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Techno-economic comparison for the use of syngas in internal combustion engine, PEM fuel cell and SOFC fuel cell

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Abstract

In this thesis, a techno-economic analysis of the use of syngas as fuel for internal combustion engine, pem fuel cell combined with internal combustion engine and sofc is developed. In particular its aim is to calculate the flow rate (Nm3/h) of syngas necessary for each path to produce 50 kWe. The composition of syngas used for the simulations is 14% H_2, 53% N_2, 4% CH_4, 17% CO, 12% CO_2 and with LHV is 1.15 kWh/Nm3. These are typical values for a commercial gasifier fed by dry M10 biomass with a feeding rate of 49 kg/h. The resulting flow rates needed are 143,5 Nm3/h for internal combustion engine, 95,57 Nm3/h for PEMFC combined with internal combustion engine and 69,1 Nm3/h for SOFC. The electrical efficiencies of these processes, without considering electricity auto-consumption, are respectively 30%, 37% and 52% while considering electricity auto-consumptions are 26%, 25% and 50%. Thermal efficiencies are respectively 60%, 36% and 41% while considering thermal auto-consumptions are 60%, 36% and 15%.

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List of acronyms

LHV = lower heating value

TRL = technology readiness level

BoP = balance of plant

MREF = membrane reforming reactor

PEMFC = proton exchange fuel cell

SOFC = solid oxide fuel cell

PSA = pressure swing adsorption

MR = membrane reactor

CHP = cogeneration

2 Introduction

Nowadays topics of pollution and clean energy are diffused and discussed. Innovative ideas are needed to fight the problem of pollution and new ways to produce energy are necessary to guarantee a slowing down of carbon dioxide that traditional ways to produce energy emits, in particular fossil fuels, coals,etc. Imagine that the world is producing 51 billions of tons of CO2 each year. This is a very high number and it has to decrease if life on this planet wants to be preserved. Many innovative ideas have been found in the years and for sure one of the first action that can be approached is the use or improvement of what already is. In this occasion, the concept of cogeneration comes out. But what does cogeneration mean? Very simply, as the word suggests, cogeneration is the production of electricity and heat at the same time. It seems to be easy as an idea, but it is not this diffused. Many large plants are producing electricity for example but, since they do not need heat supply, the do not exploit the heat generated by the machine that produces electricity. This is both a big loss and a clue that heat would not be wasted, there may be another reality that would use it as a "fuel" for its activity. By thinking, for example, to an internal combustion engine, it does not produce only electricity but also heat and more precisely 2/3 of the product is heat. The first idea comes from the action of using both products (heat and electricity) and do not waste them and this is the exact meaning of cogeneration. Cogeneration is not done only with engines, but can be done with many production methods. In this thesis, in addition to internal combustion engine, fuel cells of type PEMFC and SOFC are used and they are both able to cogenerate. In this case the production of heat comes from the fact that the system has to be kept at high temperature and electrochemical reactions themselves produce both movement of electrons and heat. In Italy, to show some numbers, the investment in 2018 in terms of energy efficiency has been equal to 7,1 billlions, with a growth of 6,3% respect to the previous year due to the entering in the market of new units of combustion engines. In fact, internal combustion engine is the most developed technology used and covers the 84% of units connected to district heating whose production represents 17% of the total thermal energy given to networks. After 4 years of growth at double number, a slowing down has been observed in 2018 mainly due to the slowing down of growth in the industrial sector. Considering the three different ways to cogenerate, the thesis goes to investigate which path is better from the technical aspect and which other one from the economical one. The comparison from the technical point of view of the three paths is done with the implementation of models in Aspen Plus for what concerns PEMFC and SOFC. Both models rely on some assumptions and simplification of the process well explained in the next paragraphs. For the internal combustion engine instead literature is valid and consolidated and data from it are used to evaluate the results. The project is developed with the help of the office Iris s.r.l. where the internship took place. This small reality deals with innovation and, for this particular project, is developing prototypes to collect marine litter and transform it into syngas through pyrolysis. Its work is briefly explained in the next pharagraps.

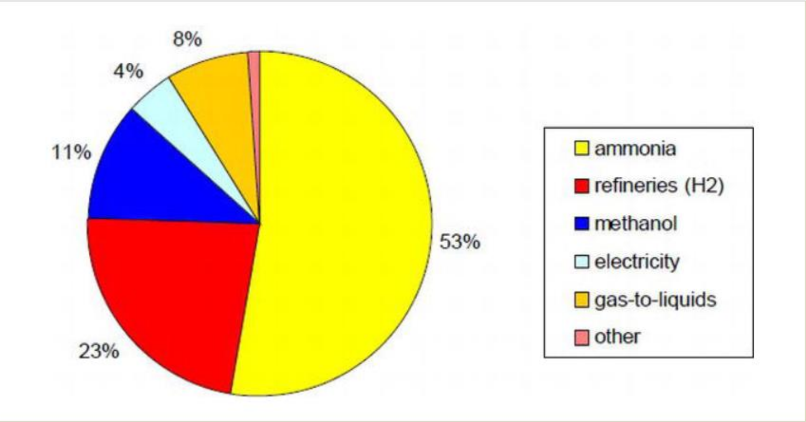
3 Syngas from pyrolysis and gasification

3.1 Syngas

The syngas, abbreviation for synthesis gas, is a mixture that can be produced by pyrolysis or gasification of a wide variety of feedstock that contains carbon such as biomass (wood gas), plastics, coal, municipal waste, marine litter or similar materials. Its main components are CO and H2 in variable proportions and some other gases, in lower amount, which are mainly CO2, CH4 and N2.

In the chemical industry this gas is an intermediate product and, in particular, its main chemical applications are the production of synthetic natural gas (SNG) and production of ammonia and methanol. Each year around 6 EJ (2% of world's primary energy consumption) are produced globally [1] and the current market distribution of it is shown in Figure 1.

Figure 1.Syngas share of usage [2]



Moreover, the quality and characteristics of the synthetic gas produced from gasification can vary a lot and this variation can be addressed to the feedstock material and its particulate size, the feedstock flow, the chemical reactor configuration and gasifying agent and in general the operation conditions of the process. The different paths and operating conditions from feedstock to syngas are explained later in more details.

Even tough syngas is mainly used as an intermediate material in the industry, being a combustible, it can also be used as fuel for internal combustion engines. From literature the value of LHV of syngas goes from 10.4 MJ/kg to 27.8 MJ/kg. By comparing its range of calorific value with a conventional fuel as natural gas (LHV=47.1 MJ/kg [20]), it can be noticed that the power per kilogram is significantly lower so the combustion will require a greater flow of syngas fuel to obtain the same power of a standard combustion engine. But the combustion is not the only solution in the use of this gas that, thanks to the precious species that it contains, can offer a wide spectrum of use also in the field of energy production without any combustion process, which means clean production of energy. The reference in this case in the production of energy via fuel cells that are particular machines to produces energy that, instead of using combustion, use electrochemistry of some species and more properly rely on reduction and oxidation of some species to produce electrons and further products. In fact, being it composed by hydrogen in a certain volume fraction usually between 10-15% vol, the separation of hydrogen from it is doable in order to obtain pure hydrogen as fuel for example for fuel cells at low temperatures (PEMFC). Syngas can also be used as fuel for high temperature fuel cells (SOFC) and in this last case it can be used directly as fuel for them since they can tolerate fuel flexibility.

For what concerns the limitations of this gas, tar, contaminants and humidity are the key point in the usage of this gas as a fuel. Each technology needs a different cleaning process of the gas that will be explained in the following paragraphs.

3.2 Pyrolysis and gasification

Pyrolysis and gasification became very important and in particular plastic is a fundamental support for today's lifestyle. Thanks to the low cost of production and the properties of it as low density, long duration and high resistance to corrosion, plastic is substituting many traditional materials such as wood, metals and ceramics.

More wildly, there are two different ways to produce energy from plastics and other materials: pyrolysis and gasification. Pyrolysis, which is a thermal treatment in inert atmosphere, is considered the main solution to produce fuels and chemical products. Even though the interest in pyrolysis increased a lot in the las years, its usage is still not this common and, in addition to that, some plastic materials are not suitable for this kind of process due to the fact that they bring to the production of toxic materials and/or of difficult usage. For example, pyrolysis of PVC brings to the production of aromatic hydrocarbs and HCl and in the case of PET high quantities of char and CO are produced.

Pyrogasification, differently from pyrolysis, is a thermal treatment where an oxidant (usually air) or steam (gasifiying agent) are introduced. In these conditions the process self-sustains and, compared to oyrolysis, the energy that has to be provided from the external is lower. Temperatures reached are usually higher with a minimum production of char and liquid and a gas composed mainly by H2, CO, CO2, CH4 and N2 is produced. The main interest of pyrogasification process lays in their flexibility of producing energy, energy vectors as H2 and chemical substances deriving from the syngas produced. another great advantage of gasification compared to pyrolysis is the greater flexibility to produce energy with plastics of different compositions or plastic materials mixed with other waste materials such as biomass. The application and so the composition of the syngas produced depends on the gasifying agent. For example the gasification of plastic materials with air produces a syngas with an average calorific value of 6-8 MJ Nm from where energy can be produced. Nevertheless, gasification with steam allows to produce syngas without N2 with a calorific value greater than 15 MJm-3 with composition useful for synthesis applications.

The major challenge of gasification of plastic wastes is he high concentration of tar in the gaseous product compared to the one obtained with biomass and so a great and very efficient cleaning system of syngas is necessary in order to allow the use of this product as a chemical product.

