (e.g. rheological properties [56] applied to slurry processes and the effects of design choices to the polymer characteristics[57]).

Lifecyle studies on polypropylene, like the one published periodically by PlasticsEurope [58], lack of the detail needed to discriminate the effect of process design choices, and focus mainly on factors as nature of raw materials and polymer waste recycling.

Moreover, the metrics used in these LCA studied are not directly suitable for application as design support tools in polymerization process development. In facts, LCA metrics are suited to the analysis of the whole environmental performance of the lifecycle system, which is only one of the aspects of concern in process design: they are not, alone, able to analyse the way energy and material are used within the specific process sections and the margins of improvement still available, given the physical (e.g. thermodynamics) constraints, which would require different metrics (e.g. exergy analysis).

The following method describes an adaptation of PDAM to the review of the main commercial processes for polypropylene production. This required specific assumptions and modifications of the method as information and data availability for these schemes is limited, if compared with the inputs typically required by PDAM.

The analysis is based on the definition of reference schemes based on proposed technologies and assessed for carbon footprint and exergy destruction performance. The proposed methodology aims at supporting decision making and directing future design and development activities toward more sustainable options.

Procedure outline

The method proposes an extended LCA approach tailored to polymerization technologies analysis. This method provides comparative information regarding different design choices among the principal polypropylene production industrial processes. This methodology is intended to be a support strategy for feasibility study of new processes during decision making activities and technologies selection. Through the schematization and simulation of reference polymerization scheme, material and energy balances are carried out for environmental and exergy analysis. Aspen HYSYS is utilized as support program. This methodology is intended to support design choices for future polymerization technologies by monitoring the currently state-of-the-art principal processes and highlighting strength and weaknesses. Two different approaches are adopted to perform the analysis:

- Cradle-to-gate to express environmental results of the entire polymer production lifecycle chain. This strategy allows to characterize each specific polypropylene productive chain tailored to different polymerization processes. In this way, the performance of each process is evaluated within its background activities quantifying the repercussion of polymerization design choices to external auxiliary units (e.g Cracker for monomer production, electric power plant)
- Gate-to-gate to carry out exergy analysis and provide specific information about the maintenance of energetic quality due to the different polymerization strategies. Thus, this approach allows to monitor specific polymerization operation defining the best options for polypropylene productions.

The following flow chart represents the outline of the methodology. (Fig. 7)

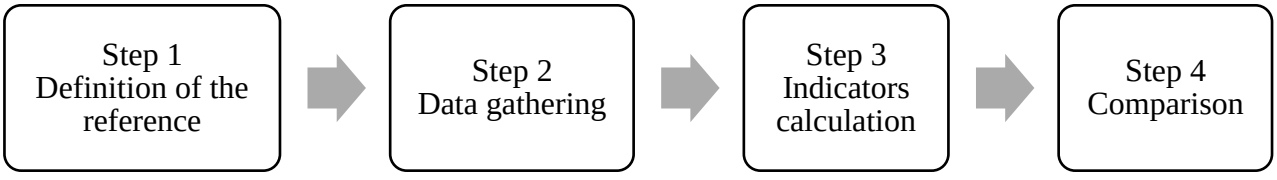


Figure 7: Flow chart of the Screening method for polyolefin technology comparison

The comparative assessment is based on 3 different indicators:

- Estimated Global Warming Potential (GWP): This indicator expresses the mass of CO_2 per mass of polymer produced. Technology input are converted to CO_2 by literature coefficients.
- Excess of raw Hydrocarbons (Monomers & Inerts): This indicator is a measure of the hydrocarbon's exploitation of the technology. It's expressed as sum of the mass of monomers and hydrocarbon's inert per mass of polymer produced.

- Overall Exergy destruction/loss: This indicator measures the overall quantity of exergy destructed and loss of each technology is divided by its production capacity. The introduction of this index offers the opportunity to quantify an overall technological performance of polypropylene and polyethylene processes.

Definition of the reference

As most of the Life Cycle Assessment and PDAM the procedure starts with the definition of the reference scheme and the selection of the appropriate boundary which identifies processes inside the context of the analysis. It's essential to define uniquely which are the units and operation considered in the domain. This procedure is tailored to polymerization activities and provide comparative information about different polymerization strategies. In particular, polypropylene is selected as reference polymer and the principal polymerization process are schematized and simulated to monitor their performances. All propylene polymerization technologies share the same generic process block diagram, schematized in Figure 1. The reaction stage is aimed at the conversion of the monomer into polymer. Depending on the technology it can be performed as Gas or Bulk phase [59]. Bulk polymerization is carried out in the absence of any solvent or dispersant, and polymer granules are formed from a liquid monomer phase [60]. The monomer itself acts as a solvent which guarantees high purity of the products. However, the relatively high viscosity of the system can be relevant issue for the reaction management (e.g. stirring, reaction control). Gas phase processes are characterized by an heterogeneous polymerization where usually an initiator is required [60]. Gas phase polymerization is typically carried out in fluidized-bed or stirred reactors where high fluidization velocity or mechanical agitation is provided.

Due to a reaction yield lower than 100%, the outlet stream of the reaction section is a mixture of polymer and unreacted monomers. Traces of hydrogen, catalyst and co-catalyst could be present as well. The recovery section is devoted to separation, and possibly recycle into reaction, of the unreacted components. Different procedures could be implemented in this section. However, separation is typically performed by the increase of temperature and the decrease of pressure. Recovered monomer can be stored in a tank or directly recycled to the reaction section. The Polymer finishing section treats the stream with a catalyst deactivator agent (i.e. steam or CO_2) and dries the product with hot nitrogen. This operation also allows striping the last traces of adsorbed monomer. Finally, an extrusion section provides for the homogenization of the polymer, for the blending with specific additives and for a consistent pellet shape to the final product. Beside the process sections shown in Fig. 8, a production plant also contains auxiliary units required for storage and feed of raw materials and final product, supply of thermal energy and cooling, and treatment of waste streams.

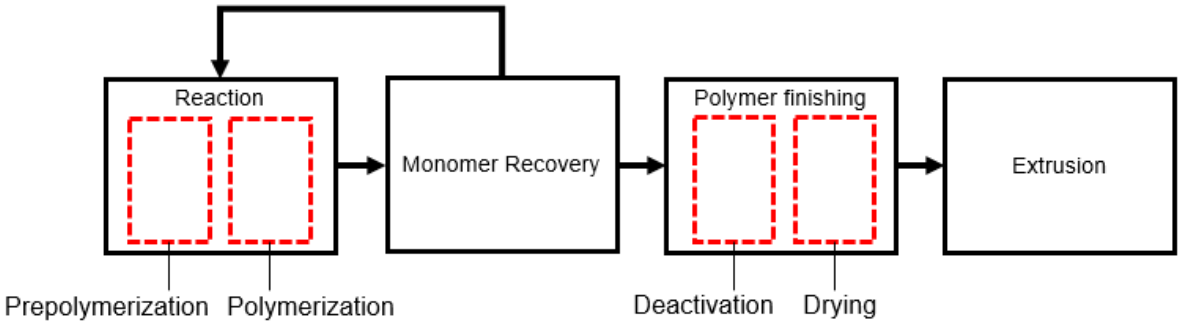


Figure 8: Block flow diagram of a generic propylene polymerization process

The process described in Fig. 8 is usually applied to the production of different types of final product, according to specific production campaigns that alternate during the year as for market demand. The Homopolymer (Homo) is the simplest form of polymer and is obtained by the polymerization of propylene alone. Heterophasic Impact Copolymer (Heco), is a more complex polymeric structure where at least 2 monomers are required (e.g. propylene and ethylene, with typically up to 21% of ethylene) [61]. Homo and Heco are actually macro categories of products, which include a huge variety of polymers with particular physic-chemical properties. As this analysis is focused mainly on the process rather than on the products, each technology is characterized only considering only a single reference formulation for Homo and Heco production.

The polymerization process (Fig. 8) is part of a greater polymer production chain schematized in Fig. 9. Processes involved in this assessment are a restricted set of units considered in the application of PDAM to the polymer production chain. The lack of detailed information about specific polymeric chain forced to consider the same set of background processes for each technology. This chain includes the auxiliary processes for the supply of raw materials and energy. The definition of the entire polymer production chain (i.e. lifecycle thinking [62]) is necessary for the computation of the GWI indicator. Other processes could be considered by the introduction of new data tailored to specific application (i.e off-gas, Waste..)

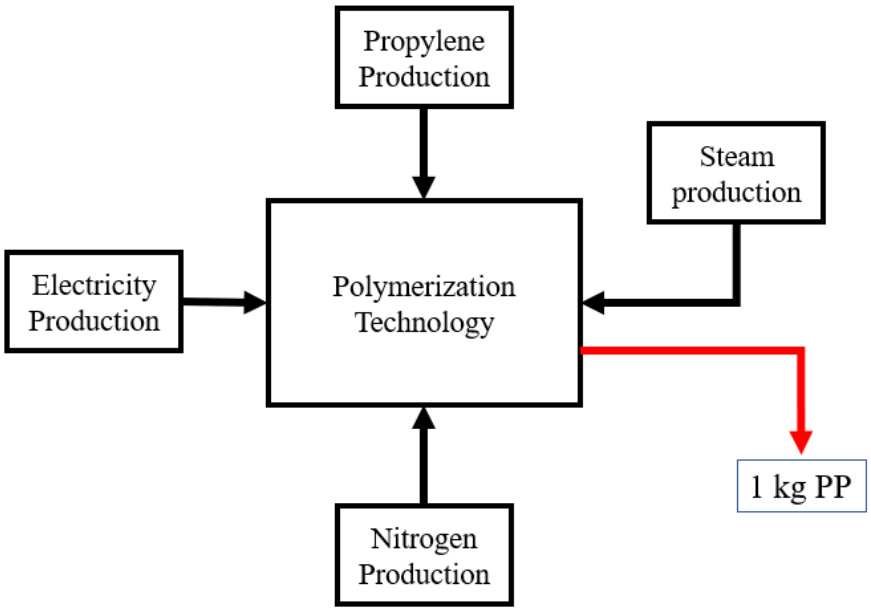


Figure 9: Schematization of the polypropylene (PP) production chain

Data gathering

Data derived from literature [53] [58] [59] are processed and utilized to carry out Energy and Material balances for each technology. The lack of detailed information forced to estimate some required input and output streams. Reference capacity is assumed for each process (400 kt/y of polypropylene). The electrical consumption of the main equipment (i.e. compressors, pumps) was estimated. Streams exergy values were calculated using SRK equation. Results are summarized in section 3 and were used for the computation of industrial performances based on the presented indicators. Polymer exergy value is calculated based on literature correlation [65].

Assumptions

The lack of detailed data plans to introduce several hypotheses to compute the results:

- The consumption of low-pressure steam (LP), medium pressure steam (MP) or high-pressure steam (HP) is considered equal from environmental standpoint. It's possible to improve the assessment introducing a new unit process (i.e Steam turbine) that evaluate the electricity saving for technologies that use lower pressure steam.
- Monomers and Inerts are converted to CO_2 by considering PlasticsEurope data. Tab. 8 reports the adopted coefficients.
- The operativity annual working hours are assumed constant and equal to 8000 h/y
- Hydrogen required is not considered due to its low mass flow rate.
- Boiler water is summed with the quantity of cooling water, however the process water is not considered.
- This application doesn't involve the use of characterization factors for the first indicator. Hydrocarbons have equal weight for the computation of Excess of Hydrocarbons (Monomers & Inerts)
- Emission factors coefficients for Steam and Electricity conversion to CO_2 are constant and represent average carbon footprint. These coefficients are used for each technology.
- The mass of monomers involved in the reactions is equal to the mass of polymer produced.

$$m_{M,R} = 1000 \ {}^{kg,monomers}/_{t,\ polymer}$$

Indicators calculation

A set of indicators was developed to allow for a quantitative comparison of key environmental performance aspects of the alternative technologies for polypropylene production. This allows for the characterization of the principal state-of-the art processes regarding environmental impacts and energy efficiency, defining criteria to evaluate the repercussion of design choices specific of each technology. Two impact indicators were proposed to characterize each technology by its environmental footprint and energy performance: Global Warming Indicator (GWI) and Exergy destruction (Ex,d). Detailed information about these indicators is presented in the following chapter.

Environmental performance indicators

The computational of the estimated GWP is based on the conversion of each technology's input to CO_2 by coefficients. This calculation methodology is simple and it requires almost zero computational time. However, results could be strongly influenced by adopted coefficients which have huge geographical dependence. This method is tailored to process alternatives comparison, in this direction emissions coefficients are fixed and are not influenced by specific plant location and auxiliary technology selection (e.g Electricity power plant). In addition, coefficients are kept constant over the time. In a short-scale period, this assumption is true, however, considering a long-time frame, coefficients could be changed and as a consequence, results of the analysis. For future applications, it's mandatory to check literature updating for emissions coefficients. Assumed coefficients are presented in the following:

- The first one is the emission factor for electricity production. $EF_e = 0{,}39\ tCO_2/MWh$
- The second one represents the emission factor for steam production $EF_s = 0{,}224\ tCO_2/MWh$
- The last coefficient expresses the average electricity consumption per NM^3 of Nitrogen produced [66]. $EF_{N2} = 0{,}478\ MWh/Nm^3$
- For Monomers and hydrocarbon inerts table x allows the conversation of the required process stream to the emitted quantity of CO_2.

Table 8: CO_2 Conversion coefficients for principal polymerization raw materials and energetic input

Hydrocarbons	Coefficients [$kgCO_2/kg$]	Source
Propylene	1,374	PlasticsEurope
Ethylene	1,374	PlasticsEurope
1-Butylene	0,341	PlasticsEurope
1-Hexene	0,341	Equal to 1-Butylene
1-Octene	0,341	Equal to 1-Butylene
Vinyl Acetate	1,848	Equal to Cyclohexane
Cyclohexane	1,848	Catalytic hydration of benzene
Propane	0,409	PlasticsEurope
Isobutane	0,341	Equal to 1-Butylene
Hexane	0,341	Equal to 1-Butylene

List of Inputs:

- Cooling Water (CW): the estimated electric power for handling the water mass flow rate is converted by EF_e in tCO_2/y
- Electrical Feed: the electricity required is converted by EF_e in tCO_2/y
- Steam: the input mass flow rate of steam is converted first in MWh by its latent heat at pressure = 1.8 bar (2,112 MJ/kg) and by EF_s in tCO_2/y
- Monomers and Hydrocarbon inerts: the required mass flows rate of monomers is converted in tCO_2/y by table x.
- Nitrogen: the mass flow rate of nitrogen is converted first to MWh by multiplication of EF_{N2} then to tCO_2/y by EF_e.

This procedure is applied to the most widespread technologies for polypropylene production, computing the *overall* tCO_2/y for each process as a sum of all the input contributions. Furthermore, each *overall* tCO_2/y is divided by its plant's capacity in order to compare technologies with different polymer's production capacity. Eq. (6) reports the computational step.

$$Estimated\ GWP = \frac{overall\ tCO_2/y}{tP} \quad [\frac{kgCO_2}{kgPolymer}] \qquad (6)$$

P plant's capacity [tPolymer/y]

Excess of raw material (Hydrocarbons)

The second indicator measure the excess quantity of hydrocarbon's raw material exploited for each technology per tonne of polymer produced. Eq. (7) stabiles the excess of monomers.

$$m_{EM} = \left(m_{M,I} - m_{M,R}\right) \qquad (7)$$

- m_{EM} excess of monomers [kg,monomers/t,polymer]
- $m_{M,I}$ Input monomers [kg,monomers/t,polymer]
- $m_{M,R}$ monomers required in reaction [kg,monomers/t,polymer]

this result is summed with the mass of hydrocarbon inert to compute this indicator. Eq (8) shows the calculation step.

$$EH = m_{EM} + m_{I,I} \qquad (8)$$

- $m_{I,I}$ Input hydrocarbon inert [kg,hydrocarbon inert/t,polymer]
- EH Excess of Hydrocarbons (Monomers & Inerts) [kg,hydrocarbons /t,polymer]

Exergy destruction and loss

The last indicator is based on exergy balance. The sum of annual overall exergy destructed and loss of each technology is divided by its production capacity. The Exergy theory is presented in the following chapter.

Exergy Indicator: focus on calculation and interpretation

Energy issue is becoming increasingly crucial for industrial sector and in particular for chemical plants that consumes large quantities of utilities every day [67]. Although the scientific community is looking for alternative energy resources, a short-term solution would rather rely on a more rational use of energy. To face this challenge, Exergy analysis is an efficient method for the identification of process inefficiencies, the first indispensable step for a possible energy improvement.

The traditional energy analysis is based on the evaluation of transfer and/or conversion of energy involving physical or chemical processes. Typically, this analysis entails an energy balance based on the First Law of Thermodynamics with the goals of define possible heat recovery, evaluate the heat lost towards the environment and define the heat transfer performance of the system [68]. However, an energy analysis provides no information on the degradation of resources or energy content in the material streams. The exergy analysis based on the Second Law of Thermodynamics overcomes this limitation. The exergy of a system is defined as the maximum shaft work that can be done by the composite of the system and a specified reference environment [69]. Therefore, exergy balances identify and quantify energy degradation in a system and can therefore lead to improve operations and technologies.

The Exergy analysis is a method based on the conservation of mass and conservation of energy principles, combined with the Second Law of Thermodynamics. The application of the method to a system allows to define the Exergy destruction as an index of the irreversibility of the process and the exergy efficiency of the system. Aim of the method is the identification of the causes, locations and magnitudes of process inefficiencies for furthering the goal of more efficient energy-resource use.

Specific provisions on step 1 and 2 of PDAM

Step 1. Definition of the reference scheme

In literature, several application of exergy analysis are carried out to open [69] [70] [71] and closed [72] [73] [74] systems. In this framework, only closed systems are considered. It's essential to define the boundary of the analysis, for example it's possible to perform an exergy balance of the entire plant or carry out balances at equipment level. The crucial point is the definition of material and energetic inlet and outlet streams of the considered system.

Step 2.1 Data gathering

Material streams' characterization is generally based on the Material balance of conceptual design phase and the specific equipment datasheet when it's required. Instead, the electrical consumption of plant or equipment could be defined at three levels of detail:

- For ordinary equipment (Centrifugal pumps, Compressors, fans) via process simulation

- In case of more complex equipment (i.e Reactor pumps) the electrical consumption could be defined by specific guidelines derived from Process Design package (i.e Conceptual design phase)
- Sometimes a more detailed electrical consumption report from a basic design package could be used for the definition of the electrical load of equipment (i.e internal supporting Package). This report could be used in case of lack of data from early conceptual design phase or for a more accurate analysis (e.g., Basic design package).

Furthermore, a new level of detail could be introduced by the basic design or benchmark reports where the specific operative consumption of monomers, electricity, steam and nitrogen are presented for several plant. This data could be used only when the boundary of the reference scheme is the entire plant. This data could be used only when the boundary of the reference scheme is the entire plant. The accuracy of the analysis is defined by the quality of data. In addiction it's possible to evaluate the exergy performance of equipment or plant during a specific run of a polymer or its average performance during a whole year.

Step 2.2 Process simulation

This step is essential for two fundamental reasons: the evaluation of Thermodynamic properties of components (Exergy, Enthalpy and Entropy) and the verification of local material and energy balances while it's possible.

Calculation of Exergy Indicator

Step 3.1 Application of the Exergy Balance

By the combination of the conservation law for energy (FLT) and no conservation law for entropy (SLT), the exergy balance can be obtained as follows Eq. (9) [69]:

Exergy input – Exergy output – Exergy consumption = Exergy accumulation (9)

Eq. (9) demonstrates that for a process occurring in a system, the difference between the total exergy flows into and out of the system, less the exergy accumulation in the system, is the exergy consumption *I*, expressible in Eq. (10):

$$I = T_0 \dot{S}_{gen} \qquad (10)$$

T_0 is the reference environmental temperature, $\dot{S}_{gen}$ is the entropy generative term due to irreversibility. Eq (10) points out the Exergy consumption is proportional to entropy creation which is known as the Gouy-Stodola theorem[75].

In this framework, exergy balance is applied only at equipment or process level, therefore Eq. (11) could be simplified by considering a closed system with a constant volume in steady state:

Exergy input (material) – Exergy output (material) ± Exergy (electricity) ± Exergy (thermal power) = Exergy destruction (11)

The signs of the exergy due to electricity and thermal power exchanged towards the environment depends on the direction of the reference stream (input or output from the system). For example, considering a pump or a compressor, electricity is required by the equipment, so the exergy term associated with the electrical power is positive. Vice versa for turbines this term is outgoing by the system so it's negative.

The following table (Tab. 9) reports the equations used to define exergy terms. The strategy is in accordance with literature approach [67]

Table 9: Definition of Exergy for the commonly used unit operations

Exergy terms	Symbols	Formulas	Notes
Exergy input (material)	EX_{IN}	$\sum_{i=1}^{Ncomp} \dot{m}_{i,IN}\left[\widehat{H}_i - \widehat{H}_{i,0} - T_0\left(\hat{s}_i - \hat{s}_{i,0}\right)\right]$ • $\widehat{H}_i$ Specific enthalpy of component i at stream's conditions (T, p) • $\widehat{H}_{i,0}$ Specific enthalpy of component i at the environmental reference state 0 • $\hat{s}_i$ Specific entropy of component i at stream's conditions (T, p) • T_0 Environmental Temperature • $\hat{s}_{i,0}$ Specific entropy of component i at the environmental reference state 0	
Exergy output (material)	EX_{OUT}	$\sum_{i=1}^{Ncomp} \dot{m}_{i,OUT}\left[\widehat{H}_i - \widehat{H}_{i,0} - T_0\left(\hat{s}_i - \hat{s}_{i,0}\right)\right]$	
Exergy (electricity)	$EX_{\dot{W}}$	$\dot{W}$ • $\dot{W}$ Electrical power required	
Exergy (thermal power)	$EX_{\dot{Q}}$	$\dot{Q}\left(\left\|1 - \frac{T_0}{T_S}\right\|\right)$ • $\dot{Q}$ heat exchanged with the environment. • T_S Absolute temperature of the boundary where heat rate crosses	For an adiabatic system It's assumed that $\dot{Q} = 0$
Exergy destruction	EX_d	$T_0\dot{S}_{gen}$	

The application of the exergy balance introduced in the Step 3 allows to quantify the Exergy destruction of each equipment as the amount of [kW] losses due to the irreversibility of the operation. In case of adiabatic system, Eq. (11) could be simplified as follows:

$$EX_{IN} \pm EX_{\dot{W}} - EX_{OUT} = EX_d \qquad (12)$$

This simplification is admissible as long as the considered system is adiabatic, which means that the equipment is well insulated from the environment. During its useful life, the insulation can lose the effectiveness and the term may no longer be negligible.

The exergy balance can be visualized in Fig. 10, this is the typical configuration of pumps, compressors and fans. In this case $EX_{OUT} > EX_{IN}$ due to $EX_{\dot{W}}$ which increases the pressure and/or the temperature in the process stream. Vice versa, in case of turbine, $EX_{OUT} < EX_{IN}$ due to $EX_{\dot{W}}$ outgoing the system.

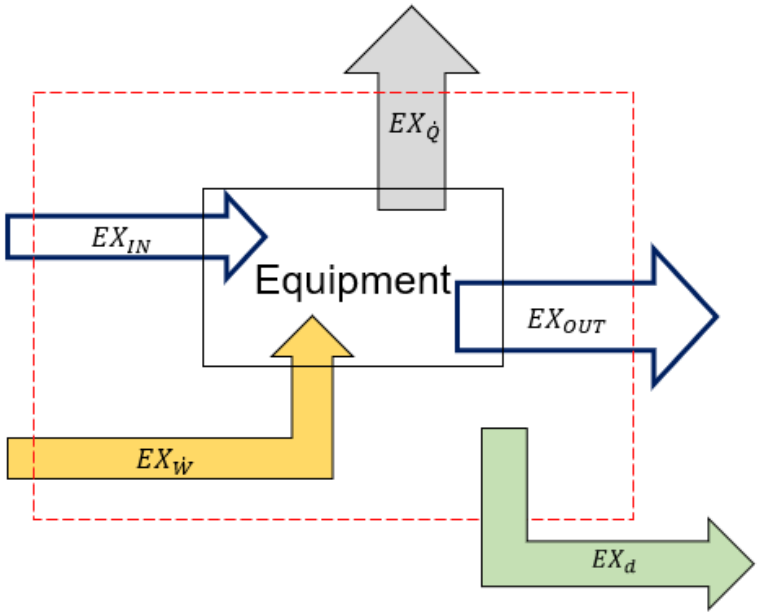


Figure 10: Identification of principal input-output from a general process system

Reference environment

Exergy is evaluated with respect to a reference environmental state. The intensive properties of the reference environment determine the exergy of each stream. The assumed environmental conditions are:

Table 10: Environmental conditions for the dead state identification

T_0	p_0
25°C	1 atm

The reference environment is in stable equilibrium, with all parts at rest relative to one another. This state acts as an infinite system and is a sink and source for materials and heat. No chemical reactions can occur between substances at environmental conditions. Tab. 9 shows that the exergy of each stream at the environmental reference conditions is zero. Tab. 11 reports enthalpy and entropy at environmental reference conditions of the principal substances involved in the analysis.

Table 11: Enthalpy and Entropy at reference environmental conditions for the main substances involved in the analysis

Substances	State	Thermodynamics model	$\widehat{H}_{i,0}\,(T_0, p_0)\,{}^{kJ}/_{kg}$	$\hat{s}_{i,0}\,(T_0, p_0)\,{}^{kJ}/_{kg\,K}$
Water	L	SRKKD	208,9	0,702
Propylene	G	SRKKD	634,5	2,915
Propane	G	SRKKD	631,8	2,852
Polymer*	S			
Nitrogen	G	PR	310	6,441

*Polymer's exergy is derived from literature correlation [65]

Step 3.2. Calculation of Exergy destruction and Exergy efficiency

Exergy destruction (EX_d) and Exergy efficiency (η^{EX}) are the two key results of the procedure. The computational of these two quantities for a system is essential to characterize the energy degradation and the system performance associated with its irreversible operation. These two concepts are used in all the case-studies to perform a comparative analysis of the systems, defining where process inefficiencies are located for future technological improvements.

The exergy balance introduced in Step. 3 allows the determination of exergy destruction of each system. Eq. (13) introduces the Exergy efficiency (η^{EX}) [69] as a consequence of the definition of each exergy terms:

$$\eta^{EX} = \frac{Useful\ exergy\ outgoing\ the\ system}{Total\ exergy\ entering\ the\ system} \qquad (13)$$

In accordance with literature [76] the following Exergy efficiency formulas are adopted for the assessment. Tab. 12 reports the assumptions.

Table 12: Exergy efficiency of the principal chemical process equipment

Pumps, Compressors and Fans	$\eta^{EX} = \frac{EX_{OUT} - EX_{IN}}{EX_{\dot{W}}}$
Turbines	$\eta^{EX} = \frac{EX_{\dot{W}}}{EX_{IN} - EX_{OUT}}$
Heat Exchangers	$\eta^{EX} = \frac{EX_{OUT}^{cold} - EX_{IN}^{cold}}{EX_{IN}^{hot} - EX_{OUT}^{hot}} = \frac{\Delta EX^{cold}}{\Delta EX^{hot}}$
Other equipment or Systems	$\eta^{EX} = \frac{\sum EX_{OUT}}{\sum EX_{IN}}$

Interpretation of Exergy Indicator results

Exergy has the specific characteristics that it is conserved only when all processes involved in the reference system and environment are reversible. Exergy is destroyed whenever an irreversible operation occurs. In this context, the application of exergy analysis to a chemical process can quantify the thermodynamic imperfection related to the unit operations involved in the system. In the specific, the quantification of Exergy destruction measures the thermodynamic irreversibility rate of the process which represents losses in energy quality or usefulness. Exergy analysis is an efficient method to define critical issues along with a process chain, highlighting strength and weaknesses of a reference schemes. The introduction of this calculation procedure during early process design activities can monitor each equipment performance, quantify process alternatives solutions from energetic efficiency standpoint and identify optimal thermodynamic conditions among available ranges. Exergy analysis can be a practical tool for early design activities, monitorization of operating phases or improvements assessment projects.

Database of energy sources

General overview

In this section a database of energy source is proposed based on Environmental, Safety, Economic and Energy efficiency indicators. Several renewable and non-renewable technologies for electricity production are analysed to characterize impacts and efficiencies of principal state-of-the art processes. Baseline information for future PDAM applications is proposed. In particular, this assessment provides KPIs regarding Environmental protection, safety and economy of the most widespread technologies for electric power production.

