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Techno-economic analysis of mixed plastic waste-to-chemical plants

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Abstract

The accumulation of plastic waste represents a significant environmental issue, requiring innovative strategies for its effective management and conversion. This thesis explores the gasification of mixed plastic waste into methanol by using two different configurations of chemical reactor: the FastOx gasifier and the fixed bed.

Different process design configurations are considered for each reactor typology, to assess the best options with the aim of maximising the techno-economic performance of the overall system. In particular, the technical performance is assessed by analysing indicators such as efficiencies and performance metrics (e.g. the *carbon conversion efficiency* and the *cold gas efficiency*), while the economic evaluation is carried out to determine the capital cost, operational expenses, and revenues of the plastic-to-methanol plant.

The findings indicate that while both reactors have distinct advantages, the choice of gasification technology largely depends on specific operational objectives and economic limitations. The FastOx reactor exhibits superior efficiency and requires a lower amount of oxygen, making it more suitable for applications requiring high-quality syngas. Differently, the fixed bed reactor provides a more cost-effective solution with simpler operational demands, although with slightly lower performance metrics.

Riassunto esteso

L'accumulo di rifiuti di plastica rappresenta un problema ambientale significativo, richiedendo strategie innovative per una gestione e conversione efficaci. Questa tesi esplora la gassificazione di rifiuti plastici misti in metanolo utilizzando due diverse configurazioni di reattori chimici: il gassificatore FastOx e il tradizionale fixed bed.

Vengono considerate diverse configurazioni di design del processo per ciascuna tipologia di reattore, al fine di valutare le migliori opzioni con l'obiettivo di massimizzare le prestazioni techno-economiche dell'intero sistema. In particolare, le prestazioni tecniche sono valutate analizzando indicatori come le efficienze (e.g. *carbon conversion efficiency* e *cold gas efficiency*), mentre la valutazione economica viene effettuata per determinare il costo del capitale, le spese operative e i ricavi dell'impianto di conversione della plastica in metanolo. I risultati indicano che, sebbene entrambi i reattori abbiano vantaggi distinti, la scelta della tecnologia di gassificazione dipende in gran parte dagli obiettivi operativi specifici e dalle limitazioni economiche. Il reattore FastOx mostra una maggiore efficienza e richiede una minore quantità di ossigeno, rendendolo più adatto per applicazioni che richiedono syngas di alta qualità. Al contrario, il reattore a letto fisso offre una soluzione più economica con richieste operative più semplici, sebbene con metriche di prestazione leggermente inferiori.

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Introduction

The management of the plastic waste is a significant global problem. For this reason, a sustainable waste control is nowadays one of the most challenging issues to be tackled by the modern generations. While the accumulated global waste generation accounted for 267.8 million metric tons in 2017, only 12.7% was processed for energy recovery, and more than 52% of generated plastic waste was landfilled (Sajid et al., 2022). Alternatively, the collected plastic waste can be mechanically treated to recover the valuable polymers. However, due to the limited efficiency of such treatments, the residual ‘untreated’ plastic, a mixture of potentially valuable polymers, represent a significant fraction, and is called ‘mixed plastic waste’.

There are several technologies to convert mixed plastic waste into valuable products, such as mechanical and thermal treatments. Thermal treatments are the best options to deal with waste management because it contributes to energy sustainability improving the environmental management. Among these (direct incineration, gasification, thermal power plant), gasification can convert mixed plastic waste into syngas that can be used to produce chemicals. This work builds on mixed plastic waste gasification to develop and compare different plant configurations for the production of methanol, which is a building block for many of everyday products and a clean energy resource, that can be used as green fuel. In particular, this study proposes a techno-economic analysis of two different technologies of gasification reactor: a traditional fixed bed configuration and a lower technology readiness level (TRL) one, namely labelled as ‘FastOx reactor’, both using oxygen and steam as gasification agents. In addition, for each type of reactor two sub-configurations are considered: one with the implementation of a specific separation technique, called pressure swing adsorption, and the other case without it. The separation technique allows to remove nitrogen and methane from the syngas, that are not involved in methanol production process, allowing to increase the lifetime of the catalyst and avoiding the accumulation of inert inside the plant. Independently from the chosen configuration, downstream syngas generation, the plant involves the methanol production and purification section. The final aim of this work

Introduction

is to compare the techno-economic performance of the investigated plant configurations, to provide insights into the best mixed plastic waste-to-methanol options.

This thesis is structured into three primary chapters that collectively highlight the advantages and disadvantages of the gasification configurations under study. The first chapter provides a comprehensive overview of these gasification methods, along with a rationale for the decisions made throughout the project. The second chapter details the technical and economic methodologies and assumptions employed in the plant simulations, as well as the approach taken to compare the resulting data. The third chapter presents the technical and economic outcomes derived from these simulations.

Chapter 1

Chemical recycling of mixed plastic waste

1.1 Technologies for plastic recycling

Plastics, with its characteristics of being flexible and lightweight, can be used for a huge variety of functions, and it represents one of the most important materials for the modern society. The continuous increase of the plastic waste generation is due to the urbanization, modernization, population growth, its low production cost and its resistance, in addition this is underlined from the increasing of the plastic global production that reaches 322 million tons in 2015 (Lopez et al., 2018).

Due to the intense use of plastic for a daily-use and the short-life applications of this material, the sustainable plastic management, at the end of its life, must include some segregation and a separate collection of valuable materials that can be reused, remembering that the recycling process causes the change of the main properties of the products.

Traditionally, plastic waste was discarded in landfills, but the landfill regulations are becoming more stringent due to the dangerous problems that it causes to the environment, especially to the marine one, due to its low degradability. To diminish the amount of plastic sent to landfill, different approaches can be considered such as reuse, recycling and energy recovery.

To better explain the technologies used to recycle solid plastic waste, a classification of the four main approaches can be listed (Singh et al., 2017):

- *Primary recycling* involves the recycling of single type uncontaminated polymers, that have properties comparable to virgin materials. Typically, it considers injection moulding, re-extrusion and other mechanical techniques.
- *Secondary recycling* includes the mechanical transformation of plastics to become a less demanding products through cutting, shredding and extrusion.

- *Tertiary recycling* does not require the sorting of materials, and it is important for the contribution to the energy sustainability with pyrolysis, cracking and gasification.
- *Quaternary recycling* is carried out when several cycles of primary, secondary and tertiary recycling processes are already applied, because plastics has lost most of its main properties. At this point plastic is used to recover energy through incineration, reducing the volumes of waste that will be sent to landfill.

The focus of this thesis is related to a specific technique of the *tertiary recycling*: the gasification of a particular type of plastic, called mixed plastic waste. The generalities of this process are developed in a subsequent section.

1.1.1 Mixed plastic waste

The large amount of waste is not the only problem connected to plastic, because it also important to consider the large amount of hazardous chemical additives, such as stabilizers and solvents, that are typically utilised to produce polymers of high quality.

Generally, once the plastic waste is collected it is treated through mechanical procedures to recycle the most valuable polymers. The residual part coming from these treatments is a mixture of polymers that is called “mixed plastic waste” (MPW), or “Plasmix” in Italy, and consists of both the undersieve plastic from the size separation equipment and the residual part of mechanical sorting (Figure 1.1).

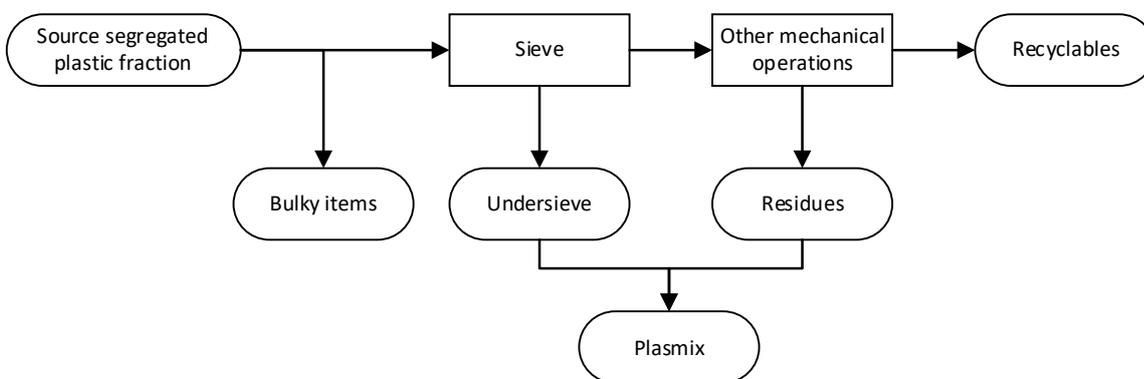


Figure 1.1. General layout of a facility for the selection of material derived from plastic recycling (Cossu et al., 2017).

1.2 Gasification

Chemical recycling of MPW is one of the best possible options for large scale implementations, because products like chemicals, fuels and syngas can be obtained from this class of processes (Seo et al., 2018). In particular, considering the above-mentioned *tertiary recycling*, starting from gasification, different options are available, as outlined in Figure 1.2.

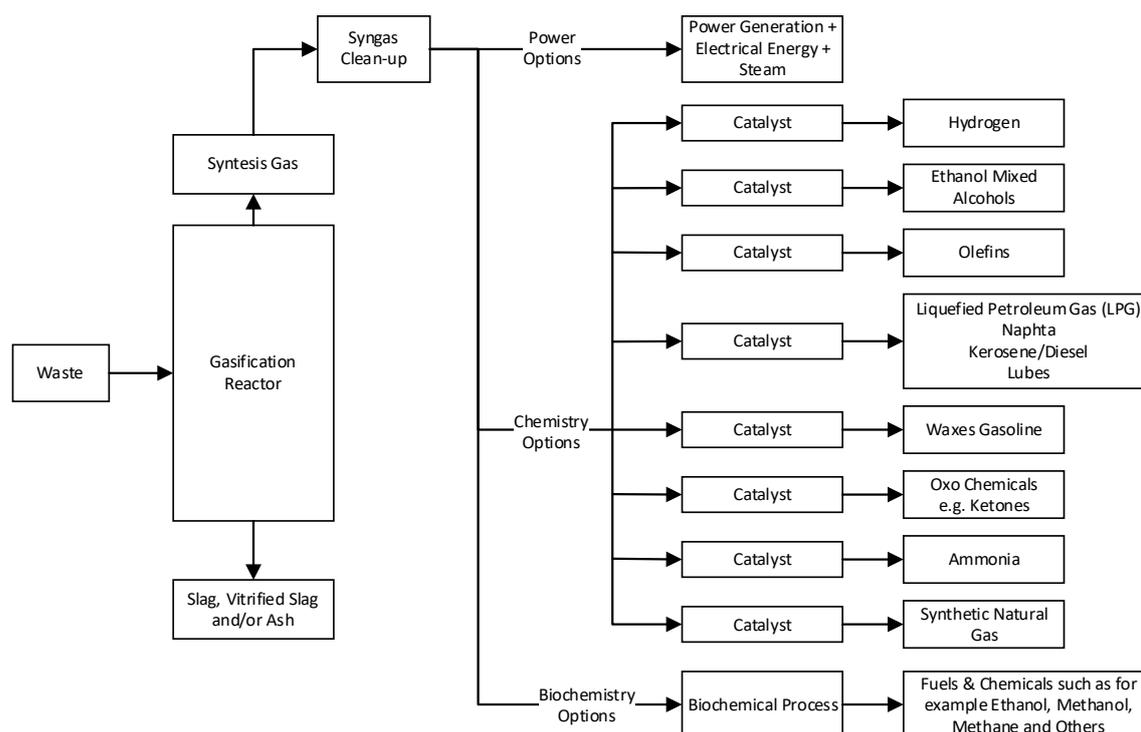


Figure 1.2. Pathway of waste to energy by gasification (Seo et al., 2018).

Advanced thermochemical technologies like pyrolysis and gasification are the most used because of their robustness and good economics, even if the quality of the products is strongly affected by the temperature, waste input and by the specifications of the overall process.

Pyrolysis is not considered here, because of the limited implementation of this technology. This work focusses on MPW gasification.

Gasification represents an important option for MPW management, as it is widely recognised as a method for converting non-recyclable and unsorted MPW into fuels and valuable chemicals, being very versatile in terms of feedstock processing.

In traditional gasification process, MPW together with a gasification agent, is converted into a colorless, odorless and flammable gas mixture, called syngas, made primarily of hydrogen, methane, carbon monoxide and carbon dioxide (and some higher hydrocarbons), that is suitable as heat source, as fuel for combustion, or as feedstock to chemical processes. When syngas is obtained, through the partial combustion of carbonaceous feedstock, at temperatures higher than 750°C and atmospheric pressure, a severe cleaning before its use is necessary if the aim is to reach high-valuable products. In general, the gasification is an endothermic process that transforms carbon-based raw materials into syngas through the following series of chemical reactions in Table 1.1.

Table 1.1. Thermochemical gasification reactions (Santos et al., 2022a).

Reaction	Name
$C + \frac{1}{2}O_2 \rightarrow CO$	Partial oxidation
$C + CO_2 \rightarrow 2CO$	Boudouard reaction
$C + H_2O \rightarrow CO + H_2$	Water gas reaction
$C + 2H_2 \rightarrow CH_4$	Methanation reaction
$CO + \frac{1}{2}O_2 \rightarrow CO_2$	Complete oxidation
$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$	Oxidation of hydrogen
$CO + H_2O \rightarrow CO_2 + H_2$	Water gas shift reaction
$CH_4 + H_2O \rightarrow CO + 3H_2$	Steam reforming reaction

The main drawback of performing the gasification is the formation of tar and ash, that are the main by-products of the reactions, that cause corrosion of the reactor and its blockage. Specifically, tar is a mixture of organic compounds that contains aromatics, polycyclic aromatics, whose decomposition and reforming reactions are the ones named in Table 1.2. The quality of the syngas is connected to the amount of tar present inside of it: lower is the quantity of tar in the syngas and the more is the hydrogen content inside of it, obtaining a high-quality gas.

Generally, the temperature has an effect on the amount of tar formation: higher temperatures lead to low tar content and a higher carbon conversion of the waste into gas phase, but the gas obtained is characterised by a lower heating value.

Table 1.2. Decomposition and tar reforming reactions (Sajid et al., 2022).

Reaction	Name
$C_nH_{2n+2} \rightarrow C_{n-1}H_{2(n-1)} + CH_4$	Cracking
$C_nH_m \rightarrow C + C_xH_y$	Thermal cracking
$C_nH_m + (2n - 0.5m)H_2 \rightarrow nCH_4$	Hydrocracking
$C_nH_m + nCO_2 \rightarrow 2nCO + 0.5mH_2$	Dry reforming
$C_nH_m + nH_2O \rightarrow nCO + (n + 0.5m)H_2$	Steam reforming
$C_nH_m + xH_2O \rightarrow C_xH_y + qCO + pH_2$	Steam dealkylation
$C_nH_m + xH_2 \rightarrow C_xH_y + qCH_4$	Hydro dealkylation
$C_nH_{2n+2} \rightarrow nC + (n + 1)H_2$	Carbon formation

Not only the temperature has an impact on the formation of by-products, but also the gasification agents play an important role (Wang et al., 2023).

1.2.1 Gasification agents

Syngas can be characterised by a wide range of compositions and, for this reason, it can be used for several applications. Different gasification agents can be used to carry out the gasification and improve yield and quality of the syngas. Typically, air, steam, oxygen and carbon dioxide are the most used gasification agents. For simplicity air gasification is the most implemented process because it does not require additional external energy. The drawback of using air as gasification agent is the large amount of nitrogen present, that has an important impact in the gas composition that, in these conditions, is mainly used for energy generation. Sometimes steam gasification is used to obtain a low tar content and hydrogen rich syngas, that can be considered more suitable for chemical applications, with respect of using air. A valuable alternative solution is the use of pure oxygen, instead of air or steam, because it allows not to put nitrogen inside the reactor and to have the benefits of the use of steam, such as the increase of the amount of hydrogen in the product. The only problem related to the use of oxygen is that it is the more expensive solution caused by the high costs related to the operating and the air separation costs, even if the reactor rate and the temperature increase, leading to a higher thermal efficiency (Sajid et al., 2022).

Typically, there is not a univocal choice to carry out the oxidation. In general, the gasification of waste has a restricted number of research due to its early stages of study. Being a globally

endothermic process, there are two pathways to provide the necessary heat: direct (autothermal) gasification in which the heat is generated directly inside the reactor through exothermic reactions, or indirect (allothermal) gasification where the required heat is supplied from an external source.

1.2.2 Gasification reactors

The gasification process can be carried out in different types of reactors. In the past few decades, many types of gasifiers have been developed and ongoing research and studies focused on the improvement of gasifiers. Most of these studies have predominantly examined main gasifier categories including, fluidized bed, plasma gasification and fixed bed (Arena, 2012a; Chanthakett et al., 2021).

1.2.2.1 Fluidized bed reactors

In gasification processes, two classes of fluidized bed reactors have traditionally been utilized: circulating fluidized beds (CFBs) and bubbling fluidized beds (BFBs). Despite the intriguing characteristics of CFBs for the gasification of plastic waste operations, particularly the ability to achieve low tar and high conversion yields, plastic gasification research has been mostly focussed on BFBs due to its advantages. The primary benefits of BFBs are their excellent gas–solid contact, high mass and heat transfer rates, good temperature control and flexibility, and good solid-mixing regime. Their primary drawbacks are their limitations in particle size both in feed and bed, high investment cost, unreacted material entrainment, and defluidization issues (Shah et al., 2023). The advantages and disadvantages are represented in the Table 1.3 below:

Table 1.3. Pros and cons for fixed bed as gasification reactor.

Pros	Cons
Well suited for biomass	Feedstock sorting is necessary
Some feedstock flexibility	Process typically uses only one form of feedstock
	Organic materials require drying
	Low moisture compatibility
	Limited efficiency
	Unable to process large amount of metals or glass

BFB reactors run in a continuous mode and have a high scale and development degree, with various research being conducted in pilot plant scale units. They are usually composed of granular solids such as sand, dolomite, olivine while the temperature is between 540 and 980°C (with small gradients of temperature). The gasses and remaining solids are later separated (e.g., in a cyclone).

1.2.2.2 Plasma reactors

Plasma reactors are a recent technological development aimed to increase efficiencies by increasing temperature over conventional gasifiers (Chanthakett et al., 2021), by passing pressurised gas through a high-voltage electric arc. All the main characteristics of this type of reactor are presented in Table 1.4. The main advantage of plasma reactors for plastic gasification is the high temperature reached (up to 4 425°C), which promotes an almost complete cracking of tar compounds, and therefore high gas yields by enhancing the elimination of harmful and toxic compounds.

Table 1.4. Pros and cons for Plasma as gasification reactor.

Pros	Cons
Low emissions	Low efficiency
Well proven	Large capital investment
Reducing sorting needs	Complicated design and processes
Little to no landfill disposal	Large footprints
Produces useful materials	Multiple units necessary for large capacities
	Expensive to operate

Plasma gasifiers produce syngas and slag, and they have a good feedstock flexibility and a high range of materials that they can process. However, their capital and operating costs are prohibitive, and they use 40-50% of the energy they produce to run the system. This technology has been scarcely applied to the gasification of plastic wastes and, furthermore, the studies have generally been performed in small scale units.

1.2.2.3 Fixed bed reactors

Fixed bed gasifiers are the simplest technology, and this type of reactors includes two different configurations: updraft and downdraft. These different configurations are related to the input of the feedstock and the gasifying agent. The traditional fixed bed reactors operate

at a pressure between 1 and 100 bar and temperature from 500-1200°C (Santos et al., 2022a). Generally, the traditional fixed bed needs sorting of waste before entering the reactor, waste particle diameter up to 100 mm, due to the poor temperature control, there is risk of sintering (Arena, 2012b) and it cannot handle more than 20% moisture.