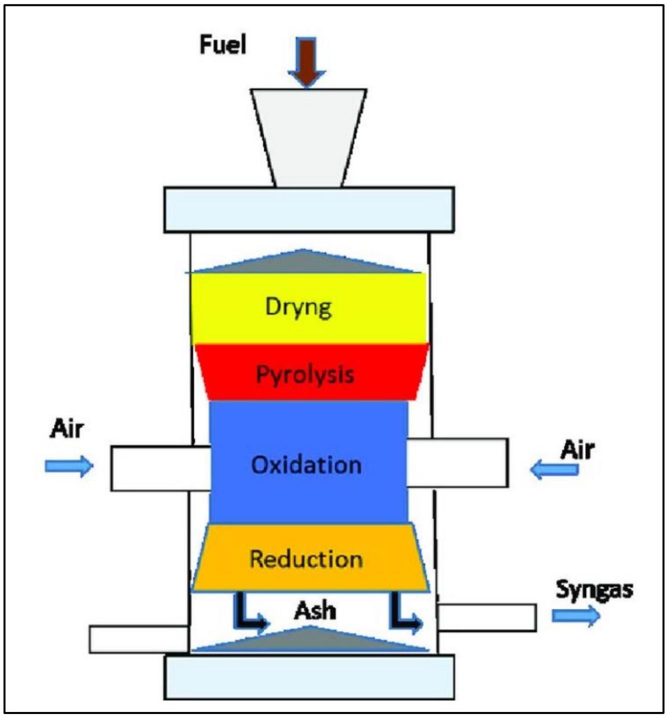
3.3 Typologies of plants

Of great interest for this thesis is the production of syngas from biomass and plastic which happens through the so-called gasification or pyrolysis. Bad products of combustion are not created since the thermal treatment does not burn but oxidizes the feedstock. The product of the gasification process is a gas called syngas which is composed mainly by carbon monoxide, hydrogen, methane, carbon dioxide and nitrogen and some other end-products are created such as contaminants, ash and tar.

The process of gasification takes place into a reactor called gasifier and an oxidizing agent is supplied to make the reaction happen. This last can be pure oxygen, air or a combination of them and it is chosen according to the purity and composition of syngas required at the end.

The gasification occurs in four steps that are briefly described below: drying, pyrolysis, oxidation and reduction [3].

Figure 1. Scheme of a gasifier [4]



- Drying. Biomass, before entering in the reactor, is not totally dry but it has a moisture percentage ranging from 5% to 35%. At high temperatures, in particular greater than 373 K, water becomes steam and the feedstock is dried. In this step, the feedstock is not subjected to any thermal decomposition yet.
- Pyrolysis. This step it the thermal decomposition of biomass without any oxygen. Volatile components of the feedstock are vaporized by the heating producing also char and ash. The

production yield and quality and composition depend on the operating conditions of the gasifier as temperature, pressure, etc...

- Oxidation. In this section, air or oxygen or a mix of them is sent to the reactor (as it can be observed in Figure 1, blue zone). The oxidation takes place at temperatures of 975 to 1275 K. By injecting air, some inert gases as nitrogen and argon are introduced in the reactor but they do not interact so they remain as they entered at the reactor. Another heterogeneous reaction takes place and produces carbon monoxide.

$$C + O_2 \rightarrow CO_2 \quad (1)$$

While hydrogen reacts according to (2).

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O \quad (2)$$

- Reduction. It is the last step and many reactions happen at high temperature in absence of oxygen. The main reactions that happen in this section are the Bodudouard reaction (4), steam-reaction (3) and methanation (5).

$$C + H_2O \rightarrow CO + H_2 \ (3)$$

$$C + CO_2 \rightarrow 2CO \ (4)$$

$$C + 2H_2 \rightarrow CH_4 \ (5)$$

Since most of the reactions are endothermic, it means that heat has to be supplied to the reactor in order to make the gasification happen. If the gasification is complete, all the carbon is converted into carbon oxide and carbon monoxide. The remaining matters are ash and some char [5].

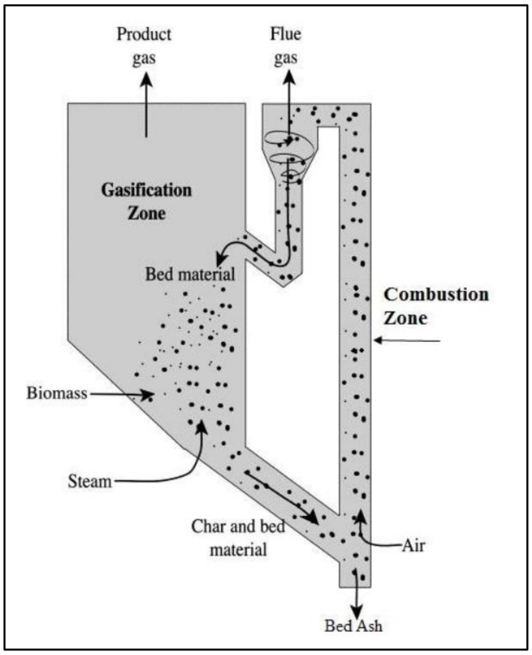
There are then many types of gasification reactors.

3.3.1 Fluidized bed reactors

Mainly two typed of fluid bed reactors are used for gasification processes which are circulating fluid beds and bubbling fluid bed. Most of research and applications focuses on the bubbling fluid bed because their main advantages are high transfer speed of heat and mass, excellent contact gas-solid, great control of the temperature and flexibility. The main disadvantages of these type of reactors are connected to their high investment cost, limit of grain size both on the bed that on the feeding side, dehumidification problems and non-reacted material problems. These types of rector work at stagnant regime and their flow and degree of development is usually very high, with many ongoing studies at industrial scale. These reactors are usually run with common air as gaseous fuel (also for plastic wastes). Even though they cannot guarantee an high heating of the produced gas, this strategy causes many operative advantages as the ones connected to the self-heating process and the reduction of carbon in the gaseous product.

Here it is an illustration of a fluidized-bed gasifier. In this type of reactor, the bed of solid particles is suspended by an upward flow of gaseous reactants and products. This scheme of operation guarantees a great mixing between feed and oxidant. The operating temperature of this reactor is below the softening point of the ash (900 to 1050 C) otherwise it would cause an agglomeration of the ash that may interfere with the bed-fluidization [6].

Figure 2. Internal fast circulating fluidized bed reactor [7]

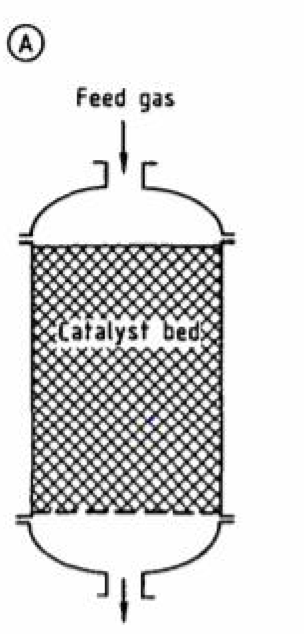


3.3.2 Fixed bed reactors

The use of this type of reactor is related to their easiness of project and functioning at limited investment costs. The main disadvantages of these reactors are the difficulty of scalability, the functioning in a continuous regime, the low speed of transfer of heat and the limited contact gas-solid. Among the fixed-bed reactors there is a huge variety of design with the common point of being used in small scale.

Here it is an illustration of the typical fixed-bed reactor. As it can be seen, they make the use of a catalyst and the reaction takes place in the for of a heterogeneously catalyzed gas reaction on the surface of the catalyst that are placed is the reactor as a so called fixed-bed.

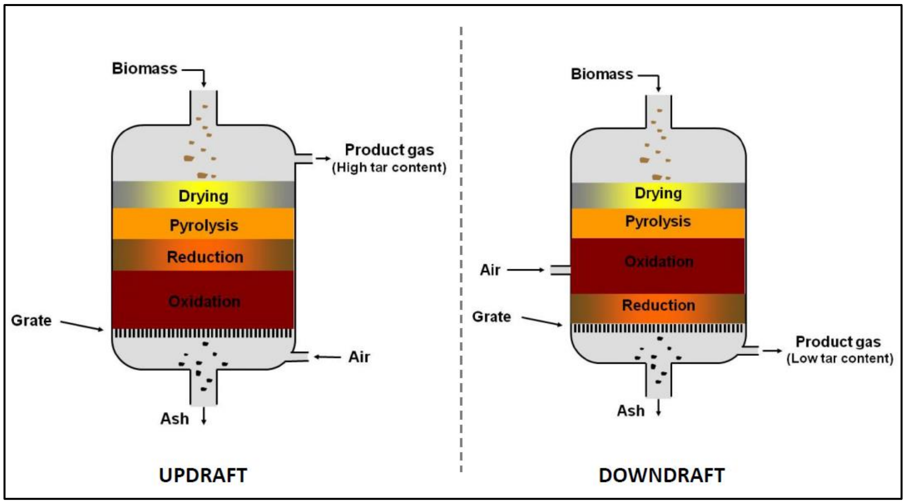
Figure 3. Fixed-bed reactor



3.3.3 Moving bed reactors

There are two types of moving-bed gasifiers, downdraft and updraft. The downdraft moving-bed gasifier is a reactor in where the fuel moves downwards driven by gravity and it is gasified by a countercurrent blast. A relatively high temperature is reached in the oxidation region (800 to 1200 C). Due to the high temperature, this type of moving bed gasifier is better able to crack tars, thus producing a syngas with low amount of tars. In the updraft gasifier, the fuel moves always down driven by gravity but lower temperatures are reached in the oxidation zone and thus this gasifier is less able to fully crack tars. The result of this gasifier is a syngas with a higher amount of tars.