The quantification of electricity source impacts is a key aspect for chemical process lifecycle analysis as one of the indispensable inlets. In this direction, the performances of the major widespread electricity production technologies are defined. Aim of this assessment is to support design decision making for future polymerization plant during their early feasibility study and technology selection facing a sustainability progress.

Definition of the Reference

In this assessment technologies for electric power production are considered as black boxes and characterized only by their principal input and output. In this context, a lifecycle boundary is assumed to monitor the whole performances of the reference. 1 kWh of electricity produced is assumed as reference unit to express KPIs and allow technology comparison. Fig. 11 presents the reference scheme

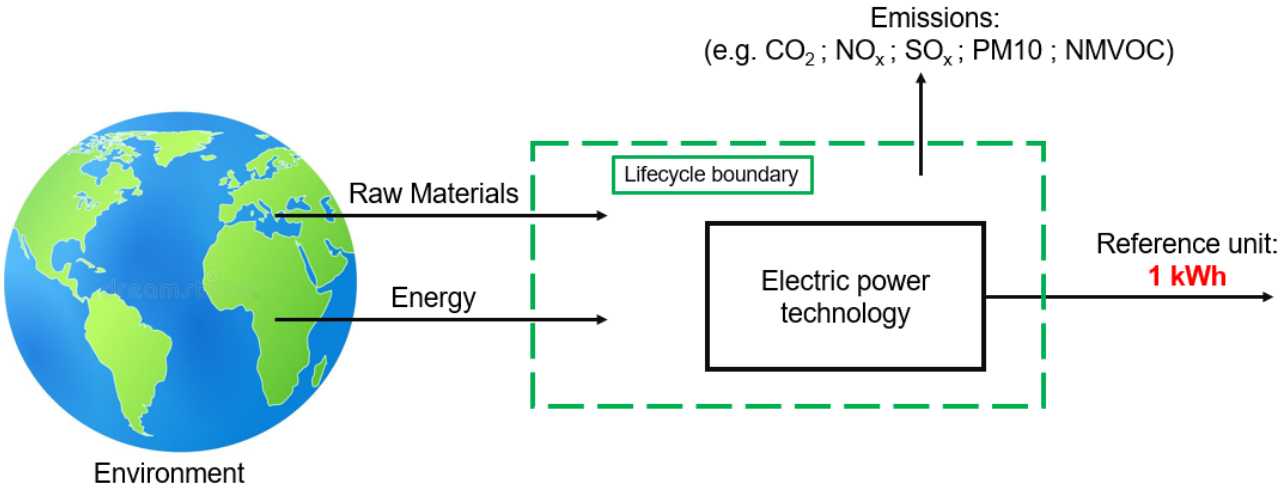


Figure 11: Reference scheme for the characterization of Electric power production technologies

Lifecycle boundary is comprehensive of all the activities and operations required to produce the reference unit. In this framework, it's important to highlight that: emissions, raw materials and energy consumptions may not be allocated directly in the electric production plant, but also in auxiliary background processes (e.g., Oil Extraction and pre-treatment for oil-based electricity technologies). This assumption allows to include all the facilities required for each technology, promoting consistent KPIs.

Tab. 13 reports the list of technologies considered for the analysis and the geographical location. Due to the lack of detailed data, not all the combinations (site-location / technology) are mentioned. At list, each country is characterized by the average grid mix performance.

Table 13: Reference technologies and site-location for the assessment

Non-Renewable technologies	**Renewable technologies**	**Average**	**Countries**
Coal Gas	Biogas	Grid Mix	EU-28 (Europe)
Lignite	Solar Thermal		GB (Great Britain)
Hard Coal	Geothermal		CN (China)
Heavy Fuel Oil (HFO)	Waste		ES (Espania)
Nuclear	Photovoltaic		NL (Netherlands)
Natural Gas	Hydro power		IT (Italy)
	Wind power		DE (Deutschland)
	Biomass (Solid)		GR (Greece)
			FR (France)
			US (United States)
			BR (Brasil)
			MY (Malaysia)
			TH (Thailand)
			JP (Japan)
			GR (Greece)
			IN (India)
			NZ (New Zeland)

Indicators calculation

Environmental impacts indicators

Environmental KPIs are intended to monitor the environmental footprint of the reference. In this assessment the following indicators are assumed:

- Land Use [m^2 y / kWh] that evaluate the total area required to produce 1 kWh for 1 year (e.g., Grassland, Industrial area, Urban area). This indicator is intended to support the identification of required area during the early technology selection and feasibility study.
- Overall energy required [kWh/kWh] which measure the energy required (e.g thermal) to produce 1 kWh. This KPI monitors the energetic performances of the reference technologies. In addition, it's mentioned also the % of renewable energy that are converted into electricity.
- Emissions of pollutants into atmosphere: GWI, POCI, AI, Dust in accordance with Tab. 6

Environmental KPI are calculated in accordance with Eq. (1).

Safety Indicator

Preliminary considerations about safety aspects are introduced in this assessment by the evaluation of the risk associated with the introduction of each technology. In this assessment, risk is intended to evaluate the number of human fatalities per year Eq. (14) reports the calculation step:

$$Risk = Frequency * Severity \qquad (14)$$

Frequency measures the number of fatality incidents per year [event/y], Severity expresses the number of deaths per incident [death/event]. Once Eq (14) is applied, a time frame of electrical production of the last 20 years is considered as basis for the calculation of Risk KPI [death/TWh] in accordance with the considered functional unit. Electrical grid mix of the last 20 years is derived by literature [77].

Economic indicator

Economic aspects are introduced by the definition of the LCOE (Levelized cost of Energy) [78] of each technology option. LCOE is a measure of the net present cost of electricity generation during the entire lifecycle of the reference related by the total amount of electricity produced. Eq. (15) reports the calculation step:

$$LCOE = \frac{sum\ of\ costs\ over\ lifetime}{total\ electricity\ produced\ over\ lifetime} \qquad (15)$$

Data gathering

Data collection is based on literature databases and reports. In particular, information about environmental emissions and land utilization are obtained by LCA databases (Thinkstep, Sphera [79]). Safety parameters (frequency and Magnitude) are derived by reports [80], [81] or calculated by the list of events. Regarding economic aspects, several information about LCOE of each technology are obtained in literature [82], [83]. However, LCOE of technologies is strongly influenced also by the site-location of the reference electric power plant. In this assessment, average indicators are assumed in order to reduce the geographical dependence on the indicator.

Results

Table 14: KPIs obtained for Non-Renewable technologies utilized for Electric power production.

Non-Renewable Resources	Grid Mix	Coal gas	Lignite	Hard coal	Heavy Fuel Oil (HFO)	Nuclear	Natural Gas
Land Occupation [m2y/MWh]	29,8	1,4	1,3	1,3	0,5	0,1	0,2
Overall Energy Required [kWh/kWh]	2,9	3,1	3,0	2,9	3,4	2,8	2,4
% Of Renewable fraction [kWh/kWh]	27,22%	0,35%	0,79%	0,35%	0,39%	0,06%	0,15%
GWI [kg CO_2,eq/kWh]	4,8E-01	1,1E+00	1,1E+00	9,7E-01	9,3E-01	4,4E-03	4,8E-01
AI [kgSOx,eq/kWh]	1,3E-03	1,5E-03	7,6E-03	3,0E-03	6,3E-03	2,8E-05	3,6E-04
Dust [kg PM10,eq/kWh]	1,2E-03	2,4E-03	4,2E-03	2,8E-03	4,2E-03	2,5E-05	5,0E-04
POCI [kg C2H4, eq/kWh]	2,4E-05	2,6E-05	2,8E-06	2,5E-05	8,6E-05	3,0E-06	2,4E-05
Frequency [Accidents/year]		Not Estimated	Not Estimated	44,1	13,4	0,2	4,6
Magnitude [Death/Accidents]		Not Estimated	Not Estimated	20,1	44,2	356,4	15,7
Risk [Deaths/year]	353,1	Not Estimated	Not Estimated	887,2	592,4	77,8	71,4
Risk [Deaths/TWh]	2,4E-02	Not Estimated	Not Estimated	1,6E-01	5,0E-01	3,4E-02	2,6E-02
LCOE Average [$/MWh]	104,1	109,0	104,5	116,0	Not Estimated	155,0	56,0

Table 15: KPIs obtained for Renewable technologies utilized for Electric power production.

Renewable Resources	Grid Mix	Biogas	Solar Thermal	Geothermal	Waste	Photovoltaic	Hydro power	Wind power	Biomass (Solid)
Land Occupation [m2y/MWh]	29,8	753,5	1,5	0,1	2,8	5,6	0,3	0,9	1019,1
Overall Energy Required [kWh/kWh]	2,9	8,0	9,1	4,5	2,2	6,2	1,2	2,5	4,0
% of Renewable fraction [kWh/kWh]	27,22 %	95,76%	98,25%	99,85%	87,03%	96,90%	99,60 %	98,74 %	95,63%
GWI [kg CO_2,eq/kWh]	4,8E-01	9,1E-02	3,9E-02	6,4E-02	7,5E-01	4,9E-02	6,6E-03	8,6E-03	3,7E-02
AI [kgSOx,eq/kWh]	1,31E-03	2,45E-03	9,05E-05	4,96E-06	6,08E-04	1,80E-04	4,18E-06	2,11E-05	1,64E-03
Dust [kg PM10,eq/kWh]	1,2E-03	2,7E-03	9,1E-05	6,5E-06	8,9E-04	1,5E-04	4,9E-06	1,9E-05	1,9E-03
POCI [kg C2H4, eq/kWh]	2,4E-05	4,4E-05	3,6E-06	6,7E-07	1,4E-05	3,9E-05	2,2E-07	1,4E-06	2,1E-04
Frequency [Accidents/year]	9,3	Not Estimated	Not Estimated	0,03	Not Estimated	Not Estimated	0,4	2,2	Not Estimated
Magnitude [Death/Accidents]	395,4	Not Estimated	Not Estimated	21,0	Not Estimated	Not Estimated	2309,3	1,1	Not Estimated
Risk [Deaths/year]	353,1	Not Estimated	Not Estimated	0,5	Not Estimated	Not Estimated	833,9	2,3	Not Estimated
Risk [Deaths/TWh]	2,4E-02	Not Estimated	Not Estimated	1,1E-02	Not Estimated	Not Estimated	3,2E-01	2,8E-02	Not Estimated
LCOE Average [$/MWh]	104,1	147,0	141,0	90,5	125,0	93,0	75,0	58,5	82,5

Results presented are representative of the average impacts and performances of the reference countries. In order to compare results obtained and define a hierarchy of electric power production technologies from sustainability standpoint, a new calculation step is introduced by Eq (16). In this context, KPIs obtained for each reference technology is compared directly with Grid Mix performance defining strength and weaknesses.

$$KPI_{\%} = \frac{KPI_{tech.} - KPI_{GridMix}}{KPI_{GridMix}} \qquad (16)$$

Furthermore, classes of improvements/worsening are defined based on $KPI_{\%}$. This assessment is based on multiple assumptions (average upon all the countries, literature datasets). In this framework, the definition of classes allows to compare not the specific results but the trend. Classes of impacts are reported in the follow (Tab. 16). The applications of Eq (16) to the reference technologies are presented in Tab. 17 and 18.

Table 16: Definition of classes of impact

> + 100%	[+40%;+100%]	[+10%;+40%]	[-10%,+10%]	[-40%,-10%]	[-90%,-40%]	[-100%,-90%]

Table 17: Non-renewable technologies performances compared to the Grid Mix

	Coal gas	Lignite	Hard coal	Heavy Fuel Oil (HFO)	Nuclear	Natural Gas
Land Use						
Energy Efficiency						
CO_2 Emission Index						
Other Emission Index						
Risk	N.A	N.A				
LCOE				N.A		

Table 18: Renewable technologies performances compared to the Grid Mix

	Biogas	Solar Thermal	Geothermal	Waste	Photovoltaic	Hydro power	Wind power	Biomass (Solid)
Land Use								
Energy Efficiency								
CO_2 Emission Index								
Other Emission Index								
Risk	N.A	N.A		N.A	N.A			N.A
LCOE								

Conclusions

Nowadays multiple process options are well defined and implemented at industrial level for electric power generation and supplying. However, new renewable solutions are continuously growing, increasing their performances and reducing their economic impacts. In this framework, this assessment monitors the state-of-the art of electric power technologies in order to compare alternative solutions for primary processes PDAM. Furthermore, the current study can be defined as the starting point for future assessment, delineating strength and weaknesses of new potential electric power generation options.

In detail, KPIs regarding environmental impacts, energetic performances, safety and economic impacts are calculated for the principal renewable and non-Renewable technologies for electric power production. The comparison with average Grid Mix KPIs allows to monitor entirely their performances. The principal problematic related to the use of non-renewable technologies is the high environmental impacts (emissions of toxic and pollutant substances). This problematic is partially overcome by Natural Gas and Nuclear based plants. The Strength of non-renewable resources is their high energetic efficiency, low MJ are required to produce 1 kWh of electricity. Natural Gas based plant represents the most performing non-renewable technology. Results obtained are comparable with renewable technologies. Furthermore, good results are obtained also for nuclear technology, however, it's still quite expensive and even if the risk is considerably low, the severity of fatal incidents is considerably high. Renewable technologies are principally characterized by low emissions, except for Biogas and Biomass which are responsible of high NOx, SOx and Dust emissions. These technologies are also characterized by high use of Land. In general, the principal weakness of renewable sources-based plant is the Energetic efficiency of the plant. The most promising technologies for the incoming future are photovoltaic and wind power. It's clear that site specific conditions are required to build efficient solar and wind-based plant (good solar incidents, ventilated area). However, these technologies are becoming more and more profitable. In detailed, the price of electricity from solar declined by 89% in these last 10 years, while onshore wind by 70% [84]. These trends increasingly encourage business to frame future decisions including renewable resources for electricity supply, even at chemical industrial scale.

Section 3: Case Studies

This section is dedicated to the application of methods presented in Section 2. Case-studies try to represent industrial facilities and interconnection of chemical processes inside the polymer production chain. Some of the case-studies were defined in collaboration with industrial company.

The development and analysis of the case studies aims at three main goals:

- Demonstration: the introduction of several case studies allowed to apply each presented methodology and offers the chance to demonstrate the efficacy of developed procedures. Moreover, case-studies cover a wide range of design aspects, encompassing three dimensions: different polymerization technologies, stages of the plant design and boundary levels. The applicability of the methods at any of these studies demonstrates the flexibility and the simple use of the developed portfolio of approaches.
- Computation: the profitable collaboration with industrial company allowed to carry out analysis with real plant data and schemes. The computation of performance indicators provides the chance to quantify operating processes efficiency and industrial technology improvements. Therefore, case-studies form a rich database of examples that will be helpful for future industrial application of the methodologies.
- Validation: in the analysis of the case studies, constant attention is paid at final and intermediate results to match the expected literature impact profiles. Results were presented and discussed to LCA and Circularity experts with industrial experiences.

Table 19: Proposed assessment methods used in the case-studies

Case Study	Assessment methods		
	PDAM: Process design assessment method	Screening method for polyolefin technology comparison	Database of Energy Sources
Environmental impact evaluation of polypropylene production chain	X		
Screening of principal polypropylene polymerization technologies		X	
Comparison of polymerization processes based on reaction phases	X		
Application of Exergy analysis to a polypropylene productive plant	X		
Analysis of potential polypropylene process improvements		X	
Analysis of Electric power technologies			X

Case Study 1: Environmental impact evaluation of polypropylene production chain

Case-study description

The following case-study concerns the quantification of polypropylene productive lifecycle chain environmental impacts. This application of PDAM is tailored to 450 kt/y polypropylene slurry plant. In detailed, conceptual design data and other relevant design information are used as method inlet information to monitor the sustainability profile of the plant and defining critical issues along the polymeric productive chain. Different level of detailed are investigated to measure emissions and principal locations inside and outside the polymerization plant battery limit. This analysis is carried out following the procedure presented in section 2.

Definition of the reference scheme

Reference layout is derived by polypropylene productive chain [58]. In this context, polymerization technology is the focal point of the assessment and is assumed as Primary process. Background processes are introduced to simulate external technologies for raw material and energy supply, waste management and supporting facilities. A certain level of detailed is adopted to interpretate real processes interaction matching available information. A reference unit of 1 kg of polypropylene pellet produced via polymerization is assumed. This assumption allows to express environmental results per kg of polymeric pellet and compares KPI with literature data. In order to monitor environmental impacts and provide critical issues at different levels, three nested System boundaries are defined. In particular, 2 design boundaries are adopted focused on polymerization activities (design boundaries of Fig. 4) and an extended framework is introduced to incorporate all the polymer productive units (lifecycle boundary of Fig. 4). A representative layout of the reference scheme is presented in Fig. 12 where principal connections between units and reference boundaries are illustrated.

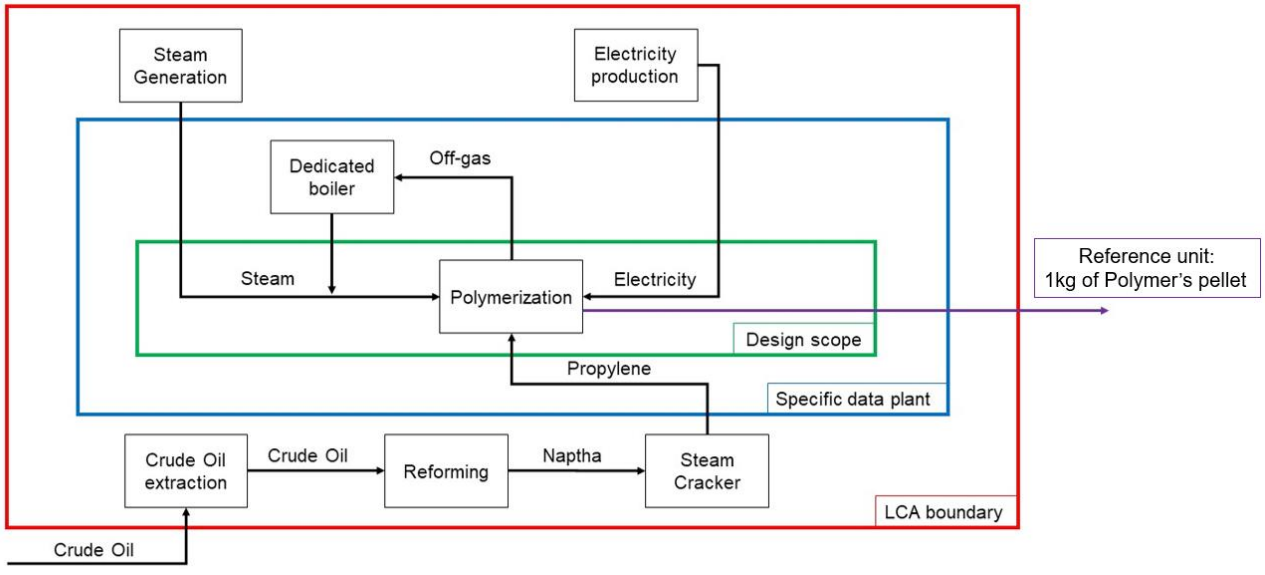


Figure 12: Reference polypropylene productive process for the application of the PDAM

In detail, boundaries are divided as followed:

- The inner boundary, the "Design scope" evaluate only the process in the scope of the design or operative phase (e.g. Polymerization process within a PDP). This framework is comprehensive of polymerization principal activities that convert monomer into the polymer.
- The second boundary, the "Specific data plant" is set in the middle and coincides with the battery limit of the reference plant. Therefore, it encloses site-specific unts and utilities (for example, dedicated boilers for the steam production or optional Gas Phase Reactor of a reference plant). This second boundary divides the plant battery limit which is the physical limit of the primary process from external out of control operations.
- The more extended system boundary, the "Lifecycle boundary", contains all the units process required for the polymer production outside the battery limits for supplying of raw materials and utilities, disposal of waste and by-products.

Environmental indicators are computed at the three nested boundary level (Fig. 12) The method was applied repeatedly using the following documents for data collection:

- PDP (process design package) of the reference slurry loop plant reference plant This document allows to compute two set of indicators using the minimum or the maximum electrical load required.
- A vendor proposal inside a basic design package for the electricity required of each equipment.

Definition of input data

Two different approaches are adopted for data collection of the presented assessment. A certain level of detail (compatible with the information available in the FEED design phase) is required to characterize energy and material consumption of the Primary process. Background processes are instead out of the control of designer, and generic datasets that measure the average technologies performances can be used. However, the methodology is completely versatile and different plant size or polymerization technologies could be adopted. Furthermore, no particular restrictions are imposed for data collection, but it's clear that results reliability depends on input data quality.

Data gathering for Unit process within the Design Scope

The methodology requires to characterize at least input and output material and energy stream that crosses the Design scope boundary. This information is derived by material and energy balances. Data required are strongly influenced by the polymer run of the plant and the level of design involved. There are huge differences in terms of energy and material consumption between polymer's type (Homo, Raco, Heco). In addiction, within the same type of polymer, there are minimal differences for the specific polymer produced. A reference polymer run is assumed in accordance with PDP stream characterization.

In this particular application, several sources are used to characterize polymerization consumptions. Table 20 and 21 present a list of input and output of the design scope that are produced or treated

outside this boundary. In the LCA methodology they are called “process flows” and allow to correlate each unit process.

Table 20: List of required input for the Design Scope

Input	Source
Monomers and Reactants	
Propylene	PDP
Ethylene	PDP
Butene	PDP
Hexene	PDP
Octene	PDP
Vinyl-Acetate	PDP
Hydrogen	PDP
Inert	
Propane	PDP
Ethane	PDP
Hexane	PDP
Nitrogen	PDP
Catalyst, Co-Catalyst and other components	
Catalyst	PDP
Co-Catalyst 1	PDP
Co-Catalyst 2	PDP
Oil/Grease	PDP
Antistatic Agent	PDP
Additives	PDP
Utilities	
Water	PDP
Steam	PDP
Electricity	PDP / Basic Design Package (BDP)

Table 21: List of output from the Design Scope

Output	Source
Direct Emissions	
Vent to atmosphere	PDP / Integrated Environmental Authorization
Liquid waste/by-products	PDP / Integrated Environmental Authorization
Solid waste	PDP / Integrated Environmental Authorization
Purges	
Off-gas	PDP
Liquid purges	PDP
Other output	
Oil/Oligomers	PDP
Wastewater	PDP

The input data required for the application of the proposed methodology to this case study are derived from a specific Process design package (PDP). Input and output data that cross the *design scope* boundary (green) are obtained from material and energy balances during early design phases of the plant. Ordinary plant emissions and vents to the atmosphere or water can be estimated from *Plant integrated environmental authorization.* Emission of micro-pollutant from utilities and auxiliary processes (monomer production, power and steam generation, water treatment, etc.) are evaluated by emission factors from available databases [PlasticsEurope]. Geographical and technological decisions have been taken for emission factors matching data availability and specific plant location. The main material and energy flows across the system boundaries are reported in Tab. 22.

Table 22: Material and Energetic input for the application of the PDAM to the reference polymerization process

Input	Mass or Energy flow	Source
Propylene	57415 kg/h	PDP
Ethylene	2000 kg/h	PDP
Electricity	28160 kW	BDP
Steam	12685 kg/h	PDP
Nitrogen	600 kg/h	PDP

Results from methodology application

The current section presents the results obtained in this specific case study. The environmental KPIs applied to the reference scheme are summarized in Tab. 23. As shown in the table, relevant differences are monitored for the three defined boundaries. In particular, the major quantity of pollutant emissions is located in the Lifecycle boundary where background processes operate to support polymerization activities. In this specific application, lack of detailed data didn't allow to quantify Design Scope emissions (e.g., vent to atmosphere). However, in accordance with specific plant integrated environmental authorization, these emissions are negligible compared to the entire polymer lifecycle.

Table 23: Environmental KPIs obtained by the application of the methodology to the polypropylene lifecycle chain

KPI	Unit of measurement	**LCA boundary**	**Specific Data Plant**	**Design Scope**	**Total indicators**
ADI,f	[MJ/kgPolymer]	7,26E+01	6,40E-01	0,00E+00	7,33E+01
ADI,e	[kgSb,eq/kgPolymer]	2,08E-07	1,84E-09	0,00E+00	2,10E-07
RwEC	[MJ/kgPolymer]	2,78E+00	5,96E-04	0,00E+00	2,78E+00
WC	[kgWater/kgPolymer]	2,67E+01	1,49E-01	0,00E+00	2,69E+01
CO_2	[kgCO_2/kgPolymer]	1,68E+00	3,63E-02	0,00E+00	1,72E+00
GWI	[kgCO_2,eq/kgPolymer]	1,77E+00	4,03E-02	0,00E+00	1,81E+00
ODI	[kgCFC-11/kgPolymer]	3,01E-08	5,70E-13	0,00E+00	3,02E-08
AI	[kgSO_2-,eq/kgPolymer]	4,10E-03	2,77E-05	0,00E+00	4,13E-03
POCI	[kgEthylene,eq/kgPolymer]	4,51E-04	4,08E-06	0,00E+00	4,55E-04
EI	[kgPO_4---,eq/kgPolymer]	1,17E-03	6,37E-06	0,00E+00	1,18E-03
PM	[kgPM10,eq/kgPolymer]	3,53E-03	2,88E-05	0,00E+00	3,56E-03
HTI	[kg 1,4-Dichlorobenzene eq / kgPolymer]	3,68E-01	3,23E-03	0,00E+00	3,71E-01
FETI	[kg 1,4-Dichlorobenzene eq / kgPolymer]	1,02E-01	3,27E-04	0,00E+00	1,03E-01
MAETI	[kg 1,4-Dichlorobenzene eq / kgPolymer]	1,94E+02	2,30E-02	0,00E+00	1,94E+02
TETI	[kg 1,4-Dichlorobenzene eq / kgPolymer]	1,35E-03	4,89E07	0,00E+00	1,35E-03

These results offer a general overview of the environmental problematics related to the polymerization activities. Further considerations can be carried out considering different location and technologies for background processes (e.g renewable resources), analysing the specific operation within the design scope and comparing KPIs with literature or previous analysis indicators.

Interpretation and sensitivity

Focusing on GWI result, selected as reference example, it is possible to quantifying the percentage of contribution of each process to the indicator and defining a hierarchy of more impactful processes. This approach allows to define critical issues along with the polymer chain pinpointing the principal processes that required technological intervention to reach more sustainable results. In this analysis, principal processes required to support the polymer production process are considered. Results are reported in Fig. 13 where the contribution of each unit to the GWI are reported based on the reference scheme (Fig. 12). In this case, a HECO polymer run is considered to quantify the ethylene production impact compared to the principal monomer (propylene). First of all it's possible to appreciate that the largest quantity of GHG is emitted during the monomers production chain (about 83.6%) in accordance with PP Ecoprofile [58]. Other relevant emissions are allocated in the Electric power generation plant (11%) and for steam production (5.4%). Considering the overall PP lifecycle chain, other raw materials have negligible impact compared to the main processes (e.g Hydrogen, Nitrogen).