In downdraft reactor, the feedstock enters at the top of the reactor, but the gasification agents enter from the side or top of the gasifier as shown in Figure 1.3 (Santos et al., 2022b). With this configuration synthesis gas is moved down at the bottom of the bed, in fact it is possible to distinguish the same zones of the updraft one (Arena, 2012b).

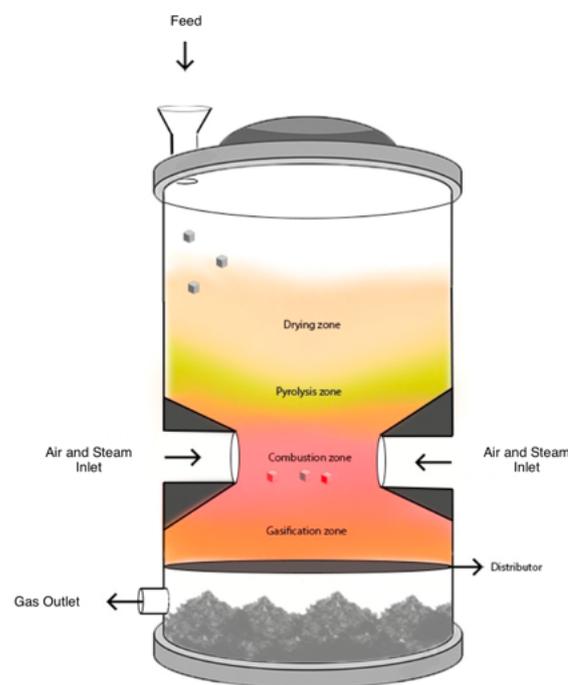


Figure 1.3. Fixed bed downdraft gasifier (Santos et al., 2022b).

In updraft reactors the feed is introduced from the top of the gasifier while the gasification agents enter from the side bottom of the reactor. The syngas is produced along the reactor, passing through different zones (drying, pyrolysis, gasification and combustion), and the output is placed in the upper part of the reactor (Santos et al., 2022b), while ash is deposited and dropped at the bottom. The design of the traditional updraft fixed bed is clarified with Figure 1.4.

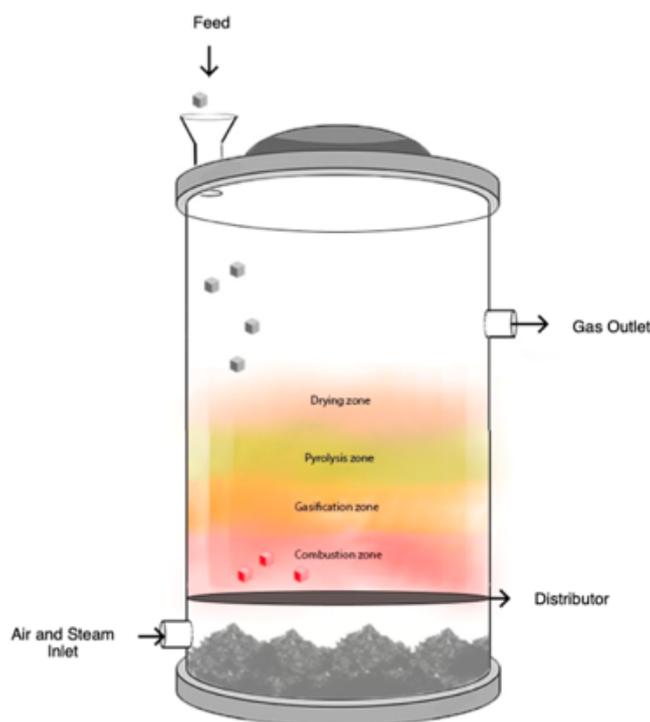


Figure 1.4. Fixed bed updraft gasifier (Santos et al., 2022b).

An industrial application of the updraft fixed bed reactor is the FastOx developed by Sierra Energy. The gasification with this new technology is developed to directly address the limitations of the traditional reactors (Sajid et al., 2022), FastOx gasification combines the high-temperatures of plasma gasification with the streamlined simplicity of low-temperature gasifiers according to the design proposed by Figure 1.5. FastOx gasification is a fixed bed (updraft) gasification system that breaks down feedstock at the molecular level by injecting highly concentrated streams of oxygen and steam at rapid rates. The injections result in extremely high temperatures (around 2,200°C) without capital intensive plasma-arcs or difficult-to-operate molten baths. FastOx gasification drives off 90% of the components in waste (the organic fraction), directly reforming it to clean and high-quality syngas. The syngas is an intermediate fuel used to produce valuable energy products such as electricity, diesel, hydrogen and more. The high temperature of FastOx gasifier allows the remaining 10% of the components in the waste (the inorganic fraction and metallic compounds) to be melted and recovered as recycled metal and inert stone, that can be used or sold as construction aggregate. A key innovation of FastOx gasification is the optimised rate and position of oxygen and steam injection into the gasifier. This drives the complete conversion of waste into its molecular constituents without the production of any major byproducts that

require additional disposal. The average FastOx system is more cost-effective than competing technologies, both as to capital needs and operating costs over the life of the system. This is due in part to its low parasitic load and low maintenance costs related to the fact that it is designed for continuous operation with few moving parts.

The FastOx reactor can deal with a significant variety of wastes (with an approximate size of 1-3 inches), except radioactive and explosive materials, in addition it can handle wastes with moisture up to 50% by weight, even if the optimal moisture content is 20% because higher content will consume large amount of energy with a loss in efficiency.

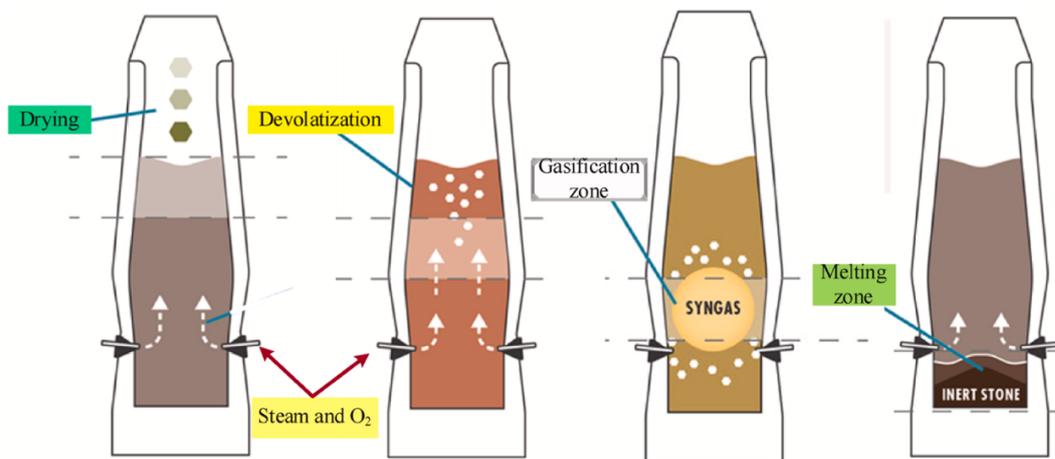


Figure 1.5. FastOx gasification furnace and different stages of gasification process (Sajid et al., 2022)(adapted from Sierra Energy).

The four zones along the new technology reactor can be described as follows:

- *Drying* happens in the top zone of the unit, where hot syngas rises and moves through the waste, evaporating free moisture in the process.
- In the *pyrolysis* zone (704°C), most of the volatile matter is released into syngas. This zone is where a significant amount of the waste's chemical energy is released as a mixture of light gases, hydrocarbons, and condensable tars.
- The *gasification* zone involves the reaction of the remaining carbon-containing materials in the waste (char/fixed carbon and ash) with the injectants. This exothermic reaction generates high temperatures ranging from 1731°C to 2200°C,

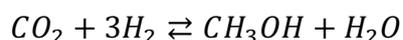
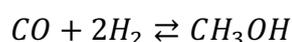
enabling the complete conversion of the remaining carbon into syngas. The energy produced in this stage makes FastOx gasification self-sustaining.

- Inorganic compounds and metals melt due to the high temperatures in the *partial oxidation zone*. These materials collect at the bottom of the unit in a molten state and are continuously removed as inert stone and recycled metals.

At the base of the gasifier, inorganic materials and metals collect in a molten state. This molten liquid is periodically tapped out and cools into a vitrified stone that is very similar in appearance to volcanic rock and suitable for use in landscaping or as construction material aggregate.

1.3 From syngas to methanol

Once the syngas is produced with the conditions described by the gasification process, the production of methanol is carried out and it consists of the hydrogenation of carbon oxides through the following exothermic reactions:



The reactions are carried out using a Cu/Zn/Al catalyst and they are characterised by a decrease of the molar volume, for this reason the favorable conditions for the equilibrium conditions are high pressure and low temperature, respectively 90 bar and 240°C (d'Amore et al., 2023). The catalyst that permits to operate at these conditions is more selective respect to the ones previously used, but it is more sensible to poisons. The activity of the catalyst decreases due to the physical blockage of the active sites, caused from the formation of by-products, that causes the loss of active copper. In fact, the release of heat from the reaction must be kept under control to maintain the optimal reaction rates of the reactions and to maintain the catalyst in its optimal operating conditions. The quality of hydrogen that enters the methanol reactor is important to avoid the poison of the catalyst, and a process called pressure swing adsorption (PSA) can be implemented to remove impurities: it separates

components from a gas stream by selective adsorption to a solid at high pressure, and subsequent desorption at low pressure.

Usually, the reactor for methanol production is gas phase fixed bed reactor, the design of which is reported in Figure 1.6 (Hamelinck & Faaij, n.d.). For methanol production it is assumed that the process is steady-state at thermodynamic equilibrium conditions. To keep the reactor at isothermal conditions, cooling water is used in the shell of the reactor. The catalyst is loaded into tubes and the cooling medium circulates around the outside of the tubes. This type of configuration permits to perform a nearly isothermal operation.

The high sensibility of the catalyst to temperature and the equilibrium condition, determine the conversion of methanol inside the reactor, for this reason a recycle of unreacted reactants is necessary to obtain a high overall conversion.

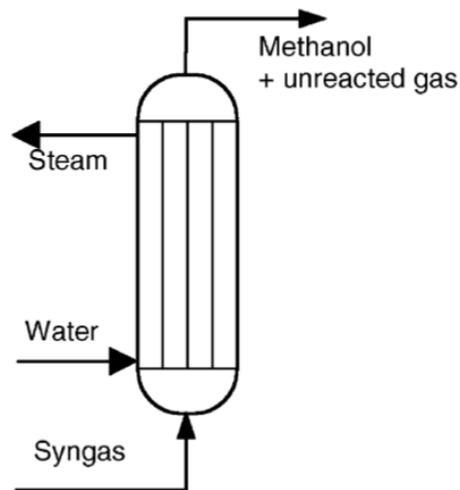


Figure 1.6. Steam raising reactor type (Hamelinck & Faaij, n.d.).

Generally, the methanol that exits from the reactor is separated through a flash drum. The flow rate that exits from the top is partially recycled to the methanol reactor, to convert the remaining reactants, while, from the bottom of the flash the flow rate is sent to a tray separation column, necessary to separate methanol from water, that is a byproduct.

1.3.1 Pressure swing adsorption

To produce syngas suitable for methanol production, it must undergo purification process, to achieve the desired composition, which is called pressure swing adsorption. This purification process involves a series of separations, resulting in syngas enriched with hydrogen, carbon monoxide, and carbon dioxide, and eliminate methane and nitrogen, which are not required for the methanol synthesis reactions. This way, before entering the methanol section, the ratio between hydrogen and carbon monoxide is adjusted (Puig-Gamero et al., 2018). This process involves the use of a zeolite, LiX, that can absorb molecules with the following order: $\text{CO}_2 \gg \text{CO} > \text{N}_2 > \text{Ar} \gg \text{H}_2$. The adsorption affinity of CO_2 is too strong that leads to high regeneration energy requirement, for this reason activated carbons instead of the zeolite are used for removing carbon dioxide. PSA processes often utilise layer beds of multiple adsorbents due to differences in adsorption affinities, and high purity products from multicomponent feeds. In such operations, the zeolite layer must be protected from CO_2 propagation, by placing activated carbons (to remove CO_2 and Ar) in the bottom and the zeolite (that removes CO and N_2) at the top of the layer, because of the challenges in regeneration and the high heat of adsorption (Moon et al., 2016).

1.4 Literature review on MPW gasification

The gasification of MPW is an evolving area of research and technology development. It presents an opportunity to transform non-recyclable plastics into valuable syngas for energy, chemicals, or fuel production.

Research is looking at advanced strategies for plastic waste management, focusing on technologies such as gasification, pyrolysis, and carbon capture to convert waste into valuable resources such as syngas, hydrogen, and fuels. Gasification and pyrolysis have proven to be important methods, with gasification producing syngas through partial oxidation and pyrolysis of plastics. Both approaches contribute to the circular economy by treating complex and contaminated plastics that cannot be mechanically recycled and reducing pollution. However, challenges such as reactor optimization remain significant for their efficiency (Cossu et al., 2017; Dogu et al., 2021; Singh et al., 2017). Research had highlighted the environmental benefits of combining gasification with carbon capture and storage (CCS), which significantly reduces greenhouse gas emissions and produces clean

hydrogen, providing a more sustainable solution compared to traditional incineration (Xu & Shi, 2022). Another study highlighted the potential of supercritical water gasification (SCWG), especially for plastics with high moisture content, to minimize unwanted by-products such as tar and increase syngas yields, especially when combined with biomass or coal (Chari et al., 2023). Further analysis compared six management scenarios for non-recyclable MPW waste and showed that using it as an alternative fuel in cement kilns and blast furnaces provides environmental benefits, while incineration and gasification alone increase emissions (Ciuffi et al., 2020). Furthermore, advances in separation technologies such as laser-induced plasma spectroscopy and magnetic density separation have improved sorting of mixed plastic waste and supported more effective recycling methods. Overall, that study highlighted the importance of optimizing these technologies to improve sustainability and resource recovery in plastic waste management. Gasifying mixed plastic waste using a two-stage gasifier to produce a clean, energy-rich, low-tar, high-calorific value product gas solves the environmental problems of traditional waste management methods such as landfilling and incineration. This two-stage process improved tar removal by using the lower reactor for the primary reaction and the upper reactor for tar cracking with additives such as activated carbon and dolomite. Results showed that tars are significantly reduced, and the gas produced has a high calorific value and low heat release, indicating the possibility of a sustainable energy recovery process (Kim et al., 2011). Another study investigated steam gasification in a dual fluidized bed gasifier to understand how different types of plastics, such as polyethylene and polypropylene, behave during gasification. That study found that plastic blends produce more hydrogen and carbon monoxide than pure polymers due to enhanced reforming reactions, but the production of tars creates operational challenges (Wilk & Hofbauer, 2013). Another work focused on steam-oxygen gasification in a large pilot-scale reactor, to determine the efficiency of the process and its impact on waste-to-hydrogen applications. The significant effects of operating parameters on syngas composition and reactor stability were considered, and kinetic models are validated to optimise the large-scale process (Parrillo et al., 2024a). Assessment of advanced thermochemical processing of mixed plastic waste through life cycle analysis had identified gasification with carbon capture and storage (CCS) as the most promising option to significantly mitigate the emission of greenhouse gases (Arena et al., 2023). This comprehensive assessment highlighted the potential of integrating CCS into various thermochemical processes to improve sustainability in plastic waste management. That paper explored the feasibility of

gasification as a method to convert mixed plastic waste (MPW) into valuable products such as methanol and hydrogen and evaluated two gasification pathways using a dual analysis: techno-economic analysis (TEA) and life cycle analysis (LCA) considering a fluidized bed reactor (Afzal et al., 2023). Results indicated that the minimum selling prices for methanol and hydrogen produced by MPW gasification would be \$0.70/kg and \$3.41/kg, respectively. It also emerged that gasification could help reducing the supply chain energy consumption (in this context, supply chain refers to the comprehensive consideration of all processes involved in the production of methanol or hydrogen, from the initial stages through to the final products) by 52% for methanol and 56% for hydrogen, compared to traditional fossil fuels, but results in higher greenhouse gas emissions. Nevertheless, steam and electricity cogeneration has advantages, such as reduced smog formation and ozone depletion, and gasification is positioned as a promising alternative for the sustainable management of MPW. Another study explored the possibility of converting MPW to hydrogen and methanol in the geographic setting of the European Union, estimating that this technology could produce 2.8 million tons of hydrogen and 14.4 million tons of methanol per year (Zsiborács et al., 2024). This represents a significant opportunity for the EU to diversify its energy sources and improve the efficiency of waste management, while highlighting the need for economic analysis to support sustainable energy solutions (Zsiborács et al., 2024). The feasibility of gasifying MPW for hydrogen production, combined with carbon capture and storage (CCS), has been investigated, which indicates that hydrogen from this process can be economically competitive with fossil-fuel-derived hydrogen and current electrolysis technologies (Lan & Yao, 2022). Life cycle assessments have shown that using CCS reduces environmental impacts, supporting a sustainable way of managing plastic waste while producing low-carbon hydrogen (Lan & Yao, 2022).

1.5 Characteristics of the processes

Related to the gasification technology insufficient knowledge already exists, caused by the multi-scale nature of the process, and the unique properties of the plastic materials and feedstock complexity caused by additives and contaminants.

In addition, these technologies are being investigated quite recently and at an early stage of implementation, a deeper study of the chemistry, of the reactors design and of the overall

process should be carried out to maximise their economic and, most importantly, environmental performance (e.g., by reducing the greenhouse gas emissions).

An interesting point is that usually fixed bed reactors are often used in small scale gasification processes, but it is characterised by the ease in their operation and design, and their low investment cost. Considering these advantages, even if the key problems are the scale up, the limited gas–solid contact, the continuous operation, and a low heat transfer rate (Shah et al., 2023), here is presented a possible large-scale implementation of this type of configuration.

One of the main purposes of this study is the comparison between two different types of fixed bed reactors: the traditional one and the FastOx, underling as operating conditions can change the results. Both are updraft fixed bed reactors, and they can use more than one gasification agent: oxygen and steam are used in this work.

This study operates the traditional fixed bed reactor at a pressure equal to 1 bar and at a temperature of 900°C, determined through a sensitivity analysis, in order to obtain a syngas with a maximised content of hydrogen, and with a low amount of carbon dioxide. The operating conditions of FastOx reactor is determined from theory already expressed in paragraph §1.2.2.3.

This study considers two autothermal gasification processes where the energy, necessary for the endothermic steam reforming reactions, is mainly provided by the partial oxidation of an amount of the feedstock. Most of the industrial waste-fueled gasifiers are developed as steam or air-blown rather than oxygen-blown, and only a very limited experience exists in autothermal steam-oxygen operations, particularly on industrial plants (Parrillo et al., 2024b). This study proposes a large-scale implementation of the use of both oxygen and steam as gasification agents. The first component is necessary to give the required heat, allowing to reach high temperatures through a partial oxidation reaction (it also allows to control the gasification temperature, because too much oxygen would lead to a complete oxidation, and this must be avoided). The presence of steam allows to produce more hydrogen and to decrease the formation of coke. The combination between the two permits to improve the efficiency of the overall process.