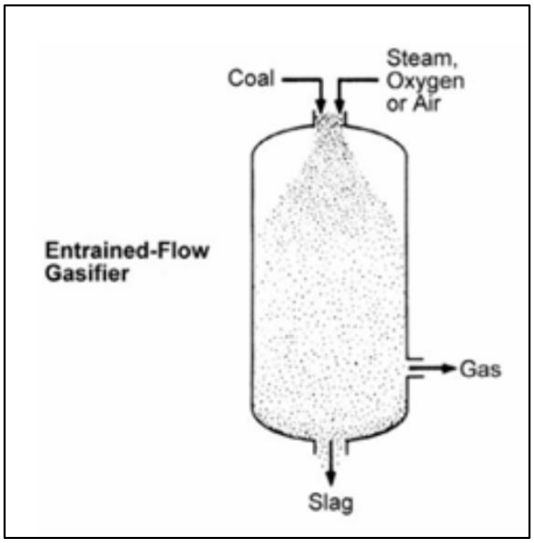
Figure 4. Moving-bed gasifier: updraft and downdraft



3.3.4 Entrained flow reactors

Entrained-flow gasifiers. In this type of gasifier particles are dispersed and carried around by a blast of reactants and products in co-current flow. The operating temperature is high (1250 to 1600 C) and this operating condition guarantees high fuel conversion and low methane in the gas. The size of particles is very small (order of hundred micrometers) so that it can ensure the complete burnout of particles.

Figure 5. Entrained flow gasifier [8]

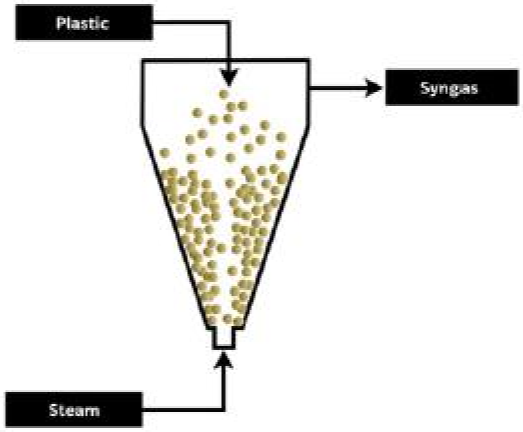


3.3.5 Spouted bed reactors

The characteristics of spouted-bed reactors make them a good alternative to the fluidized-bed reactors in particular for the valorization of waste. These types of reactors are characterized by a high speed of transfer of heat and mass, good mixing and suitable contact gas-solid. More that that, their vigorous cycling circulation of the solid avoids of de-fluidification and softens problems of manipulation of irregular particles and particles with wide grin distribution. The main disadvantages for their application are the short stay of volatile substances which can be an obstacle for cracking of tar.

Here it is an illustration of a spouted-bed reactor.

Figure 6. Spouted-bed reactor



3.3.6 Plasma reactors

Processes of gasification of plasma consist in the transformation of wastes in products into an oxiding environment. The main advantage of this technique is the very high temperature reached which favors an almost complete cracking of tars and consequently an high efficiency of gas, improving the elimination of toxic substances. Plasma technologies are divided into three categories according to the way of discharge of plasma, in particular: continuous current, radiofrequency and microwaves.

3.4 Typologies of fuel

3.4.1 Biomass

The European Directive 2009/28/EC defines biomass as “The biodegradable fraction of products, waste and residues from biological origin from agriculture (including vegetal and animal substances), forestry and related industries including fisheries and aquaculture, as well as the biodegradable fraction of industrial and municipal waste”. It is then possible to talk about it as a great feedstock because it is natural and of plant origin and it does not require any energy-intensive production processes and pollutants. In addition to that, it is also considered a CO2 net zero emission feedstock since the carbon dioxide that biomass produces when burns is equal to the one that it absorbed during its growth. The emission of this carbon dioxide would be impossible even if the biomass would not be burned because it would stay otherwise in the root of the biomass specie and would enter in the atmosphere either way. The European Union considers the biomass the most efficient system to produce energy to reduce carbon monoxide emissions.

3.4.2 Fossil fuels

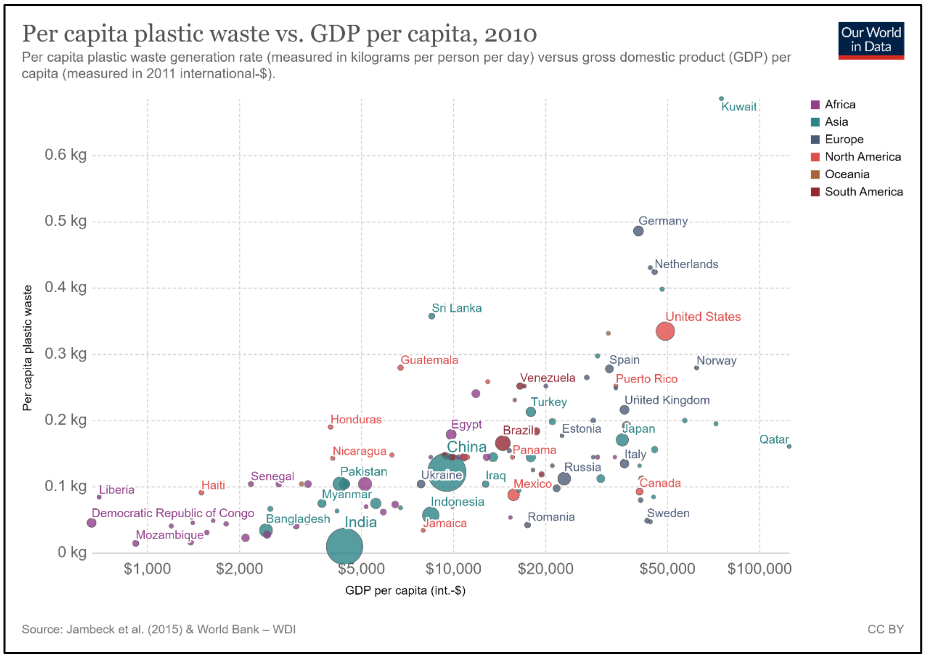
A fossil fuel is a fuel formed by natural processes, such as anaerobic decomposition of buried dead organisms, containing organic molecules originating in ancient photosynthesis that release energy in combustion. Such organisms and their resulting fossil fuels typically have an age of millions of years, and sometimes more than 650 million years. Fossil fuels contain high percentages of carbon and include petroleum, coal, and natural gas. Commonly-used derivatives of fossil fuels include kerosene and propane. Fossil fuels range from volatile materials with low carbon-to-hydrogen ratios (like methane), to liquids (like petroleum), to nonvolatile materials composed of almost pure carbon, like anthracite coal. Methane can be found in hydrocarbon fields alone, associated with oil, or in the form of methane clathrates. Although peat shares many characteristics with fossil fuels, including its decayed organic structure and release of greenhouse gas upon usage, whether it can be considered a true fossil fuel is debated. As of 2018, the world's main primary energy sources consisted of petroleum (34%), coal (27%), and natural gas (24%), amounting to an 85% share for fossil fuels in primary energy consumption in the world. Non-fossil sources included nuclear (4.4%), hydroelectric (6.8%), and other renewables (4.0%, including geothermal, solar, tidal, wind, wood, and waste). The share of renewables (including traditional biomass) in the world's total final energy consumption was 18% in 2018.Most air pollution deaths are due to fossil fuel combustion products: it is estimated that this pollution costs over 3% of global GDP, and that fossil fuel phase-out would save 3.6 million lives each year.The use of fossil fuels causes serious environmental damage. The burning of fossil fuels produces around 35 billion tonnes (35 gigatonnes) of carbon dioxide (CO2) per year. Natural processes on Earth can only absorb a small part of this amount, therefore there is a net increase of many billion tonnes of atmospheric carbon dioxide per year. CO2 is a greenhouse gas that increases radiative forcing and contributes to global warming and ocean acidification. A global movement towards the generation of low-carbon sustainable energy is underway to help reduce global greenhouse gas emissions. [9]

3.4.3 Waste and marine litter

The presence of plastic debris is one of the major concerns that came up in the last fifty years. The accumulation of these materials is dangerous not only for nature environment but also for human society and health [10]. It is interesting to investigate which are the specific impacts of plastic on wildlife and on human life. This is a topic that is being studied since 1980s when a peer-reviewed on plastic impacts was published. It is clear that this is a very old field of study and many data have been collected. Even though, the real impact of this plastic is not yet well known. For what concerns the wildlife, there are three different pathways by which plastic can affect wildlife and these are entaglement (the entrapping, encircling or constricting of marine animals by plastic debris), ingestion and interaction [11]. By analyzing then effects of microplastic (particles smaller than 4.75 mm of diameter) and nanoplastic it can be stated that the greater danger is the ingestion of it both for humans and animals. There are not few evidences for humans yet but the ingestion of it can be possible in many different ways such as ingestion of water (orally), consumption of marine microplastic, skin cosmetics or also inhalation of particles in the air [12]. These dangers are a great alarm and it is clear that the production of plastic and its recycle should gain importance.

To better analyze the scenario here it is the production of plastic per-capita.

Figure 7. Per-capita plastic waste vs. GDP per capita [13]



Per capita plastic waste vs. GDP per capita, 2010

Per capita plastic waste generation rate (measured in kilograms per person per day) versus gross domestic product (GDP) per capita (measured in 2011 international-$).