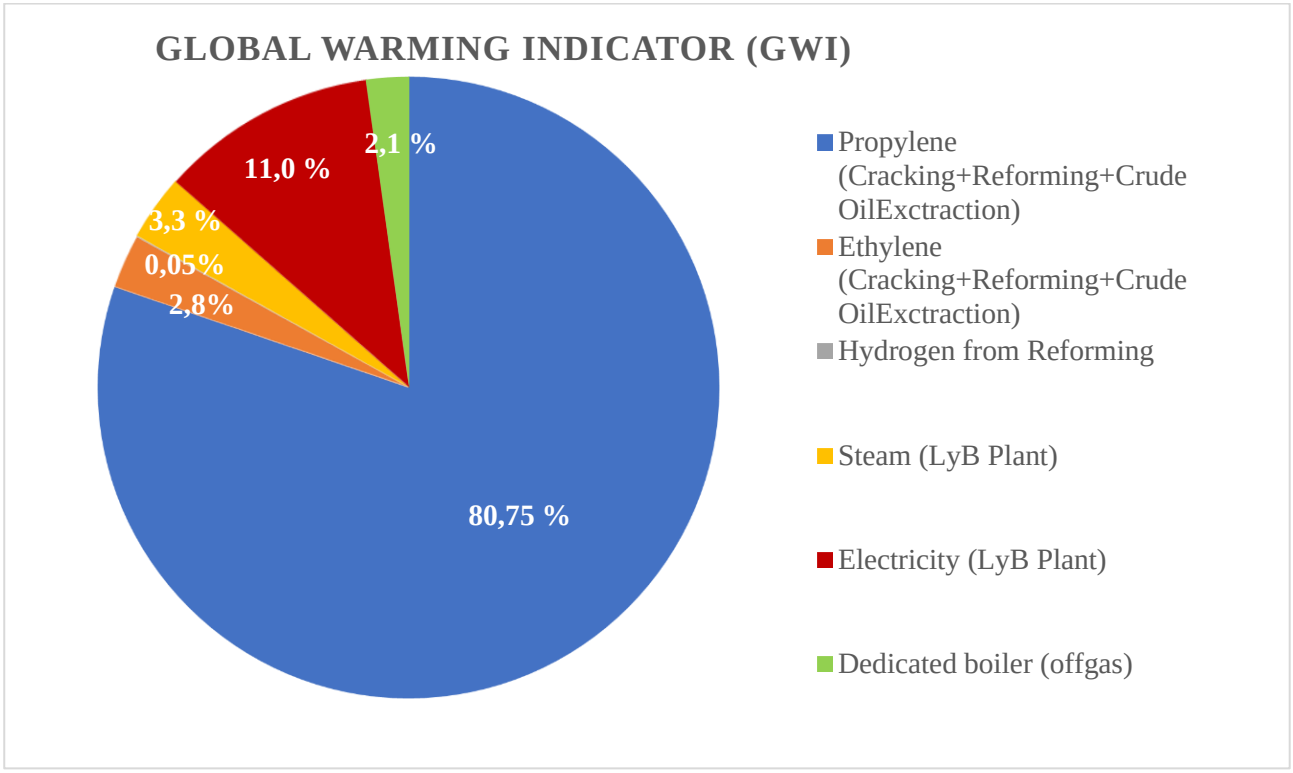


Figure 13: Allocation of GWI of the polypropylene productive chain

This result highlights that the potential environmental GWI impact for PP is dominated by monomer (and co-monomer) productions with the current non-renewable technologies. However, before planning new process layout and investigate alternative solutions, it's mandatory to identify the potential minimum impact of each contribution to the environmental indicator. In order to quantify the minimum impact related to the monomer production plant, it's assumed a stoichiometric consumption of propylene and ethylene. This configuration is figured as an ideal case and the overall percentage of contribution related to monomers production (80,75%+2,8%=83,6%) is lowered to 78,1%. The Gap between the current monomer production impacts and the minimum stoichiometric one is only 5,5%. This percentage evaluates the potential improvements margin related to the reduction of monomers consumption with the current technologies. In this direction, improvements focused on the reduction of monomer consumption can be comparable with new configurations that

reduce steam and electricity required for polymerization activities. In addition, in order to interpretate the results and define critical issues along with the polymer chain, alternative options are considered for energy and raw material supply. This approach allows to overcome the minimum configuration related to current activities evaluating new strategies for raw material and energy supply. Further considerations are presented in the following section.

Moreover, deeper analysis can be carried out with particular focus to primary process activities. Primary process can be divided into its principal operations and correlate their consumptions of raw material and energy directly to the environmental KPI. For example, considering the contribute of electricity to the reference process GWI (about 11%), it's possible to allocate directly the contribute to each primary operation. In this specific example, Tab .24 reports the electrical power consumption of primary activities inside the polymerization process and Fig. 14 the graphical representation of each contribution.

Table 24: Electrical power consumptions of primary operations

Primary Process Activities	kW
Catalyst Preparation	17
Reaction (Step 1)	2650
Monomer Recovery & Storage	1220
Reaction (Step 2)	1606
Polymer Finishing	522
Safety Blow down	845
Monomer Pre-treatment	479
Extrusion	20117
Polymer final treatment	706
Total	28161

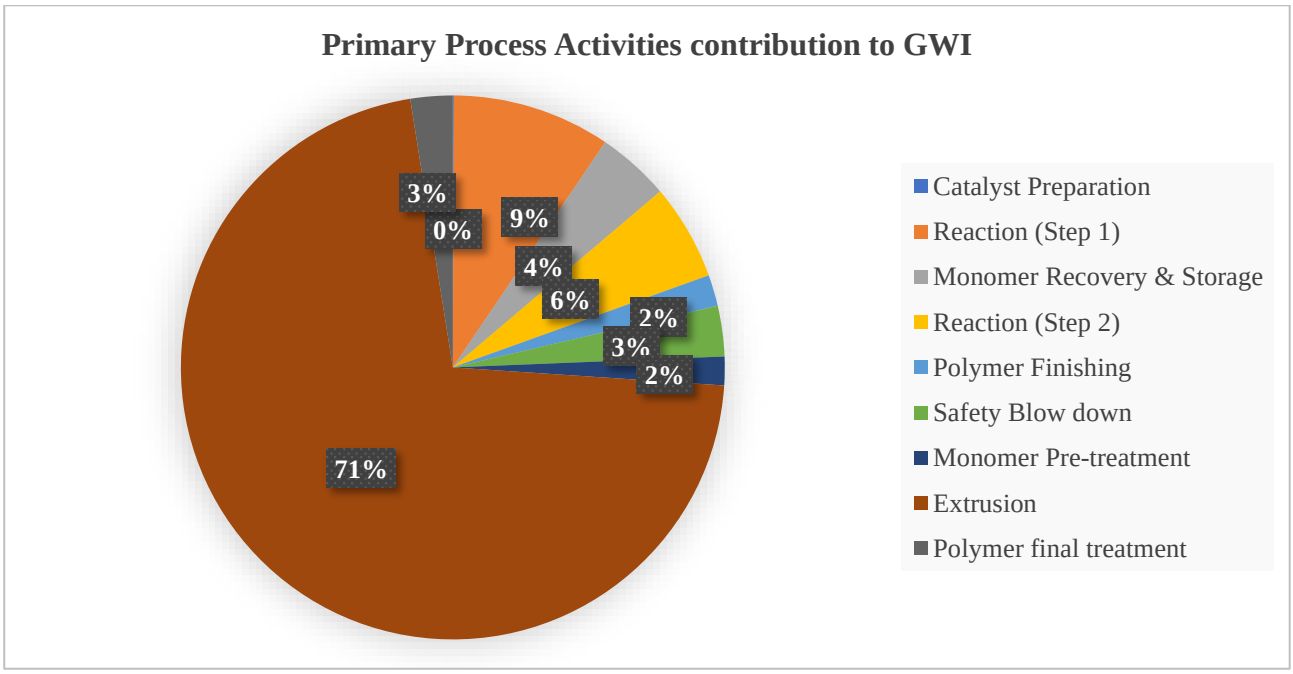


Figure 14: Percentage of contribution of primary activities to the GWI

This strategy is intended to monitor the environmental impact related to primary activities and define a hierarchy for future improvement study. In this specific example, about 70% of GHG emitted by external electrical power plant that support primary activities is allocated in the final extrusion section. Extrusion is by far the most energy-consuming operations within the polymerization process and could be the starting point for future improvement study.

Results are compared with literature available information regarding environmental profile of polypropylene productive plant [58]. In particular, focusing of GWI, PlasticsEurope reports a KPI of 1,63 $kgCO_2$,eq/kg PP which is about 8% lower than the value calculated and reported in Tab. 23. However, different approach is adopted in the current work for GWI calculation compared with literature procedure. PlasticsEurope reports an average impact of about seven different technologies, so the indicator is tailored to products and not characterize the specific technologies. Furthermore, net monomer consumptions are assumed for the PP Ecoprofile, so off-gas and purges are not considered in the assessment. In addiction, PP Ecoprofile assumed a cut-off rules of 98%, so not all the GHG emitted are considered to characterize the polypropylene environmental footprint.

Results obtained are used to populate a database of plant environmental impact indicators. Future analysis will use other PDP results for internal consistency check.

Final remarks

In this chapter, the methodology developed and presented in section 2 is demonstrated by the application to a polyolefin productive process. Multiple options for input data can be selected spanning from early feasibility study to operative material and energy balances. This versatility allows to monitor the environmental footprint of the reference scheme at any operative level and design phases. A certain level of detail is suggested to characterize primary process which is the principal scope of the assessment. In this specific case-study, conceptual design and basic design data are utilized to quantify respectively material consumption and electrical power required for the reference process. Literature datasets are utilized to populate background processes and characterize the entire scheme.

Result obtains is a set of Key Performance Indicators regarding the principal environmental problematics (e.g., Climate change, Ozone depletion layer, toxicity). Deeper analysis can be carried out with the aim of monitoring the environmental impact of single operations within the reference process. This approach drives and establishes a hierarchy for future improvement study. For polymerization specific case-study, the final extrusion area is the most energy-consuming.

In conclusion, results can be compared with literature available information in order to compare processes and technological alternatives from environmental footprint. This approach generates new benchmark and targets to face the progress in a sustainability perspective.

Case study 2: Screening of principal polypropylene polymerization technologies

The comparative methodology presented in section 2 is applied to the principal reference polymerization scheme. The analysis of available literature about the proposed technologies allowed to identify the key features of each process scheme highlighting strengths and weaknesses of different polymerization strategies. Results obtained are intended to support the technology selection phase and preliminary feasibility study for the design of future plant.

Overview of current propylene production technologies

An analysis of the current market of polypropylene production allowed to identify twelve leading technologies currently implemented in production at industrial scale [64] [85]. The generic scheme presented in Fig. 8 is applicable to each technology, though specific design choices make every process unique. Tab. 25 reports the world production capacity of the main polypropylene technologies.

Table 25: World production capacity of the principal polypropylene technologies. Adapted from [85]

Technology	Owner Company	Type	Industrial application since	World Capacity 2017 [kt/y]	World Capacity 2022 [kt/y]	Increase of Capacity (2017-2022)
UNIPOL	Grace	Gas Phase	1985	12 546	17 250	+37 %
INNOVENE PP	INEOS	Gas Phase	1979	6 600	9 681	+47 %
HORIZONE	JPP	Gas Phase	1979	1 962	2318	+18 %
SPHERIZONE	Lyondellbasell	Gas Phase	2002	2913	3 818	+31 %
NOVOLEN	Lummus Novolen Technology	Gas Phase	1967	7 908	8863	+12 %
SUMITOMO	Sumitomo	Gas Phase	1977	1427	1840	+29 %
BORSTAR	Borealis	Bulk	2000	2 378	2386	+0 %
EXXONMOBIL	Exxonmobil	Bulk	1989	1 605	1704	+6 %
SPHERIPOL	Lyondellbasell	Bulk	1983	20 037	23659	+18 %
HYPOL II	Mitsui	Bulk	1984	2 854	3272	+15 %
Sinopec	Sinopec	Bulk	1996	6 124	8931	+46 %

Nowadays UNIPOL and SPHERIPOL are the market leaders respectively of Gas Phase and Bulk technologies. Grace company was able to transfer in UNIPOL process the great knowledge developed in the polyethylene production. Lyondellbasell developed Spheripol technology introducing innovation in the reaction configuration and the adopted catalyst since the ‘80s, when polypropylene market was expanding.

Globally, all the processes are growing their production which is a symptom of the increase of the plastic demand [86]. However, more recent processes show a higher growth rate (e.g SPHERIZONE,

SINOPEC). They are still experiencing their initial start-up phase, if compared to more mature technologies.

Information on the technologies in Table 1 was retrieved from literature reports [63], [85], [87] and specific technologies patents [88], [89], [90].

Principal industrial state-of-the art processes for polypropylene production are classified and presented in Tab 26 and 27. Gas and Bulk phase technologies are compared regarding the main equipment involved and conditions.

Table 26: Principal equipment and design conditions of polymerization gas phase processes

Gas Phase processes						
Technology	UNIPOL	INNOVENE PP	HORIZONE	SPHERIZONE	NOVOLEN	SUMITOMO
Owner Company	Grace	INEOS	JPP	Lyondellbasell	Lummus Novolen Technology	Sumitomo
Reaction section – 1st or main Reactor (principal polymerization equipment)						
Reactor technology	Vertical Fluidized bed	Horizontal stirred bed	Horizontal stirred bed	Multi-Zone Circulating (MZCR)	Vertical stirred bed	Vertical Fluidized bed
Heat Removal	External Cooler (CW)	External Cooler (CW)	External Cooler (CW)	External Cooler (CW)	External Cooler with partial condensation (CW)	External Cooler (CW)
Operative conditions	• P = 33.8 bar • T = [65-75] °C • τ = 1h • C3 feed grade = 99,5%	• P = [21-24] bar • T = [63-85] °C • τ < 1h	• P = [20-24] bar • T= n.a.	• 2 reaction zones • P=30 bar • T=85°C	• P = [2.2-3.2] MPa • T = [70-80] °C	n.a.
Reaction section - Optional Polymerization equipment (required e.g., for HECO polymer)						
2nd Reactor (Copolymer)	Vertical Fluidized bed	Horizontal stirred bed	Horizontal stirred bed	Gas Phase	Vertical stirred bed	Vertical Fluidized bed
Powder Transfer System (R1->R2)	Transfer Station	Powder Transfer System	Gas Lock	High pressure degasser	Not present	Transfer Station
Monomer Pre-treatment	Splitter (accepts low propylene grade)	Not present	Not present	Not present	Not present	Not present
Polymer recovery, Polymer finishing and Extrusion Sections						
Powder Deactivator	Purge Bin (Steam + Nitrogen)	Powder Deactivator (Water + Nitrogen)	Purge Column (Water + Nitrogen)	Steamer (Steam) Dryer (Nitrogen)	Purge vessel (Nitrogen)	Powder Deactivator (Steam + Nitrogen)
Monomer Recovery	Degassing	Separator	Separator	LP Filter	Membrane recovery unit Deethanizer	Vent recovery
Pelletizing	Extruder	Extruder	Extruder	Extruder	Extruder	Extruder

CW: cooling water; P: pressure; T: temperature; τ: residence time of solid phase; n.a.: information not available.

Table 27: Principal equipment and design conditions of polymerization bulk/slurry phase processes

Bulk Phase processes				
Technology	BORSTAR	EXXONMOBIL	SPHERIPOL	HYPOL II
Owner Company	Borealis	ExxonMobil	Lyondellbasell	Mitsui
Reaction section – 1st or main Reactor (principal polymerization equipment)				
Reactor technology	1 Slurry Loop 1 Gas Phase	2 Slurry Loops	1 or 2 Slurry Loops	2 Slurry Loops
Heat Removal	Jacket (CW)	Jacket water	Jacket water	Jacket water
Operative conditions	• P = [2.2-3.2] MPa • T = [70-80] °C • τ < 1 h	n.a.	• P = [4.1-4.6] MPa • T = [75-80] °C • τ = [1-2] h	• P = n.a. • T = n.a. • τ = [1-1.5] h
Reaction section - Optional Polymerization equipment (required e.g., for HECO polymer)				
2nd Reactor (Copolymer)	Vertical Fluid bed Gas Phase	Vertical Fluid bed Gas Phase	Vertical Gas Phase	Vertical Fluid bed Gas Phase
Powder Transfer System (R1->R2)	Not present	Not present	Not present	Not present
Monomer Pre-treatment	Not present	Not present	Not present	Not present
Polymer recovery, Polymer finishing and Extrusion Sections				
Powder Deactivator	Purge Bin (Steam + Nitrogen)	Dryer (Nitrogen) Purge Bin (Steam + Nitrogen)	Steamer (Steam) Dryer (Nitrogen)	Steamer (Steam) Dryer (Nitrogen)
Monomer Recovery	Separator Separation Columns	Heater High P Degasser Deethanizer C3- Scrubber	Heater High P Degasser	Heater High P Degasser
Pelletizing	Extruder	Extruder	Extruder	Extruder

The principal advantage of bulk phase processes is the high monomer concentration in the reactor, which leads to a higher conversion per pass if compared to gas phase technologies. Another key difference regards the inventories usually present in a reactor, which are typically larger in bulk reactors due to higher densities involved: this can be a severe drawback for safety (higher inherent hazard potential) and for emergency management (e.g., sizing of the blowdown system). In addiction, Bulk processes typically require a higher thermal input in the monomer recovery section to vaporize the unreacted monomer.

In general, one or two reactors are required in the reaction section, depending on polymer type and production capacity. A single reactor solution is typically preferred for medium or low HOMO production capacity (e.g up to 300-400 kt/y). For greater plant size, two parallel reactors are usually employed, allowing higher versatility during maintenance. Sometimes, a configuration with two reactors in series is proposed to maintain different operative conditions in the two reaction stages. When two reactors are used in HOMO production process, they are typically designed as two identical pieces of equipment.

When plant design considers possibility of production of HECO polymer a second reactor downstream the configuration used for HOMO is required. This reactor is typically a gas phase technology in order to increase the homogenization of monomers.

In bulk phase processes, reactor design typically exploits vertical tubular reactors. The design introduced by Spheripol technologies inspired other polymerization technologies (e.g Borstar,

ExxonMobil). On the other hand, gas phase processes are characterized by greater variability in the design of the reaction stage. Several configurations are possible with use of vertical/horizontal stirred bed reactors and fluidized reactors.

Reaction section includes some pieces of equipment dedicated to Catalyst and Co-Catalyst preparation which are technology specific. Generally speaking, this involves mixing of catalysts with solvents and additives in order to increase the catalyst performance, ensure greater resistance and make it more accessible for the reaction stage.

Reaction area usually include a prepolymerization phase [91], which is aimed to slowly encapsulate the catalyst particle in a polypropylene shell, preventing the excessive production of fines by mechanical degradation of catalysts in the reactor. Prepolymerization is typically carried out in agitated small vessels at low temperature.

Production of HECO requires to operate two reactors at different conditions (e.g., composition of the monomer phase, pressure). In plant designs for HECO production, a powder transfer system is present between the reaction stages. Powder transfer system or Gas Lock system is constituted by process vessels and rotary valves that disconnect the reaction stages. The introduction of a gas lock system also prevents the monomer back-flow from the second to the first section. Main drawbacks in these systems are the extra electricity and maintenance requirement. Some Technologies (e.g., NOVOLEN) discharge onto the second reaction thanks to a lower pressure in downstream reactor thus avoiding the need of such system. Monomer recovery section consists in depressurization (typically through a valve) and physical separation of monomer from polymer. The equipment involved in physical separation are technology specific: high- or low-pressure filters (e.g. Spheripol, Spherizone), degassing vessels (e.g Unipol) and powder/gas separators (e.g. Novolen). The separated monomer is then compressed and sent back to the reaction section. Compression is the main responsible of electric energy consumption of this section and is strongly affected by the pressure and recycle flowrate typical of each technology.

Regarding the polymer finishing section, the operations of catalyst deactivation and polymer drying could be performed in a single or in two separated pieces of equipment. Processes that adopt the single stage configuration reduce the initial capital cost, but also introduce a limit in the versatility of the operation when different polymer formulations are produced. A schematic representation of the two possible process configuration is given in Fig. 15.

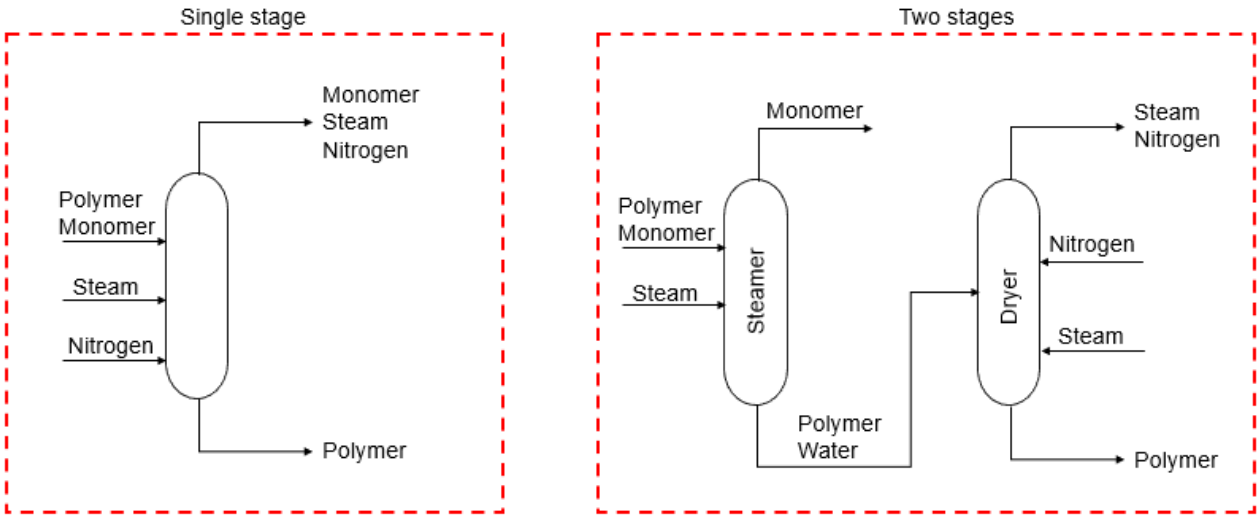


Figure 15: Polymer finishing alternative configurations

Considering two separated pieces of equipment, the outlet gas stream of the steamer is richer in monomer and could be more easily recycled to the reaction stage or exploited as feedstock in other process (e.g., as fuel for boilers, or as feed for propylene cracker). Recycle into the reaction stage would require dehydration and, possibly, distillation (i.e., monomer splitter) when accumulation of inert gases (e.g. propane and ethane present in the raw monomer feedstock) in the system is an issue. This solution with two separated pieces is adopted e.g., by UNIPOL technology.

The gas outlet stream from the dryer in two-stage technologies is typically rich of nitrogen. Though it can be considered for venting, potential exists for closed loop use of nitrogen. This requires removal of water (e.g., by condensation) and re-heating of nitrogen before recycle to the drier. On the other side, it allows for high mass flow rate of nitrogen in the drier with a low make-up of fresh nitrogen.

A greater level of simplicity is achieved in the single stage operation; however, the outlet gas stream is composed of a mixture of monomer, nitrogen, steam and hydrocarbons (e.g propane) and separation for recovery or energy use is more complex. Notably, NOVOLEN proposed a membrane unit for the separation of hydrocarbons from nitrogen in this stage.

UNIPOL process introduces an extra operation of monomer purification upstream the reaction section. This section uses reflux distillation (splitter) for improvement of the grade of the reactor feed stream. Typically, polymerization technologies operate with monomer at polymer grade (99.5%) as lower monomer purities will reduce the catalyst yield. The introduction of a splitter, allow to accept monomer streams at lower grades (e.g., chemical grade 95-97%) as battery limit inlet stream. This increases the versatility of the process for raw material supply. In addition, the same splitter section can be used to separate vent streams rich in monomer (e.g., monomer stream for the first column of a two sages polymer finishing section), enhancing material efficiency of the process.

Identification of reference schemes for technologies

Preliminary reference schemes were defined for a selected set of 5 technologies, representative of some key choices in process design (e.g., reactor type, polymer finishing strategy, etc.). This section illustrates the reference schemes adopted for each technology. The general polymerization layout proposed in Fig. 8 is developed into five process options inspired to industrial polymerization technologies analysed in section 3.1. In particular, Technology 1 is adapted from Unipol process, Technology 2 from Innovene, Technology 3 from Novolen, Technology 4 from Spheripol and Technology 5 from Spherizone. As not all the details on these technologies are available on the open literature, some assumptions based on good process engineering practice were considered for the definition of the missing information in the schemes.

Technology schemes and stream characterization tables proposed in the following refer to the Homopolymer (HOMO) production. A reference polymer capacity is adopted (400 kt/y) in the material and energy balances. In the reference schemes, units are assigned to specific sections of the polymerization process (see block diagram in Fig. 8 of the main text) according to a colour code: green for reaction section, blue for monomer recovery section, red for polymer finishing and black for extrusion section. The catalyst preparation and prepolymerization stages are not presented due to the negligible contribution to the assessment.

<u>Technology 1</u>

Technology 1 is characterized by a vertical fluidized-bed reactor with an expanded upper section for minimizing the carryover of polymer particles. The monomer gas stream is circulated through the bed, compressed and cooled in an external circuit. A recycle blower and a condenser are required to provide reaction heat removal and bed fluidization. The fresh liquid polymer-grade propylene is combined with recycled monomer stream. Produced polymer and residual gas are discharged in a lower pressure vessel.

The monomer-polymer mix is fed to a Purge Bin (as reported in Fig. 16). Steam and Nitrogen provide the catalyst deactivation and polymer drying before the extrusion section, while recovered reactants are compressed and condensed at low temperature. Process purge allows to remove incondensable components (e.g Nitrogen). Condensed hydrocarbons are separated by distillation. Monomer are recycled to the reaction area, while propane is removed from the system. Stream characterization is reported in Tab. 28. Tab. 29 illustrates the thermal duty of each area.

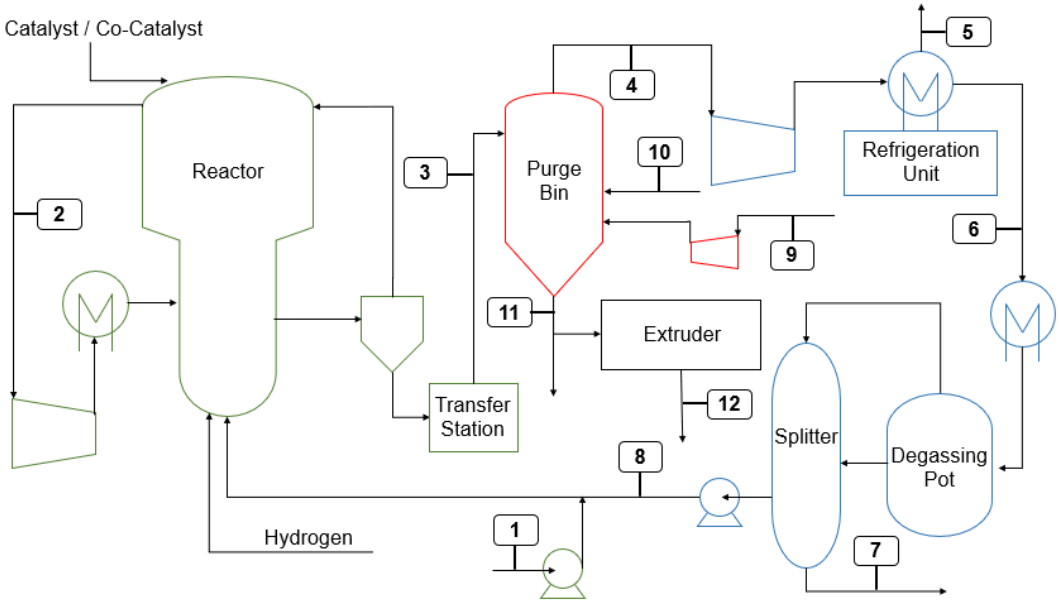


Figure 16: Technology 1 (T1) reference scheme for HOMO production

Table 28: Technology 1 stream characterization

	1	2	3	4	5	6	7	8	9	10	11	12
Propylene [kg/h]	50844	1037996	2241	2241	355	1886	489	1397				
Propane [kg/h]	256	278865	821	821	113	708	143	565				
Polypropylene [kg/h]			50000								50000	50000
Water [kg/h]										1250	1250	
Nitrogen [kg/h]		232387	63	2163	2100	63		63	2100			
Total Mass Flow [kg/h]	51100	1549247	53125	5225	2568	2657	632	2025	2100	1250	51250	50000
T [°C]	40	70	70	85	-30	-30	50	35	25	150	85	25
p [bar]	27	29,5	7,5	1,5	20	20	20	30	1,1	4,5	1,5	1

Table 29: Technology 1 Thermal duty per area

Technology 1		
Area	Duty [kW]	Thermal vectors
Reaction	26504	Removed (Cooling Water)
Monomer Recovery	3964	Removed (Cooling Water)
	1811,3	Provided (Hot Water)
Polymer finishing	0	
Extrusion	10181	Removed (Cooling Water)

Technology 2

Technology 2 performs the reaction in a horizontal gas stirred-bed reactor. Mechanical agitation guarantees the homogenization of the system. Polymerization heat is quenched with liquid monomer produced by an external partial condensation. The first reactor output is directly fed to a high-pressure separator where monomer is partially separated by polymer (as shown in Fig. 17). Gas stream is recycled back to the reaction area, while polymer is deactivated and dried in the polymer finishing section before extrusion. This process lacks a low-pressure monomer recovery system and, as a consequence, high amount of monomer is lost in the two process purges. Stream and Thermal duty characterizations are reported respectively in Tab. 30 and Tab. 31.