The interesting thing of this study, that makes this work even more innovative, is not only the comparison between two different technologies of the reactor, but the study also leads to the comparison of the performances implementing or not a PSA separation before the

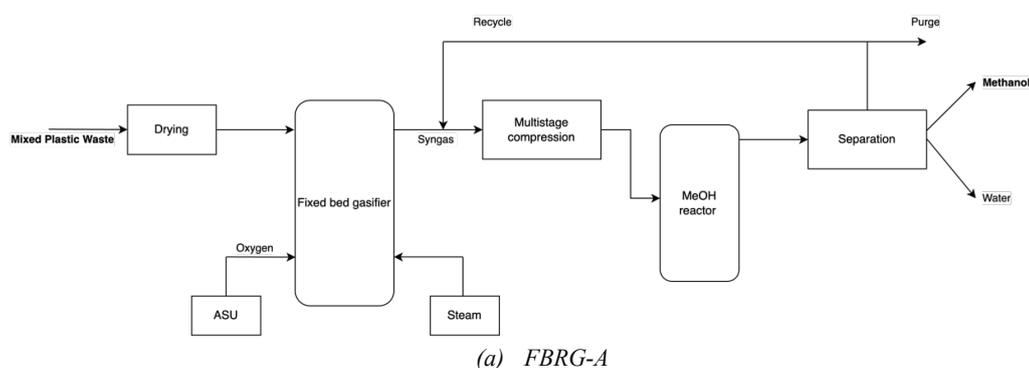
methanol section of the plant. An additional innovation presented in this thesis is the simulation of the entire plants, that permits to obtain methanol, a valuable chemical, from mixed plastic waste that cannot be reused anymore.

Chapter 2

Materials and methods

2.1 Process concept

As the techno-economic assessment of MPW-to-methanol is the final goal of this work, this chapter presents a detailed technical description of the considered design configurations, alongside the methodology employed for the economic evaluation of the plant. In particular, this study compares a total of four different configurations, two of which comprise either a traditional fixed bed reactor (Figure 2.1) and are named as FBRG, or a FastOx fixed bed reactor (Figure 2.2), labelled as FORG. Considering that the new technology FastOx reactor is a particular type of updraft fixed bed gasifier, it is important to compare these two types of reactors in order to understand how the gasification process is improved with respect to the traditional technology. Each reactor type (i.e., FBRG and FORG) is simulated in two scenarios: one involving pressure swing adsorption (i.e., FBRG-B and FORG-B) as a part of the process, and one without the PSA implementation (i.e., FBRG-A and FORG-A). The rationale behind the choice in PSA implementation, or not, is based on the presence of methane and nitrogen in the syngas obtained. These two components are not required for the production of methanol and with the implementation of the PSA, these two components are removed and do not enter the methanol process, avoiding the presence of inert.



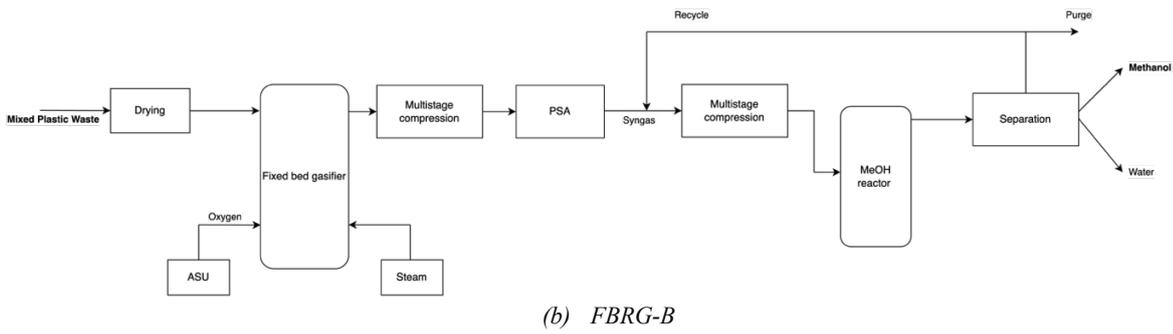


Figure 2.1. Simplified schemes of the process which involves the traditional fixed bed reactor without the PSA (a) and with the PSA (b).

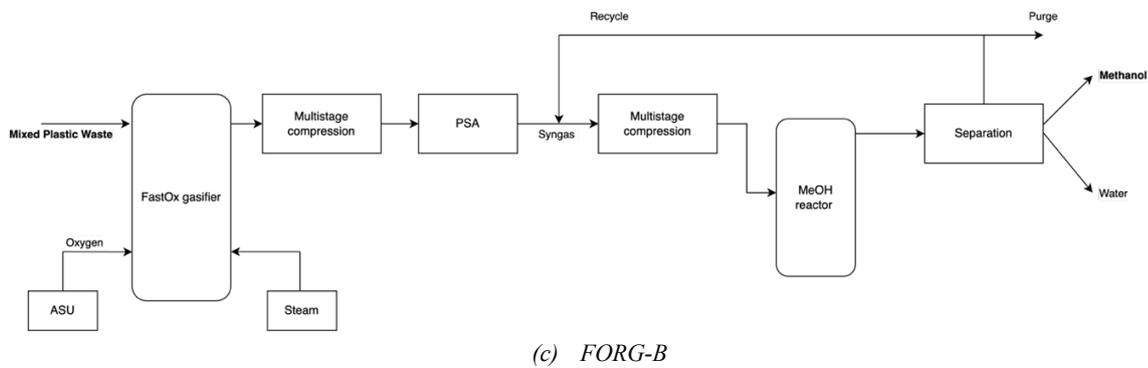
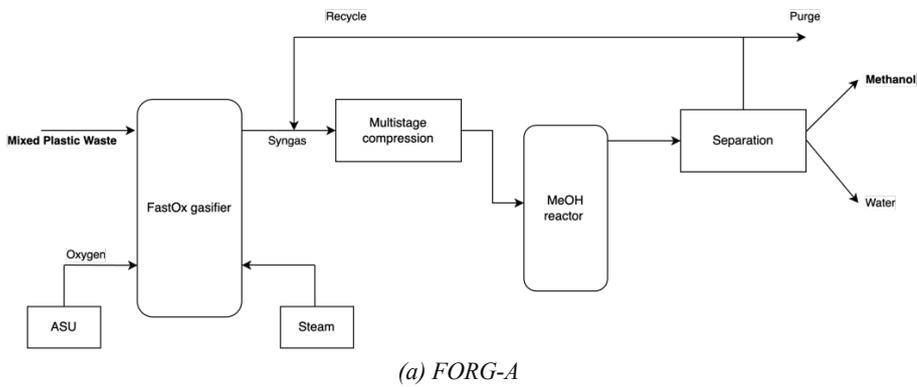


Figure 2.2. Simplified schemes of the process which involves the new technology FastOx reactor without the PSA (a) and with PSA (b).

2.2 Technical plant design

2.2.1 Model properties

The plants are simulated in Aspen Plus software by choosing components for the simulations such as carbon, carbon monoxide, carbon dioxide, hydrogen, methane, methanol, nitrogen, oxygen, sulfur, and water, as well as ash, MPW, and tar as non-conventional ones. The

Redlich-Kwong-Soave (RKS) cubic equation of state with the Boston-Mathias alpha function is utilised for all thermodynamic properties. This model is recommended for gas-processing, refinery, petrochemical applications, and it ensures reasonable results across various pressures and temperatures (Aspen Technology, Inc., 2023). Additionally, it is necessary to define the enthalpy model (HCOALGEN) and the density model (DCOALIGHT) for all non-conventional components in the simulation. The model operates under the assumptions of steady-state conditions, equilibrium state chemical reactions within the gasifier, no pressure loss, ideal gas behavior for all gases, and that carbon and ash remain in the solid phase.

In the study the feed is the same for all the plants considered and it is defined as non-conventional component, as it is previously explained. It is described through the proximate and ultimate analysis (Dogu et al., 2021) with the composition reported in Table 2.1.

Table 2.1. MPW ultimate and proximate analysis.

	MPW Ultimate analysis [wt%]		MPW Proximate analysis [wt%]
Carbon	79.77	ASH	13.3
Hydrogen	15.47	Fixed carbon	0.4
Nitrogen	2.76	Volatile matter	85.7
Sulfur	0.00	Moisture	0.6
Oxygen	2.00		
Gross calorific value [MJ/kg]			39.46

To realistically simulate the actual process, it is essential to account for the amount of tar formed during gasification. It is assumed that 17% by weight of the waste is converted into tar due to pyrolysis reactions in the traditional FBRG (Jamro et al., 2023), whereas the new FORG technology reduces tar formation to 10% [1]. The flow rate of the MPW that enters the processes is calibrated to have the same amount of feedstock really converted into syngas, despite of differences in the amount of tar formed. The considered feedstocks are 5000 kg/hr for FBRG configurations and 4630 kg/hr for the FORG ones.

In the case of the FBRG configuration, before entering the reactor, the feedstock must be dried to reduce the moisture content. The amount of moisture content in the MPW is very low in the proximate analysis considered, but the MPW composition is not uniquely defined and the moisture content can be higher than the one in this study, for this reason the drying

unit is important to implement a standard gasification procedure, that can deal with different compositions of the feedstock.

2.2.2 FBRG plants design

This section highlights the pathways to convert MPW into methanol according to the different configurations: FBRG-A and FBRG-B plants.

2.2.2.1 FBRG-A

Starting considering FBRG-A plant (Figure 2.3) the MPW is initially dried before entering the gasification reactor, which is performed using the saturated steam obtained from the process, (stream #16 in Figure 2.3). Together with the main feedstock also the gasification agents, steam and oxygen (#26 and #5 respectively), enter the reactor, once they are heated up to gasification temperature. The use of air as gasification agent is usually preferred due to its low cost but the presence of nitrogen has a negative effect in the composition and in the heating value of the syngas. The use of pure oxygen, instead of air, allows to increase the thermal efficiency even if the purification of oxygen is an expensive process. The incorporation of steam as gasification agent produces a syngas richer in hydrogen that is more suitable for chemical applications with respect to the syngas obtained through air or pure oxygen gasification (Shah et al., 2023).

The required amount of oxygen for the gasification is obtained using a cryogenic air distillation process through several steps. The ASU involves the use of two distillation columns: one that operates at high pressure, and the other, that is used for the purification of the oxygen, that works at low pressure. The air, whose composition based on molar fraction is 22% of oxygen and 78% of nitrogen (while the presence of argon is neglected) is compressed to 5.5 bar by a three-stages centrifugal compressor with intercooling that permits to keep air at the ambient temperature. The pressure achieved is now the operating pressure of the high-pressure column (HPC) and it is cooled down with a heat exchanger to reach cryogenic temperatures to keep the stream in the safe limit of vapor fraction. With the HPC the cold air is separated in gaseous nitrogen, which is liquefied in the condenser unit, that exits from the top of the column and oxygen enriched liquid from the bottom.

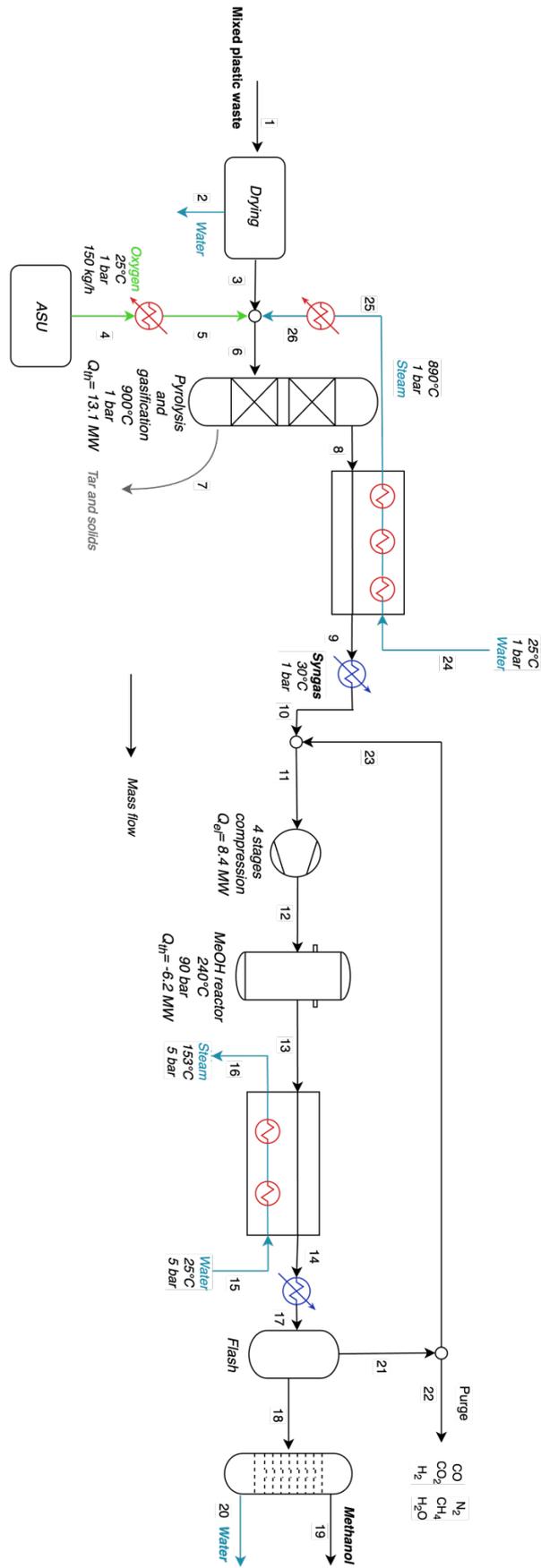


Figure 2.3. FBRG-A.

Both the nitrogen and oxygen streams are expanded to 1.52 bar which is the operating pressure of the low-pressure column (LPC) that is used to obtain pure gaseous nitrogen from the top and pure liquid oxygen from the bottom (with a purity of 99%) (Elhelw et al., 2020). The oxygen is then heated up, with a floating head heat exchanger, to the gasification temperature (by burning natural gas) and the necessary amount is 150 kg/hr that correspond an air flow rate of 777 kg/hr.

The optimal amount of oxygen required for the gasification is determined for all the configurations through a sensitivity analysis (Figure 2.4) in order to maximise the amount of hydrogen and carbon monoxide and minimise the amount of carbon dioxide that exits from the reactor.

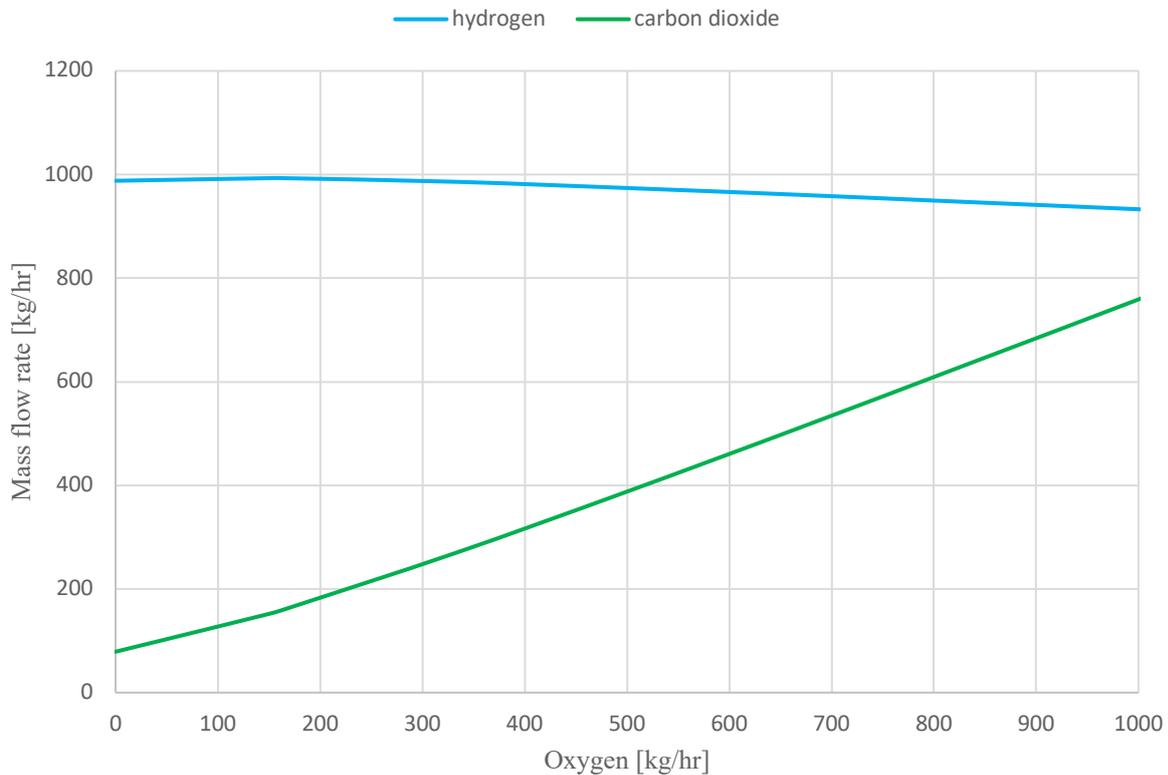


Figure 2.4. Variation of H₂ and CO₂ mass flow rate by the variation of the amount of O₂ injected.

In the same way, through a sensitivity analysis, the optimal amount of steam for the gasification is determined and highlighted in Figure 2.5, showing that the optimal *steam to feed ratio* is equal to 1 for all the configurations and equal to 4142 kg/hr (#26).

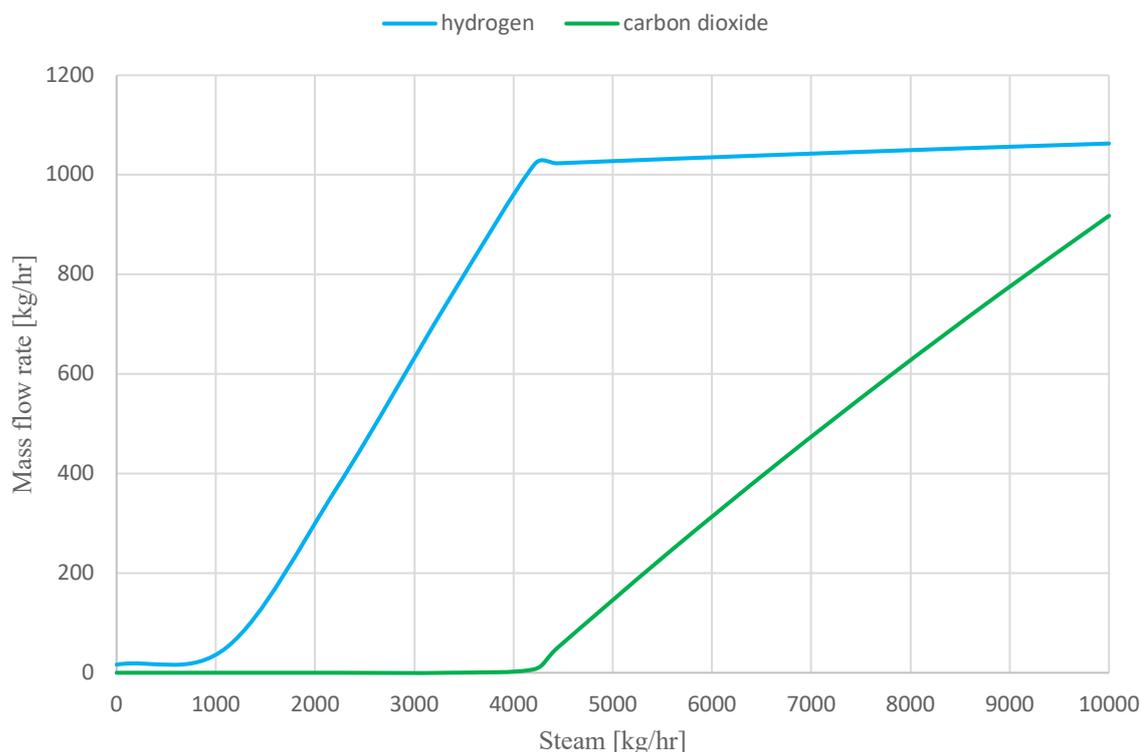


Figure 2.5. Variation of H_2 and CO_2 mass flow rate by the variation of the amount of steam injected.