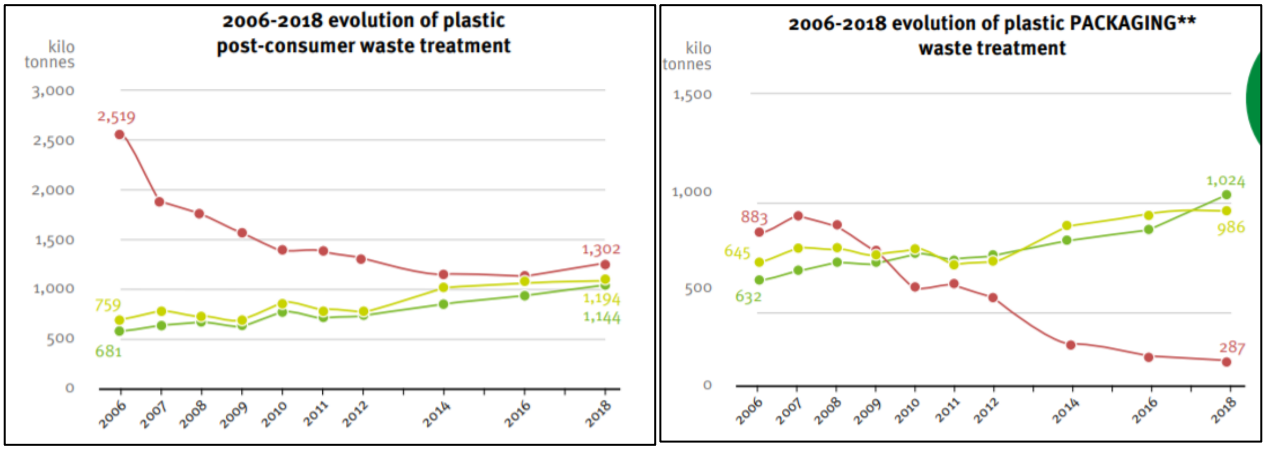
Source: Jambeck et al. (2015) & World Bank – WDI

CC BY

Higher is the GDP, higher is the per-capita plastic waste production so plastic production is directly correlated to richness of the country. Italy has a high production of plastic that, with time, can become dangerous for its recycling issues and quantity. Attention has to be addressed to the topic and it is also starting to raise awareness in population and government.

The Italian scenario remains still positive, even if the consumption of plastic is really high. In fact, in 2018 Italy 3.6 million of tons of plastic post-consumer waste were collected in order to be treated and from 2006 to 2018 the volumes for recycling increased by 68%, energy recovery increased by 57% and landfill decreased by 48% [14]. In addition to that, 2.3 million tones of plastic post-consumer packaging from households, industrial and commercial packaging were collected through official schemes in order to be treated. From 2006 to 2018 the volume of plastic packaging that has been collected for recycling increased by 62%, energy recovery by 53% and landfill decreased by 67% [15].

Figure 8. Evolution of plastic post-consumer waste treatment (left), evolution of plastic packaging waste treatment (right) [16]



3.5 Syngas cleaning

3.5.1 Particulate removal

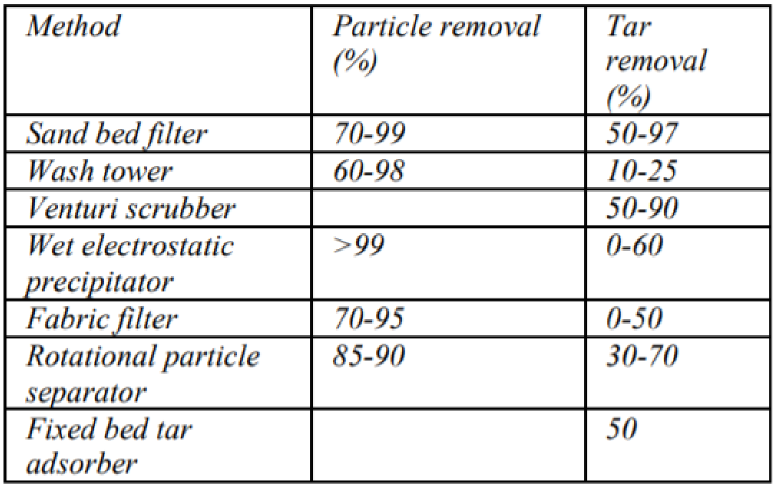
Particulate matter is the bigger in size impurities that is contained in the syngas. The concentration of it depends a lot on the design of biomass gasifier and the presence of it in the gas may cause the bad-functioning of the chain of devices that the syngas feeds. For this reason, particulate removal is important and there are currently two main technologies for particles removal: dry gas cleaning or dry gas collectors like cyclone separators, barrier filters, electrostatic precipitators and wet gas cleaning or wet scrubbers (spray towers, cyclone spray scrubbers, venturi scrubbers and packed bed scrubbers) [17]. The only problem that can be encountered during the process is the cooling of the gas and so the condensation of tars. The solution is to keep the temperature of the syngas above the tar dew point.

3.5.2 Tar removal

They are organic impurities that can be produced from petroleum, coal wood and peat. If they condense or polymerize they may transform in more complex structures that risk to chock and compromise the functioning of the device increasing the need f maintenance and decreasing the efficiency.

Tar removal technologies could be classified into five groups: mechanism methods (cyclones, filters, granular beds, RPS, electrostatic precipitators and scrubbers), self- modification, catalytic cracking, thermal cracking and plasma methods (Pyroarc, corona, glidarc) [17]. The efficiencies of these mechanism are reported in table XX.

Table 1. Tar and particle removal efficiency of some mechanism methods [18]



Method	*Particle removal (%)*	*Tar removal (%)*
Sand bed filter	*70-99*	*50-97*
Wash tower	*60-98*	*10-25*
Venturi scrubber		*50-90*
Wet electrostatic precipitator	*>99*	*0-60*
Fabric filter	*70-95*	*0-50*
Rotational particle separator	*85-90*	*30-70*
Fixed bed tar adsorber		*50*

3.5.3 HCl removal

The removal of HCl from synthesis gas is very important for any final application of it since it has a great corrosion potential when in contact with metal components. In order to do it, a filter hosts a sorbent material which is able to capture the HCl and clean the synthesis gas that passes through it. To obtain tolerance limit of 1 ppm sorbents as Na2CO3, K2CO3 and NaAlO2 are suitable. Krishnan et al. (1994) evaluated many other carbonate materials such as nahcolite, shortite and dawsonite able to rapidly capture HCl vapor at temperatures around 400 up to 600 C, temperature easily reachable since the synthesis gas exits from the gasifier at a temperature of around 650 C for commercial downdraft gasifiers. In the coal market, the most used adsorbents are CaO based sorbents [19].

HCl removal commercial adsorbents are generally expensive and they have to be changed after a certain amount of hours of operation which means that also they do not imply only capital costs but also operation costs.

3.5.4 H2S removal

The removal of H2S is necessary to protect the devices from high temperature corrosion , caused by the formation of alkali sulfates that in a normal combustion engine can be dangerous but also in the application field of fuel cells is poisoning and deactivates Ni catalyst, action that brings to a drop of the voltage. It has been tested that high temperature desulphurization processes could imply lower capital and operating costs compared to low temperature processes.

The method to remove H2S from the synthesis gas is with the auxilium of a sorbent. The hot gas desulphurization process based on sorbents metal oxide-based should reach a good efficiency and should not lower the quality of the syngas.

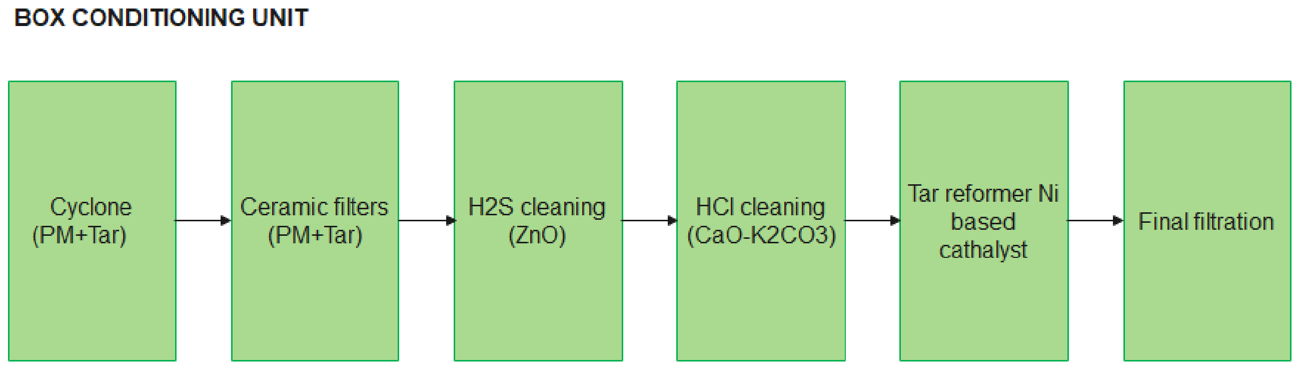
Some sorbents have been found in literature to be feasible, in particular Fe, Zn, Mn, Mo, Ca, Sr, Ba, Co , Cu metal oxides and especially sorbents containing Zinc, Copper, iron and manganese. The only problem for these metal oxides is their thermal instability shown at high temperature values.

3.5.5 For internal combustion engine application

Internal gas combustion engine tolerates up to certain values of contaminants and being the exiting gas from gasifier contaminated, it has to be treated in a particular cleaning unit.

The cleaning unit used for the simulation of this thesis is the one represented in figure below.

Figure 9. Cleaning-unit for internal combustion engine application (PATH 1)



Cyclone and ceramic filters are designed to remove particulates and tars, filter with ZnO sorbent to clean from H_2S, filter with $CaO-K_2CO_3$ to remove HCl and a final tar reformer (Ni-based catalyst) performs the final tar filtration.

This cleaning unit for syngas feeding the internal combustion engine can guarantee an exiting cleaned gas with HCl content < 5 ppm, H_2S content < 1 ppm, PM < 0.1 mg/Nm3, Particle size < 10 µm, Tar < 10 mg/Nm3.