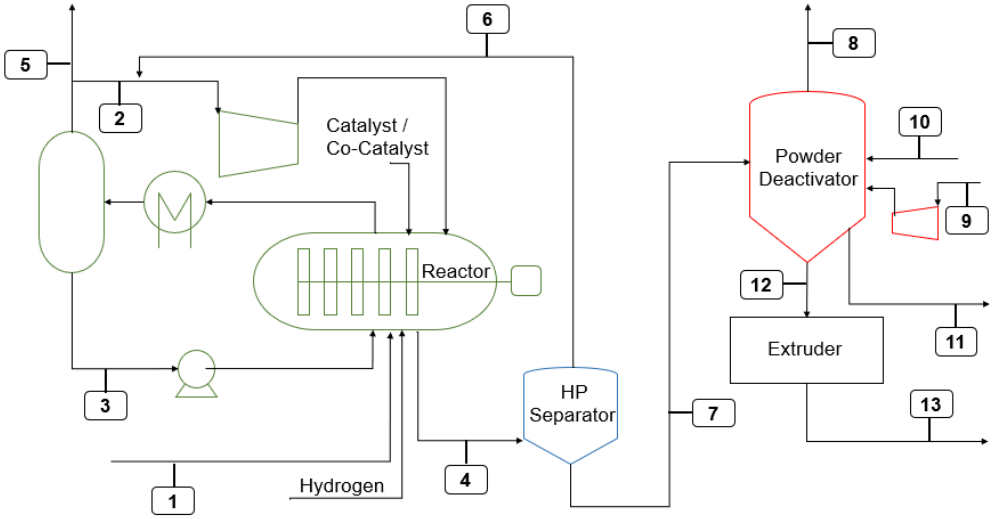


Figure 17: Technology 2 (T2) reference scheme for HOMO production

Table 30: Technology 2 stream characterization

	1	2	3	4	5	6	7	8	9	10	11	12	13
Propylene [kg/h]	51487	243547	240330	7324	447	6284	1040	1040					
Propane [kg/h]	259	41009	44801	1293	75	1109	184	184					
Polypropylene [kg/h]				50000			50000					50000	50000
Water [kg/h]								0		1250	1250		
Nitrogen [kg/h]								360	360				
Total Mass Flow [kg/h]	51746	238853	285131	58617	522	7393	51224	1584	360	1250	1250	50000	50000
T [°C]	40	46,7	46,7	70	46,7	70	70	82	25	150	82	82	25
p [bar]	27	19	19	22	19	19	19	1,5	1,1	4,5	1,5	1,5	1

Table 31: Technology 2 Thermal duty per area

Technology 2		
Area	Duty [kW]	Thermal vectors
Reaction	27463	Removed (Cooling Water)
Monomer Recovery	0	
Polymer finishing	0	
Extrusion	10181	Removed (Cooling Water)

Technology 3

Technology 3 features a vertical stirred reactor to perform the polymerization. The reaction medium homogenization is guaranteed by a mechanical agitator. External circuit is required to remove the reaction heat via gas condensation and its sequential vaporization inside the reactor. Polymer-gas outlet stream is fed to the monomer recovery area (as shown in Fig. 18). A preliminary separator allows to recovery the most quantity of monomer. The final phase of monomer recovery is performed by a membrane unit followed by a deethanizer. Propylene is separated by propane and nitrogen and pumped back to the reaction area. Polymer finishing is carried out in a single equipment as in Technology 1 and 2. Final extrusion is required. Stream and Thermal duty characterizations are reported respectively in Tab. 32 and Tab. 33.

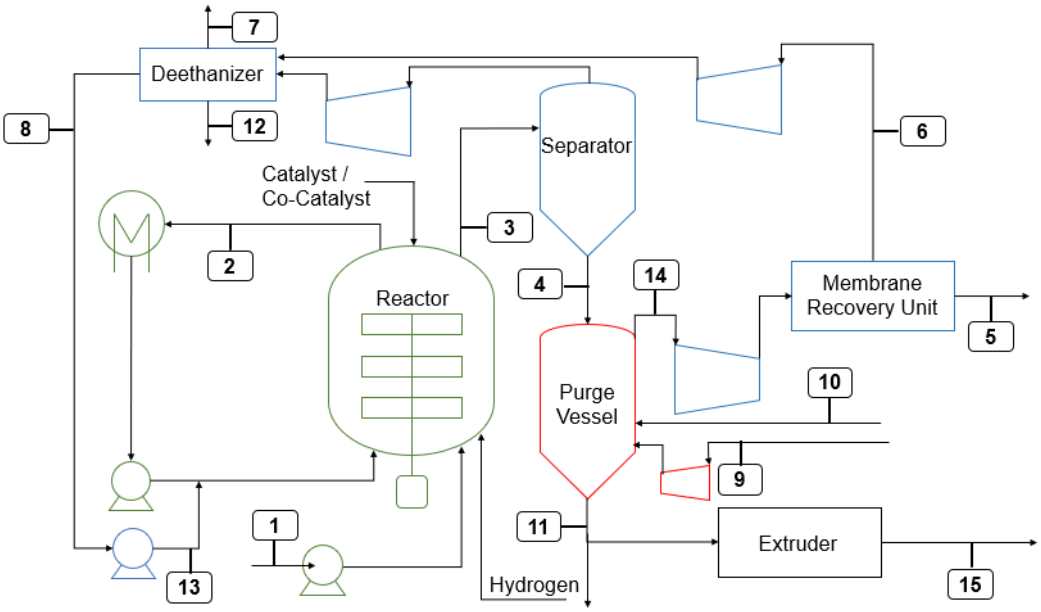


Figure 18: Technology 3 (T3) reference scheme for HOMO production

Table 32: Technology 3 stream characterization

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Propylene [kg/h]	50844	339579	9869	1401	70	1331	774	9025					9025	1401	
Propane [kg/h]	256	56201	1632	232	12	220		1376				244	1376	232	
Polypropylene [kg/h]			50000	50000							50000				50000
Water [kg/h]										1250	1250				
Nitrogen [kg/h]					304	16	16		320					320	
Total Mass Flow [kg/h]	51100	395779	61501	51633	386	1567	790	10401	320	1250	51250	244	10401	1953	50000
T [°C]	40	75	75	75	50	50	48	49	25	150	87	56	50,4	87	25
p [bar]	27	27	28	19	19	1,5	20	20	1,1	4,5	1,5	20	28	1,5	1

Table 33: Technology 3 Thermal duty per area

Technology 3		
Area	Duty [kW]	Thermal vectors
Reaction	27272	Removed (Cooling Water)
Monomer Recovery	1388	Removed (Cooling Water)
	857	Provided (Hot Water)
Polymer finishing	0	
Extrusion	10181	Removed (Cooling Water)

Technology 4

Technology 4 exploits a bulk phase loop reactor for the polymerization. Fresh monomer is mixed with recycled reactants. An axial pump homogenized the reaction medium. Heat removal is guaranteed by utility jacket water. Reactor output stream is fed to the monomer recovery area (as reported in Fig. 19). Liquid monomer is preliminary separated from the polymer granules by a flash in a heat exchanger and then by two sequential degassers. Recycled monomer is condensed and pumped to the reaction area. Polymer is deactivated and dried is two separated units. As a consequence, the output gas stream from the steamer does not contain nitrogen and can be easily recovered in external auxiliary process (e.g Boiler, Cracker). Stream and Thermal duty characterizations are reported respectively in Tab. 34 and Tab. 35.

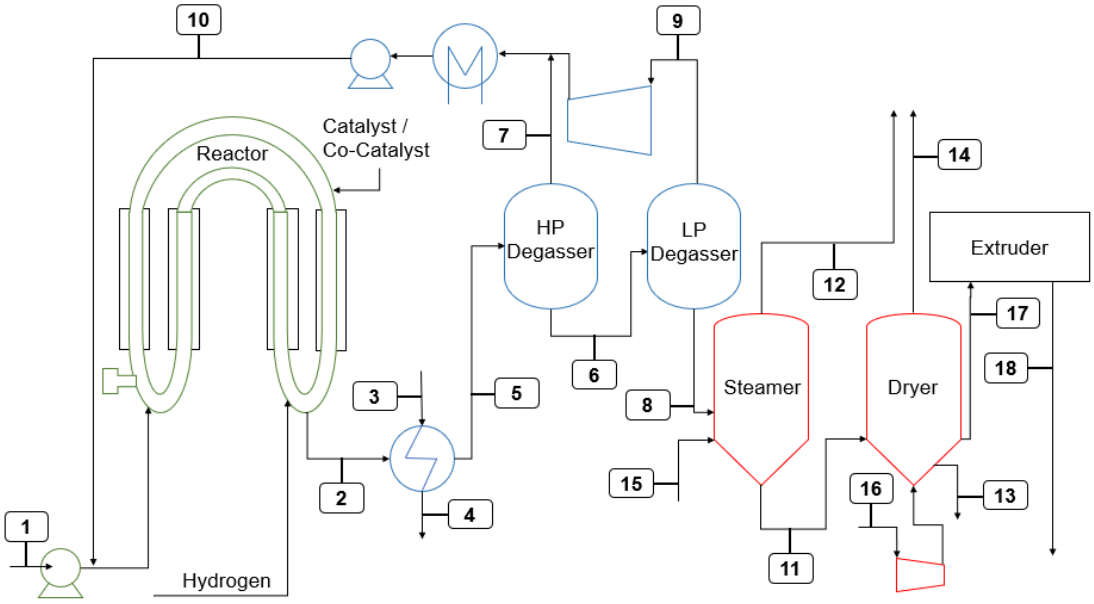


Figure 19: Technology 4 (T4) reference scheme for HOMO production

Table 34: Technology 4 stream characterization

	1	2	3	4	5	6	7	8
Propylene [kg/h]	50844	34691			34691	3955	30736	844
Propane [kg/h]	256	6218			6218	709	5509	256
Polypropylene [kg/h]		50000			50000	50000		50000
Water [kg/h]			6155	6155				
Nitrogen [kg/h]								
Total Mass Flow [kg/h]	51100	90909	6155	6155	90909	54664	36245	51100
T [°C]	40	75	150	150	90	85	90	82
p [bar]	27	43	4,5	4,5	19	1,5	19	1,5

	9	10	11	13	12	14	15	16	17	18
Propylene [kg/h]	3111	33847			844					
Propane [kg/h]	453	5962			256					
Polypropylene [kg/h]			50000						50000	50000
Water [kg/h]			1250	1250			1250			
Nitrogen [kg/h]						750		750		
Total Mass Flow [kg/h]	3564	39809	51250	1250	1100	750	1250	750	50000	50000
T [°C]	82	50	90	55	90	87	150	25	87	25
p [bar]	1,5	43	1,5	1,5	1,5	1,5	4,5	1,1	1,5	1

Table 35: Technology 4 Thermal duty per area

Technology 4		
Area	Duty [kW]	Thermal vectors
Reaction	25547	Removed (Cooling Water)
Monomer Recovery	1185	Removed (Cooling Water)
Polymer finishing	0	
Extrusion	10181	Removed (Cooling Water)

Technology 5

Technology 5 is characterized by a unique gas-phase reactor design. Polymer particles continuously circulate between two interconnected zones, each with distinct thermodynamic conditions and fluid dynamic regime. A fluid barrier system maintains the two reaction zones allowing the production of unique polymer. Reaction external mass flow rate is required to remove polymerization heat and feed the barrier section. The polymer-gas output is fed to a gas-phase reactor for HECO production or directly separated by two sequential degassers (as reported in Fig. 20). Monomer is compressed and recycled back to the reaction area, while polymer is deactivated and dried before extrusion. This process, as Technology 4, performs the polymer finishing section in two sequential operations. This strategy facilitates the purge recovery. Stream and Thermal duty characterizations are reported respectively in Tab. 36 and Tab. 37.

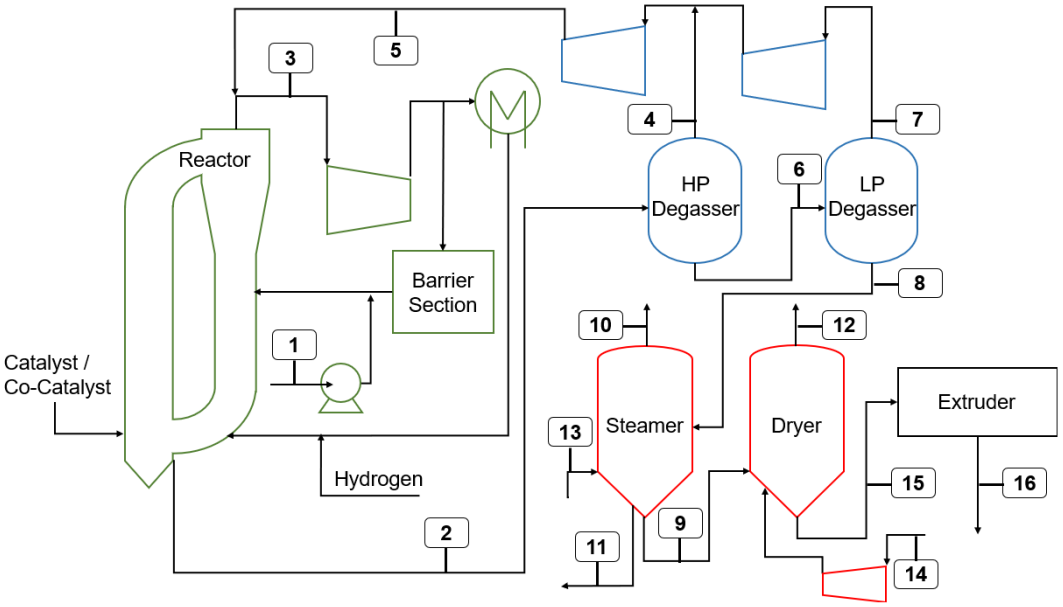


Figure 20: Technology 5 (T5) reference scheme for HOMO production

Table 36: Technology 5 stream characterization

	1	2	3	4	5	6	7	8	9
Propylene [kg/h]	50844	17084	2114016	14026	16240	3058	2214	844	
Propane [kg/h]	256	2825	256182	2319	2569	506	250	256	
Polypropylene [kg/h]		50000				50000		50000	50000
Water [kg/h]									
Nitrogen [kg/h]									
Total Mass Flow [kg/h]	51100	69909	2370198	16345	18809	53564	2464	51100	50000
T [°C]	40	85	75	85	80	85	85	85	85
p [bar]	27	30	29	19	31,5	19	1,5	1,5	1,5

	9	10	11	12	13	14	15	16
Propylene [kg/h]		844						
Propane [kg/h]		256						
Polypropylene [kg/h]	50000						50000	50000
Water [kg/h]			1250		1250			
Nitrogen [kg/h]				750		750		
Total Mass Flow [kg/h]	50000	1100	1250	750	1250	750	50000	50000
T [°C]	85	90	85	90	150	25	90	25
p [bar]	1,5	1,5	1,5	1,5	4,5	1,1	1,5	1,5

Table 37: Technology 5 Thermal duty per area

Technology 5		
Area	Duty [kW]	Thermal vectors
Reaction	27455	Removed (Cooling Water)
Monomer Recovery	694	Removed (Cooling Water)
Polymer finishing	0	
Extrusion	10181	Removed (Cooling Water)

Benchmark ideal process

An ideal case for polypropylene production was introduced to serve as a benchmark for other technologies. This is an ideal case, characterized by extreme hypothesis aimed to represent the best desirable case in terms of GHG emission reduction given the current technologies on feedstock and operative conditions of the reactor. It thus provides the minimum value of GWI, that is impossible to further lower with the current conditions for supply of raw materials and energy. The ideal case was built considering the following hypothesis:

- Reaction occurred in 1 reactor (this was modelled on the basis of Technology 3 and 4 assuming average data for reaction conditions from Tab.3 P=27 bar, T=75°C)
- Overall reaction yield per pass is assumed equal to 100% and raw material feed is stoichiometric. No monomer recovery section is therefore required.
- Raw material feed is 100% propylene. No Off-gas or purge streams are required.
- No agitation of the reactor is required. The powder finishing section is performed with the minimum required amount of steam and nitrogen.
- Monomer is fed at the battery limit temperature and reach the reaction temperature due to the reaction heat. Steam is not required for the polymerization section.

The reference scheme for the ideal process is presented in Figure 21. Tab. 38 reports the stream characterization with reference to a production capacity of 400 kt/y of HOMO polymer.

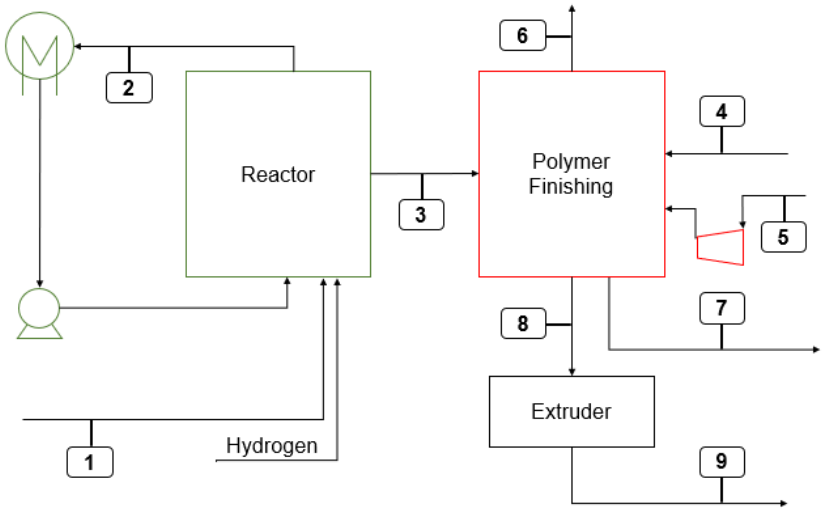


Figure 21: Ideal process reference scheme for HOMO production

Table 38: ideal process stream characterization

	1	2	3	4	5	6	7	8	9
Propylene [kg/h]	50000	339579							
Propane [kg/h]	251	56201	251			251			
Polypropylene [kg/h]			50000					50000	50000
Water [kg/h]				1250			1250		
Nitrogen [kg/h]					320	320			
Total Mass Flow [kg/h]	50251	395779	50251	1250	320	571	1250	50000	50000
T [°C]	40	75	75	150	25	87	87	87	25
p [bar]	27	27	27	4,5	1,1	1,5	1,5	1,5	1,5

Indicator results

The indicators defined in Tab. 6 were calculated for a set of 5 technologies, deemed representative of the broader set of technological options presented above. The description of the technologies and the results of the material and energy balances that were reconstructed on the basis of available information are presented in the follow. A summary of the main features is reported in Tab. 39.

Table 39: Summary of the main features of the 5 technologies used in indicator evaluation.

Technology ID	Reaction type	Operative conditions reactor	Monomer recovery	Polymer finishing	Similar commercial processes
Tech. 1	Gas	T=70°C, P=30 bar	Compression (P=20 bar), Condensation to liquid (T=-30°C) and Distillation	Purge Bin	Unipol
Tech. 2	Gas	T=70°C, P=22 bar	High pressure separation (P=19 bar)	Powder Deactivator	Innovene
Tech. 3	Gas	T=75°C, P=28 bar	Separation (P=19 bar), Compression, Membrane Unit and Distillation	Purge Vessel	Novolen
Tech. 4	Bulk	T=75°C, P=43 bar	Monomer thermal flash (P=19 bar, T=90°C) High pressure separation (P=19 bar), Low pressure separation (P=1,5 bar) Compression and Condensation	Steamer and Dryer	Spheripol
Tech. 5	Gas	T=85°C, P=30 bar	High pressure separation (P=19 bar), Low pressure separation (P=1,5 bar) and Compression	Steamer and Dryer	Spherizone
Ideal Process	Gas	T=75°C, P=27 bar	Not included	Single equipment (Deactivation/Drying)	-

The results of the two considered sustainability indicators are reported in Tab. 40 with reference to the production of 1 kg of polymer for GWI and 1 kgPP/s for Ex, d. GWI is selected as reference KPI for the environmental impact comparison.

Table 40: Indicators results to produce HOMO and HECO polymers of the analysed technologies

		GWI [$kgCO_2/kgPP$]	Ex,d per Area [kJ / kgPP] - Homo production				
Technology ID	Ref. Tech.	HOMO	Reaction	Monomer Recovery	Polymer Finishing	Extrusion	Total
Tech. 1	Unipol	1.489	197	67	18	624	906
Tech. 2	Innovene	1.504	248	2	17	624	890
Tech. 3	Novolen	1.482	186	23	17	624	850
Tech. 4	Spheripol	1.502	177	110	16	624	926
Tech. 5	Spherizone	1.503	376	34	14	624	1048
Ideal Process		1.451	138	0	14	624	776

The GWI presents a narrow range of variability among the considered options, which implies that the choice of the polymerization technology only moderately affects the GHG emissions of the whole polymer production chain. As a matter of facts, the polymerization process is a minor direct source of greenhouse gasses as these are limited principally to fugitive emissions. It shall be noted that all the considered process schemes produce a hydrocarbon rich off-gas stream that, if flared, would produce CO_2 emissions (0.11 $kgCO_2/kgPP$ for technology 2, 0.07 $kgCO_2/kgPP$ for all the other technologies) contributing up to +4.5% (+6.8% in technology 2) to overall GWI. However, this stream is usually a by-product valorised in other processes (e.g. fuel use, feedstock to cracker), so no GHG emission associated to its combustion is accounted in the current study (i.e. potential emissions are allocated to the by-product use that is out of the system boundaries of current analysis[25]).

Tab. 41 reports the percentage contribution of units inside the boundary for the computation of the GWI for the HOMO PP production of each analysed technology. The main contribution to the indicator is given by the production of the monomer, as it relies on a cracking process that is currently very intensive in terms of fossil energy requirements. This behaviour confirms that the monomer production unit (e.g Steam Cracker) is the principal responsible of the CO_2 emission in the polymer lifecycle chain. This result is supported by literature assessment [58] and let to the exploration of less impacting technologies (e.g Propane Dehydrogenation) [92].

On the other hand, energy consumption of the process itself defines GHG emissions that are strongly bond to the choice of technology used in providing that energy. Nevertheless, with the emission factors considered in current analysis, GHG emissions from energy requirement counts for less than 10% of the total.

Table 41: Percentage contribution of each unit for the computational of the GWI of the analysed technology

	% Monomer	% Electricity	% Steam
Technology 1	94,3%	5,4%	0,3%
Technology 2	94,6%	5,2%	0,3%
Technology 3	94,7%	5,0%	0,3%
Technology 4	93,5%	4,9%	1,6%
Technology 5	93,4%	6,3%	0,3%
Ideal Process	95,2%	4,5%	0,3%

In the current analysis, the steam consumption for polymer deactivation and, in bulk processes (e.g., Spheripol), the steam required to vaporize the unreacted monomer. Even if other minor uses of stream can be present in actual plants (e.g., reaction start-up, utilities area), they are not expected to significantly change the profile reported in Tab. 40. The same can be said for other minor users of electricity in actual plants (e.g., polymer handling and final homogenization systems, prepolymerization unit).

An "ideal process" for polypropylene production was introduced to serve as a benchmark for other technologies. This is an ideal case, characterized by extreme hypothesis aimed to represent the best desirable case in terms of GHG emission reduction. The ideal process thus provides the minimum value of GWI, that is impossible to further lower with the current conditions for supply of raw materials and energy.

GWI results for considered processes are inevitably greater than benchmark ideal process. The results, however, suggest that all technologies are already quite close to a high level of efficiency in limiting direct GHG emissions. Significant reduction of GWI can therefore be obtained only by reduction of direct emissions from monomer production or by use of less carbon intensive sources of electrical power.

Analysed technologies consumed globally an amount of monomer relatively close to the stoichiometric considered in the ideal process, therefore the variation between GWI of each process and the benchmark minimum GWI quantifies mainly the reduction of electric power and steam consumptions.

The exergy indicator is affected by the combination of process and thermodynamic aspects. The minimization of process pressure and temperature is a key factor for the reduction of the exergy destruction. However, this effect is better appreciated at equipment level by the application of exergy balance to the single process sections. Results obtained by the application of exergy balances presented in section 2 to the five reference schemes are reported in Tab. 40. The same table reports the contribution to exergy destruction of individual process section.

Regarding the reaction area, the single bulk process (Technology 4) demonstrates the lower exergy destruction. This is obtained due to a good arrangement of the utility water service system (avoiding excessive temperature differences among reactor and coolant) and a moderate low temperature for the monomer recycled stream (50°C).

Technology 1 and Technology 3 introduces other interesting design choices that lead to a low exergy destruction. Technology 3 minimizes the electricity consumption of the heat removal system through the total condensation of the external recycled stream. This design choice allows to introduce a pump rather than a compressor to guarantee the external stream circulation reducing the electrical consumption. On the other hand, Technology 1 performs the polymerization without the introduction of a mechanical agitator, reducing the overall electrical consumption of the reaction area.

Technology 5 is responsible of a high amount of energy destruction in the reaction area. This result is related to a significantly higher electrical consumption at the fluidization compressor. This equipment guarantees the circulation for bed fluidization and heat removal as in other alternatives, but also feeds the barrier section which represents a unique section of this technology. The flexibility in product formulation (e.g., product with broad molecular weight) that Technology 5 process can provide in comparison with other processes, is therefore guaranteed at the expense of major electrical consumption. In this context, further considerations can be included based on products portfolio.

It can be concluded that key winning factors in reducing exergy destruction in reaction section are the adoption of a low temperature for the reaction and a heat removal strategy, in gas phase technologies, that exploits the total condensation of the circulating stream. In addition, processes requiring agitators are disadvantaged form the exergy point of view, as they result in net exergy dissipation.

These considerations apply for process that make no use of the thermal energy removed from the reactor.

The exergy indicator for the reaction section of the ideal process, evidence that, as long as reaction heat is dissipated to the environment, exergy destruction cannot be lower than 138 kJ/kgPP. When the possibility of reaction heat recovery is considered, that shall occur at the highest possible temperature to minimize loss of energy quality. Potentially the polymerization heat of reaction can be recovered and generate a thermal vector (e.g utility water), but low reaction temperature forces to obtain a thermal vector with a temperature not greater than 65°C which finds little applications inside a polymerization plant. In an integrated plant scenario, this thermal vector can support the operability of a secondary processes or civil uses, guaranteeing optimal exergy destruction profiles.

Regarding the Monomer recovery section, the gas phase processes present a high range of variability even if this section is conceptually very similar among considered technological options: in all cases it consists of depressurization of the polymer-monomer mixture, separation, and recycle of the recovered monomer at the reaction pressure. However operative conditions (temperature, pressure, flowrate) change among technologies, affecting exergy destruction. In general, processes that operate at lower pressure in the reactor (22 bar, 28 bar), require less electrical power for the compression of the monomer recycle, which leads to lower exergy destruction (e.g., Technologies 2 and 3). More in detail, Technology 2 performs a moderate pressure monomer recovery operation (19 bar); as a consequence, Technology 2 is responsible of a higher monomer loss which affects negatively GWI.

Technology 3 introduces a membrane unit to support the monomer recovery. This strategy, combined with a distillation operation, allows to separate nitrogen from monomer and recover only reactant to the reaction, differently from Technology 1. Therefore, considering equal monomer partial pressure inside the reactor, Technology 3 can operate at lower reaction pressure respect to Technology 1, minimizing the electrical consumption of the monomer recovery unit and the feed pump. This effect is directly related to a minimization of the exergy destruction, which can be otherwise 0,31% higher for Technology 3 Monomer Recovery and Reaction areas if it operates at Technology 1 reaction pressure.

Altogether, electrical consumption for the compressors required in Technology 3 for membrane operations appears to be lower than the one for the refrigeration unit used for monomer condensation in Technology 1. Hence, membrane separation appears to be a valid strategy for monomer recovery, able to minimize the exergy destruction for technologies that perform the polymer finishing in a single equipment.

The splitter (distillation column) required in Technology 1 for the monomer recovery process, also introduces the possibility for greater versatility in the supply of raw monomer (i.e., feed monomer at lower grades can be accepted). Moreover, due to the low dew point temperature of the mix propylene-propane, the thermal energy at the reboiler of the splitter could be easily provided by internal heat recovery, avoiding the consumption of a dedicated steam. In this framework, the introduction of a splitter provides a good management avoiding an increase of CO_2 emitted and exergy destruction

An appreciably higher level of exergy destruction is identified in this section for Technology 4. It is due to the energy demand for vaporization of the unreacted monomer: almost 60% of the exergy destruction of the Technology 4 monomer recovery is allocated to the steam powered heater. However, the use of a thermal vector with a temperature closer to the one of the process streams (90°C) can be identified as an option to reduce this term: clearly enough this improvement shall be considered against implications on other factors, as fixed costs (e.g., heat exchange areas).

As discussed earlier, the polymer finishing section could be performed in a single or in two sequential equipment units. Technologies 4 and 5 obtained better results in terms of exergy destruction thanks to the introduction of two sequential equipment. Process configurations proposed by these technologies allows to obtain hydrocarbon purges at higher temperature, reducing the overall exergy destruction of the polymer finishing section. In addition, hydrocarbons and nitrogen are purged in separated streams which simplifies the downstream treatment. It shall be stressed that, even in the case of ideal process, some exergy destruction is expected in this section, as a result of heat balance.