Part of the steam is obtained using the water coming from the bottom of the distillation column used to separate methanol from water (#20), due to low presence of impurities. This quantity is not enough to generate the necessary steam, so the missing quantity is made of fresh water.

The steam must be at the same temperature of the gasification reactor, for this reason water has to be heated up and vaporised to achieve the desired temperature. Considering both plants, water at 25°C and 1 bar becomes steam at 890°C through a multiple pipe heat exchanger that allows to increase the steam temperature by cooling the syngas that exits from the gasification reactor (#8), that is cooled down from 900°C to 83°C. The T-Q diagram for both FBRG configurations is reported in Figure 2.6 where the red line represents the hot stream that should be cooled down, while the light blue line is related to steam heating, and flat line is the heat necessary for the evaporation of water.

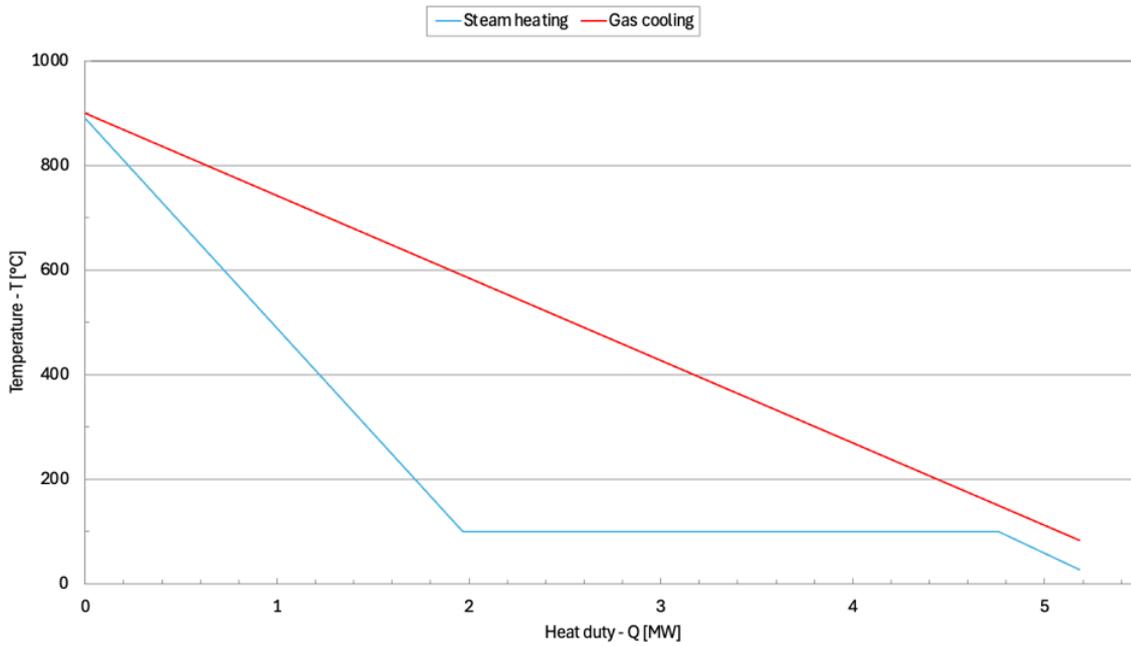


Figure 2.6. T-Q diagram for the FBRG configurations.

The plot shows that the temperature achieved from the steam is lower than the temperature required from the gasification reactor. To increase the temperature to the required one a non-reactive furnace is used, which gives thermal heat by burning natural gas. After the gasification, the temperature of the syngas should be reduced to 30°C using a floating head heat exchanger with refrigerated water (#10) to enter the methanol section.

After the production of the syngas, its composition has the specifications that allow to enter in the production of methanol part of the plant (Ali et al., 2023). The configurations for the methanol production are the same in FBRG and FORG cases (independently on the implementation or not of the PSA). The mole composition of the syngas that enters the process satisfy the module defined as:

$$M = \frac{H_2 - CO_2}{CO + CO_2} \quad (2.1)$$

whose value of 2.05 represents the correct composition for the subsequent methanol synthesis (d'Amore et al., 2023).

Initially the syngas is compressed from 30 bar to 90 bar, through a multistage compressor, pressure necessary to carry out the following desired reactions already mentioned in paragraph §1.3.

The compression is performed using a four stages isentropic compressor, with an efficiency of 0.8 and intermediate cooling. The cooling between stages is operated with tower water that allows to obtain, at the outlet of the compressor, a syngas with a pressure of 90 bar and a temperature of 240°C, that are the required conditions to enter the fixed bed methanol reactor, whose design is shown in Figure 1.3.

The products obtained (#13), that are mostly made of hydrogen, carbon monoxide, carbon dioxide, water and methanol, have to be cooled down. Taking into account that recover heat in any possible part of the plant is important, because it could be used to heat up other flows, in all the configurations is implemented a multiple pipe heat exchanger that allows to cool down methanol, from 250°C (that is the outlet temperature of the methanol reactor) to 162°C. This type of exchanger allows to heat up water (at 25°C and 5 bar) to form low pressure steam (LPS) at 153°C. After this exchanger, an additional one (floating head) is required to cool down the methanol to the flash temperature, equal to 30°C, using refrigerated water as utility. The production of steam is important because it could be used to dry the plastic waste before its entrance to the reactor.

Once that the products are cooled down, they enter the flash, that separates components by reducing the pressure to 1 bar. From the top of the flash, 8% of the stream is purged, which is the lower possible amount to ensure process stability. The recycle is mixed with fresh syngas and the total stream is sent to the compression stages before the methanol reactor (the recycle is not directly sent to methanol reactor because the flash has decreased the stream pressure to 1 bar, while it is necessary high pressure to obtain methanol).

The liquid phase that exits from the bottom of the flash is rich in water and methanol and it is send to the separation section, made of a distillation column, that allows to obtain pure methanol.

2.2.2.2 Distillation column

The liquid stream that exits from the bottom of the flash must be separated through separation column to obtain pure methanol. The tray column allows to separate mainly

methanol, that exits from the top of the column (the boiling point at atmospheric pressure is 65°C), from water that exits from the bottom of the column. The water obtained from the distillation column is used to produce steam as mentioned in paragraph §2.2.2.1 together with fresh water.

Considering that pure methanol is used with a percentage equal or higher than 99.8%, only one distillation column, whose design is presented in Table 2.2, is required to reach the desired purity.

Table 2.2. FBRG-A, distillation column specifications.

FBRG-A	
Number of trays	20
Feed tray number	14
Reflux ratio	1.5
Distillate rate [kmol/hr]	215

The column has an efficiency equal to 0.5 and both, the condenser and reboiler, are floating head heat exchangers that use tower water and low-pressure steam, respectively, as utilities.

2.2.2.3 FBRG-B

Considering the case of FBRG-B the PSA is implemented requiring an additional compression and cooling units respect the FBRG-A configuration. These units are necessary at the exit of the gasification reactor, because the operative pressure of PSA is 30 bar.

For this reason, the syngas that exits from the reactor, once it is cooled down (stream #9 in Figure 2.7), must be compressed through a two stages isentropic compressor, with intermediate cooling and an efficiency of 0.8. The PSA operative temperature is set to 35°C achieved with a floating head heat exchanger that cools down the syngas temperature, with refrigerated water as utility. With the purification of the syngas, through the PSA, almost the total amount of methane and nitrogen is removed together with little amount of carbon monoxide, carbon dioxide and hydrogen. The purified syngas enters the methanol section (#13) that was previously described. The only differences are the split fraction of the purge and the characteristics of the distillation column.

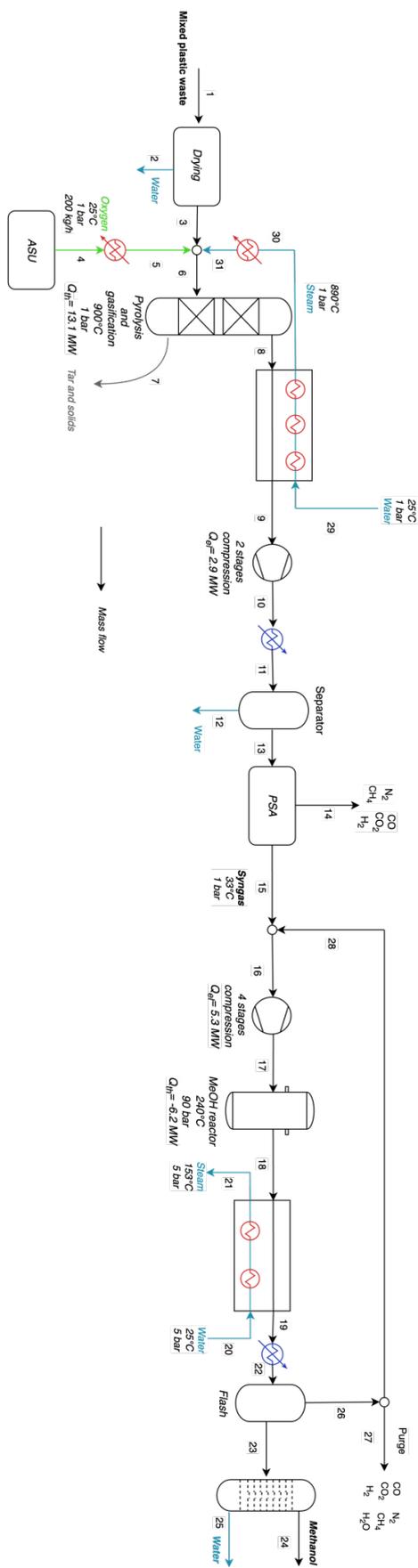


Figure 2.7. FBRG-B.

From the top of the flash, 10% of the stream is purged, while the distillation column design is reported in Table 2.3.

Table 2.3. FBRG-B, distillation column specifications.

FBRG-B	
Number of trays	27
Feed tray number	21
Reflux ratio	0.3
Distillate rate [kmol/hr]	216

2.2.3 FORG plants design

The same procedure is applied for both the FORG plants, but in these cases the gasification operates at 2200°C, that is a higher temperature with respect the gasification temperature in the FBRG configurations, to combine the advantages of plasma and low-temperature gasifiers. In these two cases the drying unit is not necessary because the FastOx can accept a huge types of wastes, with the exception of radioactive and explosive materials. The gasifier can handle wastes with moisture contents of up to 50% by weight although optimal moisture content is 20% and below.

2.2.3.1 FORG-A

As in FBRG configurations, the MPW (stream #1 in Figure 2.8) enters the gasification reactor with oxygen (#3) and steam (#23) as gasification agents. Oxygen is obtained from the same ASU explained before but, in this case, a sensitivity analysis shows that lower amount of oxygen is required for the gasification. The necessary amount of oxygen is 50 kg/hr (Figure 2.9) which correspond to an amount of air equal to 677 kg/hr, that is heated up to the gasification temperature by a non-reactive furnace that burns natural gas that gives the required heat.

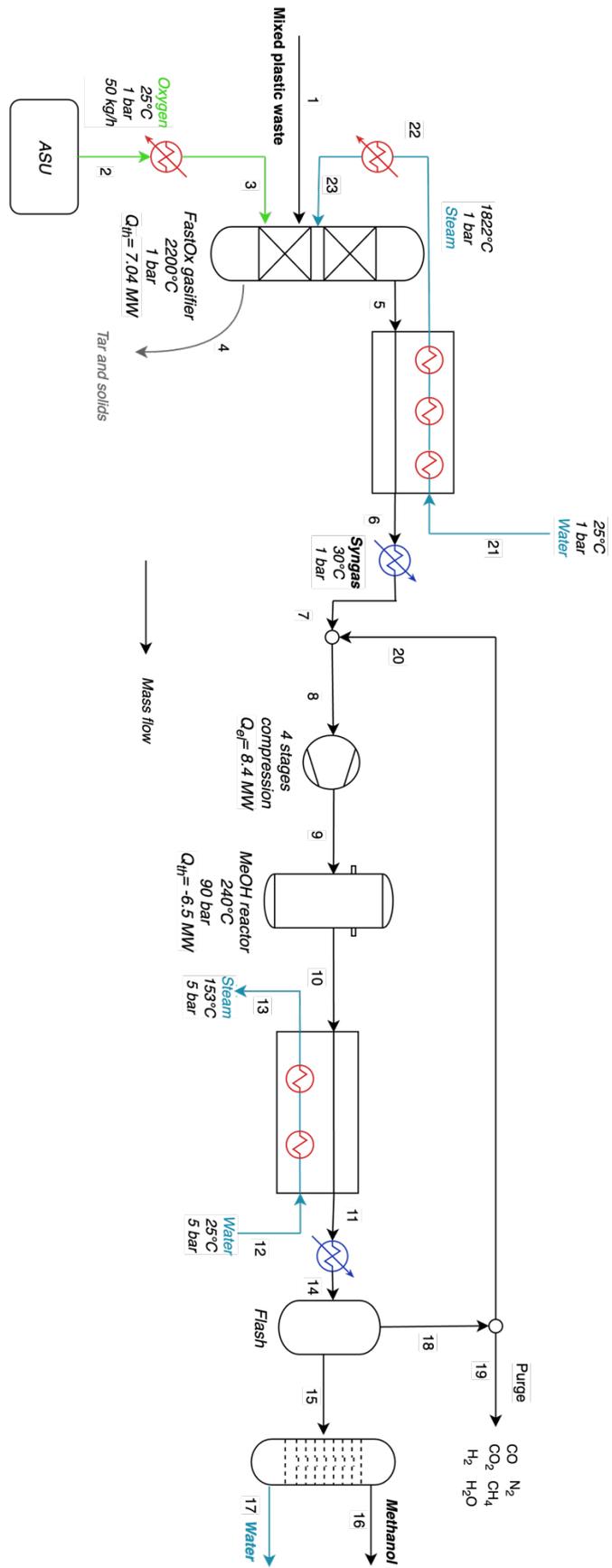


Figure 2.8. FORG-A.

Materials and methods

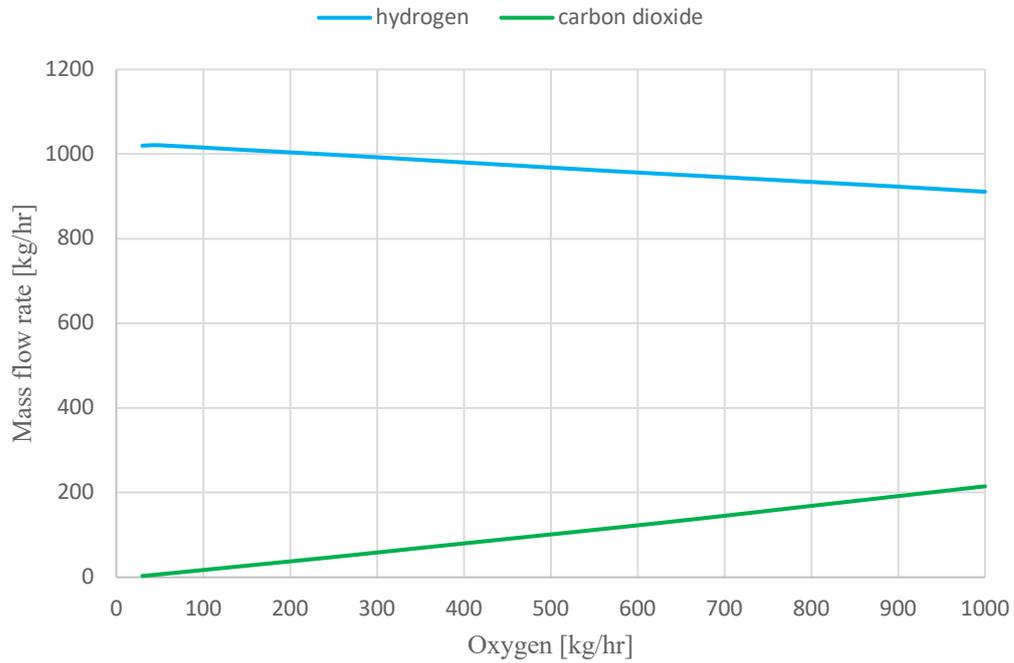


Figure 2.9. Variation of H_2 and CO_2 mass flow rate by the variation of the amount of O_2 injected.

Referring to the steam conditions, a multiple pipe heat exchanger is used to heat up the steam from 25°C to 1821°C , while the syngas that exits from the reactor is cooled down from 2200°C to 1100°C , as shown in Figure 2.10 which represents the thermal situation of both FORG configurations.

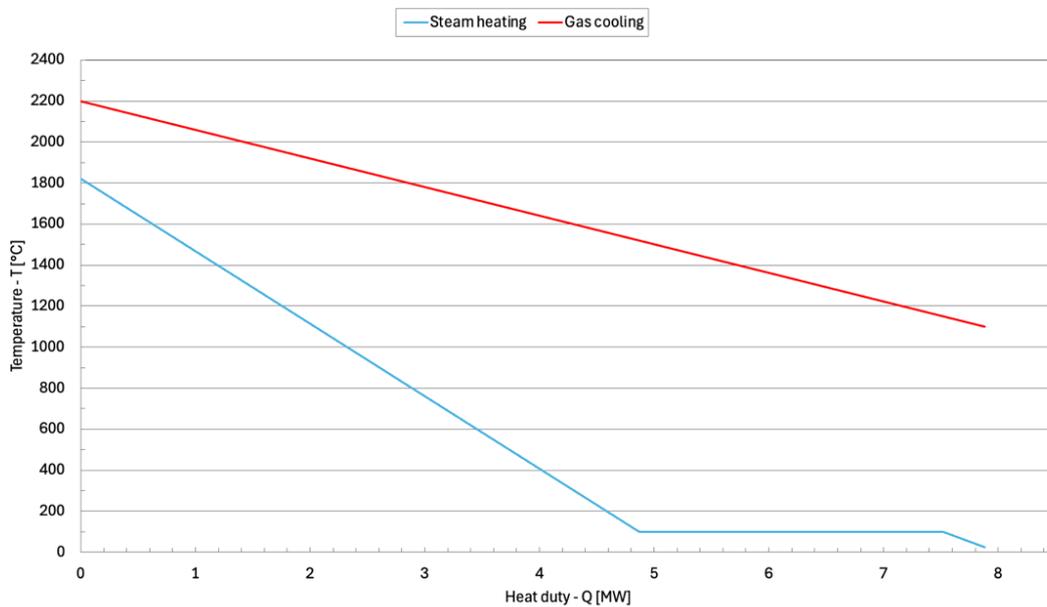


Figure 2.10. T-Q diagram for the FORG configurations.

As the previous case, the temperature reached by the steam is not sufficiently high to enter the gasification reactor, so it is heated up again through a non-reactive furnace that burns natural gas.

Before entering the methanol section, the temperature of the syngas should be reduced to 30°C using a floating head heat exchanger with refrigerated water as utility (#7).

The split fraction of the purge that ensures process stability is 7% and the design of the methanol separation column is reported in Table 2.4.

Table 2.4. FORG-A, distillation column specifications.

FORG-A	
Number of trays	26
Feed tray number	17
Reflux ratio	1.5
Distillate rate [kmol/hr]	222

Differently from FBRG configurations, the FORG ones do not involve the drying section. For this reason, the steam produced by cooling the methanol that exits the reactor (#10) can be used in other parts of the plant, for example in the reboiler of the distillation column, necessary to separate methanol from water.

The cases of FORG configurations, to better represent the reality, the heat considered for the gasification is not the one resulted from the simulation.