3.5.6 For PEMFC application

After evaluating many opinions of experts and reading from literature, the more efficient but not cheaper solution to clean the syngas for PEMFC application is the use of palladium or palladium-alloy membranes which are able to separate pure hydrogen at very high percentage (around 99.9%) from the flow of syngas. A brief explanation of the application of these membranes is exposed in the following paragraphs and, after the explanation of the functioning of these tools with their application in special reactors able to also increase the percentage of hydrogen useful to feed the PEMFC, the complete layout is exposed and explained.

HYDROGEN SEPARATION TECNIQUE

There are three different ways in which hydrogen can be separated from a syngas stream:

1) PSA (Pressure Swing Absorbing)

2) selective membranes

3) cryogenic distillation

The most common, commercial and large-scale processes used for hydrogen separation are PSA and cryogenic distillation but the market is changing, looking always forward to create more compact and less energy-consuming techniques. In fact, by getting in contact with some experts on this topic and by analyzing the literature, the new most efficient and less energy intensive technique to produce pure hydrogen is the use of membranes which are highly selective to hydrogen. In particular it has been proved that high purity of hydrogen can be obtained through dense metallic membranes and especially Palladium and its alloys are highly permeable to hydrogen [20]. The only problem is that these metallic membranes are sensible to some gases such as carbon monoxide and hydrogen sulfide. For this reason, cleaning and upgrade of the fuel (in this case syngas from CO rich to CO poor) have to performed. Therefore, it would be preferable to use inorganic membranes since they are inert to poisoning materials but Pd-alloy membranes are proved to have a greater proportionality of hydrogen permeated to pressure compared to inorganic membranes.

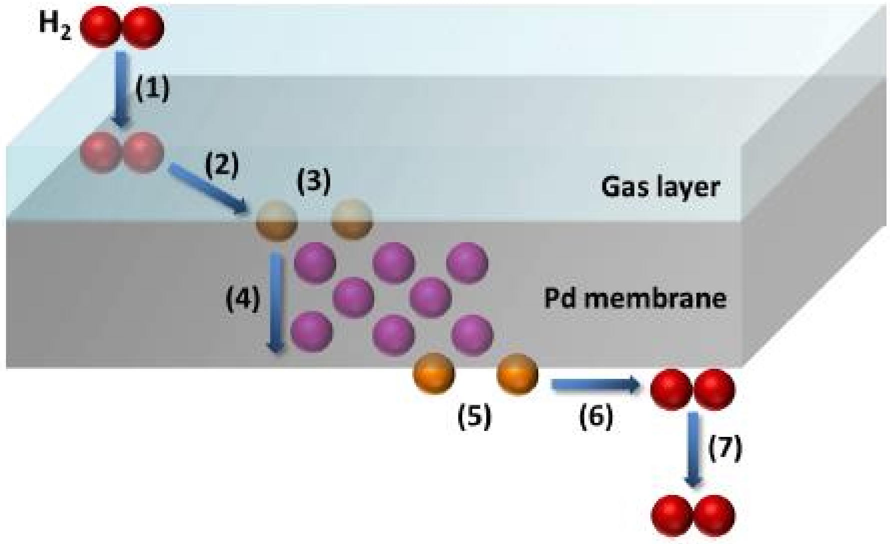
PALLADIUM BASED MEMBRANES

Dense Palladium-based membranes have been of great interest in the last decades and there is still a lot of research going on. This is due to the application that they may have. The fact that they are permselective to hydrogen makes them one of the most attractive method for hydrogen separation, since pure hydrogen can be used for several applications related to the carbon neutral transition and in particular it can be used for low temperature fuel cells PEMFC.

Hydrogen permeation across the membrane is based on the solution-diffusion mechanism that can be described in five steps:

1. Hydrogen molecule is adsorbed on the Pd surface on the feeding side of the membrane
2. Hydrogen dissociates into atomic hydrogen
3. Atomic hydrogen enters in the palladium-based lattice and diffuses across it, while electrons interact with the metal lattice
4. Once on the permeation side of the membrane, hydrogen leaves the lattice and recombines in order to be desorbed as molecule

Figure 10.Schematic of H2 permeation steps through a Pd membrane [21]



The entire process can be described through the following equation:

$$J_{H_2} = \frac{P_{H_2}}{\delta} \cdot \left({P^n}_{H_2,feed} - {P^n}_{H_2,perm}\right) \qquad (6)$$

Where J_{H_2} is the hydrogen molar flow per membrane surface (mol/sm2) and ${P^n}_{H_2,perm}$ is the permeability of the membrane. The term in the bracket is the driving force of hydrogen permeation, n is the hydrogen partial pressure exponent and it depends on the rete-determining step of the permeation process. Assuming that n is constant at any temperature, permeability follows the Arrhenius-type law

$$P_{H_2} = {P^0}_{H_2} \cdot e^{(-\frac{E_a}{RT})} \qquad (7)$$

In this simplification, the selectivity of the dense Pd-based membrane is supposed infinite and the concentration of carbon monoxide in the feeding fuel (in this case syngas) has to be lower than 10 ppm in order to be considered a non-poisoning element for the membrane [22]. If the concentration of carbon monoxide is grater then that value, its presence causes an inhibition of the permeation of the membrane in the whole range of concentration (0.2 – 9% vol). the poisoning happens for temperatures lower than 300 °C and increases a lot with the reduction of temperature. Inhibition effect il very lighter instead for operating temperatures above 375 °C, but for the WGS-MR it has to be taken into account that the WGS reaction is slightly exothermic so it is not favored at high temperatures. Even though the poisoning from carbon monoxide is dangerous for the properly functioning of the membrane, it is reversible and the membrane can be cleaned and brought to initial conditions by bringing it under vacuum at temperatures higher than 250 °C [23].

WATER GAS SHIFT REACTOR

Water Gas Shift reaction is a slightly exothermic reaction and follows the stoichiometry

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \Delta H = -41.1\ kJ/kmol$$

This reaction gained a lot of interest in the last years due to the fact that it guarantees a good conversion of carbon monoxide into carbon dioxide.

The reaction, being exothermic, favors the conversion of reagents at lower temperatures but as it is clear from physics, the kinetic of the reaction, which is favored at high temperatures, is not favored. Being the number of moles constant in the reaction (# moles reactants = # moles products) pressure does not influence the reaction.

There are two main categories of catalyst used in Water Gas Shift process and the use of one instead of the other depends on the temperature of operation.

1) Fe/Cr based catalysts
2) Cu based catalysts

The first ones are used for HT WGS and they operate in a range of temperature from 350 to 450 °C. The second ones are the Cu based. Cu has not stable at high temperatures because subjected to thermal sintering. This type of catalyst is in fact used for LT WGS.

This is the state of the art for WGS reaction, but when it is implemented into a membrane reactor, some parameters and behaviors change. Most of the experimental works found in literature investigate the behavior of this reaction with membranes od Pd-Ag alloy.

Mendes et al. studied the behavior of the WGS reaction in MR Pd-Ag alloy for temperatures from 200 to 300 °C. They observed that CO conversion increases for temperatures greater than 250 °C because the permeation of hydrogen is eased by the higher temperature.

Cornaglia et al. studied the behavior of WGS reaction in MR Pd-Ag alloy for temperatures greater and equal to 400 °C. For WGS happening at 400 °C the adsorption of carbon monoxide on the Palladium film increases reducing the permeability of the membrane while for temperatures greater than 400°C the permeance of hydrogen reduces the lifetime of Pd film increasing cracks and defects in the material.

To improve the operation of these membranes in the reactor many studies have been carried out and some possible corrective parameters have been identified.

The first and most important is the operating pressure of the two sides of the membrane. When the pressure of the gas flow increase in pressure, this brings a positive effect because it increase the partial pressure of hydrogen at the level of the membrane and, as it is explained in the state of the art of the Pd-alloy membranes, the process of hydrogen permeation is lead by its partial pressure. In this way, not only the hydrogen permeates better due to its higher partial pressure but also the conversion of carbon monoxide is enhanced because, by removing hydrogen from the reaction zone, thanks to the mass transport principle the WGS happens more easily and the production of hydrogen increase [24].

The second is the S/C ratio which represents the division of steam and syngas carbon quantity. It is confirmed by several studies that a S/C ratio greater than 1 has beneficial effects on WGS reaction and brings to a greater conversion of carbon monoxide. A too high S/C ratio decrease the quantity of hydrogen yield. This means that a trade-off value of S/C ratio has to be adopted for the reaction and according to several studies this trade-off value ranges between 1.5-2. For values of S/C ratio lower than 1, the permeance of Pd membrane tends to decrease due to the deposition of C on the membrane. For high values of S/C ratio (from 3 to 4) deposition of C is observed by Liguori et al. and this is addressed to Boudouard reaction. At the end, Cornaglia et al. stated that a S/C ratio between 2 and 3 and a Pt-based catalyst helps in stopping C deposition [24].

The third and last is the use of an inert sweep gas on the permeated side with the aim of removing the hydrogen produced once that it is separated from the membrane. In this way, a pressure difference between the two sides of the membrane of hydrogen is kept along the whole length of the membrane and the hydrogen yield increases.

MEMBRANE REACTOR

Integration of membranes in the chemical industry and processes brought to a significant boost of process and product, offering opportunities for a sustainable industrial development. This happens because there are many possibilities to integrate this technology into already existing processes in favor of compactness of the plant, quality of the products and reduced energy consumption being the device concentrated in smaller size. Behind this there is the famous logic of the Process Intensification Strategy that can lead to development and re-design of new processes more compact and efficient that allow better exploitation of material, lower energy consumption and reduced plant volume [25]. For this reasons MR attracted the attention in substituting the traditional existing plants.