The extrusion area is by far the main source of exergy destruction in a polymerization plant. About 98% of the exergy destruction of this area is related to the extruder electrical consumption, while the remaining 2% is originated to polymer cooling to environmental conditions. Extruders basically convert electricity into heat, melting the polymeric material and providing the homogenization and its final product shape. However, from the exergy standpoint, the huge amount of electricity required is lost, as no increase of the energy quality of the final product is provided by the operation (e.g., the final output of the extrusion area is a polymeric pellet at environmental conditions which has, by definition, zero amount of exergy). As this section is the same for all the schemes considered, no appreciable differences are obtained in technology comparison.

When the overall exergy destruction indicator calculated is calculated (i.e., sum of the contributions of all the sections of the process for each technology) the differences between technologies become less apparent because of the large contribution of the extrusion section, which is the same for all of them (including the ideal reference). Technology 3 results in the lower overall exergy destruction indicator. This is only 9.5% higher than the ideal process result, confirming that electrical consumption of the extruder and the dissipation of heat from polymerization reaction are key exergy destruction sources. Given their nature inherent to process operations, they are somehow inevitable and are not affected by choices of auxiliary processes for the supply of raw materials and energy (e.g., use of renewable resources).

Role of the context

In this section the role of the energy sources on the performance of the Global Warming Indicator is demonstrated, allowing to explore the sensitivity of the environmental performance of the technology to the context of application. In particular, GWI was calculated under different assumptions as regard the GHG emission factors for electricity and steam production. Five scenarios were simulated, accounting for situations typical of different geographical areas and penetration of renewable energy sources. The same technology for monomer production (Steam Cracker) was instead maintained in all the options, as the GHG emissions from this process are less likely to be affected by the plant context [59].

The scenarios considered are:

1) Electricity from Italian Grid mix / Steam from Natural Gas (Italy)
2) Electricity from United States Grid mix / Steam from Natural Gas (US)
3) Electricity from Italian Grid mix / Steam from Heavy Fuel Oil (Italy)
4) 25% of Electricity from Photovoltaic, 75% from Italian Grid mix / Steam from Natural Gas (Italy)
5) Electricity 100% from Photovoltaic / Steam from Natural Gas (Italy)

Emission factors for the considered scenarios were defined according to the data reported in Tab. 8. Tab. 42 shows the GWI results with reference to the five analysed technologies and the ideal process.

Table 42: GWI calculated for the five analysed Technologies HOMO production and ideal process for the five presented scenarios

GWI – [kg CO_2/kgPP]						
Scenario	Technology 1	Technology 2	Technology 3	Technology 4	Technology 5	Ideal Process
1)	1.489	1.504	1.482	1.502	1.503	1.451
2)	1.518	1.531	1.508	1.529	1.536	1.474
3)	1.490	1.505	1.484	1.509	1.504	1.452
4)	1.472	1.487	1.466	1.486	1.482	1.436
5)	1.419	1.436	1.418	1.438	1.420	1.393

The comparison of scenario 1 and 2, clearly shows as the geographical location considered for the technology affects the results. In facts, GWI increases of about 2% due to the use of a US electricity grid mix for electricity. By converse, the use of larger shares of renewable electricity production (scenario 4 and 5) will reduce the GWI of at least 4.2% if compared to scenario 1.

The variations of GWI due to different scenarios for energy production reported in Tab. 42 exceed the ones identified in Tab. 40 for differences among the technologies. For example, comparing Technology 4 in scenario 4 and Technology 5 in scenario 1, there is and evident inversion of the GWI ranking of technologies if compared with the one presented in Tab. 40. This result demonstrates that, though it is the technology that defines the requirements for energy and utilities of the process, the design of the auxiliary processes and the supply of utilities of a site plays a key role in the actual GHG emissions.

Considering scenarios 1, 3 and 5 the environmental benefits are 1 order of magnitude greater in case of use of renewable resources for electricity production rather than the use of greener fuels in steam generation. This can be linked to the relatively low use of thermal energy (steam) if compared with electrical energy in the considered polymerization technologies. This result establishes a hierarchy of impact reduction for auxiliary units in polymerization plants.

This finding shall support design decisions for process improvements inside the entire polymer production chain. For example, as Technology 4 uses higher quantity of steam and lower electric power in comparison to Technology 5, moving from scenario 3 to 1, the effect of a more sustainable steam source is more remarkable for Technology 4 rather than Technology 5 one (respectively +0,47 % and +0,08%). Indeed, moving from scenario 1 to 5, the adoption of a renewable resource for electricity generation has more impact to Technology 5 rather than Technology 4 (respectively -4,27% and -5,51%).

Design choices and optimal configurations to define the best GHG reduction strategies for polymerization technologies are therefore site specific, and it is necessary to contextualize the polymer production plant.

As shown in Fig. 13 the technology for monomer production deeply affects GHG emission performance. However, from the point of view of the designer of the polymerization plant, the supply of raw materials is typically characterized by lower degrees of freedom in comparison with the supply of energy (e.g., self-production, cogeneration, use of waste energy stream), making the latter aspect a “tool of choice” toward GHG emission reductions in design activities.

Role of process improvement

The analysis of polypropylene processes, evidence relatively similar performances in terms of efficiency for all the technologies analysed. Moreover, if compared to the ideal process the margin for further improvement, though possible, is relatively limited, in particular for GWI.

The high level of performance achieved by current polymerization technologies can be tracked back to the constant effort toward process optimization all along the industrial application history of polypropylene technologies. In the last 30 years, polymerization technologies have studied and introduced new process configurations to reduce consumptions and waste [59]. In this case, the adoption of more performing systems in terms of yields and costs is directly connected to environmental benefits.

Fig. 22 shows the results from the calculation of GWI over time for a selected technology (Spheripol), based on the average material and energy demand of operative plants recorded over the last twenty years. The emission factors used in calculation of GWI were kept constant to the values considered in Annex 1: this assumption allowed appreciate the effect of improvements in the polymerization process, disregarding the evolution of the auxiliary processes (e.g., electric power generation).

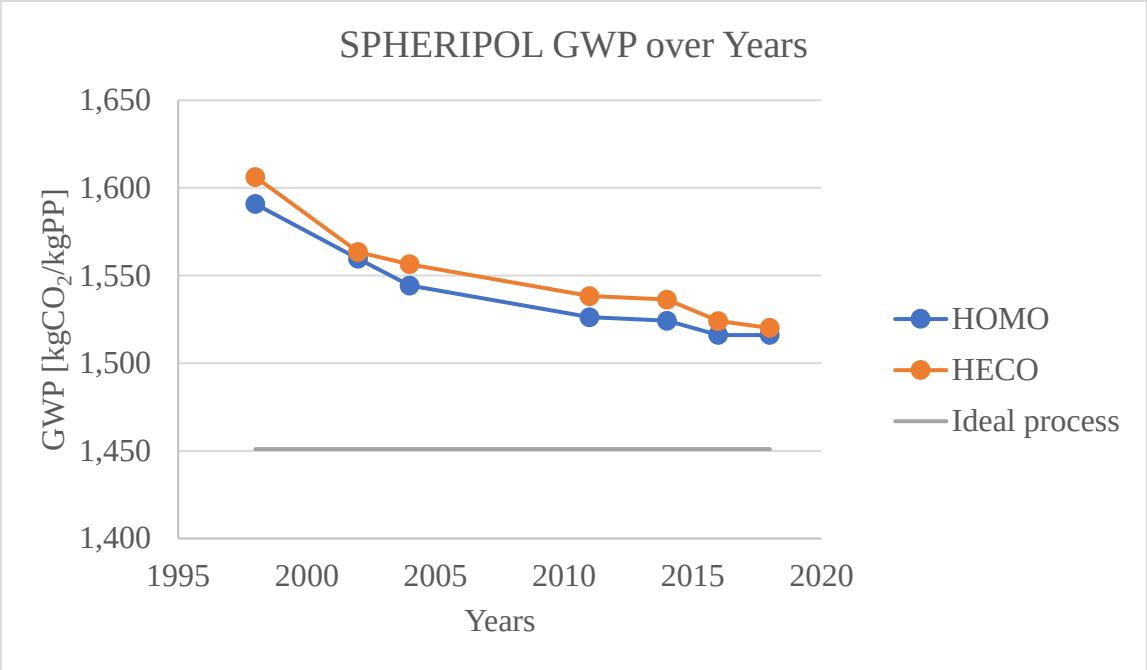


Figure 22: Evolution of the GWI applied to Spheripol technology over the time (1998-2018).

It can be observed a clear reduction over time, both for HOMO and HECO products, with a progressive approach to the performance of an ideal process. Fig. 22 shows that improvements made in the first decade, have a more significant impacts in the global scenario of the polymer production chain. The two presented curves are characterized by high slope in this time period, which means that the reduction of polymerization consumptions have significant impacts in the polymer chain. Instead, in the last ten years the two curves' slopes are less steep: polymerization consumptions are getting progressively closer to the ideal minimum, which means lower margins of improvement are possible and at a higher cost.

Different causes of can be identified for the GWI reduction trend. First, a decrease of the process energy demand stemming from scale up effect in production plant. It is well known that increase in plant capacity allows to reduce specific consumption [93]. From 1998 to 2018, Spheripol plants were designed with capacities that went from 100 ktPP/y to 600 ktPP/y

Another significant improvement was the increase of reaction yield by the use of higher reaction temperatures and pressures. This design choice allows also to reduce the capital cost of heat exchangers dedicated to the removal of the reaction heat. Considering equal capacity, the use of higher reaction temperatures allows to increase the heat removal driving force and, as a consequence, the required area of the heat exchangers.

In 2000 the introduction of phthalates and ethers as co-catalyst allowed to increase the overall reaction yield. Furthermore, approximately every 10 years, a new catalyst and co-catalyst generation was developed allowing for better process configurations (reduction of consumptions, increase of product portfolio).

Between 2005 and 2010 a high-pressure degasser was introduced in the monomer recovery section (as shown in Fig. 21). The introduction of this equipment allowed to reduce the consumption of the recycle compressor as a relevant portion of the gas to be recycled is available at higher pressure.

The maturity of polypropylene technologies is also accompanied by an increase in plant reliability. Enhancing reliability allows to reduce the number of shutdowns over the years. Shutdowns are

responsible of generation of off specification products and energy demand in non-productive operations, which negatively affect yearly GHG emission of operative plants.

Final remarks and results overview

The main commercial processes for polypropylene production were reviewed and compared form the point of view of environmental sustainability. Two indicators were applied to a set of 5 reference technology schemes in order to characterize each process by its carbon footprint and energy use efficiency. In all cases the principal impacts of the polypropylene production chain are related to the emissions form raw material supply and auxiliary processes (cracker, electric power and steam production). However, design choices in the polymerization process emerged to influence the demand for auxiliary processes consumptions and, consequently, the impacts. An ideal process was defined as benchmark for the existing technologies, pointing out the potential for improvements and the inherent limits of the current polymerization process.

In this context, different design choices of polymerization technologies are analysed performing a comparative assessment based on sustainability aspects. Reference Technology 2 (based on Innovene process) proposes only a partial polymer-monomer separation, which implies higher monomer consumption. This technology is characterized by the highest GWI result, as monomer production technology (e.g Steam Cracker) is the principal responsible of CO_2 emissions. In this perspective, the minimization of required monomer is a key aspect for polymer lifecycle. Furthermore, the prevention of excessive reaction pressure can reduce the electric power consumption of monomer recovery unit. This consideration is fundamental is case of non-renewable technologies for electricity supply.

The exergy indicator identified that Technology 3 (based on Novolen process) as an optimal configuration for polymerization operations, as the choice of the simplicity for the reaction area reduces global electrical consumptions and improve the monomer-polymer separation. However, also other technologies propose efficient strategies: for example, Technology 4 (based on Spheripol) reduces the exergy destruction for the reaction area due to the reduced energy demand for circulation in bulk phase reactor and the good management of temperature profiles.

The monomer recycle section consumes large amounts of steam, leading to high exergy destruction and GHG emissions; hence new strategies for monomer-polymer separation are required.

Membrane unit and distillation operation can enhance the monomer separation and recycling sections. Low electrical consumption and potential heat recovery can improve the lifecycle perspective compared to conventional strategies.

The GHG emission from auxiliary process that supply electrical power and steam to the polymerization system is identified to present a variability potentially greater than the difference of GHG emissions among alternative polymerization technologies. Hence the design of the utilities present on site shall be carefully considered in defining overall production chain environmental performance. Moreover, as all the technologies considered have a relatively low use of thermal energy (steam) if compared with electrical energy, greening of electricity production is identified as a priority.

The comparison with a reference ideal process allowed to understand the margins for improvement available to the different technologies. These have been reduced significantly over the last twenty years of technology improvement. In facts, for the polypropylene production process we can

recognize a strong synergy between environmental and economic improvement, stemming from the fact that reduction of energy demand and improvement of yields is a key factor for both domains of sustainability.

The main directions of further future improvement of the sustainability of the process can be tracked in higher levels of recovery (e.g., energy recovery from reaction, use of membrane for off gas-separation), use of green auxiliary processes (e.g. electricity from renewable sources), and use of recycled feedstocks (e.g. monomer form de-polymerization or pyrolysis processes).

Annex 1 – Emission factors for GWI computation

Emission factors required for Eq (1) are defined by literature databases [94] and report [95]

Tab. 43 reports the emission factors adopted for the computation of the GWI indicator. The three pressure levels of steam (low pressure, medium pressure and high pressure) were assumed to have the same emission factors. The same table specifies which factors were used in baseline analysis (Scenario 1 of section 3) and analysis of the role of the context (Scenarios 1 to 5 discussed in Section 3).

Table 43: Emission factors for GWI computation

	Emission Factor	Unit	Used in scenario	Source
Propylene	1.374	$kgCO_2/kg$	1, 2, 3, 4, 5	PlasticsEurope [95]
Nitrogen	0.0590	$kgCO_2/MJ$	1, 2, 3, 4, 5	literature report [96]
Steam – Nat.Gas (IT)	0.0774	$kgCO_2/MJ$	1, 4, 5	Sphera, Thinkstep [79]
Steam – Nat.Gas (US)	0.0819	$kgCO_2/MJ$	2	Sphera, Thinkstep [79]
Steam – HFO (IT)	0.1000	$kgCO_2/MJ$	3	Sphera, Thinkstep [79]
Electricity – Grid mix (IT)	0.1064	$kgCO_2/MJ$	1, 3, 4	Sphera, Thinkstep [79]
Electricity – Grid mix (US)	0.1653	$kgCO_2/MJ$	2	Sphera, Thinkstep [79]
Electricity – Photovoltaic (IT)	0.0135	$kgCO_2/MJ$	4, 5	Sphera, Thinkstep [79]

Annex 2 - Assumptions for the calculation of Ex,d

The computation of the exergy destruction indicator is based on a thermodynamic concept [69] which requires some level of knowledge on the streams of each process. In this preliminary analysis, some assumptions are introduced to carry out exergy balances and define the exergy destruction term. Tab. 44 reports pressure, temperature and exergy content of polymerization input and output streams. Polymer exergy is assumed equal to zero due to its atmospheric temperature.

Table 44: Thermodynamic conditions of principal polymerization input and output

Substance	Aggregation State	Temperature [°C]	Pressure [MPag]	Specific Exergy content [kJ/kg]
Steam	Gas	150	P*(T)	720,7
Condensate	Liquid	150	P*(T)	81,7
Propylene	Liquid	40	2,6	138,9
Nitrogen	Gas	29	0,6	2552,4
Cooling Water IN	Liquid	36	0,45	1,30
Cooling Water OUT	Liquid	46	0,45	3,13

Case study 3: Comparison of polymerization processes based on reaction phases

Case-study description

The current section presents the application of the PDAM methodology to the principal average polymerization technologies for polypropylene and polyethylene production. This case-study offers the opportunity to demonstrate the versatility of the methodology and classify different technologies from environmental standpoints based on their reaction phases. Results obtained in this section generate a reach database for internal studies and allow to compare consolidated and operative technologies with new processes schemes and literature results.

Definition of the reference

This assessment characterizes the environmental footprint of several average technologies for polypropylene and polyethylene production based on their reaction phases. A plant size of 400 kt/y of polymer is assumed as reference for each technology.

Data collection is based on literature information. Average material and energy balances are utilized to perform the assessment. Tab. 45 report the adopted values. Specific Units process within the boundary of the assessment are Monomer productions, Electricity and Steam generation. Literature datasets [PlasticsEurope] are utilized for the characterization of Background processes. Literature available information are used to measure the carbon footprint of hydrocarbon monomers [58]. Environmental KPIs are calculated in accordance with Eq. (1). For lack of specific information, average net monomer consumption is adopted for each technology to carry out the analysis. This assumption allows to monitor the interaction between specific reaction phase and environmental footprint.

Table 45: Raw material and energy consumption of the reference technologies based on Reaction phases

Consumption of PP technologies			
Reaction Phase	Monomer [kg/h]	Electrical Feed [MWh]	Steam [kg/h]
Bulk	50500	17,7	18000
Gas Phase	50500	21,8	6840
Alternative Gas Phase (AGP)	50500	28	0
Consumption of PE technologies			
Reaction Phase	Monomer [kg/h]	Electrical Feed [MWh]	Steam [kg/h]
Gas Phase	50500	24	10500
Slurry	50500	27	19151
High Pressure	50500	41,2	-60000*

*Generation of Steam as polymerization by-product. In this context, its environmental impact is subtracted by the lifecycle footprint of the scheme.

Results

The set of KPIs presented in Tab. 6 is calculate for the reference technologies to monitor the environmental performances of different polymerization reaction solutions. KPI calculation step is presented in section 2 and reproposed in the current assessment. The following Tab. 46 reports the KPIs obtained for the current case-study.

Table 46: Environmental KPIs for the reference PP and PE production technologies

KPI	Unit of measurement	PP - Bulk	PP – Gas Phase	PP - AGP	PE – Gas Phase	PE - Slurry	PE – High Pressure
ADI,f	[MJ/kgPolymer]	9,83E-01	9,78E-01	9,90E-01	1,00E+00	9,99E-01	9,36E-01
ADI,e	[kgSb,eq/ kgPolymer]	4,71E-01	5,60E-01	6,90E-01	7,08E-01	6,86E-01	1,00E+00
RwEC	[MJ/kgPolymer]	4,88E-01	5,77E-01	7,27E-01	7,56E-01	7,31E-01	1,00E+00
WC	[kgWater/ kgPolymer]	8,10E-01	8,42E-01	8,89E-01	8,96E-01	8,87E-01	1,00E+00
CO_2	[kgCO_2/ kgPolymer]	9,49E-01	9,38E-01	9,73E-01	1,00E+00	9,97E-01	8,30E-01
GWI	[kgCO_2,eq/ kgPolymer]	9,48E-01	9,36E-01	9,72E-01	1,00E+00	9,97E-01	8,22E-01
ODI	[kgCFC-11/ kgPolymer]	9,98E-01	9,99E-01	9,99E-01	9,99E-01	9,99E-01	1,00E+00
AI	[kgSO_2-,eq/ kgPolymer]	9,51E-01	8,80E-01	9,27E-01	9,98E-01	1,00E+00	3,64E-01
POCI	[kgEthylene,eq/ kgPolymer]	9,75E-01	9,39E-01	9,63E-01	9,99E-01	1,00E+00	6,80E-01
EI	[kgPO_4---,eq /kgPolymer]	9,89E-01	9,77E-01	9,87E-01	1,00E+00	1,00E+00	8,94E-01
PM	[kgPM10,eq/ kgPolymer]	9,70E-01	9,00E-01	9,34E-01	9,97E-01	1,00E+00	4,12E-01
HTI	[kg 1,4-Dichlorobenzene eq / kgPolymer]	9,76E-01	9,80E-01	9,89E-01	9,91E-01	9,90E-01	1,00E+00
FETI	[kg 1,4-Dichlorobenzene eq / kgPolymer]	9,85E-01	9,88E-01	9,91E-01	9,92E-01	9,91E-01	1,00E+00
MAETI	[kg 1,4-Dichlorobenzene eq / kgPolymer]	9,61E-01	9,55E-01	9,82E-01	1,00E+00	9,98E-01	8,93E-01
TETI	[kg 1,4-Dichlorobenzene eq / kgPolymer]	9,45E-01	9,54E-01	9,68E-01	9,69E-01	9,67E-01	1,00E+00

KPIs are normalized with PP [58] and PE Eco-profiles [97] in order to identify strength and weaknesses of each reaction solution. Results are presented in Fig. 23 and Fig. 24. In general, environmental footprint of PP technologies are in accordance with average Eco-profile. Only slight variations are observed. The major environmental problem is related to the POCI. Globally the most performing technologies is the Gas Phase one. Instead, PE technologies results shows a wide variation from literature Eco-profile. Steam generation of High-pressure solutions demonstrate profitable results from environmental standpoint.

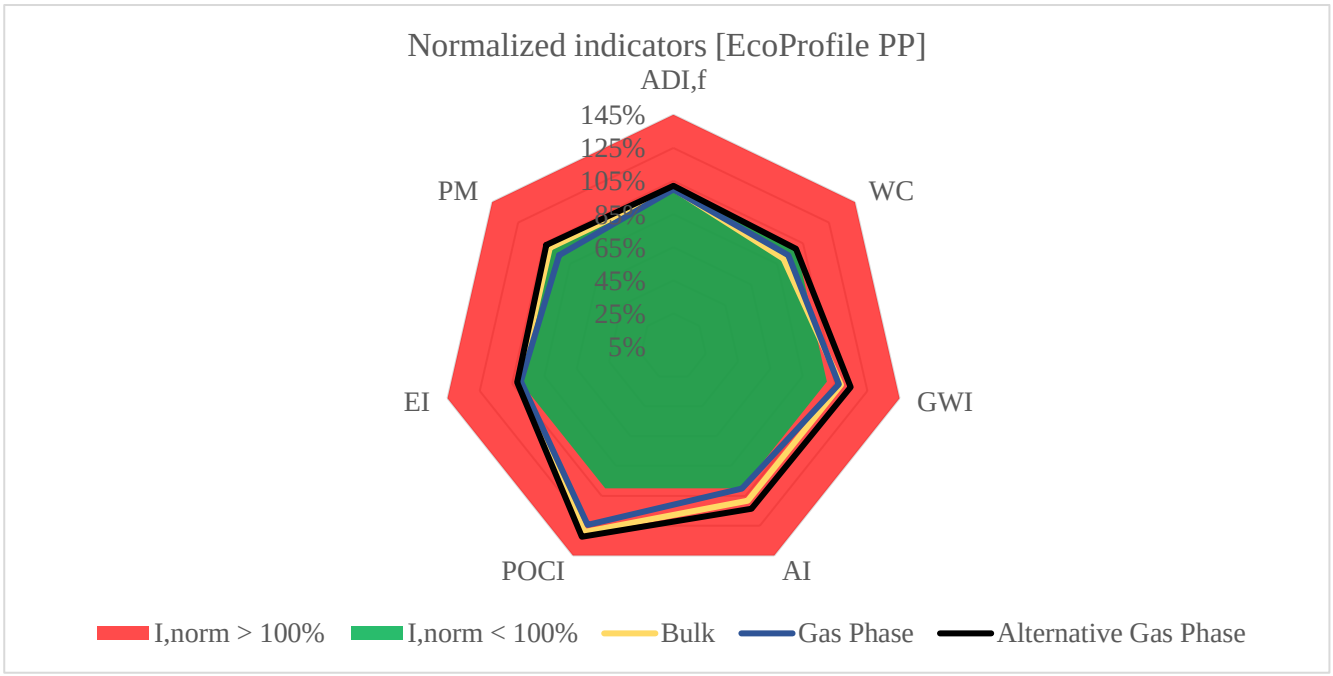


Figure 23: Normalized KPIs for PP Technologies

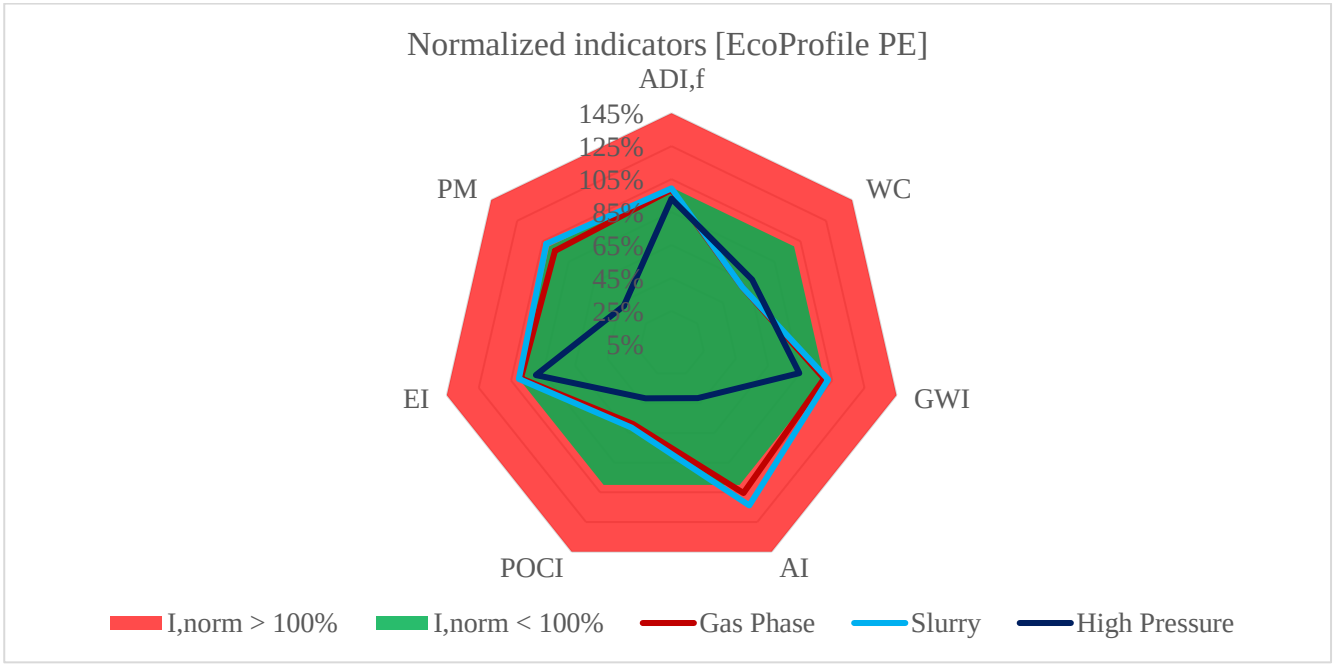


Figure 24: Normalized KPI for PE Technologies

Final remarks

This case-study provides information regarding the environmental profile of alternative strategies for PP and PE polymerizations. In general, analyzed PP technologies provides average results in accordance with PP Eco-profile. Only slight variations are registered as a function of reaction phases. Instead, different results are obtained for PE technologies, High-pressure technology guarantees the most performing environmental profile due to the steam production combined with the polymerization activities.

This result provides general information regarding the environmental footprint of polymerization technologies, however site-specific location and process selection for raw material and energy supply can modify the results (e.g. renewable resources) making some solutions more attractive.

Case study 4: Exergy case study

This section is dedicated to the application of PDAM to polymerization technologies with the aim of demonstrating the efficiency of the procedure as support strategy for energetic analysis. In this direction, the minimization of energy lost due to chemical and physical transformation irreversibility is a key concept to increase processes competitiveness and sustainability. 2 case-studies are presented to show the versatility of the methodology providing specific information and guidelines to prevent energy waste and enhance the overall efficiency. Results presented can support design activities (e.g Conceptual design, R&D, operation) in a sustainability lifecycle perspective. Some case-studies are referred to current configurations of polyolefin plants, other case-studies are representative of technological improvement or comparative assessment. The case-studies described in this chapter are briefly presented in the following.

Case-study 4A consists of the exergy analysis applied to a polypropylene productive plant. This case-study provides the opportunity of testing the new introduced methodology with the goal of demonstrating the efficiency of exergy analysis as a measure of energy quality conservation. Furthermore, results obtained generate a rich database which provides information about energetic efficiency of multiple process options. In this perspective, further considerations can be carried out considering specific plant application, potential alternative solutions, and improvements case-study.

Case-Study 4B represents the application of exergy methodology to the three process improvements presented in section 2. This case-study offers the opportunity to propose new thermodynamics criteria to measure the effects of technological choices and the potential definition of the best operative conditions.