The heat required for the gasification is related only to the amount of heat necessary to heat up the mixed plastic waste and to activate the reactor, because the FastOx reactor is self-sustainable in terms of energy, once the reactor is activated. This is related to the fact that it is quite impossible to represent a self-sustainable reaction, at specified temperature and pressure, because the data about the correct amount of oxygen, to keep the reaction self-sustainable, are not available. For this reasons the amount of oxygen considered, as gasification agent, is the one that allows to obtain the more valuable syngas in terms of quantity of hydrogen. The heat necessary to heat up the plastic wastes can be evaluated as:

$$Q = m \cdot C_p \cdot \Delta T \quad (2.2)$$

Where m is the mass of MPW considered that corresponds to 5000 kg/hr, the C_p is the specific heat approximated to the value of 2 kJ/kg °C (Handbook of Biomass Combustion and Co-firing) and ΔT is the difference between the temperature of the gasification and the temperature of the MPW that enters the gasifier.

The heat required to start the reactor its variable and depends on the specific characteristics of the plant and on the scale of the reactor, but it can be approximated to 1 MWh (IEA Bioenergy Task 33 [4]).

2.2.3.2 FORG-B

Neither in the case of FORG-B the drying unit is necessary, but the MPW enters directly the gasification reactor, together with the gasification agents. The syngas produced (stream #6 in Figure 2.11) must be compressed and cooled down to the PSA operative pressure and temperature. The units of process involved are the same as FBRG-B: a two stages compressor with an isentropic efficiency of 0.8 (with intermediate cooling) and a floating head heat exchanger to reach a syngas temperature of 35°C and the pressure of 30 bar (#8). Once the purification of the syngas is carried out, it is ready to enter the methanol production section of the plant (#10). The split fraction of the purge is equal to 10% and the distillation column specifications are presented in Table 2.5.

Table 2.5. FORG-B, distillation column specifications.

FORG-B	
Number of trays	30
Feed tray number	22
Reflux ratio	0.5
Distillate rate [kmol/hr]	222

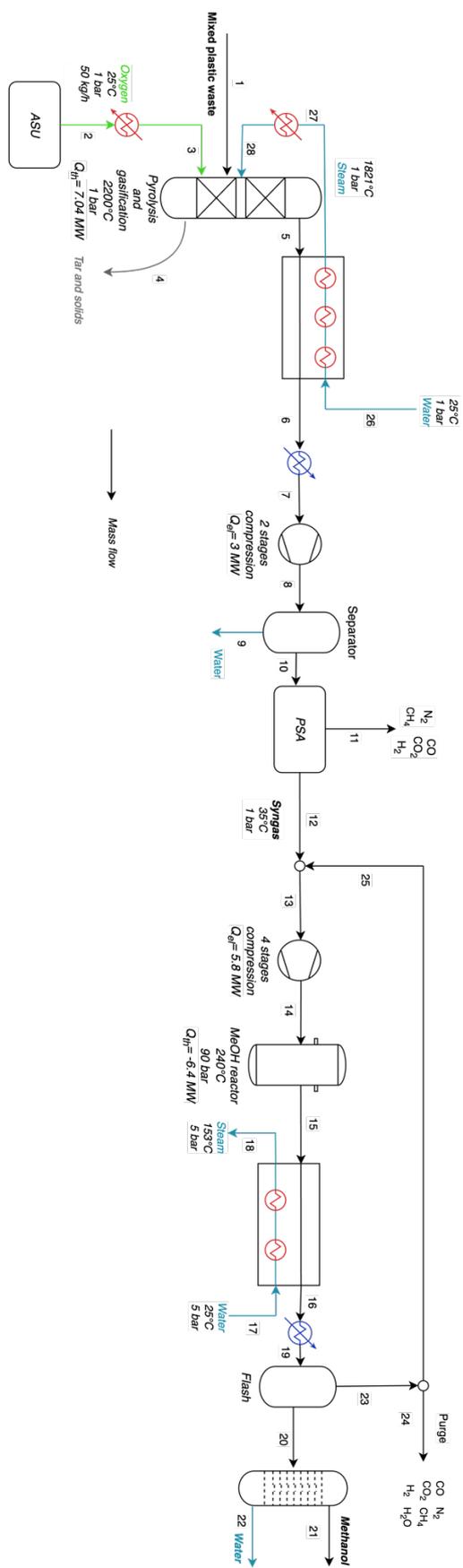


Figure 2.11. FORG-B.

2.2.4 Key performance indicators

It is necessary to calculate some indices that allow to compare and determine the performance of the four processes. The calculated indices are the LHV (*lower heating value*), the CGE (*cold gas efficiency*) and the CCE (*carbon conversion efficiency*) That are calculated according to the formulas below (Mehdi et al., 2023):

$$LHV = (38CO + 25.7H_2 + 85.4CH_4) \cdot 0.0042 \quad (2.3)$$

$$CGE = \left(\frac{LHV_{GAS}}{LHV_{FEED}} \right) \quad (2.4)$$

$$CCE = \left(\frac{\text{moles of carbon syngas}}{\text{moles of carbon feed}} \right) \quad (2.5)$$

The LHV is defined as the amount of heat released by combusting a specified quantity (initially at 25°C) and returning the temperature of the combustion products to 150°C, which assumes the latent heat of vaporization of water in the reaction products is not recovered. In this case it is calculated not only for the syngas production, but it will be calculated also for the gas that exits from the purge. Its calculation allows to determine the amount of heat that can be recovered from the purge stream.

The CCE is defined as the ratio between the carbon molar content in output streams and that in the inlet streams to the process (i.e., how much of the carbon content of the fuel gas is transferred into useful products), while the CGE is the chemical energy contained in the product gas with respect to the energy contained in the initial solid fuel and it can be calculated with respect to the LHV of the solid feedstock.

2.3 Economical methodologies

The economic analysis is performed through the results obtained from the model of the plant simulated with Aspen Plus. The method followed to carry out the economic analysis involves the evaluation of the CAPEX and both the fixed and variable OPEX of all the technical configurations presented in the previous sections.

2.3.1 CAPEX

Once that the main components of the plants are identified, the purchase cost of each piece of equipment that is calculated through the methodology proposed by Turton et al. (4th Edition 2013) based on the following equation:

$$\log_{10} C_p^0 = K_1 + K_2 \log(A) + K_3 [\log_{10}(A)]^2 \quad (2.6)$$

where C_p^0 is the purchase cost evaluated at reference conditions (with a CEPCI value equal to 397), A is a specific capacity or size parameter for the equipment and K_1, K_2, K_3 are tabulated constants. The value of the purchase cost calculated with the formula above (2.6), using parameters in Table 2.6, must be updated with the actual value of CEPCI that corresponds to 799.1 [2].

Table 2.6. Parameters to evaluate the purchase cost.

Process unit	K_1	K_2	K_3	A	Unit
Floating head heat exchangers	4.8306	-0.8509	0.3187	Area	m ²
Non-reactive furnaces	7.3488	-1,1666	0.2028	Duty	kW
Multistage compressors	2.2897	1.3604	-0,1027	Fluid power	kW
Multiple pipe heat exchangers	2,7652	0,7282	0,0783	Area	m ²
Tray columns	3,4974	0,4485	0,1074	Volume	m ³
Sieve trays	2,9949	0,4465	0,3961	Area	m ²

An important assumption is that, due to the low amount of duty required to heat up oxygen, the purchase cost of this unit is not considered in each configuration. While the purchase cost of the furnace to heat up steam is considered only in the case of FORG configurations, where the duty required is considerable. Even if these purchase costs are not evaluated, the necessary utilities are taken into account in the operating expenditure. Neither the purchase prices of the flash drum are considered due to the early stage of the design.

In the case of more complex units of process, the cost is estimated through the six-tenths rule with which the cost of a unit can be retrieved from the cost of a similar unit of different

size, whose capacity is known. In this case the equipment size is non-linearly correlated with purchase cost according to the formula:

$$\frac{C_a}{C_b} = \left(\frac{A_a}{A_b}\right)^n \quad (2.7)$$

where C is the purchase cost, A is the cost attribute for specific equipment and n is the cost exponent referred both to the equipment whose cost is to be estimated (a) and the reference equipment (b). The necessary parameters for the application of the formula above (2.7) are presented in Table 2.7. Also this cost must be updated with the actual value of CEPCI.

Table 2.7. Parameters to use the six-tenths rule.

Process unit	C_b	A_a	A_b	n	Reference
Gasification reactor	19 070	MPW input [kg/hr]	20	0.75	(Zang et al., 2019)
Methanol reactor	113 874	MeOH production [kg/hr]	2007.199	1	(Kgwedi et al., 2023)
PSA	36 560 000	Inlet flowrate [m ³ /s]	4,63	1	(Riva et al., 2018)

In general, the cost of the installed equipment is larger than the purchase cost because it is necessary to consider the piping, the control instrumentation, the building materials, the labour for installation and the insulation. Typically, the actual cost is evaluated from the purchase costs multiplied for a specific scale factor (Lang, 1948; Hand 1958):

- Distillation columns, pressurised vessels, reactors: ~ 4
- Heat exchangers: ~ 3
- Compressors: ~ 2.5

The total installed cost, which is also called *Bare Erected Cost (BEC)*, must take into account also the location factor, equal to 14% for Italy. After that, the *Total Direct Cost (TDC)* is evaluated adding the process contingencies (30% of *BEC*, considering the status of technology at concept with bench-scale data) to the *BEC*. The *TDC* with the *EPC (Engineering, Procurement and Construction)* cost and the project contingencies, allows to obtain the *Total Plant Cost (TPC)*. The *EPC* is considered equal to 14% of *TDC*, while the

project contingencies are evaluated to be 30% of *TDC*, in the case of FBRG configurations, and 40% in the case of the new FORG configurations, by the fact that a simplified design effort is considered. Furthermore, the *Owner and Start-up costs* are assumed to be 10% of *TPC*.

Having all these values, the *Total Capital Requirement (TCR)* can be evaluated, as the summation of *TPC* and *Owner and Start-up costs* (Rubin et al., 2013). At the design level it is assumed that only a fraction, equal to 1/3, of the capital investment weights on the production costs every year.

2.3.2 Fixed and Variable OPEX

The fixed OPEX involves the costs that are independent of changes in production rate, while the variable OPEX considers all the costs required for operating the plant. The calculation of these costs is necessary to determine the *Total manufacturing cost*, that is the sum of the two costs already mentioned.

Starting from the fixed OPEX, the following Table 2.8 presents the methodology used to evaluate its amount.

Table 2.8. Parameters to evaluate the Fixed OPEX.

Item	Unit price
Local taxes and insurance	2% TPC
Maintenance (M)	2.5% TPC
Operating labour (OL)	60 000 €/personnel per year
Maintenance labour (ML)	40% M
Administrative/Support labour	30% (OL+ML)
Depreciation	CAPEX/lifetime of plant

It is necessary to include the evaluation of the depreciation because the plant value decreases with time, due to physical and operational deterioration. During conceptual design, it is common practice to use the simplest depreciation approach: the straight-line method, where an equal amount of depreciation is charged each year.

The process flowsheet can be used to estimate the amount of labour required and accordingly the number of shift operators and their cost. The number N_{OL} of work positions per shift is calculated through equation (2.8).

$$N_{OL} \cong (6.29 + 31.7P^2 + 0.23N_{np})^{0.5} \quad (2.8)$$

P is the number of processing steps involving particulate solids and N_{np} is the number of non-particulate processing steps whose amounts are reported in Table 2.9 which refers to all the type of configurations.

Table 2.9. Parameters to evaluate the number of work positions per shift.

Item	FBRG-A	FIRG-B	FORG-A	FORG-B
P	2	2	1	1
N_{np}	10	12	10	12

At the end, the total number of operators is obtained considering that the number of operators required to provide all the shifts in one position is 5 and the *operating labour* is 5 times N_{OL} .

The variable OPEX involves the calculation of the cost of the utilities, which is determined using Aspen Plus, whose prices are reported in Table 2.10. It is assumed that the plant is operating 8400 hours per year, meaning a stream factor equal to ~96%. The price includes also the cost of the Cu/ZnO/Al₂O₃ catalyst used for the production of methanol, considering the lifetime of the catalyst equal to three years where PSA is implemented, and two years where the configuration does not involve the presence of the purification technique.

Table 2.10. Cost of utilities required for the process.

Utility	Cost
Refrigerated water (5-15°C)	0.14 €/m ³
Cooling water (30-40°C)	0.02 €/m ³
Process water ¹	6.04 €/m ³
Natural gas	6.5 €/GJ
Electricity [3]	125 €/MWh _{el}
Oxygen from ASU ²	0.0041 €/kg O ₂
MeOH catalyst ³	18.1 €/kg

The summation of the fixed and variable OPEX allows to determine the *Total manufacturing cost*.

¹ The cost is retrieved from (Riva et al., 2018) for both: the process water and for natural gas

² The cost is retrieved from (Ebrahimi et al., 2015)

³ The cost is retrieved from (Lacerda de Oliveira Campos et al., 2022)

In the FBRG configurations, the thermal energy required for the flash and part of the thermal energy required for the gasification reactor is given by burning the purge stream. In the FORG configurations the purge stream is used only to give heat to the flash by the fact that the FastOx reactor is self-sustaining. Natural gas is used to heat up steam and oxygen, that enter the gasification reactor, due to the high temperatures that they must reach, for these reasons the cost of natural gas is added to evaluate the total cost of the utilities.

2.3.3 Profitability analysis

The profitability analysis is evaluated considering a discounted technique which involves the determination of some indexes:

- The *discounted payback period (DPBP)* is the amount of time that the project takes to get the point in which the net cash flows generated cover the initial cost of the project.
- The *net present value (NPV)* that represents the cumulative cash position at the end of the project life, with all the cash flows discounted back to time zero. If this quantity is higher than zero, it means that the project is going to earn more than the interest rate.
- The *internal rate of return (IRR)* is the interest rate at which all the cash flows must be discounted in order for the *NPV* of the project to be equal to zero. In other words, it is the maximum interest rate that the project could pay and still break even by the end of the project life

The *interest rate* considered in the project is equal to 0.08 while the plant lifetime is 10 years, typical value of chemical industries. The cumulative cash flow is necessary to perform the profitability analysis, but its calculation requires the knowledge of some parameters. The revenues are the income earned from the sailing of methanol, whose price is equal to 0,644 €/kg (Afzal et al., 2023). It is important to consider that in the first operation years the plant capacity is lower than the nominal one: during the first year about 60% of nominal capacity is reached while the entire capacity is obtained after 3 years of operation. The taxation rate for the calculation of the taxes is considered equal to 48%. Other parameters are evaluated as follow:

$$\mathbf{Gross\ profit = revenues - manufacturing\ costs}$$

$$Income\ tax = gross\ profit \cdot taxation\ rate$$

$$After\ tax\ profit = gross\ profit - income\ tax$$

$$Cash\ flow = gross\ profit - income\ tax - Total\ Capital\ Requirement$$

The *Total Capital Requirement* considered in the evaluation of the cash flow, necessary to carry out the profitability analysis, is the annualised value. As it was mentioned above, it is obtained dividing the total amount by three years. After the first three years, its values must not be considered anymore in the calculation of the cash flow.

Chapter 3

Results and discussion

3.1 Technical analysis

This section presents the results of the simulations in terms of amounts of syngas and methanol obtained from different configurations. The Tables below (Table 3.1, Table 3.2, Table 3.3 and Table 3.4) show the main characteristics of the material flows involved in the production processes of syngas and methanol from MPW.

Starting from the comparison between Table 3.1 and 3.2, it is possible to underline the results obtained with the two FBRG configurations. For each flow, the following information are provided: chemical composition in mass percentage, mass flow rate in kg/hr, molar flow rate in kmol/hr, temperature in °C, and pressure in bar. In some cases, the amount of molar flow rate is not reported due to the fact that the processes involve also the presence of solid components, for which is not possible to determine the number of moles, due to the fact that the molar weight is not constant and clearly defined. This is also the reason why the fractions of the components are reported on mass basis and not on molar basis. The amount of methanol produced, from the same quantity of MPW as feedstock is 6714.01 kg/hr (stream #19) and 6903.61 kg/hr (#24) for FBRG-A and FBRG-B configurations, respectively. The purity of the methanol produced is consistent between these plant designs, and equal to 99%, meaning that in both the cases the desired purity is reached. This means that the presence of the PSA separation does not lead to a higher purity methanol, but it permits to obtain a higher amount of it. This outcome is also related to the amount of mass purged: the mass is almost half in FBRG-B (#27) with respect to the amount of mass that is purged in FBRG-A (#22) configuration. The presence of contaminants (e.g. methane, nitrogen) in the syngas obtained with the FBRG-A configuration requires to have a higher amount of mass flow rate that must be purged after the production of methanol, to avoid their accumulation in the plant.

Table 3.3. FORG-A configuration. Temperature T [$^{\circ}\text{C}$], pressure P [bar], molar flow rate n [kmol/hr], mass flow rate m [kg/hr], and mass ratios X_i [%] of the main streams. Stream numbers referred to Fig. 2.8.

Stream	T [$^{\circ}\text{C}$]	P [bar]	n [kmol/hr]	m [kg/hr]	X_i											
					MPW	H ₂	CO	CO ₂	CH ₄	O ₂	H ₂ O	CH ₃ OH	N ₂	ASH	TAR	
1	25	1	-	4630.00	1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2	25	1	1.56	50.00	0.00	0.00	0.00	0.00	0.00	1.00	0.00	0.00	0.00	0.00	0.00	0.00
3	2200	1	1.56	50.00	0.00	0.00	0.00	0.00	0.00	1.00	0.00	0.00	0.00	0.00	0.00	0.00
4	2200	1	-	1011.11	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.54	0.46
5	2200	1	750.76	7841.11	0.00	0.13	0.85	9.17e-4	2.07e-7	0.00	4.79e-3	0.00	0.01	0.00	0.00	0.00
6	1100	1	750.76	7841.11	0.00	0.13	0.85	9.17e-4	2.07e-7	0.00	4.79e-3	0.00	0.01	0.00	0.00	0.00
7	30	1	750.76	7841.11	0.00	0.13	0.85	9.17e-4	2.07e-7	0.00	4.79e-3	0.00	0.01	0.00	0.00	0.00
8	30	1	1556.27	17242.5	0.00	0.12	0.46	0.04	1.34e-6	0.00	4.11e-3	0.28	0.08	0.00	0.00	0.00
9	240	90	1556.27	17242.5	0.00	0.12	0.46	0.04	1.34e-6	0.00	4.11e-3	0.28	0.08	0.00	0.00	0.00
10	250	90	1089.11	17242.5	0.00	0.07	0.08	0.05	1.34e-6	0.00	2.89e-3	0.72	0.08	0.00	0.00	0.00
11	147	90	1089.11	17242.5	0.00	0.07	0.08	0.05	1.34e-6	0.00	2.89e-3	0.72	0.08	0.00	0.00	0.00
12	25	5	99.91	1800	0.00	0.00	0.00	0.00	0.00	0.00	1.00	0.00	0.00	0.00	0.00	0.00
13	153	5	99.91	1800	0.00	0.00	0.00	0.00	0.00	0.00	1.00	0.00	0.00	0.00	0.00	0.00
14	30	90	1089.11	17242.5	0.00	0.07	0.08	0.05	1.34e-6	0.00	2.89e-3	0.72	0.08	0.00	0.00	0.00
15	30	1	224.46	7160.26	0.00	0.00	0.00	2.24e-4	0.00	0.00	5.73e-3	0.99	0.00	0.00	0.00	0.00
16	40	1	222.23	7119.93	0.00	0.00	0.00	2.26e-4	0.00	0.00	2.02e-4	0.99	0.00	0.00	0.00	0.00
17	100	1	2.22	40.33	0.00	0.00	0.00	0.00	0.00	0.00	0.98	0.02	0.00	0.00	0.00	0.00
18	30	1	864.65	10082.2	0.00	0.12	0.14	0.08	2.30e-6	0.00	8.76e-4	0.52	0.14	0.00	0.00	0.00
19	30	1	60.53	705.75	0.00	0.12	0.14	0.08	2.30e-6	0.00	8.76e-4	0.52	0.14	0.00	0.00	0.00
20	30	1	804.13	9376.41	0.00	0.12	0.14	0.08	2.30e-6	0.00	8.76e-4	0.52	0.14	0.00	0.00	0.00
21	25	1	233.14	4200	0.00	0.00	0.00	0.00	0.00	0.00	1.00	0.00	0.00	0.00	0.00	0.00
22	1822	1	233.14	4200	0.00	0.00	0.00	0.00	0.00	0.00	1.00	0.00	0.00	0.00	0.00	0.00
23	2200	1	233.14	4200	0.00	0.00	0.00	0.00	0.00	0.00	1.00	0.00	0.00	0.00	0.00	0.00

Table 3.4. FORG-B configuration. Temperature T [$^{\circ}\text{C}$], pressure P [bar], molar flow rate n [kmol/hr], mass flow rate m [kg/hr], and mass ratios X_i [%] of the main streams. Stream numbers referred to Fig. 2.11.