In membrane reactors reaction and separation are integrated in the same unit in which it is also present the selective membrane. It can be then described as divided into two parts:

1) Reaction volume where the packed catalyst stays
2) Permeated where gaseous species permeated through the membrane are collected

Membrane works thanks to the effect of a pressure force created by the difference of pressure from one to the other side of the membrane (as explained in the parapgraph above about Palladium membrane physical principle behavior). The pressure force can be created either by sending a sweep gas to the membrane or by applying a difference of pressure between the two sides of the membrane. In this thesis, the incoming gas is put on pressure and there is not the need of a sweep gas. This decision rely on an experimental test. There are many advantages related to the use of a membrane reactor and part and the most important ones are listed here below:

- Improvement of the reactions limited by the equilibrium, since one or more products can be expulsed from the reaction environment (in this case the hydrogen)
- Volume of reactions are significantly reduced
- Increasing of the residence time of reagents thanks to products removal
- Lighter operating conditions

For Pd-alloy, by going into more details, the MR presents these specific peculiarities:

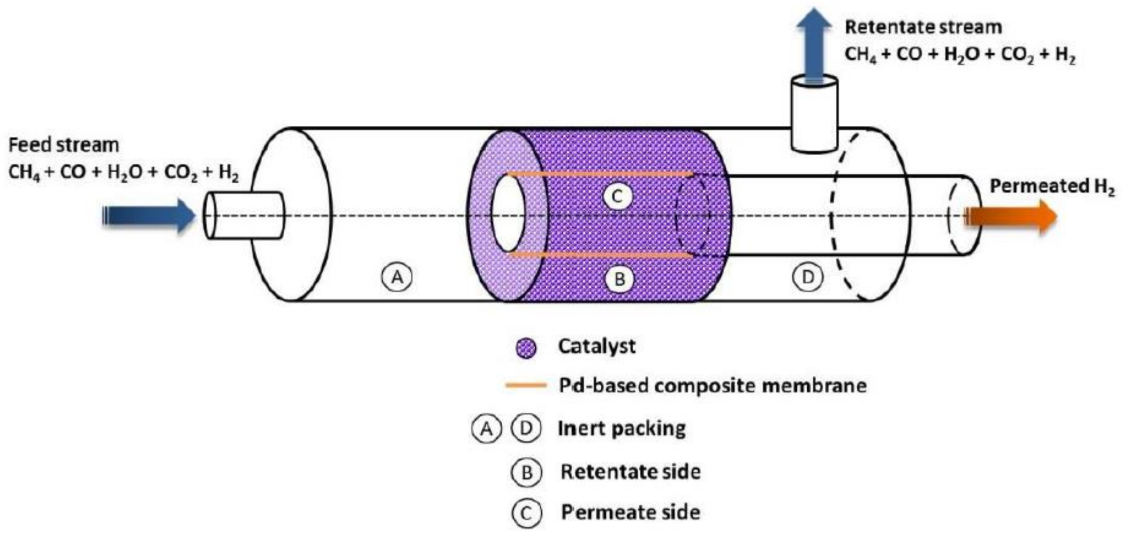
- Production of pure hydrogen
- Positive effect of pressure on the conversion, also for reactions with increasing of stationary number of moles
- Concentrated flows of retentate [23]

In conclusion it can be stated that combination of WGS reactor and Pd-alloy membrane is a good solution to provide the upgrading of carbon monoxide to hydrogen and the permeation of pure hydrogen to deliver to the fuel cell. The device takes the name of “Membrane reactor or MR”.

Membrane reactors can have different configurations.

1) Tubular shape reactor, represented by two concentric tubes. The external represents the MR shell while the internal one is constituted by the Pd-alloy dense membrane.

Figure 11. Schematic diagram of the Pd-based CMR used for H2 production



2) Plane reactor configuration. Membrane, in this case, is placed into a plane shape and the catalyst is located into one of the two chambers.
3) Tube and shell configuration

In this thesis, the first configuration is chosen as a reference model.

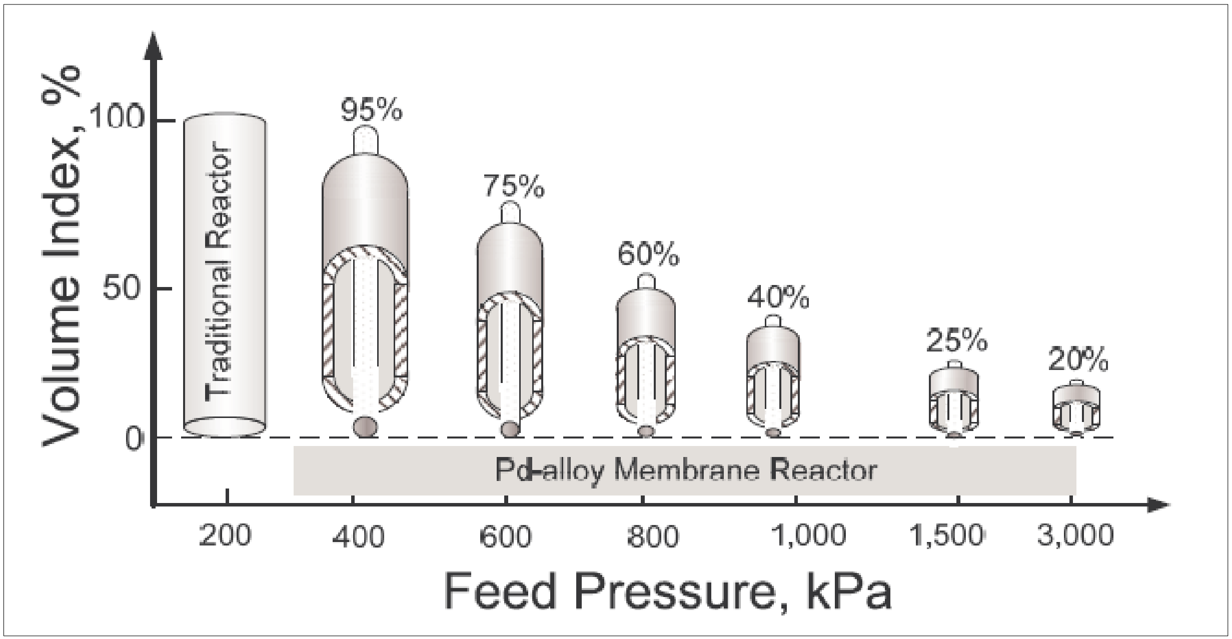
For the reaction of WGS in membrane reactors there are some new indexes that are used and that can help in understanding the strong points of their usage and the gains in their usage compared to traditional devices.

At first the Volume Index (VI) represents a relevant parameter for construction and realization of new devices. In few words, it is an indicator of the modularity of membrane reactor with respect to the traditional reactor.

$$Volume\ index = VI = \frac{V^{MR}_{reaction}}{V^{TR}_{reaction}}$$

Is has a values that ranges from 0 and 1 and it indicates, as it can be seen from the formula above, the volume of catalyst for a MR to convert a certain amount of CO compared to the volume of catalyst to convert the same amount of CO in a TR (traditional reactor).

Figure 12. VI in function of the feeding pressure. Feeding temperature = 290 °C. CO conversion = 90 %



Volume index is plotted in function of the feeding pressure of the gas. By increasing the feeding pressure, for the same obtained CO conversion and operating temperature, for example at 600 kPa the volume of the needed catalyst is 75% of the volume of catalyst necessary for a traditional reactor. So, by the application of a membrane, the quantity of catalyst is significantly reduced and it is ¼ the quantity that would be required into a traditional reactor and this is translated into a smaller reactor, lower quantity of catalyst and consequently lower cost of the material and devices.

Another important index is the conversion index.

$$Conversion\ idex = CI = \frac{Conversion^{MR}}{Conversion^{TR}} \qquad (8)$$

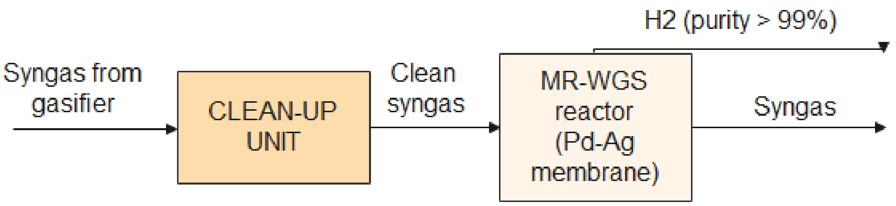
From experimental evaluations, CI is already 5 at 500 kPa. This means that the conversion of CO obtained with MR is 5 times the one obtained with a TR [23].

3.5.6.1.1 GAS CLEANING UNIT FOR PEMFC APPLICATION

Syngas coming from the gasifier has to be cleaned before entering in the process. As explained in detail in the paragraphs above, \both PEMFC and Internal combustion engine tolerate limited values of contaminants and, in this case, also the level of contaminants tolerated from Palladium-based membrane have to be taken into account being the membrane integrated in WGS reactor.

In order to have a clearer figure of the treatment section, a simplified scheme is presented in figure XX.

Figure 13. Schematic representation of upgrade and treatment section of PATH 2



As already said, the reaction/purification stage is concentrated in only one stage, the MR-WGS reactor with Pd-Ag membrane. For what concerns PEM fuel cells, allowable limits are listed in hydrogen fuel purity standards (such as J2719, Society of Automotive Engineers, or ISO 14687, International Standard Organization. In the table below, some of these contaminants allowable limits are reported.