Case-Study 4A: Application of PDAM to polymerization option with principal focalization on exergy analysis

The exergy methodology presented in Section 2 is applied to a polypropylene productive plant with the aim of mapping the energetic performance of principal operations inside the process. In particular, exergy analysis is performed at equipment level. The principal equipment of each area are simulated with Aspen Plus and Aspen Hysys in order to verify local heat and material balances. Process simulation allows to generate streams characterization of the entire plant based on their exergy value. The sequential application of Exergy Balances [69] and Exergy efficiency criteria [76] at equipment level define respectively the operational irreversibility and the performance of each process unit. Results of the analysis present a general overview of the specific plant, showing process inefficiencies, starting point for future improvement studies.

Definition of the reference scheme

A generic process for polypropylene production is assumed as reference scheme and is reported in the following simplified Block Flow Diagrams (BFD) Fig. 25-29. Heat and material balances are verified locally by process simulation. The lack of detailed literature data for Area A and F didn't allow to simulate equipment of these specific parts of the plant. In this framework, the 3 areas are considered as a whole, performing only overall exergy balances.

The following nomenclature is adopted to characterize the following Block Flow Diagram:

- The first letter identifies the location area.
- The second letter represents the unit operation associated with the considered equipment. R: Reactor, S: Separator, E: heat exchanger, P: pump, C: compressor, T: Tank
- The third character is the progressive number of equipment.
- Electric power consumption is characterized by blue arrow and the letter L

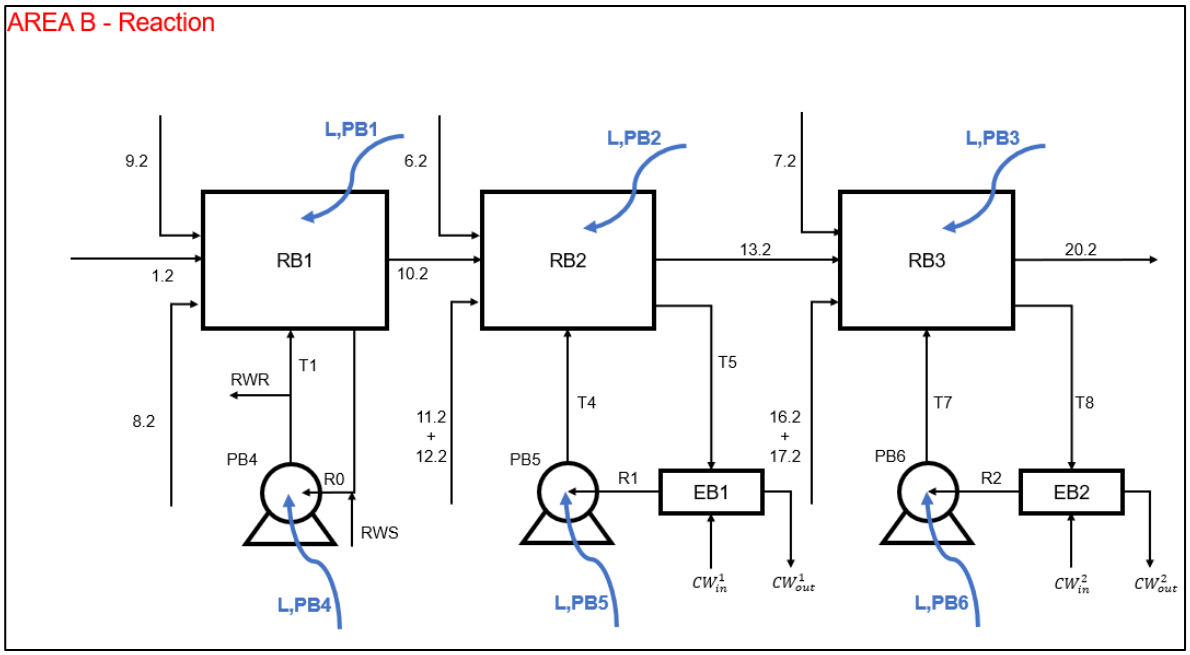


Figure 25: Block Flow Diagram of a polymerization process Area B

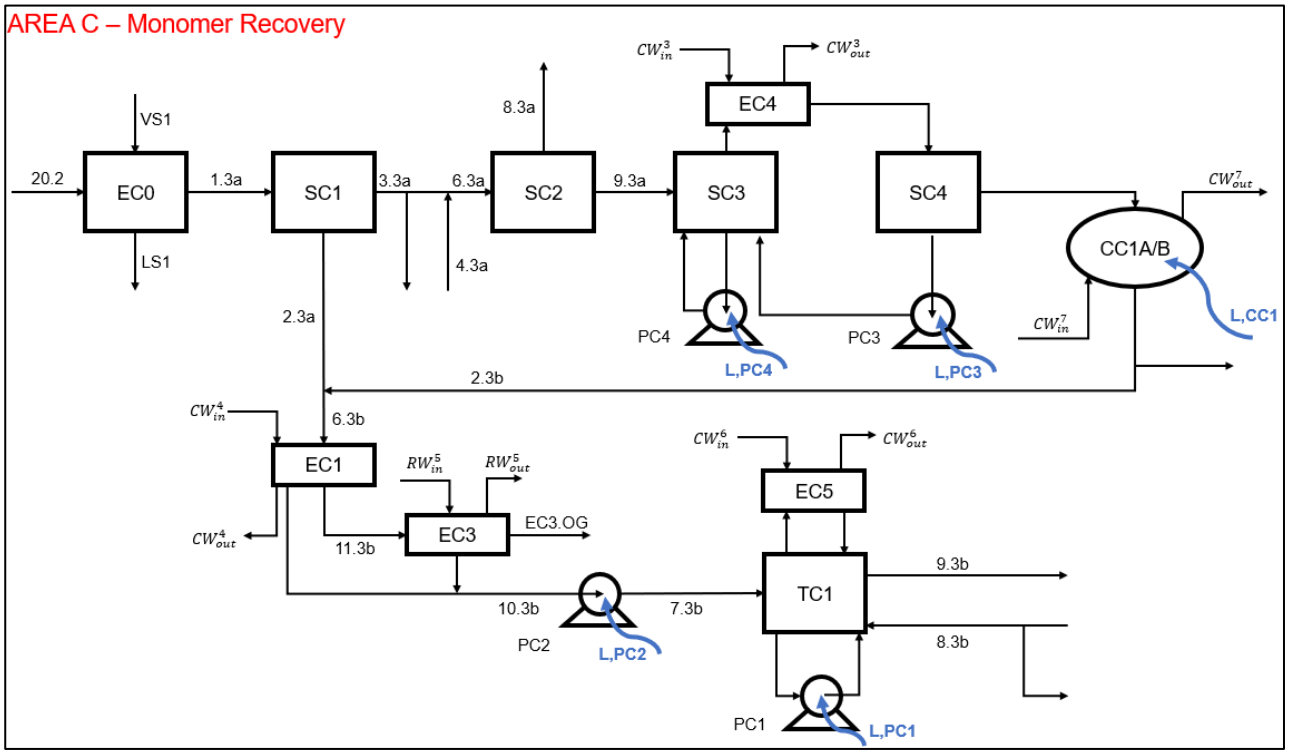


Figure 26: Block Flow Diagram of a polymerization process Area C

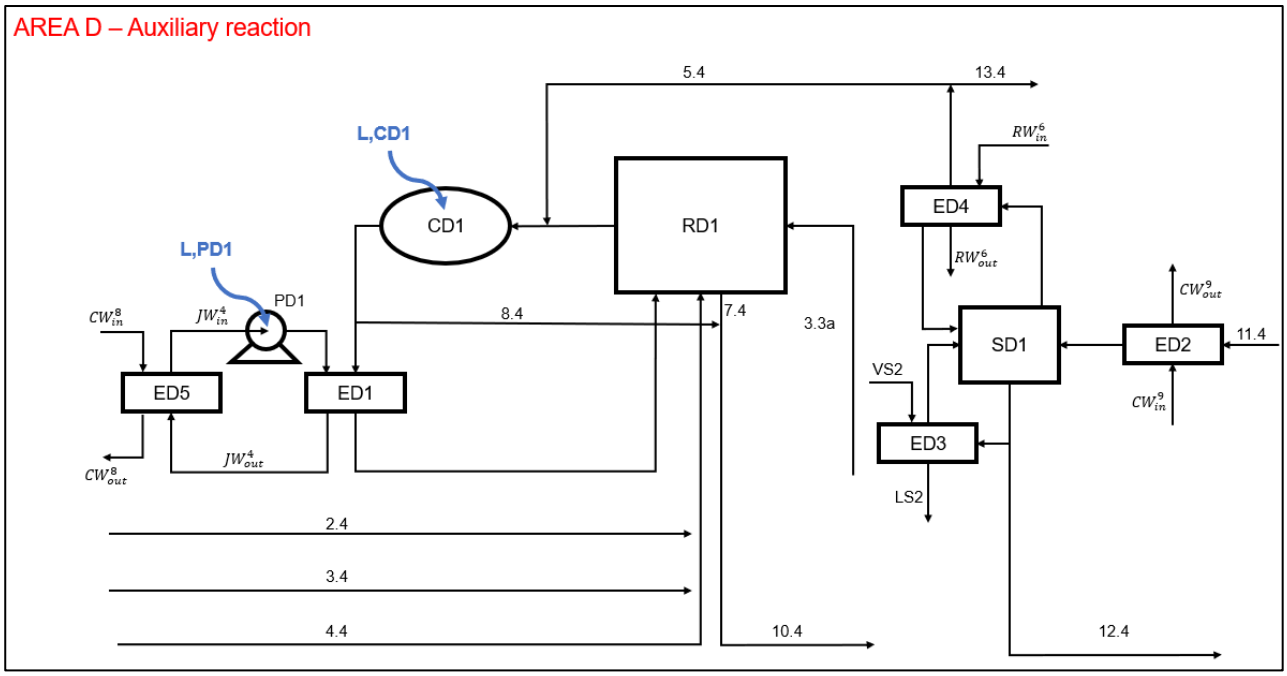


Figure 27: Block Flow Diagram of a polymerization process Area D

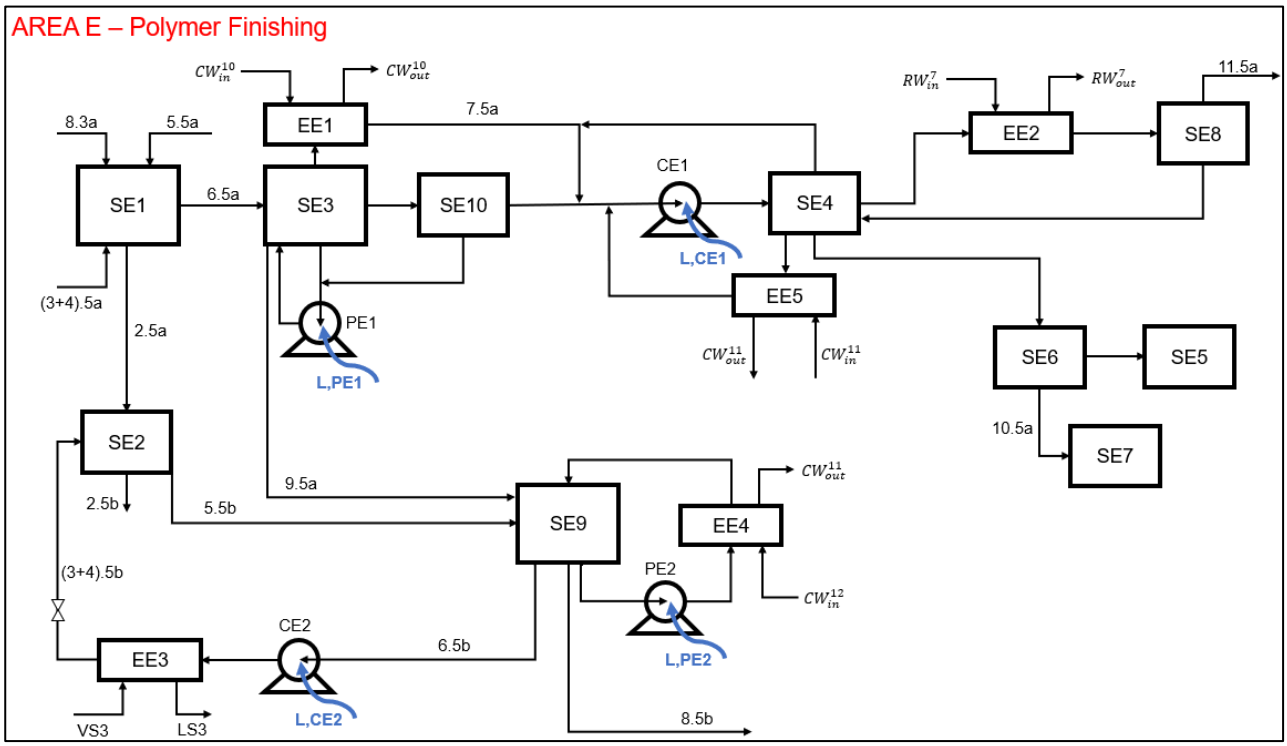


Figure 28: Block Flow Diagram of a polymerization process Area E

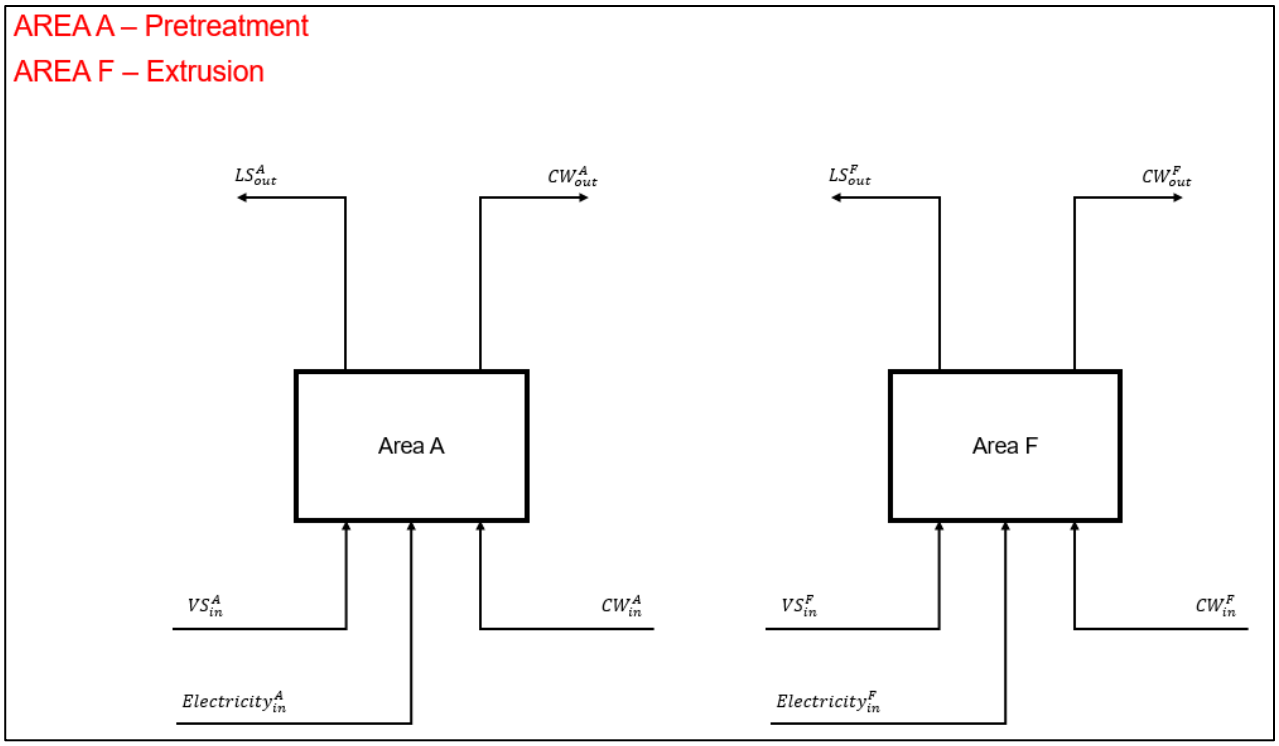


Figure 29: Block Flow Diagram of a polymerization process Area A and Area F

Data gathering e process simulation

In this study, Aspen Plus and Aspen Hysys software are employed to simulate the principal equipment of the reference process. The analysis is carried out to characterize the exergy content of the principal streams.

Thermodynamic models

The process requires different type of substances. In this context several thermodynamic models are involved to predict the behaviour of each component. The selected equations of state are:

- SRK-Kabadi and Danner [98] for hydrocarbons monomers and impurities (Propylene, Propane, Ethylene, Ethane) and Water.
- Peng-Robinson [99] for incondensable gas as hydrogen and Nitrogen
- Uniquac [100] for water-glycol solution.

In addition, the computational of polypropylene exergy value is based on literature data [65] and added to the exergetic content of streams when it is present.

Assumptions

In case of simplified applications (centrifugal pumps, heat exchangers, compressors, fans and columns) the process simulation verified locally heat and material balances. While for more complex equipment (Reactors, polymer finishers) inlet and outlet streams are defined by conceptual design material balance or specific datasheet.

Furthermore, the adiabatic efficiency assumed for the simulation of pumps, compressors and fans is reported in the following Tab. 47.

Table 47: Adiabatic efficiency for the reference mechanical equipment

Equipment	Q - Volumetric flow rate [m^3/h]	Adiabatic efficiency
Compressors	-	80%
Fans	-	50%
Pumps	< 6	20%
	6 < Q < 30	40%
	30 < Q < 70	50%
	Q > 70	70%

Exergy characterization of streams

Reference process is analysed thermodynamically incorporating energy and exergy approaches. The exergy analysis allows to identify the Exergy destruction and efficiency of each equipment. Tab. 48 reports the electricity consumption of principal mechanical equipment and their data sources while Tab. 49 the exergy characterization of principal streams.

Table 48: Electrical consumptions of principal equipment considered in the reference scheme.

Area A		
Equipment	Electrical Consumption [kW]	Source
Entire Area	23,7	PDP
Entire Area	27,5	Basic Design
Area B		
Equipment	Electrical Consumption [kW]	Source
PB1	5,0	PDP
PB2	1200,0	PDP
PB3	1200,0	PDP
PB4	7,7	Simulated
PB5	210,3	Simulated
PB6	213,2	Simulated
Area C		
Equipment	Electrical Consumption [kW]	Source
PC1	325,7	Simulated
PC2	8,2	Simulated
PC3	0,2	PDP
PC4	3,0	PDP
CC1A	163,6	Simulated
CC1B	156,0	Simulated
Area D		
Equipment	Electrical Consumption [kW]	Source
PD1	103,9	Simulated
CD1	1282,5	Simulated
Area E		
Equipment	Electrical Consumption [kW]	Source
CE1	53,5	Simulated
CE2	259,8	Simulated
PE1	13,0	PDP
PE2	9,6	Simulated
Area F		
Equipment	Electrical Consumption [kW]	Source
Entire Area	9466,4	PDP [kW]
Entire Area	19578,5	Basic Design [kW]

In order to carry out exergy balances of each equipment as described in section 2, major consumptions are considered for Area A and F.

Table 49: Exergy streams characterization of the reference schemes

Material Streams characterization								
Area A	VS,A,IN	LS,A,IN	CW,A,IN	CW,A,OUT				
Exergy [kW]	12,01	1,36	0	0				
Area B	R0	T1	8,2	9,2	10,2	11,2/12,2	13,2	17,2 /16,2
Exergy [kW]	41,29	48,09	79,28	15,85	80,99	2554	1729,76	1427,12
Area B	20,2	CWIN1	CWIN2	CWOUT1	CWOUT2	JWIN	JWOUT	R1
Exergy [kW]	2661,18	667,65	371,38	1608,93	907,00	1497,08	2503,15	1209,12
Area B	R2	T4	T5	T7	T8			
Exergy [kW]	3316,99	1396,79	2392,28	3507,78	4357,93			
Area C	1,3A	VS1	LS1	2,3A	3,3A	6,3B	7,3B	8,3A
Exergy [kW]	2978,49	1071,16	121,41	1896,08	927,07	2150,16	1745,00	788,62
Area C	9,3B	10,3A	10,3AN	10,3B	20,2	CWIN3	CWIN4	CWIN6
Exergy [kW]	4063,76	265,37	279,47	1738,86	2661,18	6,72	157,91	7,48
Area C	8,3B	9,3A	CWIN7N	CWOUT3	CWOUT4	CWOUT6	CWOUT7N	
Exergy [kW]	2229,50	55,31	3,93	18,13	426,65	13,08	10,08	
Area D	2,4	3,4	4,4	5,4	6-5,4	7,4	8,4	10,4
Exergy [kW]	118,34	357,01	1,57	118,62	39927,05	947,12	102,68	990,78
Area D	11,4	11,4T4	12,4	13,4	CWIN8	CWIN9	CWOUT8	CWOUT9
Exergy [kW]	297,23	268,70	141,09	3,21	499,48	6,29	1201,26	17,12
Area D	JWIN4	JWIN4PO	JWOUT4	JWOUT4N	LS2	RWIN6	RWOUT6	VS2
Exergy [kW]	566,29	658,94	1649,73	1647,81	10,09	106,14	73,20	88,43
Area E	2,5A	2,5B	3,4,5A	3,4,5B	3,5B	4,5B	5,5A	5,5B
Exergy [kW]	1098,78	808,23	556,41	234,40	143,25	23,44	9,94	153,59
Area E	6,5A	6,5B	7,5A	8,3A	8,5B	9,5A	10,5A	11,5A
Exergy [kW]	178,97	60,42	3,57	788,62	4,34	18,54	0,04	35,55
Area E	CWIN12	CWOUT12	LS3	VS3				
Exergy [kW]	41,58	107,60	5,52	41,65				
Area F	VS,F,IN	LS,F,IN	CW,F,IN	CW,F,OUT				
Exergy [kW]	70,07	7,94	426,72	1026,99				

Application of exergy balance

The characterization of the principal process streams allows the application of the exergy balances Eq. (12). Inlet and outlet streams are defined by the reference proposed scheme Fig. 24. This systematic approach allows the identification of exergy destruction and efficiency at equipment level.

Computational of Exergy destruction and Exergy efficiency

As a result of the application of exergy balance, the exergy destruction and the exergy efficiency are obtained for principal equipment of the plant. Tab. 50 and Tab. 51 report the results.

Table 50: Exergy destruction of the principal equipment per Area

Exergy destruction [kW] - Equipment				
Area A			AREA D	
Overall	27,52		ED1	562,38
AREA B			PD1	11,21
PB4	0,87		ED5	379,74
PB5	22,60		ED2	17,70
PB6	22,41		ED3	57,17
EB1	241,89		ED4	25,05
EB2	505,32		CD1	217,38
RB2	1109,75		SD1	41,27
RB3	845,57		RD1	15,90
AREA C				
EC0	632,43		AREA E	
SC1	155,34		SE1	77,22
SC2	83,15		SE2	303,65
CC1A/B	71,62		EE3	11,67
EC1	142,57		CE1	8,23
PC2	2,07		CE2	110,25
EC5	2,79		PE2	1,01
PC1	83,91		EE1	28,37
TC1	144,18		SE9	21,61
AREA F				
Overall	9466,35			

Table 51: Exergy efficiency of the principal equipment per area

Exergy efficiency [kW] - Equipment				
Area A			AREA D	
Overall			ED1	63,7%
AREA B			PD1	11,21
PB4	88,6%		ED5	64,8%
PB5	89,3%		ED2	38,0%
PB6	89,5%		ED3	27,0%
EB1	79,6%		ED4	95,1%
EB2	51,5%		CD1	83,1%
RB2	45,1%		SD1	100,0%
RB3	61,1%		RD1	63,7%
AREA C				
EC0	33,4%		AREA E	
SC1	94,8%		SE1	94,3%
SC2	91,0%		SE2	76,0%
CC1A/B	84,1%		EE3	67,7%
EC1	84,7%		CE1	84,6%
PC2	24,6%		CE2	57,6%
EC5	65,3%		PE2	89,5%
PC1	74,8%		EE1	69,9%
TC1	66,8%		SE9	89,6%
AREA F				
Overall				

Exergy efficiency of Area F cannot be calculated, it is assumed that outlet polymeric stream is at the environmental condition (Exergy = 0).

Final remarks

This methodology allows to monitor the entire exergy streams characterization of a reference process and therefore evaluate the exergetic performances of each equipment. In this framework, it is possible to define critical issues inside the reference scheme, highlight strength and weaknesses and propose criteria for alternative solutions comparison. In this specific case study, most of the heat exchangers present exergy efficiency lower than 50% and not negligible exergy destruction amount. This is related to a high temperature difference between the two involved fluids (process and utility water). The adoption of utility water simplifies the process scheme and operability, however, is a great source of exergy destruction due to the waste of heat in the water tower. In order to increase the energetic efficiency of the scheme, new heat recovery solutions can be analysed preventing the wasting of heat in water tower. Considering the exergy destruction per area (Tab.52), about 60% of the polymerization total amount is located in Area F due to the extrusion unit operations which is a huge source of electricity consumption. This result is in accordance with conclusion derived from Case-study 1. In a sustainability perspective, future improvement study can be focused on Area F optimization.

Table 52: Exergy destruction per Area, percentage of contribution

Ex,d - Area			%Of TOTAL
A	23,73	kW	0,2%
B	2748,4	kW	17,7%
C	1318,04	kW	8,5%
D	1386,83	kW	8,9%
E	562,02	kW	3,6%
F	9466,35	kW	61,1%
TOT	15505,37	kW	

Case-Study 4b: Analysis of potential polypropylene process improvements

The present case-study focuses on the application of PDAM to three industrial improvements studies. Aim of this assessment is to evaluate and quantify potential sustainability effects of technological improvements. Different sets of KPIs are selected to characterize each alternative. Results are intended to support design activities promoting sustainability-oriented indicators.

Improvements studies are briefly presented in the follow:

- **Introduction of a heat exchanger inside the monomer recovery section.** This first improvement foresees the introduction of a heat exchanger between the monomer separators equipment of the monomer recovery section. This solution is intended to increase the monomer recovered quantity and polymer outlet temperature. Operability benefits are principally located in the reduction of electricity required of final extruder. Other advantages can be related to a better management of monomer recovered fractions.
- **Substitution of reactors' pumps and compressors with steam turbines.** This improvement plans to substitute reactors' pumps and compressors with steam turbines equipment. This assessment also modifies the required inlet raw material of the reference process with the introduction of high-pressure steam. This study is particularly influenced by site-location specific technologies for raw material and energy supply.
- **Introduction of a splitter unit.** This last improvement analysed the introduction of a distillation column to support the operability of polymerization process. Splitter equipment plans to increase the flexibility of the process allowing lower monomer inlet grade due to a profitable off-gas separation (propane-propylene).

Introduction of a heat exchanger (2)

This process improvement plans to introduce a new equipment between the High-pressure separator and the Low-pressure separator of the monomer recovery section. The introduction of this equipment is intended to reduce the overall energy required by this section due to a better management of operative temperature. In detail, the design temperature of the outlet heat exchanger (1) stream of current configuration (Fig. 30) is settled at T0. A preliminary analysis regarding the introduction of a heat exchanger (2) (Fig. 31) has already been carried out. The following design changing are evaluated:

- Outlet heat exchanger (1) temperature reduced up to T1 (minimum temperature that avoid monomer condensation at the operative pressure)
- Outlet heat exchanger (2) temperature settle to T2
- Low pressure steam utilized as thermal utility vector for the heat exchanger (2)

The reduction of the outlet heat exchanger (1) temperature reduces the quantity of monomer separated in the first separator. Previous analysis based on energy balances demonstrate the efficiency of this equipment respect to the current configuration. In this direction, environmental benefits are quantified due to the reduction of the overall energy consumed by the system. In this section, previous analysis is enclosing in a more expanded and sophisticated methodology to define optimal configurations for the reference system. Two are the targets of this analysis:

- the definition of the optimal heat exchanger (2) conditions based on exergy analysis
- the evaluation of the best option based on exergoeconomic analysis.