Stream	T [$^{\circ}\text{C}$]	P [bar]	n [kmol/hr]	m [kg/hr]	X_i											
					MPW	H ₂	CO	CO ₂	CH ₄	O ₂	H ₂ O	CH ₃ OH	N ₂	ASH	TAR	
1	25	1	-	4630.00	1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2	25	1	1.56	50.00	0.00	0.00	0.00	0.00	0.00	1.00	0.00	0.00	0.00	0.00	0.00	0.00
3	2200	1	1.56	50.00	0.00	0.00	0.00	0.00	0.00	1.00	0.00	0.00	0.00	0.00	0.00	0.00
4	2200	1	-	1011.11	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.54	0.46
5	2200	1	750.76	7841.11	0.00	0.13	0.85	9.17e-4	2.07e-7	0.00	4.79e-3	0.00	0.01	0.00	0.00	0.00
6	1100	1	750.76	7841.11	0.00	0.13	0.85	9.17e-4	2.07e-7	0.00	4.79e-3	0.00	0.01	0.00	0.00	0.00
7	35	1	750.76	7841.11	0.00	0.13	0.85	9.17e-4	2.07e-7	0.00	4.79e-3	0.00	0.01	0.00	0.00	0.00
8	35	30	750.76	7841.11	0.00	0.13	0.85	9.17e-4	2.07e-7	0.00	4.79e-3	0.00	0.01	0.00	0.00	0.00
9	35	30	3.62	37.57	0.00	0.00	0.00	0.00	0.00	0.00	1.00	0.00	0.00	0.00	0.00	0.00
10	35	30	748.67	7803.54	0.00	0.13	0.86	9.21e-4	2.08e-7	0.00	0.00	0.00	0.01	0.00	0.00	0.00
11	35	30	29.93	245.86	0.00	0.19	0.41	2.64e-3	5.94e-6	0.00	0.00	0.00	0.00	0.00	0.00	0.00
12	35	1	718.75	7557.68	0.00	0.13	0.87	8.66e-4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
13	33	1	1052.09	11403.7	0.00	0.12	0.69	3.67e-3	0.00	0.00	1.42e-7	0.18	0.00	0.00	0.00	0.00
14	240	90	1052.09	11403.7	0.00	0.12	0.69	3.67e-3	0.00	0.00	1.42e-7	0.18	0.00	0.00	0.00	0.00
15	250	90	592.92	11403.1	0.00	0.04	0.13	3.45e-3	0.00	0.00	9.49e-5	0.82	0.00	0.00	0.00	0.00
16	161	90	592.92	11403.1	0.00	0.04	0.13	3.45e-3	0.00	0.00	9.49e-5	0.82	0.00	0.00	0.00	0.00
17	25	5	138.77	2500	0.00	0.00	0.00	0.00	0.00	0.00	1.00	0.00	0.00	0.00	0.00	0.00
18	153	5	138.77	2500	0.00	0.00	0.00	0.00	0.00	0.00	1.00	0.00	0.00	0.00	0.00	0.00
19	30	90	592.92	11403.1	0.00	0.04	0.13	3.45e-3	0.00	0.00	9.49e-5	0.82	0.00	0.00	0.00	0.00
20	30	1	222.54	7129.79	0.00	0.00	1.34e-5	2.59e-5	0.00	0.00	1.39e-4	0.99	0.00	0.00	0.00	0.00
21	42	1	222.47	7128.10	0.00	0.00	1.34e-5	2.59e-5	0.00	0.00	1.39e-4	0.99	0.00	0.00	0.00	0.00
22	79	1	0.08	1.69	0.00	0.00	0.00	0.00	0.00	0.00	0.59	0.42	0.00	0.00	0.00	0.00
22	30	1	60.53	705.75	0.00	0.12	0.14	0.08	2.30e-6	0.00	8.76e-4	0.52	0.14	0.00	0.00	0.00
23	30	1	370.28	4273.35	0.00	0.12	0.34	9.17e-3	3.79e-7	0.00	2.16e-5	0.53	0.00	0.00	0.00	0.00
24	30	1	37.04	427.34	0.00	0.12	0.34	9.17e-3	3.79e-7	0.00	2.16e-5	0.53	0.00	0.00	0.00	0.00
25	30	1	333.34	3846.01	0.00	0.12	0.34	9.17e-3	3.79e-7	0.00	2.16e-5	0.53	0.00	0.00	0.00	0.00
26	25	1	233.14	4200	0.00	0.00	0.00	0.00	0.00	0.00	1.00	0.00	0.00	0.00	0.00	0.00
27	1821	1	233.14	4200	0.00	0.00	0.00	0.00	0.00	0.00	1.00	0.00	0.00	0.00	0.00	0.00
28	2200	1	233.14	4200	0.00	0.00	0.00	0.00	0.00	0.00	1.00	0.00	0.00	0.00	0.00	0.00

In the case of FORG configurations there is not a huge difference in the amount of methanol produced: 7119.93 kg/hr (#16) in FORG-A and 7128.10 kg/hr (#21) in FORG-B. Also in this case the desired purity for methanol (i.e., 99.9%) is reached in both the configurations.

The comparison between all the configurations demonstrates that the amount of methanol obtained with FORG configurations is overall higher with respect to the amount of methanol obtained with FBRG ones.

Furthermore, the analysis of the streams permits to determine the mole composition of the syngas that enters the methanol process. The values of syngas module are reported in Table 3.5.

Table 3.5. Values of the module as a function of the configuration of the plant.

Configuration	Module
FBRG-A	2.08
FBRG-B	2.02
FORG-A	2.12
FORG-B	2.06

Considering that this value should be around 2.05, all the configurations satisfy this parameter, independently on the presence of the PSA separation.

To provide a clear and intuitive visual representation of the material flows in the methanol production process, Sankey diagrams are reported below (Figure 3.1). In particular, the mass of carbon has been evaluated where reactions that involve the conversion of carbon take place or where separations are performed. In the diagrams it is reported only the path of the components with a considerable amount of carbon. For this reason, the only component that contains a considerable amount of carbon is the carbon monoxide and methanol, the other components contain a negligible amount of carbon compared to the one present in the mass flow rates considered. This makes it easy to appreciate the changes in mass flow rates (kg/hr) between different stages of the process and allow for a visualisation of process efficiency and resource distribution, providing an immediate understanding of how raw materials and products are divided.

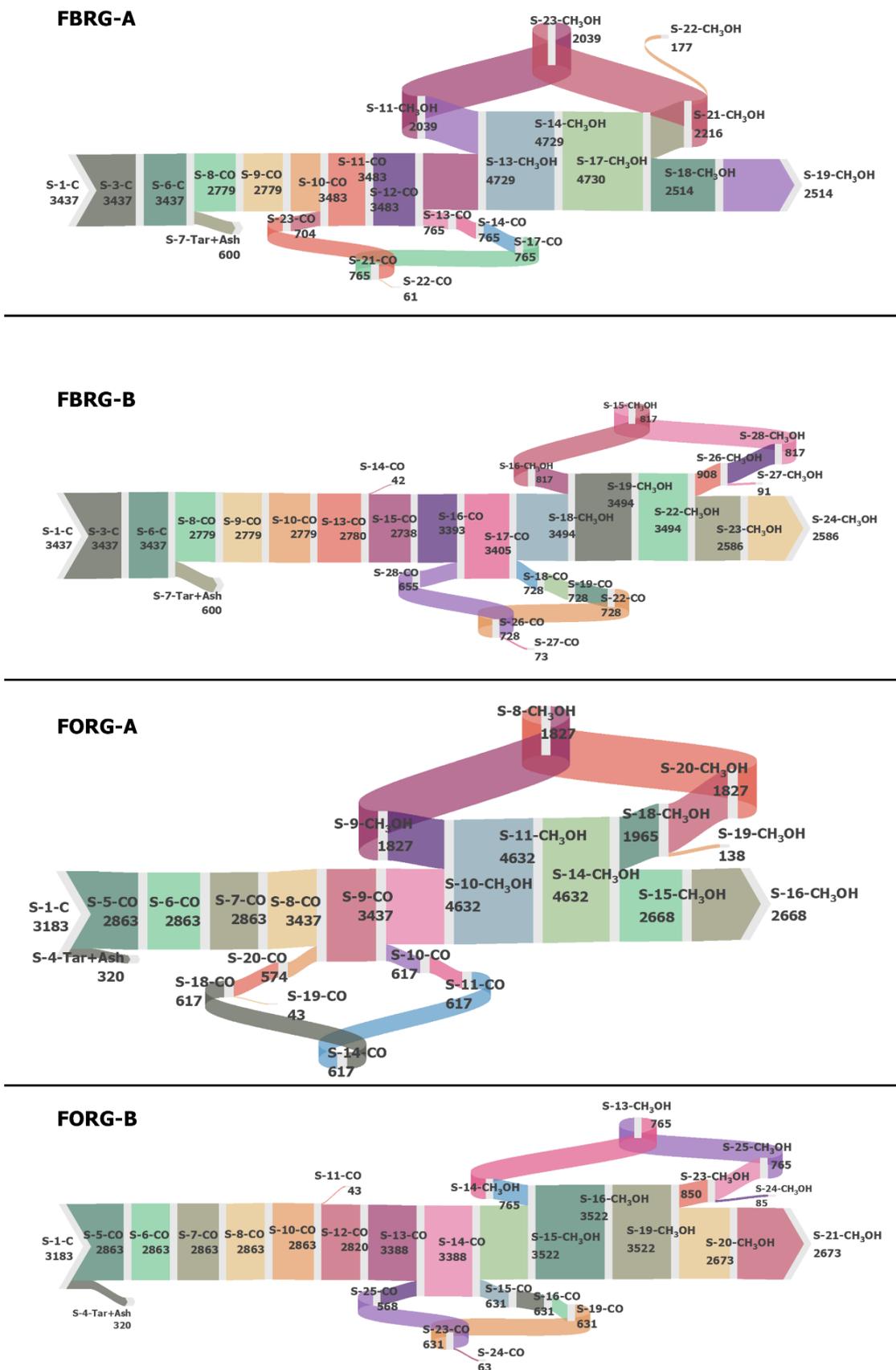


Figure 3.1. Sankey diagrams of FBRG and FORG processes.

These Sankey diagrams present the flux of the carbon that enters the overall plants, and they show how the mass of carbon is divided in different species during the processes. Particularly these Sankey diagrams show how carbon is converted in carbon monoxide and methanol. It is easy to determine that, even if there is a smaller quantity of carbon that enters the process in the case of the FORG configurations, these processes permit to obtain a higher conversion of carbon, meaning that there is a higher amount of carbon that is present in the products, in this case in methanol.

Comparing FBRG and FORG there is another important issue to take into account: the different amount of tar formed. In the case of FBRG configurations it is higher and equal to 600 kg/hr, while the new technology of the FORG allows to obtain almost half amount of tar, equal to 320 kg/hr.

These diagrams highlight also the different quantity of methanol that is purged from the different configurations: the FORG plants lead to a higher quantity of methanol to be purged, meaning that these configurations are characterised from a higher loss in valuable product.

Remembering that the *carbon conversion* and *cold gas efficiencies* are calculated to compare in a consistent way the technical results and the performances of the four different configurations, the results are shown in Table 3.6. That Table mentioned presents the values of the KPIs calculated considering only the syngas production section of the plant, in other words without considering the usage of the syngas to produce methanol.

Table 3.6. KPIs in syngas production.

	FBRG-A	FBRG-B	FORG-A	FORG-B
LHV _{FEED} ⁴ [MJ/kg]	40.2	40.2	40.2	40.2
LHV _{GAS} [MJ/m ³]	11.2	11.3	11.3	11.4
LHV _{GAS} [MJ/kg]	26.7	27.1	27.6	27.7
CGE [%]	66.4	67.3	68.6	69.0
CCE [%]	82.5	81.0	90.0	88.7

The CCE can be calculated involving also the process to produce methanol. One possibility is its calculation starting from mixed plastic waste, obtaining the performance of the overall

⁴ The value of the LHV_{FEED} is taken from literature (Arena et al., 2010)

plant. Another option or is the evaluation of CCE starting from syngas as reactant to methanol, according to the following Table 3.7.

Table 3.7. Values of CCEs in methanol production.

	FBRG		FORG	
	Methanol (A)	Methanol (B)	Methanol (A)	Methanol (B)
CCE [%] from Mixed plastic waste	73.2	75.2	83.8	84.0
CCE [%] from syngas	88.7	92.9	93.1	94.6

The higher value of CCE, considering the overall process whose transform MPW into methanol, is obtained with FORG configurations and, in particular, with the FORG-B one. This configuration, producing a purer syngas, allows to convert more carbon which is present in the waste plastic, into a valuable product.

All the plants are characterised by the presence of a purge, whose flow rate is determined by the splitting fraction defined in paragraph §2.2.4, that is different for any type of configuration considered. The purge is characterised by the presence of different elements: hydrogen, carbon monoxide, carbon dioxide, methane, methanol, water and nitrogen (only where the PSA is not performed). The amount of H₂, CO₂, CH₄ and H₂O are lower where the PSA is performed, reasonably. Due to its composition, the purge can be used to be burned to produce the heat required in some units of process. The heat available can be determined by the LHV for the purge stream. This represents an important issue for the determination of the economic analysis because it permits a lower usage of natural gas.

Table 3.8. LHV of each configuration considered.

	LHV _{purge} [MJ/m ³]
FBRG-A	8.8
FBRG-B	8.5
FORG-A	14.8
FORG-B	9.0

The CCE is connected to the amount of carbon that is present in the desired product, that in this case is only methanol, a sensitivity analysis can be performed to evaluate the amount of carbon produced as a function of the recycle fraction to the methanol reactor. Knowing the variation of the methanol production is proportional to the carbon conversion efficiency,

increasing the percentage of the recycle (meaning that the percentage of the purge decrease), the CCE will increase. Figure 3.2 represents the CCE for FBRG and FORG configurations, and its value considers the overall process, and its calculation is based on the amount of carbon that enters the process (that is the amount of carbon in MPW feedstock) (d'Amore et al., 2023).

The graph shows that the internal recycle is different considering the four processes, this is due to the fact that the process stability is reached at different values of the internal recycle rate as mentioned in the previous paragraphs, related to the processes description. In each case, the value of CCE, is quite high even if the higher values of the CCE are obtained with FORG configurations, particularly, the highest value is reached with FORG-B at its maximum value of the internal recycle.

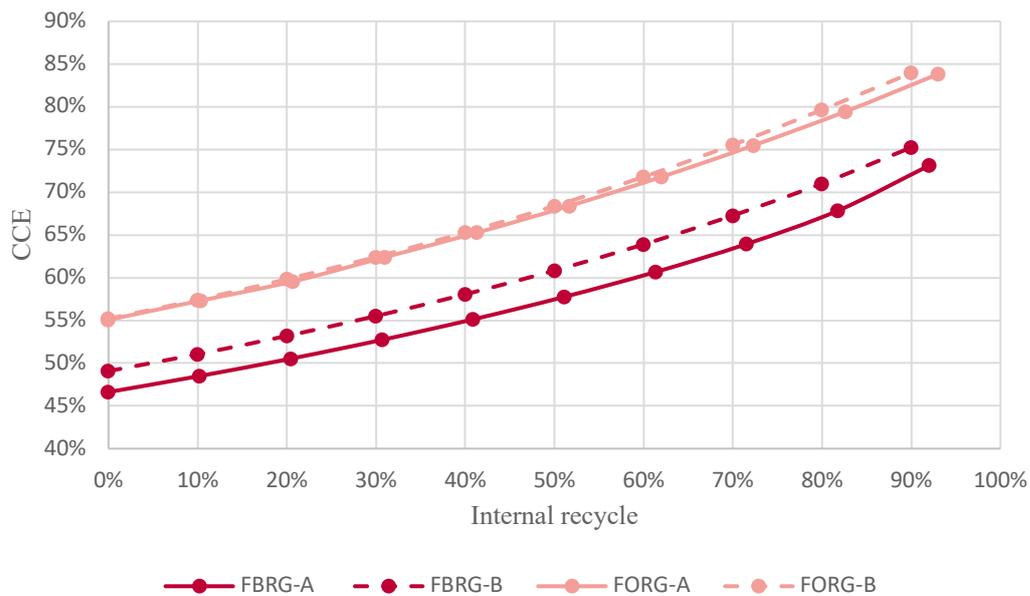


Figure 3.2. Sensitivity analysis of CCE upon variation of the internal recycle.

In industrial and chemical processes, energy management is a critical component of system design and operation. The two primary forms of energy required to maintain efficient process functionality are thermal energy and electrical power. Thermal duties are primarily concerned to the generation, transfer, and management of heat, which is essential for processes such as heating, cooling, phase transitions, and chemical reactions. These thermal requirements are often fulfilled through the use of heat exchangers, boilers, furnaces, and other thermal control systems, which ensure the process operates within the necessary temperature ranges.

Electrical duties, by contrast, involve the provision of power necessary for the operation of machinery, equipment, and control systems. This includes the activation of the compressors of the processes, which are integral to the mechanical and operational aspect. The interplay between thermal and electrical energy demands is a crucial consideration in optimising process efficiency, minimising energy consumption, and achieving sustainable operational goals. To understand the specific thermal and electrical requirements of different processes is important to analyse the values reported in Table 3.9, which underline the amounts that are necessary to give and to remove from the process, considering that the thermal integration was already performed and not take into account at this point. These quantities are essential for the development of energy-efficient designs, cost-effective operation, and the overall success of the industrial systems.

Table 3.9. Thermal and electrical requirements of processes.