Table 2. Allowable limits of hydrogen purity for PEMFC application

Contaminant	Allowable limit	Unit
Helium (He)	300	ppm
Nitrogen (N2)	300	ppm
Argon (Ar)	300	ppm
Methane (CH4)	100	ppm
Water (H2O)	5	ppm
Oxygen (O2)	5	ppm
Total Hydrocarbons (ex CH4)	2	ppm
Carbon Dioxide (CO2)	2	ppm
Carbon Monoxide (CO)	0.2	ppm
Formaldehyde (CH2O)	0.2	ppm
Formic Acid (CH2O2)	0.2	ppm
Ammonia (NH3	0.1	ppm
Total Sulfur (incl. H2S)	0.004	ppm

For what concerns the acceptance limits of contaminant for an internal combustion engine, values are shown below.

Table 3. Allowable limits of contaminants in fuel for Internal Combustion Engine

Contaminants	Accepted limit	Unit
HCl	5	ppm
H2S	1	ppm
PM	0.1	mg/Nm3
Particle size	10	µm
Tar	10	mg/Nm3

And, at last, the last acceptance limits of contaminants are evaluated from literature for Palladium membranes.

Table 4. Allowable limits of contaminants for Pd-alloy membranes gases

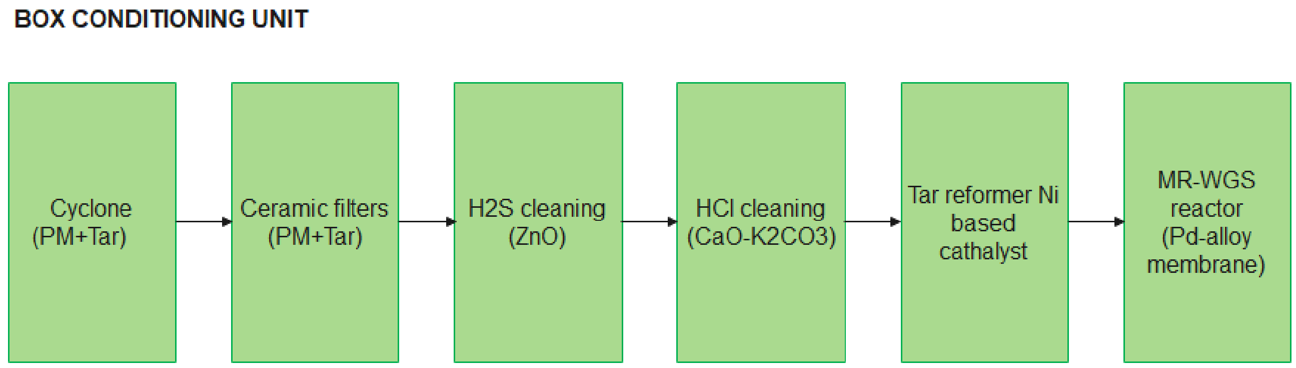
Contaminants	Accepted limit	Unit
H2S	1	ppm
CO	10	ppm

Inert gases such as CO2, Ar and N2 do not have any poisoning effect on the membrane but they decrease the level of H2 permeated.

For this type of application and for sake of simplicity, some hypothesis have been done in order to simulate the treatment process. First, the incoming syngas is considered on dry basis and it is supposed that water has already been evaporated. Then, being the total flux of syngas conveyed to the MR-WGS and being the acceptable limits for membrane and internal combustion engine similar, it is supposed that the flow of fuel receives the cleaning unit before entering the MR-WGS reactor. In this way, good functioning of the reactor-membrane and internal combustion engine are guaranteed. In addition to that, also the good operation of the PEMFC is guaranteed since the membrane guarantees the purity quality required from the fuel cell.

At this point, the cleaning unit of PATH 2 resembles the one of PATH 1, with, in addition, WGS upgrade of syngas flow and membrane separator that guarantees pure hydrogen flow on the permeated side.

Figure 14. Treatment section of PATH 2



Cyclone and ceramic filters are designed to remove particulates and tars, filter with ZnO sorbent to clean from H2S, filter with CaO-K2CO3 to remove HCl and a final tar reformer (Ni-based catalyst) performs the final tar filtration.

This cleaning unit for syngas feeding the internal combustion engine can guarantee exit conditions of the gas with HCl content < 5 ppm, H2S content < 1 ppm, PM < 0.1 mg/Nm3, Particle size < 10 µm, Tar < 10 mg/Nm3 and CO < 10 ppm.

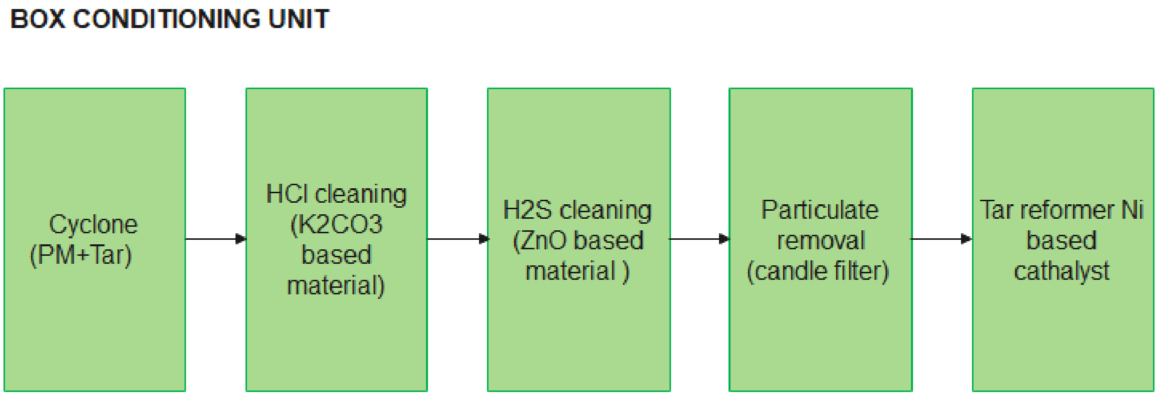
3.5.7 For SOFC application

Solid oxide fuel cells tolerate certain specific values of contaminants. The cleaning unit used for the simulation of the thesis is represented in figure below. This type of cleaning unit has been studied for the project “FLEXI FUEL SOFC”, a project that has received funding from the European Union’s Horizon 2020 research and innovation program, considering as target exiting condition of the syngas destinated to feed the SOFC the values reported in the table below.

Table 5. Allowable contaminants limits of syngas for SOFC application

Contaminant	Allowable limit	Unit
HCl	5	ppm
H2S	1	ppm
Particulate matter	0.1	mg/Nm3
Tar upgrading		

Figure 15. Cleaning unit for SOFC application (PATH 3)



FLEXI FUEL project reached the required targets of Cl and S cleaning, the tar removal reaction performed as expected and the target on the overall pressure drop (< 50 mbar) was achieved. In addition to that, also reactor target temperatures were achieved. For these reasons this particular configuration is considered as valid as a cleaning unit for this thesis, being impossible to experimentally check and build the conditioning unit for the implementation of the whole system (gasifier + conditioning unit + SOFC).

4 Production of energy

4.1 From internal combustion engine

The easier and more common application of syngas is the internal combustion engine. In particular spark ignition engine (SI) instead of compression ignition engine (CI) due to the fact that the CI still needs a petroleum feeding help while the SI engine is able to run alone with syngas thus eliminating any necessity of additional petroleum fuel.

Furthermore, the trend of syngas as a fuel for internal combustion engines is becoming more and more interesting in the last years due to the fact that the trend of the future is to shift from carbon-based to hydrogen-based energy production.

In fact, syngas is a gas composed mainly by hydrogen and carbon monoxide with low volume fraction of some other components. The combustion of hydrogen is a “clean combustion” due to its absent greenhouse emission.

The hydrogen reaction stoichiometry is

$$2\mathrm{H_2} + \mathrm{O_2} \rightarrow 2\ \mathrm{H_2O} \qquad (9)$$

$$\text{enthalpy of reaction} = -286\ \mathrm{kJ/mol}$$

It reacts with oxygen to give as product water, which is not a pollutant. Greenhouse gases are not released in the combustion of hydrogen and its enthalpy of reaction is negative and so the reaction is exothermic (heat is released during combustion). Beside this, there are some cons with the usage of pure hydrogen in particular related to the high cost of the fuel, the high difficulty of its storage, the very high flame speed and temperature which lead to an unstable combustion and knocks.

The “hydrogen issue”is not a problem in this case because, in this thesis, the combustion engine does not host pure hydrogen but the mixture of syngas. In the mixture, combustion of CO and CH4 happens in contemporary with the hydrogen’s one and these two have a really high antiknock characteristic (low flame speed) which soften the high speed flame velocity of the hydrogen combustion.

Then the trade-off position taken from the syngas as a fuel that does not have the same “clean and powerful combustion” as the hydrogen but has an easier composition which may help to ease the design of the engine makes it a valid object of study to understand the suitability of this syngas for IC engines and compare it with the traditional fuels used now for gas IC engines. The prospect of syngas as fuel for internal combustion engine is then very promising and believed to be competitive with natural gas engines. In addition to that, ICE is tolerant towards contaminants compared to gas turbines and the capital cost, reliability, high operating efficiency and modularity are very beneficial compared to other types of combustion technologies. Modularity and intermittence are two key features also if an off-grid and self-sustaining installation has to be performed which may be a great challenge for isolated places such as islands, mountain villages and so on which usually have availability of biomass feedstock.

Generally, commercial producers sell pre-built CHP unit already composed by gasifier, cleaning-unit and internal combustion engine. The cogeneration unit permits to provide electricity and also to recover the heat produced from the engine itself.

4.1.1 Mathematical simulation model

The mathematical model for the internal combustion engine is the tool that has been developed for this thesis in order to obtain, from a feeding flow of a certain fuel (in this case syngas with a characteristic LHV), power and heat produced from the device.