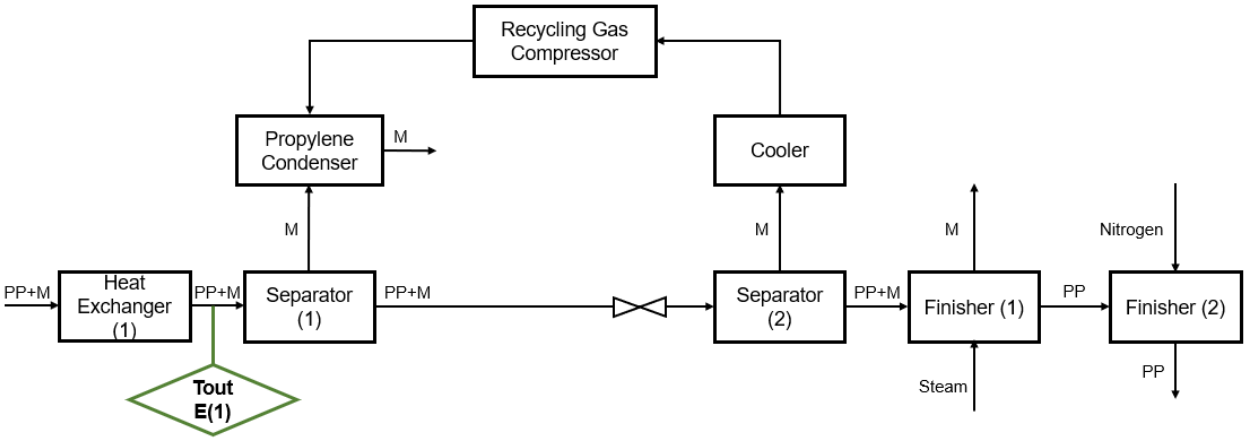


Figure 30: BFD of the current polypropylene production configuration of monomer recovery and polymer finishing sections

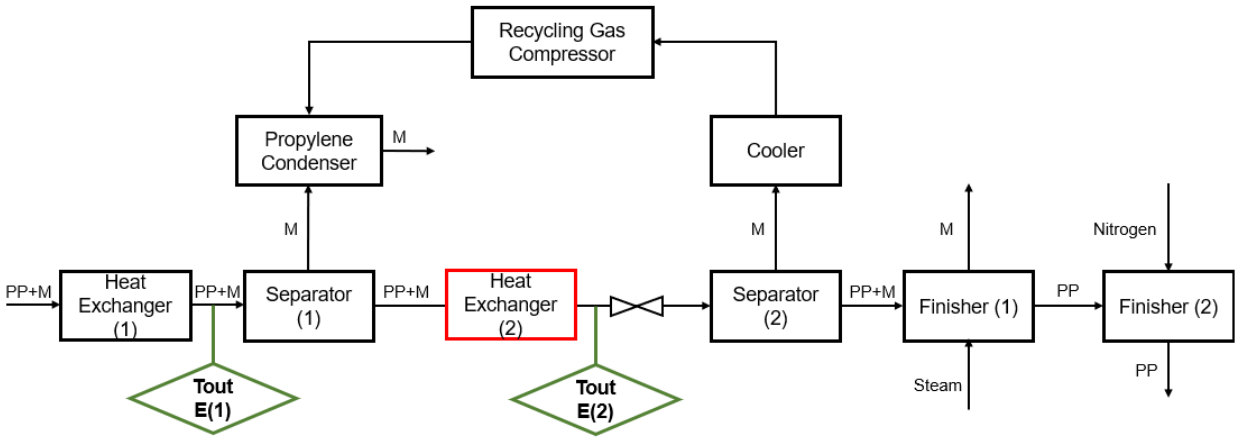


Figure 31: BFD of the new proposed polypropylene process configuration of monomer recovery and polymer finishing sections (introduction of heat exchanger (2))

Data gathering and assumptions

Stream characterization is derived by heat and material balances of a preliminary design carried out from typically information available in process design package (PDP). Process simulations are utilized to facilitate energy balances and exergy quantification. Aspen HYSYS is utilized with SRK model to predict the exergy of each stream as described in section 2. The following assumptions are introduced to perform the assessment:

- Processed stream (heat exchanger (1) inlet stream) consists of about 50% wt propylene and 50% wt polypropylene
- The monomer entrained gas quantity from HP separator and LP separator is derived by equation reported in Tab 53.
- Finisher (1) is assumed as an absorber column
- $T_{top}^{Finisher\ (2)} = T_{bottom}^{Finischer\ (1)}$
- Costs of raw materials and energy are derived from Tab. 7.

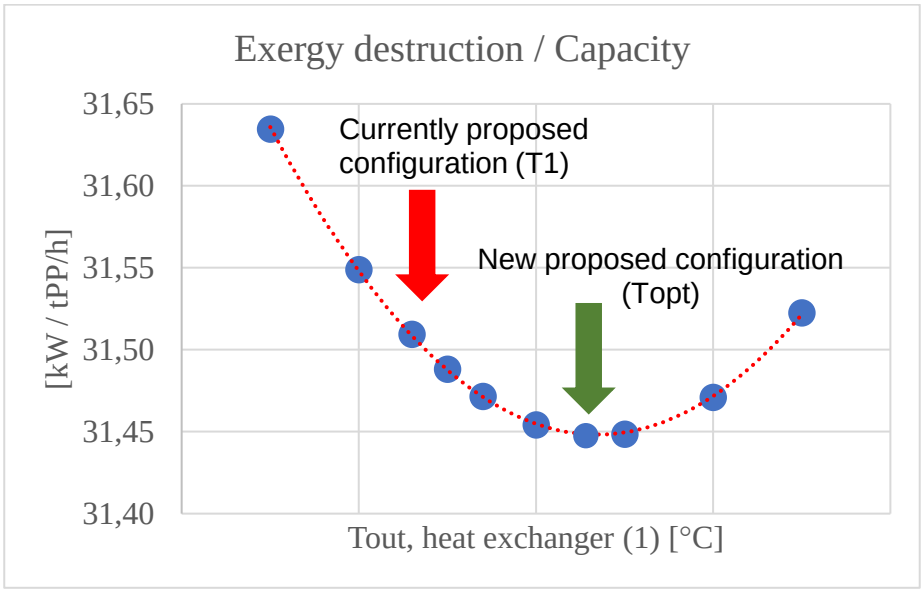
Table 53: Gas mass flow entrainment from the two separators

Gas Entrainment: $\dot{m} = f(T_{Separator}[°C])$ [kg/h]	Separator (1)	$\dot{m}_{entrained\ gas}$ (1) $= 5{,}68 \cdot 10^{-6} \cdot T^2 - 2{,}867 \cdot 10^{-3} \cdot T + 2{,}882 \cdot 10^{-1}$
	Separator (2)	$\dot{m}_{entrained\ gas}$ (2) $= -6{,}77 \cdot 10^{-3} \cdot T + 8{,}67 \cdot 10^{2}$

Definition of the optimal heat exchanger (1) outlet temperature

In this section, the exergy destruction indicator presented in section 2 Eq. (12) is utilized as metric to define the optimal heat exchanger (1) outlet temperature that minimize the overall exergy destructed by the system. In a sustainability perspective, the definition of the optimal heat exchanger (1) temperature allows to facilitate further design decisions and operate at the minimum energy consumption conditions reducing the energy depleted by the system.

A range of variability between [T1-10°C; T0] °C is assumed for the analysis. Fig. 32 illustrates the exergy destruction indicator of the reference system (Fig. 31) as a function of the outlet flash pipe temperature. Temperatures below T1 are allowed only with different pressure condition, otherwise the monomer can't be vaporized in the heat exchanger (1).



Definition of Topt	
Tout, Heat exchanger (1) [°C]	Ex,d / Capability [kW/t/h]
T1-10°C	31,635
T1-5°C	31,549
T1-2°C	31,509
T1	31,488
T1+2°C	31,472
T1+5°C	31,454
T1+10°C	31,448
T1+15°C	31,471
T1+20°C	31,523

Tout, Heat exchanger (1) [°C]	Ex,d / Capability [kW/t/h]
T1+8,5°C	31,448

Figure 32: Exergy destruction of the reference system as a function of the outlet heat exchanger (1) temperature

This study is intended to support the optimization and the definition of minimum energy working point for a process. In this application, a pre-existing improvement study is analysed adding a degree of freedom to the system. Results obtained monitors the entire performance of subsequential unitary operations defining thermodynamic conditions that minimize the exergy destruction of the system. In the specific, this assessment demonstrates the optimal working temperature (Topt) for the presented case study which is different from the currently proposed configuration (T1). This methodology

introduces a sustainability-oriented approach applicable to a sequence of unitary operations aims at the definition of the most performing working conditions. In conclusion, further considerations are required to match chemical-physical limits with assessment results to verify the operability and applicability of the proposed solutions.

Definition of the exergy minimum condition

This assessment tries to overcome the limitation imposed by the introduction of a new heat exchanger (e.g Temperature T1, Process scheme) defining new possible design conditions that minimize the exergy destructed by the system. A combination of CAPEX and OPEX of the process layout is evaluated in the NPV Eq. (5). Economic and Exergy indicators are calculated for several scenario in order to define the optimal configuration.

Previous consideration and schemes (Fig.30 and Fig.31) are integrated with a reference extruder. In this context, the outlet polymer stream from finisher (2) is processed in an extrusion section. The lack of detailed data regarding the electricity consumption of this equipment as a function of the inlet temperature and the type of the screws force to consider the following fixed consumptions.

- Extruder consumption operating at nominal inlet temperature (about 100°C) = 266,7 kW/t/h
- Extruder consumption operating at higher inlet temperature (about 109°C) = 251,7 kW/t/h.

In this section, exergy destructed by the extruder is assumed equal to its electrical consumption. This approximation is supported by results obtained in previous case-studies.

Multiple scenarios are considered for this assessment. Case 1-6 are referred to process layout that does not include heat exchanger (2), while Case 7-16 monitor the performance of the scheme that includes heat exchanger (2). Furthermore, the progressive numbering is representative of a different outlet heat exchanger (1) temperature. Letters stands for:

- a: High steam mass flow rate supplied in the finisher (1) (not all the quantity condensed). Nitrogen is supplied in the finisher (2).
- b: Steam mass flow rate is equal to the optimal configuration (all the quantity condensed). Nitrogen is supplied in the same condition as case “a”.
- c: Steam mass flow rate is the same as case “b”. Nitrogen is supplied at Battery limit condition in the dryer. In this configuration, the nitrogen heater is removed.

Due to a higher polymer temperature for Case 7-16, scenario “a” is not considered. Scenarios “a” are characterized by high operative costs related to the steam consumptions and are responsible of the same exergy destruction of cases “b”.

Table 54: List of the analysed cases for the reference scheme Fig. 30 and Fig. 31

Case	Heat exchanger (1) outlet Temperature	Heat Exchanger (2)	Steam	Nitrogen Temperature
1a	T0	not present	Nominal mass flow rate	110°C
1b	T0	not present	0,5*Nominal mass flow rate	110°C
1c	T0	not present	0,5*Nominal mass flow rate	45°C
2a	T0+5°C	not present	Nominal mass flow rate	110°C
2b	T0+5°C	not present	0,5*Nominal mass flow rate	110°C
2c	T0+5°C	not present	0,5*Nominal mass flow rate	45°C
3a	T0+10°C	not present	Nominal mass flow rate	110°C
3b	T0+10°C	not present	0,5*Nominal mass flow rate	110°C
3c	T0+10°C	not present	0,5*Nominal mass flow rate	45°C
4a	T0+15°C	not present	Nominal mass flow rate	110°C
4b	T0+15°C	not present	0,5*Nominal mass flow rate	110°C
4c	T0+15°C	not present	0,5*Nominal mass flow rate	45°C
5a	T0+20°C	not present	Nominal mass flow rate	110°C
5b	T0+20°C	not present	0,5*Nominal mass flow rate	110°C
5c	T0+20°C	not present	0,5*Nominal mass flow rate	45°C
6a	T0+25°C = T2	not present	Nominal mass flow rate	110°C
6b	T0+25°C = T2	not present	0,5*Nominal mass flow rate	110°C
6c	T0+25°C = T2	not present	0,5*Nominal mass flow rate	45°C
7b	T1-10°C	included	0,5*Nominal mass flow rate	110°C
8b	T1-5°C	included	0,5*Nominal mass flow rate	110°C
9b	T1-2°C	included	0,5*Nominal mass flow rate	110°C
10b	T1	included	0,5*Nominal mass flow rate	110°C

Table 54: List of the analysed cases for the reference scheme Fig. 30 and Fig. 31 (Continued)

Case	Heat exchanger (1) outlet Temperature	Heat Exchanger (2)	Steam	Nitrogen Temperature
11b	T1+2°C	included	0,5*Nominal mass flow rate	110°C
12b	T1+5°C	included	0,5*Nominal mass flow rate	110°C
13b	T1+10°C	included	0,5*Nominal mass flow rate	110°C
14b	T1+15°C	included	0,5*Nominal mass flow rate	110°C
15b	T1+20°C	included	0,5*Nominal mass flow rate	110°C
16b	T1+8,5C	included	0,5*Nominal mass flow rate	110°C
7c	T1-10°C	included	0,5*Nominal mass flow rate	45°C
8c	T1-5°C	included	0,5*Nominal mass flow rate	45°C
9c	T1-2°C	included	0,5*Nominal mass flow rate	45°C
10c	T1	included	0,5*Nominal mass flow rate	45°C
11c	T1+2°C	included	0,5*Nominal mass flow rate	45°C
12c	T1+5°C	included	0,5*Nominal mass flow rate	45°C
13c	T1+10°C	included	0,5*Nominal mass flow rate	45°C
14c	T1+15°C	included	0,5*Nominal mass flow rate	45°C
15c	T1+20°C	included	0,5*Nominal mass flow rate	45°C
16c	T1+8,5C	included	0,5*Nominal mass flow rate	45°C

Results and discussion

The application of exergy balances and economic considerations to the reference system allows to monitor the performance of the analyzed improvement study. Multiple scenarios are considered, spanning from current configuration (Fig. 30) with different heat exchanger (1) outlet temperature to new configuration (Fig 31) with optimal heat exchanger (2) outlet temperature derived from Case Study 4A. Fig. 33 reports the results obtained.

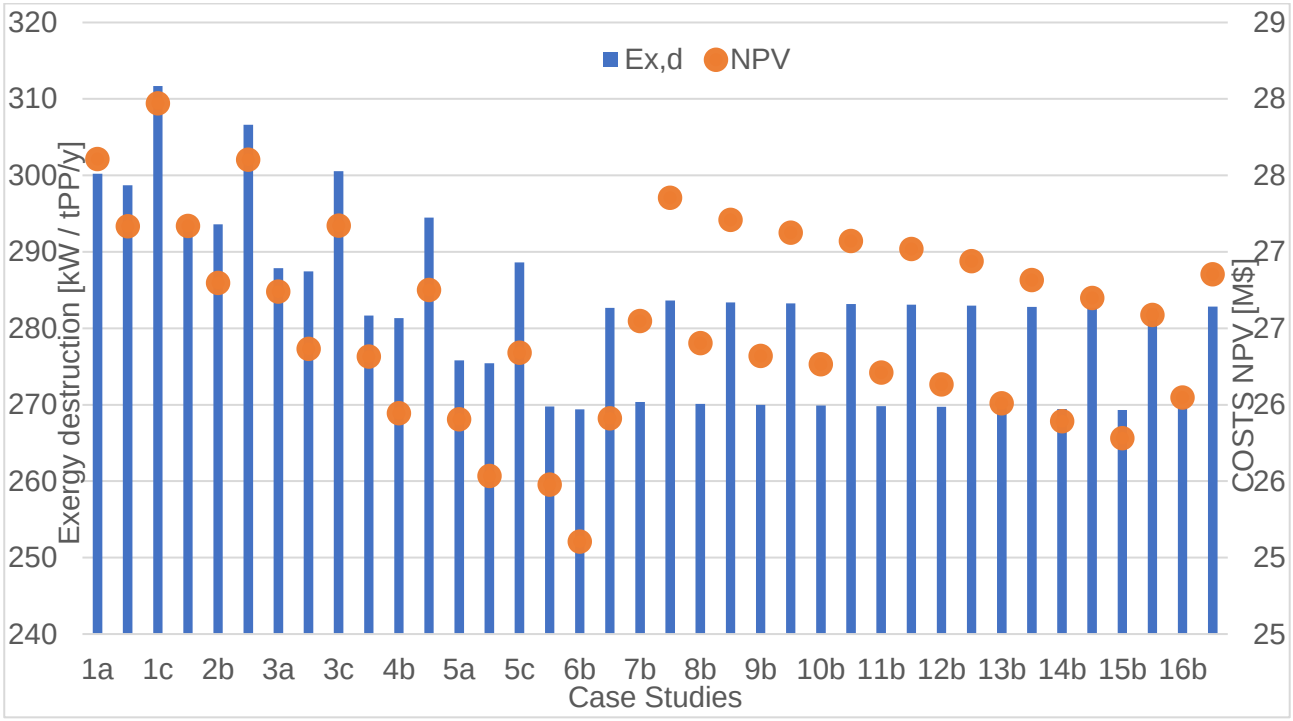


Figure 33: Exergy destruction and NPV of the analysed improvement case-studies. Comparison of heat exchanger (2) and Current configurations with different process conditions

Case 1a is representative of the current configuration with T0 as outlet heat exchanger (1) temperature and nominal mass flow rate for steam, Case 7b simulates the new layout comprehensive of the heat exchanger (2) with the outlet heat exchanger (1) temperature settle at T1. Case 16b is representative of the new optimized conditions derived from Case Study 4A. Moving from case 1a to 6a it is possible to appreciate a reduction of the exergy destructed of the system (10,1%) and overall Costs of the process (7,7%) only with a better management of the temperature in the system. Furthermore, comparing case 7b with 16b, further improvement can be obtained by the increase of the outlet heat exchanger (1) temperature up to Topt. Considering other scenarios, new optimized conditions can be defined. In general scenarios a and b of the same case study are characterized by similar exergy destruction because no relevant differences in streams' temperature are registered. However, small deviation is attributed to the finisher (1): due to the higher steam mass flow rate proposed in case a, the uncondensed quantity reduces its temperature respect to the inlet condition. This fraction of steam is a source of exergy destruction that provides unnecessary sensible heat. Furthermore, this steam fraction can be selected as a source of economic inefficiency which is the principal reason why costs NPV of cases with high steam mass flow (marked with code "a") are higher than other options (marked with code "b") for the same outlet temperature of the heat exchanger (1) (i.e., same number code of the case).

Case c is responsible of higher exergy destruction. Nitrogen is supplied at battery limit conditions to the finisher (1) establishing new equilibrium conditions at lower temperature respect to the current configuration. In this scenario, the economic benefits associated with the removal of the nitrogen heater (Capex of the equipment, Opex for the steam) are not balanced with the increase of the Opex at the extruder unit (Electricity required to reach the molten polymer temperature). In this context, considering the same case study, scenario c presents the worst results in economic and energetic terms. Moreover, comparing the entire case-studies, optimal configurations can be obtained by the increase of the outlet heat exchanger (1) temperature even without the introduction of the heat exchanger (2). In particular case study 6b presents minimized economic and exergetic indicators. The outlet heat exchanger (1) temperature is settled at T2 (as the outlet heat exchanger (2) condition). This configuration allows to separate the largest quantity of monomer from polymer in the separator (1) reducing the monomer mass flow rate collected at low pressure from separator (2), minimizing the electrical consumption of the recycle gas compressor unit. In this scheme, a source of energetic inefficiency is located in the procedure of heating the monomer quantity (heat exchanger (1)) and subsequently condensing this fraction (propylene condenser). However, the exergy destructed for monomer heating and condensation is not comparable with the reduction of electricity required in the recycle gas compressor. Furthermore, considering case studies (7-16) the heat capacity of the monomer ($\dot{m}_{c3-}\widehat{cp}_{c3-}$) is about 6% of the total heat exchanger (2) inlet stream (monomer and polymer: $\dot{m}_{mix}\widehat{cp}_{mix}$). In this context, heat exchanger (2) mainly heats polymer at T2, and the exergy benefits of the introduction of this new equipment are only related to the reduction of electrical consumption in the extruder unit. This result can be easily obtained setting the outlet heat exchanger (1) temperature at T2. In conclusion:

- Considering the design of new plant, new heat exchanger (2) outlet temperature can be considered (in accordance with case 6b).
- Considering improvement study of operative plant, the exergy benefits associated with the increase of polymer temperature can be obtained by the introduction of a heat exchanger before the extruder unit. Utility steam can be utilized as thermal vector. This configuration guarantees higher polymer temperature (as the heat exchanger (2) configuration) reducing the electrical load of the extruder, which is the principal source of exergy destruction. This configuration could be less efficient than a direct increase of heat exchanger (1) outlet temperature (case 6b), however, for operating plant, can be a valid option to reduce the overall exergy destructed without completely modifying the monomer recovery and polymer finishing sections.

Substitution of reactors' pumps and compressor with steam turbines

This improvement study plans to substitute the current reactor pumps and compressors of polypropylene process with Steam turbines that generate electricity due to the lamination of high-pressure steam. In this context, Environment, Exergetic and Economic indicators are calculated as described in section 2 respectively Eq. (1), Eq. (12), Eq. (5) to characterize the presented case study.

Definition of the reference schemes

A reference scheme is defined in Fig. 34. In this case, the polymerization process is considered as a black box and is characterized by its material and energy consumptions. A lifecycle boundary is adopted to monitor the environmental indicators, a design boundary is introduced specifically tailored to the polymerization framework to evaluate the economical and exergetic performances of the improvement. The definition of the boundary is described in the PDAM methodology (Section 2).

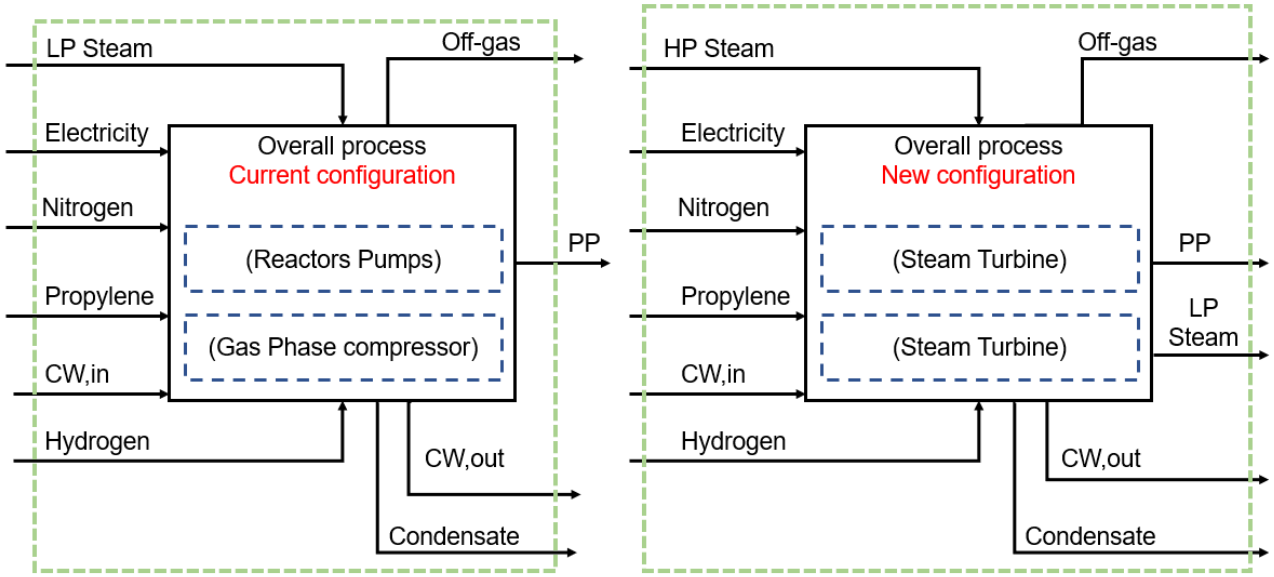


Figure 34: Reference scheme adopted for the assessment of the presented case study: Substitution of reactors' pumps and compressor with steam turbines.

Data gathering and simulations

Material and energy specific consumptions are based on average polypropylene productive process. Raw material and energy costs are assumed in accordance with Tab 7. The principal costs of equipment required to characterize the two alternatives' configurations (Current polymerization process and new process inclusive of Steam turbines) are reported in the follow (Tab. 55 and Tab. 56). In this context, a reference basis of 1000 units is assumed for the valorization of plant investment capital costs. Other costs presented in the follow are scaled from the basis. Furthermore, Steam turbine electricity production is simulated with Aspen Hysys.

Table 55: Equipment and Capital Costs of reference polymerization plant current configuration

Current configuration – Costs Estimation	
Plant Capital Costs	1000
Reactor 1 - Pump	5
Reactor 2 - Pump	5
Reactor 3 - Compressor	6,7
Overall Capex	1016,7

Table 56: Equipment and Capital Costs of polymerization new process schemes (Steam turbine options)

New process options	
Plant Capital Costs	1000
Reactor 1 – Steam Turbine	12,5
Reactor 2 – Steam Turbine	12,5
Reactor 3 – Steam Turbine	21,7
Overall Capex	1046,7

In this framework, several scenarios are considered in order to evaluate the total or partial introduction of these new equipment:

- Case 1: Current configuration.
- Case 2a: Substitution of the 2 reactors pumps (Reactor 1 and 2) and the gas phase compressor (Reactor 3) with Steam Turbines. In this case, a realistic efficiency for the steam turbines is assumed (75%).
- Case 2b: Implementation of the same equipment of Case 2a, but is assumed 100% for Steam turbine efficiency.
- Case 3a: Substitution of the 2 reactors pumps (Reactor 1 and 2) with Steam turbines (75% efficiency). In this case Reactor 3 compressor is maintained.
- Case 3b: Implementation of the same equipment of Case 3a, but is assumed 100% for Steam turbine efficiency.
- Case 4a: Substitution of Reactor 3 compressor with a Steam turbine (75% efficiency). Reactors 1 and 2 pumps are maintained.
- Case 4b: Implementation of the same equipment of Case 4a, but is assumed 100% for Steam turbine efficiency.

A reference plant capacity in assumed (400 kt/y of polypropylene) in order to characterized material and energy input and output. Streams characterization of the presented cases are resumed in Tab. 57 and Tab. 58. Input and Output streams are referred to Fig 34. In the specific, regarding cases from 2a to 4b the following assumptions are introduced:

- The Low-pressure steam (LP steam) generated by the lamination of High-pressure steam (HP steam) is utilized internally by the polymerization process.
- Electricity generated by Steam turbines are utilized internally by the polymerization process.