Equipment	FBRG-A	FBRG-B	FORG-A	FORG-B
Dryer	0.2 MWth	0.2 MWth	-	-
Gasification reactor	13.10 MWth	13.10 MWth	7.04 MWel	7.04 MWel
Steam heater	-	-	1.29 MWth	1.29 MWth
Multistage compressor 1	-	1.90 MWel	-	1.8 MWel
Compressor 2 cooling	-	-2.05 MWth	-	-1.78 MWth
Additional syngas cooler	-0.32 MWth	-0.2 MWth	-4.51 MWth	-4.34 MWth
Multistage compressor 2	8.44 MWel	5.29 MWel	7.94 MWel	5.22 MWel
Compressor 2 cooling	-5.31 MWth	-3.43 MWth	-5.08 MWth	-1.26 MWth
MeOH reactor	-6.23 MWth	-6.25 MWth	-6.49 MWth	-6.45 MWth
Methanol cooler	-5.2 MWth	-2.64 MWth	-5.27 MWth	-2.59 MWth
Flash	2.13 MWth	0.85 MWth	1.83 MWth	0.77 MWth
Tray column condenser	-4.05 MWth	-4.36 MWth	-3.86 MWth	-4.18 MWth
Tray column reboiler	4.15 MWth	4.44 MWth	3.94 MWth	4.27 MWth

The amount of thermal heat required from the flash unit is reported in the Table above, but the utilities required are not taken into account because it is assumed that the thermal heat required by this unit can be retrieved from the burning of the purge. Furthermore, the Table reports the electrical duty required to turn on the reactor considered in FORG configuration. This amount of is not necessary continuously, for the reasons already mentioned in the paragraph §2.2.3.1, but it is required only two times per year, when the reactor must be turned on after its deactivation for maintenance or other reasons.

3.2 Economic analysis

This economic analysis will critically examine key cost components, including capital expenditures, fixed and variable operational expenditures, as well as potential revenue streams, such as chemical byproducts, and carbon offset credits. Additionally, this analysis will consider external economic factors, such as fluctuating market conditions for energy and raw materials. Initially the economic analysis is evaluated considering that the price to buy raw materials is not taken into account since, as waste, they are not bought, but they are used to generate valuable products.

3.2.1 CAPEX

Starting from the evaluation of the capital expenditures, the Table 3.10 shows the results of the four considered plants, by representing the value of each process unit. The same approach, that starts from the evaluation of the *Total installed cost* is applied also to both the FBRG and FORG configurations.

Table 3.10. CAPEX of FBRG and FORG configurations.

Equipment	FBRG-A	FBRG-B	FORG-A	FORG-B
Gasification reactor⁵	1.46 M€	1.46 M€	7.55 M€	7.55 M€
Steam heater	-	-	1257 €	1903 €
Multiple pipe exchanger (syngas cooler)	424 €	422 €	232 €	232 €
Multistage compressor 1	-	3185 €	-	3103 €
Additional syngas cooler	553 €	519 €	739 €	723 €
PSA⁶	-	1.81 M€	-	1.81 M€
Multistage compressor 2	5404 €	4698 €	5309 €	4827 €
MeOH reactor⁷	2.61 M€	1.93 M€	2.56 M€	1.94 M€
Multiple pipe exchanger 2 (methanol cooler)	492 €	496 €	380 €	486 €
Methanol cooler	1242 €	920 €	1228 €	908 €
Tray column	2.64 M€	3.34 M€	2.97 M€	3.39 M€
Total purchase cost	6.72 M€	8.55 M€	13.09 M€	14.70 M€
Total installed cost with location factor (14% Italy)	7.66 M€	9.75 M€	14.92 M€	16.76 M€

⁵ The cost is retrieved through a scale up with value taken from (Zang et al., 2019)

⁶ The cost is retrieved through a scale up with the value taken from (Riva et al., 2018)

⁷ The cost is retrieved through a scale up with the value taken from (Kgwedi et al., 2023)

The results demonstrate that the presence of the PSA separation has a huge impact in the *Total purchase cost*. From the table it can be analysed that the B configurations require an additional compressor that, even if in a small percentage, impacts on the total price, that is a little bit higher. The FBRG-B takes up a *Total installed cost* that is 27.3% higher with respect to the simplest FBRG-A. While, the FORG-B, presents a cost that is 12.3% higher than the FORG-A.

An additional difference between the FBRG and FORG is that the purchase cost of the furnace to heat up steam is considered only in the case of FORG configurations, where the duty required is considerable.

The methodology presented in the section §2.3.1 permits to determine the *Total Capital Requirement* (Table 3.11) of the FBRG and FORG plants, that can be annualised dividing its value by 3.

Table 3.11. Evaluation of the TCR.

	FBRG-A	FBRG-B	FORG-A	FORG-B
Total Direct Cost	9.96 M€	12.67 M€	19.39 M€	21.79 M€
Total Plant Cost	14.34 M€	18.24 M€	29.87 M€	33.55 M€
Total Capital Requirement	15.77 M€	20.07 M€	32.85 M€	36.91 M€
Annualised Capital Requirement	5.26 M€/year	6.69 M€/year	10.95 M€	12.30 M€

By the fact that the *Total Capital Requirement* derives from the evaluation of the *Total Installed cost*, the table shows that the *Annualised Capital Requirement*, that represent the minimum capital that a company must hold on an annual basis to cover specific financial risks, ensuring its long-term stability and solvency, is higher in the case of FBRG-B as it was expected.

3.2.2 Fixed and variable OPEX

Table 3.12 reports the results of the fixed and variable operational expenditures of all the configurations. It is important to highlight that the cost of the utilities does not include the cost of the catalyst (0.19 M€). Its cost must be added every two years in the cases where the separation (PSA) is not implemented (A-configurations), while every three years in the other two cases (B-configurations). This is due to the fact that the presence of contaminants

decreases the lifetime of the catalyst. The values of the utilities considered in this table are referred to a cost of electricity that corresponds to 125 €/MWh_{el}.

Table 3.12. Fixed and Variable OPEX for FBRG and FORG, configuration, with cost of electricity equal to 125 €/MWh_{el}.

	FBRG-A	FBRG-B	FORG-A	FORG-B
Fixed OPEX				
Local taxes and insurance	0.29 M€/year	0.37 M€/year	0.60 M€/year	0.67 M€/year
Maintenance	0.36 M€/year	0.46 M€/year	0.75 M€/year	0.84 M€/year
Maintenance labor	0.14 M€/year	0.18 M€/year	0.30 M€/year	0.34 M€/year
Operating labor	5.72 M€/year	6.07 M€/year	4.91 M€/year	5.32 M€/year
Administrative and support labor	1.76 M€/year	1.87 M€/year	1.48 M€/year	1.70 M€/year
Depreciation	1.58 M€/year	2.01 M€/year	3.29 M€/year	3.69 M€/year
Total Fixed OPEX	9.84 M€/year	10.95 M€/year	10.38 M€/year	12.55 M€/year
Variable OPEX				
Utilities	11.58 M€/year	10.40 M€/year	10.47 M€/year	9.01 M€/year
Total manufacturing cost	21.80 M€/year	21.54 M€/year	21.22 M€/year	21.75 M€/year

The values of the utilities for FORG configurations involve the energy required to turn on the reactor, which is evaluated as mentioned in the methodologies, assuming that the reactor must be activated two times each year.

The *Total manufacturing cost* is almost the same for all the configurations. Typically, the absence of high number of moving parts in the new FastOx reactor, should theoretically lead to a lower maintenance cost. In this case the maintenance of the new technology is considered as the same percentage of the traditional fixed bed, obtaining a higher cost for FORG maintenance with respect to FBRG. This is due to the fact that the FastOx is a new technology and could require additional costs to unknown problems.

As previously mentioned, the economic analysis can also be performed considering a more advantageous cost for the electricity, equal to 80 €/MWh_{el}. Considering that, the utilities are the only cost that is affected by the cost of electricity, their different values, that will affect the value of the *Total manufacturing cost*, are reported in Table 3.13.

Table 3.13. Utilities and Total manufacturing cost with price of electricity 80 €/MWh_{el}.

	FBRG-A	FBRG-B	FORG-A	FORG-B
Utilities	8.38 M€/year	7.66 M€/year	7.47 M€/year	6.37 M€/year
Total manufacturing cost	18.22 M€/year	18.61 M€/year	17.85 M€/year	18.92 M€/year

Considering this advantageous price for electricity, the case of FORG-B is the configuration that presents a lower decrease of the *Total manufacturing cost* (i.e., 13%), meaning that this is the configuration that is least affected by the electricity price. Differently, the FBRG-A is the configuration mostly affected by the price of electricity, in fact, with this advantageous cost for the electricity, the decrease with respect the value reported in Table 3.11 is equal to 16.4%.

3.2.3 Profitability analysis

The profitability analysis is evaluated considering a discounted technique which involves the determination of the *discounted payback period (DPBP)*, the *net present value (NPV)* and the *internal rate of return (IRR)*, reported in Table 3.14. The *interest rate* considered is equal to 0.08 while the plant lifetime, that does not reflect the actual working life of the equipment, but the time allowed for depreciation, is 10 years, typical for chemical industry.

Taking into account that the difference value of the price for electricity causes a change in the *Total manufacturing cost*, this will also affect the profitability analysis. For this reason, the profitability analysis can be performed with both the values of the electricity, and the results are presented in Table 3.14.

Table 3.14. Profitability analysis.

	Electricity price	DPBP	NPV	IRR
FBRG-A	125 €/MWh _{el}	4.1 years	25.30 M€/year	34%
FBRG-B	125 €/MWh _{el}	4.4 years	25.82 M€/year	32%
FORG-A	125 €/MWh _{el}	5.9 years	19.53 M€/year	21%
FORG-B	125 €/MWh _{el}	6.9 years	13.66 M€/year	16%
FBRG-A	80 €/MWh _{el}	3.0 years	38.15 M€/year	54%
FBRG-B	80 €/MWh _{el}	3.5 years	36.79 M€/year	45%
FORG-A	80 €/MWh _{el}	4.6 years	31.58 M€/year	30%
FORG-B	80 €/MWh _{el}	5.5 years	24.24 M€/year	23%

Knowing that a more profitable project will have a higher IRR, in this case it can underline that the more profitable configuration is the simplest one, the FBRG-A, which considers a traditional fixed bed reactor, without the implementation of the PSA separation.

As it was expected, the IRR values of this case are higher with respect to the case in which is considered a higher value for the price of electricity. Also in this case it is obvious that the higher value of IRR is obtained with FBRG-A configuration as before. The NPV, that represents the cumulative cash position at the end of the project life, is higher with a lower price for electricity, meaning that in this case all the configurations are more profitable than the previous case, with a lower value of DPBP.

The clarification of the results presented in Table 3.14. can be obtained by plotting the trend of the cumulative cash flow, with respect the plant lifetime years, for each configuration (Figure 3.3 and 3.4).

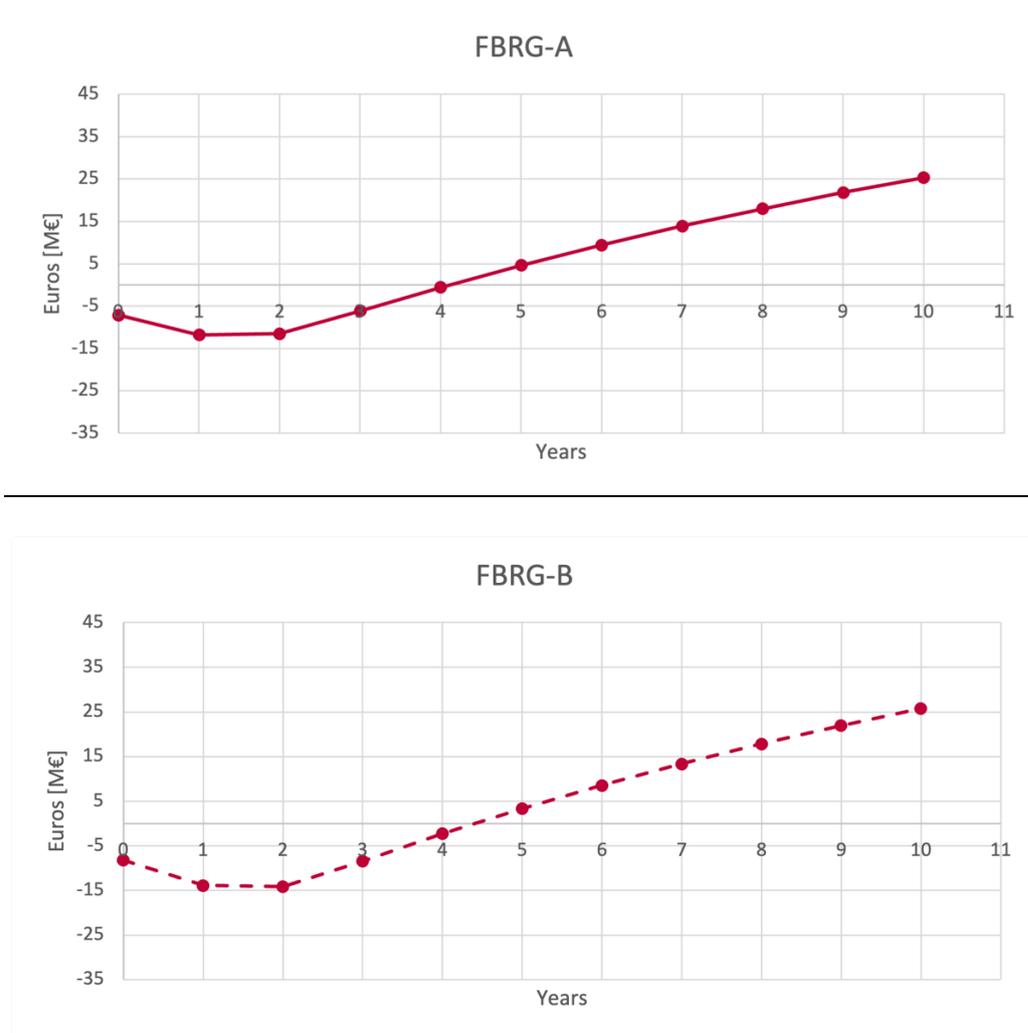


Figure 3.3. Cumulative cash flow for FBRG configurations, with the cost of electricity equal to 125 €/MWh_{el}.

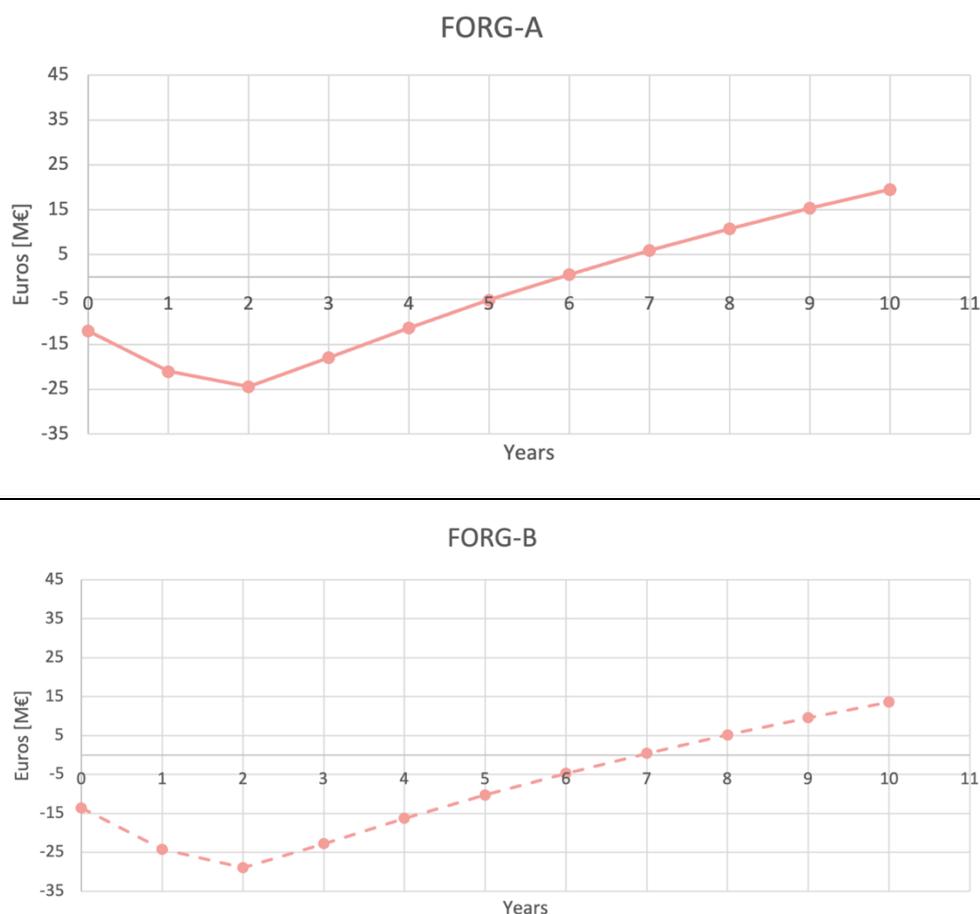


Figure 3.4. Cumulative cash flow for FORG configurations, with the cost of electricity equal to 125 €/MWh_{el}.

These plots help to visualise the trend of the cash flow, making more easily to understand that the NPV reaches a higher value in the case of FBRG configurations, with a smaller payback period.

The lower NPV is reached from the FORG-B configuration. This is caused to the fact that this configuration is characterised from the higher value of the *Total Capital Requirement* and from a high value of the *Total manufacturing cost*.

The trend of cumulative cash flow, with respect to the plant lifetime years, are reported also considering the different price of electricity as performed for the economic analysis.

As mentioned before, and highlight in Figure 3.5 and 3.6, the FORG-B is the configuration that is less affected by the price of electricity, while the FBRG-A is the one that is mostly affected.

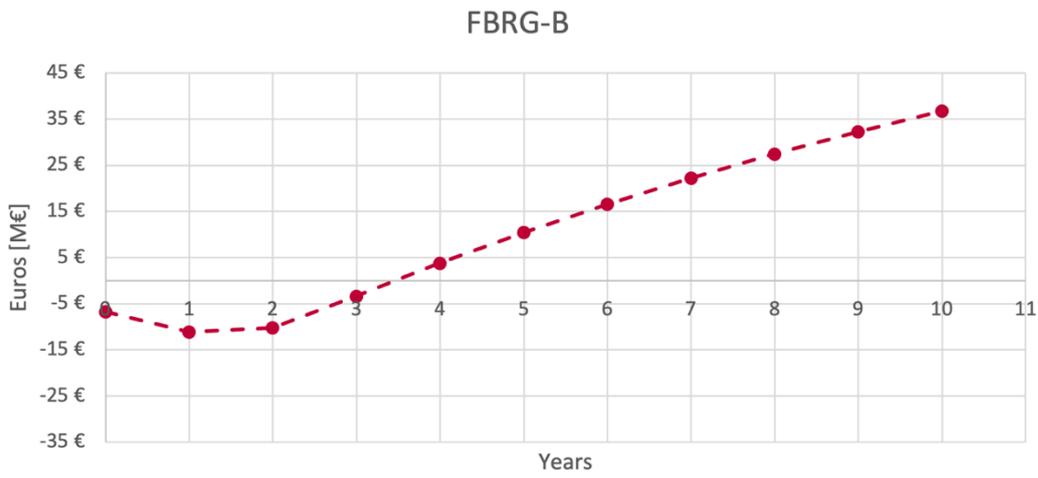
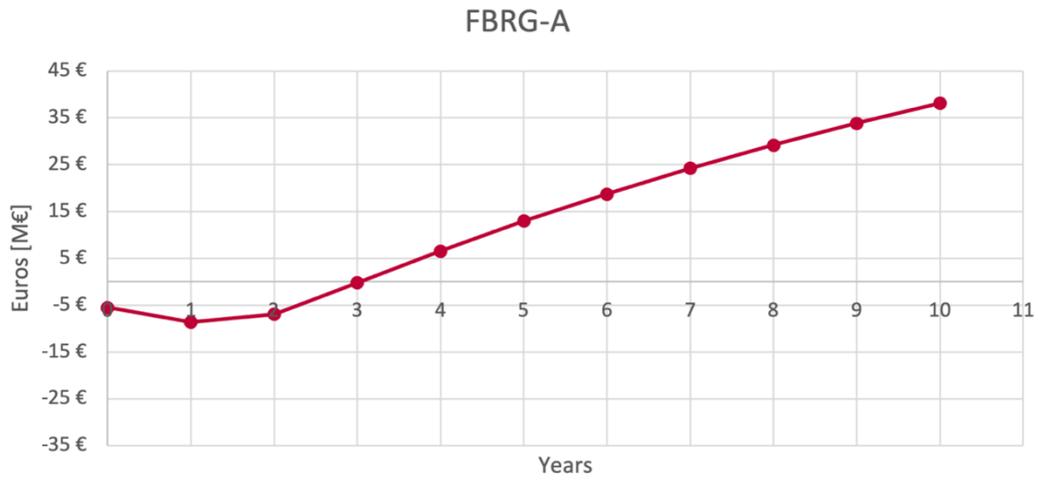
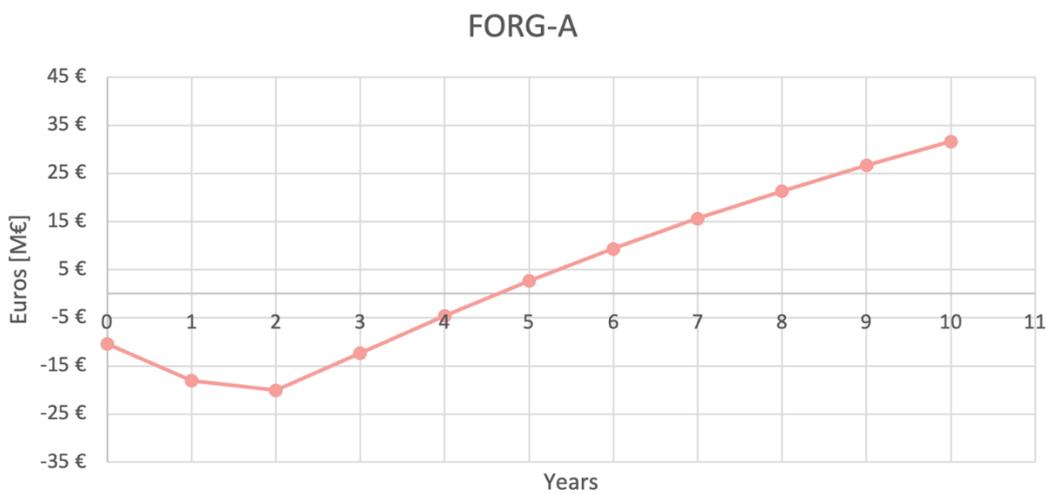


Figure 2.5. Cumulative cash flow for FBRG configurations, with the cost of electricity equal to 80 €/MWh_{el}.



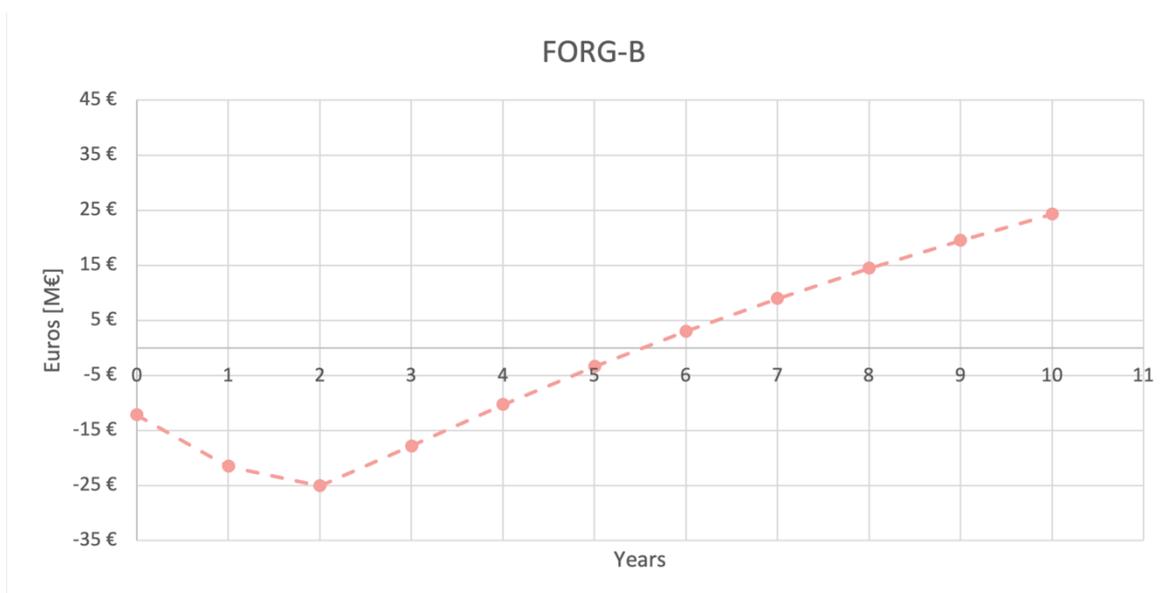


Figure 3.6. Cumulative cash flow for FORG configurations, with the cost of electricity equal to 80 €/MWh_{el}.

Comparing the amount of Euros reached at 10 years, from the plots it can be seen that the cash flow reached in these cases is quite higher with respect to Figure 3.3 and 3.4. Comparing the FBRG configurations with different prices for electricity it results that the cash flow is 48% more in the case in which the price of electricity is 80 €/MWh_{el}.

The plots that represent the cumulative cash flows allow to understand that the plant becomes profitable, in the case which consider the higher price of electricity, in almost four years. This is mostly determined by the fact that it is not taken into account the price to buy raw materials, because it is difficult to determine how they are defined. Crucially, the cost of acquiring the necessary feedstock is necessary to consider in a profitability analysis for several reasons:

- Market availability: even though mixed plastic waste may be considered a waste product, its cost can vary depending on availability, demand from recycling or recovery facilities, and the costs of collection and processing.
- Feedstock quality: Costs may depend on the purity or quality of the mixed plastic waste. The more treatment required to make it usable, the higher the costs will be.

- Competition for purchase: if multiple industries are using the same type of feedstock, there may be competition that influences pricing.
- Transportation and handling costs: even if the price of the feedstock itself is low, the costs related to logistics, transportation, and initial processing must be considered.

Ignoring these factors could lead to inaccurate estimates of operational costs, resulting in a imperfect assessment of profitability.

For this reason, considering that MPW is purchased at € 0.552 kg⁻¹ (Afzal et al., 2023) the *Total manufacturing cost* increases of a value equal to 23.18 M€, in the case of FBRG configurations that require an amount of feedstock equal to 5000 kg/hr, while it increases of an amount equal to 21.47 M€, in the case of FORG configurations where the feedstock considered is equal to 4630 kg/hr.

Considering this additional cost, the plants become unprofitable as it is clearly defined in Figure 3.7 and 3.8.

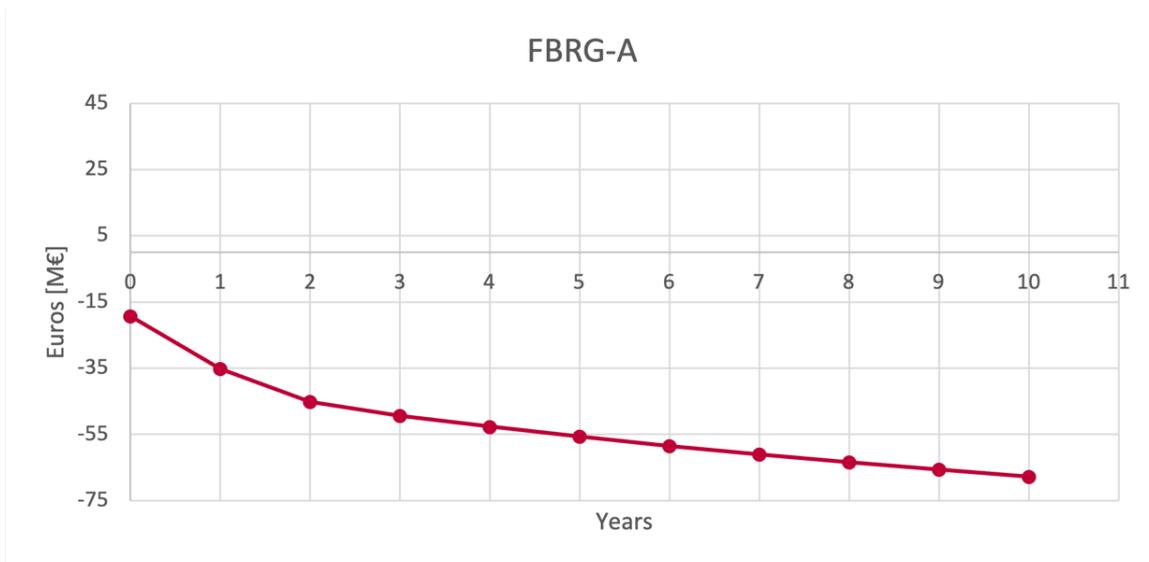


Figure 3.7. Cumulative cash flow of FBRG-A configuration with the cost of MPW equal to € 0.552 kg⁻¹.

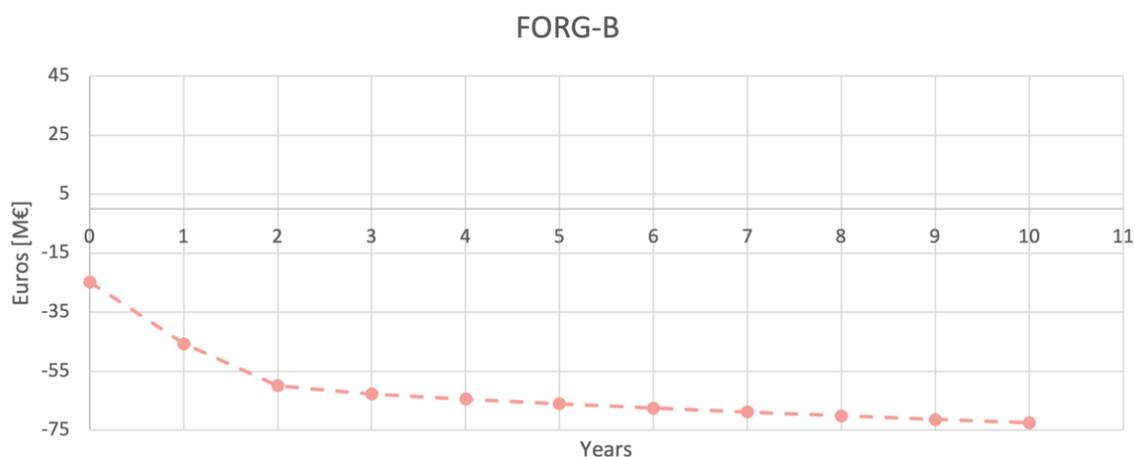


Figure 3.8. Cumulative cash flow of FORG-B configuration with the cost of MPW equal to € 0.552 kg⁻¹.

The profitability analysis performed in these conditions allows to determine how the purchase cost of MPW can impact on the cash flow. Considering this additional cost, the plants are not even more profitable. The decreasing trend of the plots underlines that the gross profit is always negative, and both the plants FBRG-A and FORG-B are affected by losses and not profits.

Conducting a more in-depth analysis on FBRG-A it is found that the maximum purchase cost of MPW, to obtain a profitable plant in 10 years, is € 0.15 kg⁻¹ and its cumulative cash flow as a function of years is presented in Figure 3.9 below.

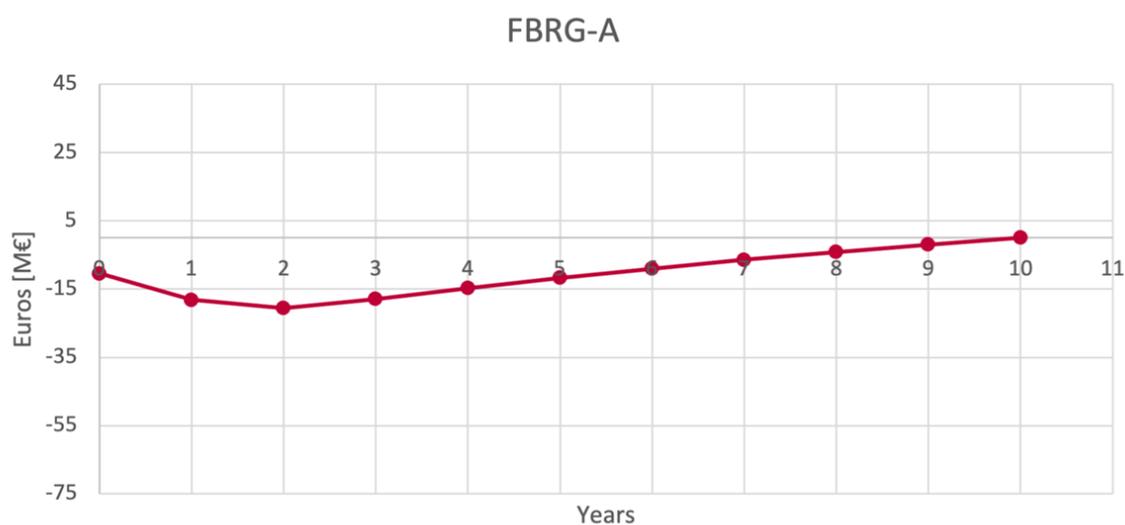


Figure 3.9. Cumulative cash flow of FBRG-A configuration with the cost of MPW equal to € 0.15 kg⁻¹.

While the case of FBRG-B, the maximum price to purchase MPW is lower, due to the fact that this plant is characterised by higher costs, and it is equal to € 0.08 kg⁻¹, obtaining a cumulative cash flow that is represented in Figure 3.10.

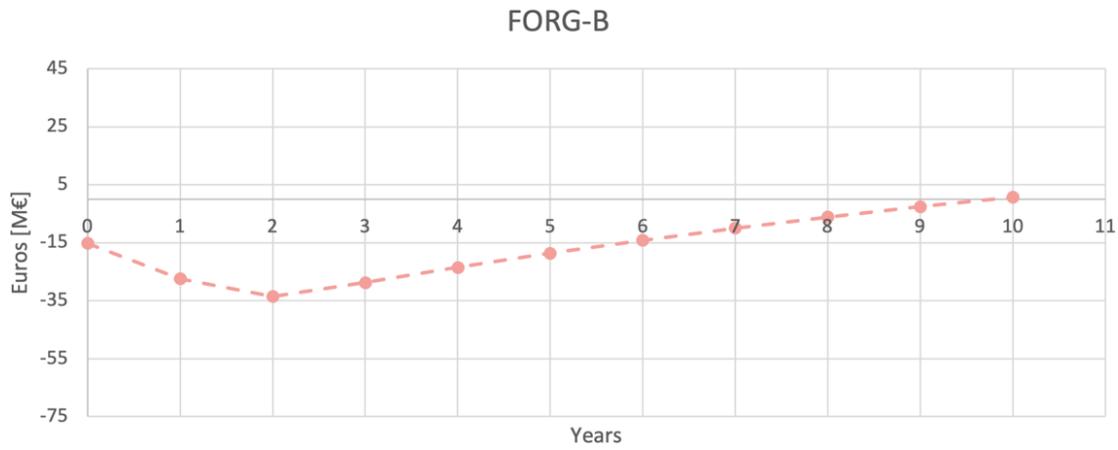


Figure 3.10. Cumulative cash flow of FORG-B configuration with the cost of MPW equal to € 0.08 kg⁻¹.

Conclusions

The primary objective of this thesis was to evaluate various reactor technologies for the gasification of mixed plastic waste to produce syngas, suitable for methanol synthesis. Additionally, it aimed to assess the impact of implementing a pressure swing adsorption (PSA) unit to purify the syngas prior to its introduction into the methanol production stage. By comparing the performance, efficiency, and costs of different gasification reactors, several key conclusions were reached. These insights provide valuable perspectives on the potential of each technology for optimising methanol production from plastic waste. This concluding section summarises the main findings, discusses their broader implications, and suggests directions for future research in this rapidly developing field.

The analysis of the various reactor technologies revealed that the newly implemented FastOx reactor, as deployed in the FORG plants, exhibits greater efficiency in methanol production, while the traditional fixed-bed reactor, utilised in the FBRG plants, demonstrates superior cost-effectiveness. Beyond the differences between these reactor designs, it is important to emphasise that, the primary distinction between configurations A and B, is the presence or absence of a PSA unit to purify the syngas prior to its entry into the methanol synthesis reactor.

Specifically, the FBRG-A configuration was found to be more effective in converting mixed plastic waste into syngas, which is critical for methanol synthesis. Conversely, the FORG-B configuration displayed significant advantages in terms of the quantity of methanol produced. Notably, the FORG-A plant achieved a methanol yield (in terms of mass flow rate) that was 6.04% higher than that of FBRG-A, while the FORG-B configuration yielded 3.25% more methanol than its FBRG-B counterpart.

These findings underscore the trade-offs between different reactor designs when applied to the gasification of mixed plastic waste. An analysis of utility costs associated with plant operation highlights the potential preference for the FORG plants, as they allow for a higher methanol yield compared to the FBRG configurations, while maintaining a nearly equivalent

Conclusions

Total manufacturing cost. Another key comparison can be made based on the inclusion or exclusion of the PSA unit. Although the FBRG-B and FORG-B configurations produce lower quantities of syngas, they enable the production of methanol with a slightly higher degree of purity.

Despite these promising results, the study is not without limitations. The performance of each reactor was evaluated under specific conditions that may not fully account for the variability of real-world plastic waste streams. Moreover, the economic feasibility of each technology was only briefly addressed and warrants further investigation. This is particularly true for the FORG configurations, where the required amounts of oxygen and steam for gasification are not uniquely defined but are instead based on achieving an optimal hydrogen-rich syngas composition. The model employed assumes steady-state operation, chemical equilibrium within the gasifier, negligible pressure losses, ideal gas behaviour for all gaseous species, and the retention of carbon and ash in the solid phase.

In summary, the FastOx reactor offers a more complete, and more efficient gasification process, producing fewer residues and a purer syngas, whereas the fixed-bed reactor, though simpler and less expensive, is theoretically less efficient in terms of conversion rate and gas purification.

Future research should focus on optimising reactor conditions for mixed plastic waste with varying compositions and exploring the integration of these reactor technologies into broader circular economy frameworks.

In conclusion, this thesis demonstrates that both reactor technologies hold significant potential for advancing methanol production from plastic waste, with each offering distinct advantages. Continued research and technological innovation in this field will be critical for developing more sustainable and efficient waste-to-methanol conversion processes, thereby contributing to global efforts in waste reduction, as well as chemical and energy production.

Nomenclature

Acronyms

ASU = Air separation unit

BEC = Bare Erected Cost

BFB = Bubbling fluidized bed

CAPEX = Capital expenditure

CCE = Carbon conversion efficiency

CEPCI = Chemical engineering plant cost index

CFB = Circulating fluidized bed

CGE = Cold gas efficiency

DPBP = Discounted payback period

EPC = Engineering, Procurement and Construction

FBRG-A = Fixed bed reactor gasification

FBRG-B = Fixed bed reactor and Pressure Swing Absorption implementation

FORG-A = FastOx reactor gasification

FORG-B = FastOx reactor and Pressure Swing Absorption implementation

HPC = High-pressure column

IRR = Internal rate of return

LHV = Lower heating value

LPC = Low-pressure column

LPS = Low-pressure steam

MPW = Mixed plastic waste

MSW = Municipal solid waste

NPV = Net present value

OPEX = Operating expenditure

PSA = Pressure swing adsorption

TCR = Total Capital Requirement

TDC = Total Direct Cost

TPC = Total Plant Cost

TRL = Technology readiness level

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