Table 57: Stream characterization of the current configuration

	Case 1		
INPUT	Mass Flow [kg/h]	Mass Exergy [kJ/kg]	Exergy [kW]
Propylene	57500	138,9	2219,1
LPsteam	16500	720,7	3303,2
HPsteam	0	0	0
Cwin	6540000	1,3	2365,1
Electricity	0	0	17700
Nitrogen	1000	171,2	47,5
Hydrogen	5,0	2552,4	3,5

OUTPUT	Mass Flow [kg/h]	Mass Exergy [kJ/kg]	Exergy [kW]
LPsteam	0	0	0
Condensate	16500	81,7	374,5
PP	50000,0	0,0	0,0
Off-gas	1650	62,1	28,5
Cwout	6540000	3,1	5692

Table 58: Stream characterization the new configuration: Substitution of reactors' pumps and compressor with steam turbines unit

	Case 2a			Case 2b		
INPUT	Mass Flow [kg/h]	Mass Exergy [kJ/kg]	Exergy [kW]	Mass Flow [kg/h]	Mass Exergy [kJ/kg]	Exergy [kW]
Propylene	57500	138,9	2219,1	57500	138,9	2219,1
LPsteam	0	720,7	0,0	0	720,7	0
HPsteam	44716,3	1178,1	14633,0	40813,5	1178,1	13355,8
Cwin	6540000	1,3	2365,1	6540000	1,3	2365,1
Electricity	0	0	13100,0	0	0	13100
Nitrogen	1000	171,2	47,5	1000	171,2	47,5
Hydrogen	5,0	2552,4	3,5	5	2552,4	3,5

OUTPUT	Mass Flow [kg/h]	Mass Exergy [kJ/kg]	Exergy [kW]	Mass Flow [kg/h]	Mass Exergy [kJ/kg]	Exergy [kW]
LPsteam	28216,3	720,7	5648,8	24313,5	720,7	4867,4
Condensate	16500	81,7	374,5	16500	81,7	374,5
PP	50000	0	0	50000	0	0
Off-gas	1650	62,1	28,5	1650	62,1	28,5
Cwout	6540000	3,1	5692,0	6540000	3,1	5692

Table 58: Stream characterization of the new configuration: Substitution of reactors' pumps and compressor with steam turbines unit (Continued)

	Case 3a			Case 3b		
INPUT	Mass Flow [kg/h]	Mass Exergy [kJ/kg]	Exergy [kW]	Mass Flow [kg/h]	Mass Exergy [kJ/kg]	Exergy [kW]
Propylene	57500	138,9	2219,1	57500	138,9	2219,1
LPsteam	0	720,7	0	0	720,7	0
HPsteam	23330	1178,1	7634,6	21294,0	1178,1	6968,3
Cwin	6540000	1,3	2365,1	6540000	1,3	2365,1
Electricity	0	0,0	15300	0,0	0,0	15300
Nitrogen	1000	171,2	47,5	1000	171,2	47,5
Hydrogen	5	2552,4	3,5	5,0	2552,4	3,5

OUTPUT	Mass Flow [kg/h]	Mass Exergy [kJ/kg]	Exergy [kW]	Mass Flow [kg/h]	Mass Exergy [kJ/kg]	Exergy [kW]
LPsteam	6830,3	720,7	1367,4	4794,0	720,7	959,7
Condensate	16500	81,7	374,5	16500	81,7	374,5
PP	50000	0	0	50000	0	0
Off-gas	1650	62,1	28,5	1650	62,1	28,5
Cwout	6540000	3,1	5692,0	6540000	3,1	5692

Table 58: Stream characterization of the new configuration: Substitution of reactors' pumps and compressor with steam turbines unit (Continued)

	Case 4a			Case 4b		
INPUT	Mass Flow [kg/h]	Mass Exergy [kJ/kg]	Exergy [kW]	Mass Flow [kg/h]	Mass Exergy [kJ/kg]	Exergy [kW]
Propylene	57500,0	138,9	2219,1	57500,0	138,9	2219,1
LPsteam	0,0	720,7	0,0	0,0	720,7	0,0
HPsteam	21386,1	1178,1	6998,4	19519,5	1178,1	6387,6
Cwin	6540000	1,3	2365,1	6540000	1,3	2365,1
Electricity	0,0	0,0	15500,0	0,0	0,0	15500,0
Nitrogen	1000,0	171,2	47,5	1000,0	171,2	47,5
Hydrogen	5,0	2552,4	3,5	5,0	2552,4	3,5

OUTPUT	Mass Flow [kg/h]	Mass Exergy [kJ/kg]	Exergy [kW]	Mass Flow [kg/h]	Mass Exergy [kJ/kg]	Exergy [kW]
LPsteam	4886,1	720,7	978,2	3019,5	720,7	604,5
Condensate	16500	81,7	374,5	16500	81,7	374,5
PP	50000	0,0	0,0	50000	0,0	0,0
Off-gas	1650,0	62,1	28,5	1650,0	62,1	28,5
Cwout	6540000	3,1	5692,0	6540000	3,1	5692,0

Economic results

The substitution of pumps and compressor for reaction plans to consider a new required source of energy as input (HP steam) reducing the electrical load from current configuration and producing LP steam as by-product. First of all, it's necessary to consider this improvement study only in cases where HP steam is available based on the process specific site location. In addition, it's necessary to identify an LP steam utilizer for the excess produced. Furthermore, economic and exergetic indicators are calculated to monitor the performance of each option and propose a quantified approach for the alternative's comparison. The Investment NPV is calculated for each case and reported in the follow (Tab. 59). In this context, differently from the previous, an investment NPV is adopted as reference KPI. In this scenario, the entire technology is considered, and costs can be compared with an estimate of the proceeds obtained from polymer sale. A timeframe of 1 year for the construction (m) is assumed and 10 years of operations (n). Discount rate is considered 10%.

Table 59: Cash flows of the reference cases and NPV

Cash Flow	Case 1	Case 2a	Case 2b	Case 3a	Case 3b	Case 4a	Case 5b
Acf,0	-1.017	-1.047	-1.047	-1.032	-1.032	-1.032	-1.032
Acf,1	161	165	165	163	163	163	163
Acf,2	147	150	150	148	149	148	148
Acf,3	133	137	137	135	135	135	135
Acf,4	121	124	124	123	123	123	123
Acf,5	110	113	113	111	112	111	112
Acf,6	100	103	103	101	101	101	101
Acf,7	91	93	93	92	92	92	92
Acf,8	83	85	85	84	84	84	84
Acf,9	75	77	77	76	76	76	76
Acf,10	68	70	70	69	69	69	69
NPV	74	70	71	71	73	71	72

Graphical representation of results is presented in Fig. 35.

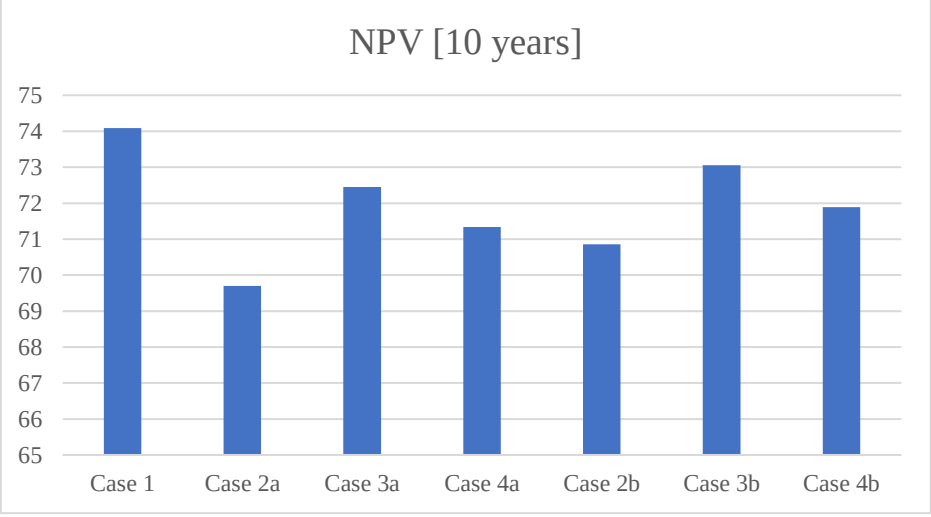


Figure 35: Economic NPV indicator of the presented cases (10 years)

This analysis highlights potential economic improvements for the substitution of Reactors' pumps and compressor by steam turbines. First, it's important to notice that cases "a" present NPV close to cases "b", so this analysis is not widely influenced by the steam turbines efficiencies. Realistic application (cases "a") can be selected as reference for results analysis. Furthermore, Case 2a presents the lower NPV value, which means that the increase of CAPEX associated with the substitution of both reactors' pumps and gas phase compressor are not balanced by the reduction of OPEX. The most attractive solution is represented by the current configuration (Case 1) which also reduces the investment capital costs (CAPEX). In this scenario, the time frame of 10 years does not justify the increase of costs required for the Steam Turbines installation. However, considering a long-term solution (30 years), different results can be obtained. In this scenario, the increase of CAPEX necessary for the steam turbines are balanced with the reduction of Operative costs making the whole project more interesting from economic standpoint. In the specific, case 2 is now the most attractive alternatives while the current configuration (Case 1) presents the lower NPV.

Fig. 36 reports the NPV of the presented cases applied to a long-term solution (n=30 years).

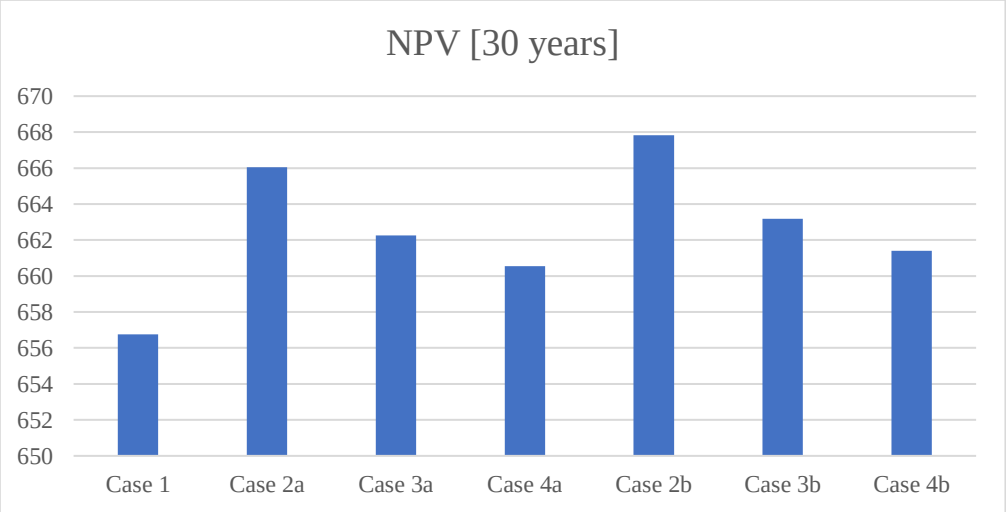


Figure 36: Economic NPV indicator of the presented cases (30 years)

Exergetic results

The substitution of current reactors' pumps and compressor offers the opportunity to apply the exergy analysis and monitor the maintenance of energy quality for the presented cases. In this configuration, the time frame does not influence the results. Exergy balances are applied to the reference schemes (Fig. 29) considering the alternatives solutions presented in the previous chapter (Case 1, 2a/b, 3a/b, 4a/b). Results are presented in Fig. 37.

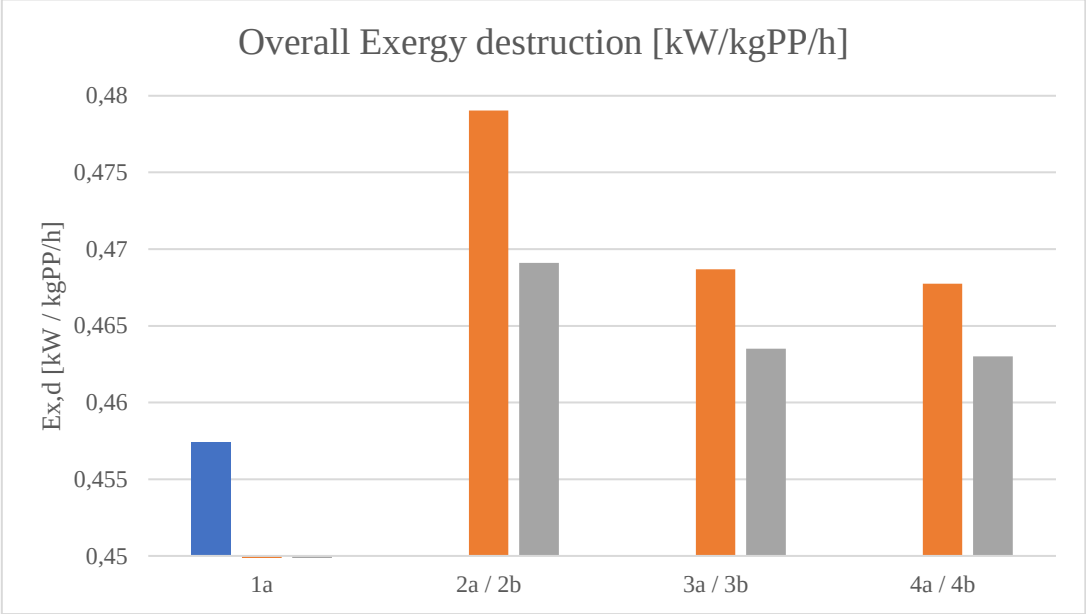


Figure 37: Overall Exergy destruction of the reference presented case.

Exergy destruction KPI demonstrates that the current configuration is the most attractive solution for the presented boundary which includes only the polymerization activities. The introduction of steam turbines units is a huge source of exergy destruction due to the reduction of temperature and pressure of the inlet steam. In this context, further considerations are required, including for example the utilizer of the excess of LP steam for cases 2,3 and 4.

Final Remarks

The presented case study offers a new point of view for the integration of polymerization activities within other external processes. Results obtained regarding Economic and Exergetic aspects are heavily influenced by the site location and geopolitical specific information. Assumptions adopted in this specific analysis provides credits to the current configuration making it globally the most sustainable and attractive solutions for a short-time investments. However, economic credits are highlighted for the new proposed schemes considering a long-term investments.

Introduction of a splitter unit

Component splitter unit are equipment that performs distillation operation. This improvement case-study is intended to analyse the introduction of a Splitter unit as auxiliary support for polymerization operability. Some industrial technologies already adopted this solution within the monomer recovery and pre-treatment section (e.g. Fig. 16). The introduction of a distillation unit allows to increase the flexibility of the process (i.e. monomer can be at chemical grade) and the quality of the process off-gas. Furthermore, the introduction of this equipment allows to increase the process purges preventing the accumulation of propane inside the reactor which is a source of inefficiency due to the volume occupation.

Definition of the reference scheme

In this case-study, the entire polymerization process is considered as a black-box and the current configuration (Fig. 38) is compared with the integrative options that foresees a splitter unit to separate propane-propylene from off-gas stream as presented in Fig. 39.

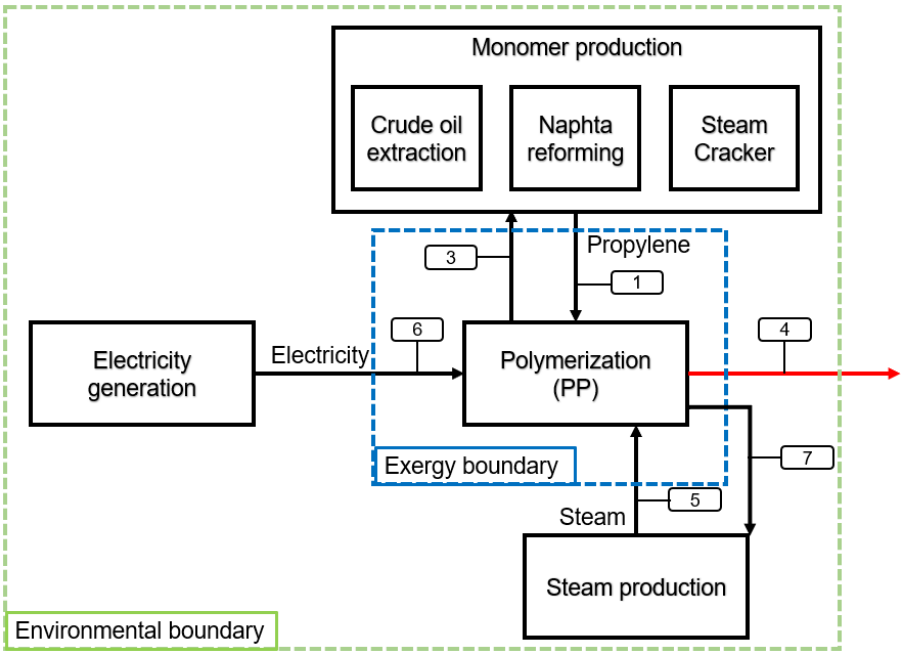


Figure 38: Reference scheme for the current configuration option

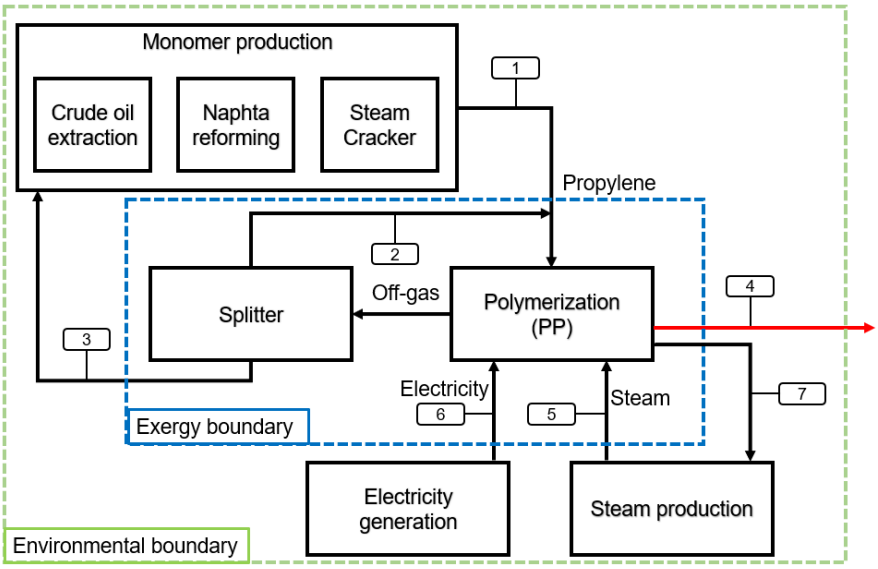


Figure 39: Reference scheme adopted for the analysis of the introduction of a Splitter unit

Data gathering and process simulation

Average polymerization raw material and energy consumptions are utilized to characterized stream for the current process options (Fig. 38). Further considerations are included to evaluate the effect of the new splitter unit. Process simulations support the local verification of heat and material balances. Distillation parameters are derived from literature [101] [102]. Tab. 60 and Tab. 61 reports the principal data required for stream characterization and the application of PDAM. Current polymerization option is compared with the new proposed scheme (Fig. 39).

Table 60: Stream Characterization for the current process option

	1	2	3	4	5	6
Propylene [kg/h]	50880		880			
Propane [kg/h]	220		220			
Polypropylene [kg/h]				50000		
Water [kg/h]					18000	
TOTAL [kg/h]	51100		1100	50000	18000	
Electricity [kWh]						17700

Table 61: Stream Characterization for the new process option (Introduction of a splitter unit)

	1	2	3	4	5	6
Propylene [kg/h]	50020	7980	20			
Propane [kg/h]	1580	420	1580			
Polypropylene [kg/h]				50000		
Water [kg/h]					18000	
TOTAL [kg/h]	51600	8400	1600	50000	18000	
Electricity [kWh]						18000

Although the two presented schemes are similar and include the same units except for the Splitter equipment, some necessary assumptions are required to perform the PDAM with available literature information:

- The new proposed scheme options reduce the monomer grade required from the Steam Cracker (Stream 1). This can reduce the energy required in the Steam Cracker process for the separation of propylene from other hydrocarbon products.
- Different mass flow rate and compositions are expected from Stream 3 which is recycled back to the monomer productive process.

The lack of detailed data regarding Steam Cracker heat and material balances doesn't allow to include in the assessment potential variation of monomer production efficiency. In general, it is expected a negligible effect of the presented assumptions for real plant operability, in any case, the adoption of the same Steam Cracker profile is conservative because the environmental benefits inside the Steam Cracker are not considered for the new proposed scheme. In this context, the application of PDAM balances the reduction of inlet monomer with the increase of electricity required for the Splitter operability.

Environmental results

The application of PDAM to the two presented process schemes allows to calculate a set of KPIs and characterize each option by its sustainability performance. In this specific assessment, the environmental set of KPIs presented in Tab. 6 is adopted as reference applied to the *environmental boundary* presented in Fig. 38 and Fig. 39. Results are presented in Tab. 62.

Table 62: Set of environmental KPIs obtained by the application of PDAM to the two presented reference schemes

KPI	Unit of measurement	Current Configuration	New Process scheme
ADI,f	[MJ/kgPolymer]	7,04E+01	6,93E+01
ADI,e	[kgSb,eq/kgPolymer]	1,55E-07	1,56E-07
RwEC	[MJ/kgPolymer]	2,10E+00	2,11E+00
WC	[kgWater/kgPolymer]	2,44E+01	2,41E+01
CO_2	[$kgCO_2$/kgPolymer]	1,63E+00	1,61E+00
GWI	[$kgCO_2$,eq/kgPolymer]	1,73E+00	1,70E+00
ODI	[kgCFC-11/kgPolymer]	2,90E-08	2,85E-08
AI	[$kgSO_2$-,eq/kgPolymer]	3,91E-03	3,85E-03
POCI	[kgEthylene,eq/kgPolymer]	4,37E-04	4,30E-04
EI	[$kgPO_4$---,eq/kgPolymer]	1,13E-03	1,11E-03
PM	[kgPM10,eq/kgPolymer]	3,42E-03	3,37E-03
HTI	[kg 1,4-Dichlorobenzene eq/kgPolymer]	3,57E-01	3,51E-01
FETI	[kg 1,4-Dichlorobenzene eq/kgPolymer]	9,87E-02	9,71E-02
MAETI	[kg 1,4-Dichlorobenzene eq/kgPolymer]	1,82E+02	1,80E+02
TETI	[kg 1,4-Dichlorobenzene eq/kgPolymer]	1,28E-03	1,26E-03

The introduction of a Splitter unit presents several environmental benefits. Except for ADI,e and RwEC which are influence more from the electricity required, the other KPIs present an average reduction of 1.5%. Further advantages are associated with the increase of process flexibility; the introduction of a splitter allows to reduce the monomer required grade and guarantee higher process purges preventing the accumulation of propane and other inerts.

Exergetic results

Exergy analysis is a powerful strategy aims at the evaluation the maintenance quality of energy source given a reference scheme as described in section 2. In this assessment, exergy balance is applied to the *exergy boundary* of Fig. 37 and Fig. 38 in order to define the exergy destruction of the two alternatives. Tab. 63 and Tab. 64 reports exergy content of the principal reference streams.

Table 63: Exergy stream characterization of the Current configuration (Fig. 38)

	1	2	3	4	5	6	7
Exergy [kW]	1971,	-	33,1	0	3604	-	408,5

Table 64: Exergy stream characterization of the New proposed configuration (Fig. 39)

	1	2	3	4	5	6	7
Exergy [kW]	1986,6	-	54,4	0	3603,5	-	408,5

The exergy destruction of each solution is summarized in the following Tab. 65

Table 65: Exergy destruction of the 2 presented schemes.

	Current configuration	New proposed scheme
Ex,d [MW]	22,8	23,1

Final Remarks

The introduction of a splitter unit is an unavoidable source of exergy destruction due to the increase of unit operations associated with polymerization procedure. In this specific case, the polymerization plant locally increases the exergy destruction amount, however the energy benefits inside the monomer production process (e.g Steam Cracker) might not be negligible in this specific case. The introduction of a splitter unit is still an attractive project due to the reduction of environmental impacts and the increase in process flexibility. In any case, further considerations might be included for the identification of potential energetic efficiency.

Conclusions

In the present study, quantitative assessment methods are developed to support the implementation of sustainability and environmental protection in process design and R&D activities. These approaches are suitable for the analysis of the early phases of conceptual and basic design, when the project is still open to changes (large number of degrees of freedom and low costs of changes).

In this context, methodologies are developed to introduce new sustainability point of view during the design of a process. Procedures are delineated to promote sustainability-oriented guidelines for the identification of critical issues along with operative chain. In the specific, KPIs based methodologies are defined for the comparison of technologies performances, delineation of optimal working conditions and generate new process schemes. The portfolio of the introduced methods is devoted to encompass different phases of the design activities and assessment targets (e.g raw material technology production, energy supply process).

The main innovations introduced in the study are listed in Tab. 66. Overall, the results obtained are expected to increase the sustainability of chemical processes, providing sustainability drivers that may be used as a support to design, paving the way to the implementation of clean, decarbonized, sustainable and safe chemical technologies.

Table 66: Innovative elements introduced in the study.

Elements	Description	Section
PDAM: Process design assessment method.	Process Design Assessment Method (PDAM) is a step-based procedure aimed at the characterization of sustainability profile of a reference process layout. First step consists of the schematization of multiple process options with particular focus on the interaction between different technologies unit. Any level of detailed is accepted for heat and material balances during the process characterization. Results consists of a set of key performance indicators aimed at monitoring the sustainability aspects of the reference schemes (Environmental protection, exergy efficiency). The proposed procedure results in a simple and flexible approach, which allows a straightforward application to practical situations offering new perspective during early design activities or implementation of new process options.	Section 2 - Process Design Assessment Method (PDAM) Pag. 15
Screening method for polyolefin technology comparison.	This procedure provides qualitative and quantitative results with particular focus on alternative solutions for polyolefin productive processes. This method is intended to schematize the most widespread technologies for polypropylene production, highlight strength and weaknesses of each solution and calculate KPI regarding environmental and energetic efficiency aspects. This method is aimed at the definition of a semiquantitative database that provides information regarding process options inside a polymerization plant. The quantification of different process options from sustainability standpoint can be a driver for the design of new technologies and plants. Furthermore, an ideal process is delineated as benchmark for theoretical minimum impact comparison and further considerations are included regarding the introduction of new renewable process options for energy supply.	Section 2 - Screening method for polyolefin technology comparison. *Pag. 28*
Database of Energy Sources.	This method provides environmental, safety, economic and energetic aspects of the current state-of-the-art technologies for electricity production of several countries all over the world. Results obtained are intended to populate a database to facilitate the technologies selection during early process design activities. In this context, renewable and non-renewable technologies are considered and compared. Results are extremely influenced by specific site location and technology selected. Further applications of this method combined with PDAM are able to monitor a specific plant environmental footprint based on the real supplied electricity source.	Section 2 - Database of energy sources. *Pag. 40*

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ANNEX A

Introduction

The following chapter is dedicated to the description of general features of polymerization process in order to frame and understand better the presented case-studies. Typically, polymerization processes are designed to achieve high versatility in the available range of products. This decision allows to respond in a short timeframe to the various market demands.

Typical products are:

- Propylene homopolymer (Homo)
- Propylene random copolymer (Raco)
- Propylene heterophasic impact copolymer (Heco or HI)

General description of the process

In this chapter, one the most worldwide spread technologies for polypropylene production is briefly described. Spheripol process is a bulk slurry process owned by Lyondellbasell. This technology is characterized by one or two in series slurry loop reactors where the polymer is dispersed and grows in a solution rich of monomer, catalyst, co-catalysts and eventually co-monomers.
Homo and Raco require only the liquid phase loop reactors with additions of hydrogen as a chain terminator. To obtain Random copolymer, it is necessary to introduce in the reactor also an amount of Ethylene equal to 3-4% of the propylene fed. Otherwise, Heco needs a third gas phase reactor where the amount of added Ethylene is increased up to 15-20%. In addition, it is possible to enhance the polymer production using also the gas-phase reactor for Homo and Raco, reducing the residence time in the liquid slurry reactors. The polymerization stage requires 5 auxiliary sections (as shown in Fig. 35):

- The catalyst preparation where the high-yield and high-selectivity catalyst paste is prepared.
- A monomer's purification section to separate monomer from pollutant and toxic components. Required equipment in that part of the plant are function of site-specific hydrocarbons' purities.
- The gas recovery stage where unreacted monomers are recovered and recycled to the feed tank.
- A Downstream section where a steam flow kills the residual catalyst and a nitrogen stream dries polymer.

- An Extrusion section which promotes the introduction of essential additives and the formation of polymeric pellets.

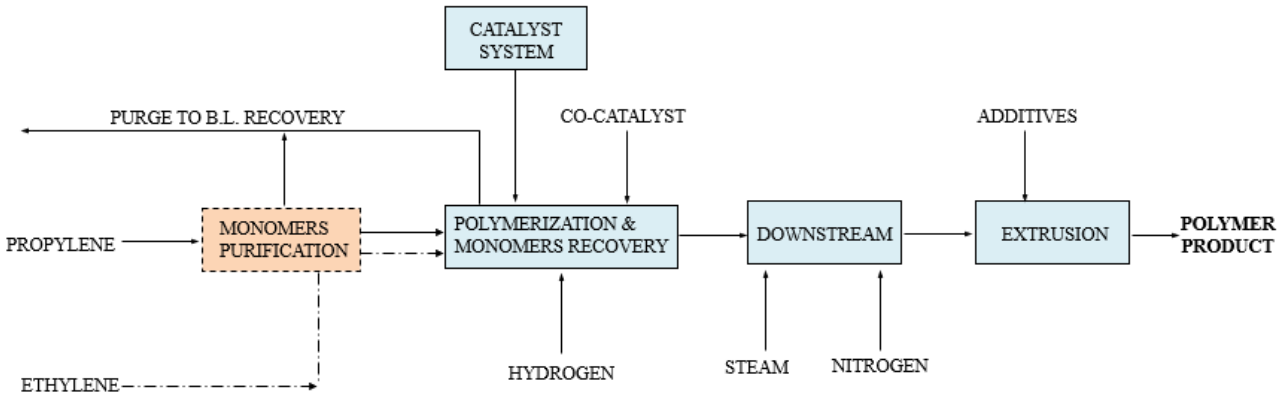

Figure 40: Typical scheme of Spheripol process (B.L. means battery limits of the plant)

Typical alternative configurations

Spheripol process is very versatile. It allows to produce a great variety of polymer pellets that can be transformed in many different products. Each polymer run, requires the introduction of different quantity of chemicals such as: additives, hydrocarbons, hydrogen, catalyst and co-catalyst. In particular, to produce heterophasic co-polymer, a second reaction stage is needed in order to increase the ethylene composition inside the polymer. Nowadays Spheripol process is the result of 40-years of continual improvements. During these years about 120 Spheripol have been licensed with a range of potentiality: from 40 kt/y to 600 kt/y of polypropylene. The annual production of polymer type is a function of the market demand and plant site location, however typically annual percentage are: 30 % of Homo, 10 % of Raco, 60 % of Heco.

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