Most of the data have been found in literature and, in addition to that, many engine producers have been investigated and asked in order to evaluate the feasibility of a working engine with the proposed concentration of syngas and the average efficiencies of these type of commercial engines on the market.

By getting in touch with some commercial suppliers of gas engines, the data below have been collected for a net electric nominal power output of around 50 kW.

Table 6. Characteristics of the commercial syngas engine

Engine	GM - G8800 -W
Fuel	Syngas
Electric power (kW)	50
Thermal power (kW)	100
Entering power (kW)	165
Electrical efficiency	30.40%
Thermal efficiency	60.80%
Total efficiency	90.10%
Cycle	Otto
Type	Aspirated
Number of cylinders	8V
Bore and stroke (mm)	114.3x107.9
Speed (rpm)	1500
Volume (lt)	8.8
Compression ratio	10.5:1

In table XX the technical specifications of the engine are reported. The electric net nominal power of the gas engine is 50 kW and the feeding fuel is clean syngas.

Syngas enters the internal combustion engine after passing through the box cleaning unit and condensate trap which has the function of drying the fuel at a temperature of 40 °C.

Knowing that the power of the entering fuel is 165 kW, depending on the LHV of the syngas, the flow of syngas required to feed the engine is calculated as

$$Volumetic\ syngas\ flow\ rate\ \left(\frac{Nm3}{h}\right) = \frac{Power\ of\ the\ entering\ fuel\ (kW)}{LHV\ syngas\ \left(\frac{kWh}{Nm3}\right)} \quad (10)$$

With the calculated volumetric syngas flow rate, gross electrical power (11) and gross thermal power (12) at the output of the engine are calculated as

$$Gross\ electrical\ power\ (kWe) = Volumetric\ syngas\ flow\ rate\left(\frac{Nm3}{h}\right) * LHV_{syngas}\ \left(\frac{kWh}{Nm3}\right) * electrical\ efficiency\ (\%) \quad (11)$$

$$Gross\ thermal\ power\ (kWth) = Volumetric\ syngas\ flow\ rate\left(\frac{Nm3}{h}\right) * LHV_{syngas}\ \left(\frac{kWh}{Nm3}\right) * thermal\ efficiency\ (\%) \quad (12)$$

Gross electrical energy (11) and gross thermal energy (12) are calculated as

$$
\begin{aligned}
&Gross\ electrical\ energy\ (kWh) \\
&= Volumetric\ syngas\ flow\ rate\left(\frac{Nm3}{h}\right) * LHV_{syngas}\left(\frac{kWh}{Nm3}\right) \\
&* electrical\ efficiency\ (\%) \\
&* \#\ operating\ hours
\end{aligned}
$$

(13)

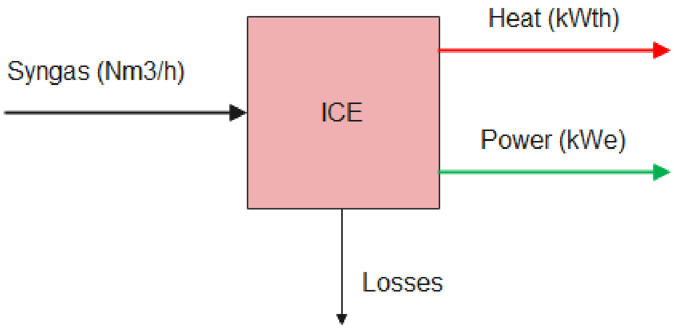
$$
\begin{aligned}
&Gross\ thermal\ energy\ (kWh) \\
&= Volumetric\ syngas\ flow\ rate\left(\frac{Nm3}{h}\right) * LHV_{syngas}\left(\frac{kWh}{Nm3}\right) \\
&* thermal\ efficiency\ (\%) \\
&* \#\ operating\ hours
\end{aligned}
$$

(14)

Where the number of the operating hours depends on the installation but usually ranges from 7000 to 7500 h.

To better visualize the functioning of the engine, a small figure represents the entering and exiting fluxes of the internal combustion engine.

Figure 16. Schematic of internal combustion engine

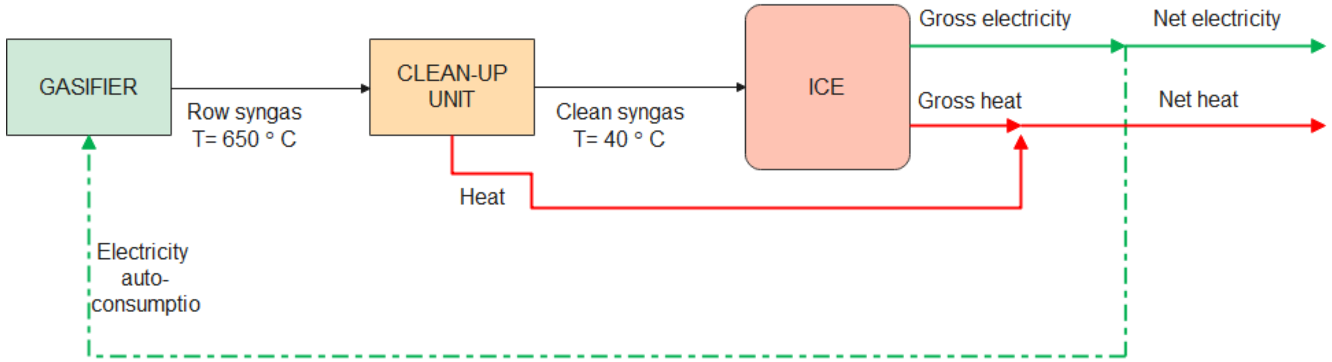


Once obtained the values of gross power (electrical and thermal) and gross energy (electrical and thermal) the engine is not considered in the model as a single device working alone, but most connected to the whole system composed by gasifier, cleaning-up section and engine.

The gasifier absorbs electrical power and this electricity is considered as the auto-consumption of the system.

The clean-up unit, being the syngas exiting from the gasifier at high temperature, does not need extra heat to work and instead it produces heat from the cooling of the syngas in the condensate trap (where it reaches the temperature of 40 °C).

Figure 17. Schematic of the internal combustion engine system



Net electricity and net heat at the output of the system are calculated as

$$\text{Net electricity (kW)} = \text{Gross electricity (kW)} - \text{Electricity autoconsumption(kW)} \quad (15)$$

$$\text{Net heat (kW)} = \text{Gross heat (kW)} + \text{Heat(kW)} \quad (16)$$

The same evaluation is done for the net electrical energy and thermal energy by multiplying the values of net electricity and heat by the number of operating hours of the plant.

Electricity auto-consumption, from experimental evaluation, is the 15 % of gross electricity.

$$Electricity\ autoconsumption\ (kW) = 15\% * Gross\ electricity\ (kW) \quad (17)$$

Thermal production from the cleaning unit is estimated as

$$\text{Heat (kW)} = \dot{m}_{\text{syngas}} * c_{\text{p,syngas}} * \Delta T \quad (18)$$

where ΔT is the difference of temperature between the exit of the clean-up unit and 40 °C (temperature at which the syngas enters the internal combustion engine after the condensate trap).

With an economical evaluation of the auto-consumption, it is possible to understand if it is convenient to sell directly the quote of gross electricity to the grid and buy from the grid the quote of auto-consumption or if it is more convenient to take from the gross electricity produced the quote of electricity auto-consumption. For this study, this calculation is not performed since it is not one of the goals of the thesis but it is a good point of development of it.

4.2 General assumptions for models of PEMFC and SOFC production of energy

The mathematical simulation model is performed with the implementation of a model in the software Aspen Plus 10 and its main goal is to obtain the technical efficiencies (%) and the volume flow of syngas required (Nm3/h) to produce a total net electric power of 50 kWe. Model is also used to calculate and estimate thermal and electric auto-consumptions (kW) in the process. The operating conditions are imposed by the layout of the system described. A brief introduction to the blocks used in the model, their function and assumptions is done in the following paragraph to ensure a good understanding of the model. Values obtained from the model are enough accurate and always compared to literature values.

Aspen Plus software uses a modular approach for the calculation of processes. In its basic computations it uses the common balances of thermodynamics but with FORTRAN it is possible to input additional calculations, constraints and parameters.

4.2.1 Blocks used in this work

In this thesis the simulations are performed by using the following Aspen blocks:

1. Stoichiometric reactor (R-Stoic): it is used either when the stoichiometry of the reaction is known, user can specify the extent of a reaction or conversion or kinetics of the reaction is not known or not important. In this block the user must enter the operating conditions, reactions and reference conditions in order to calculate the heat of the reaction.
2. Separators (Sep): this block unify the inlet streams and separate the outlet into two or more streams according to the receive input. This block can then be used when vapor-liquid equilibrium is known and other details on the reaction are not important or necessary for the calculations.
3. Mixer: this block mixes material, heat or work inlet into a single output.
4. Splitters: they split the incoming flux into two exiting flux of the same composition and properties according to the specified splitting factor.
5. Heat exchangers. They determine the heating or cooling duty required to reach a certain temperature.
6. Pressure changers. In this simulation, pump and compressors are used and they expand or compress a flow calculation the work duty.
7. Streams of material. They are the streams representing one or more material and their composition can be defined in terms of component flows, fractions or concentration.
8. Streams of heat and work. They are stream that can supply or withdraw heat or work.

4.2.2 General assumptions for PEMFC and SOFC

Gases are considered ideal and pressure drops are neglected. Furthermore, some assumptions have been done in the model for what concerns the fuel cell operation. Pressure changers are set with their own isentropic and mechanical efficiency, values taken from literature, and are here reported:

Table 7. Pressure changers input parameters

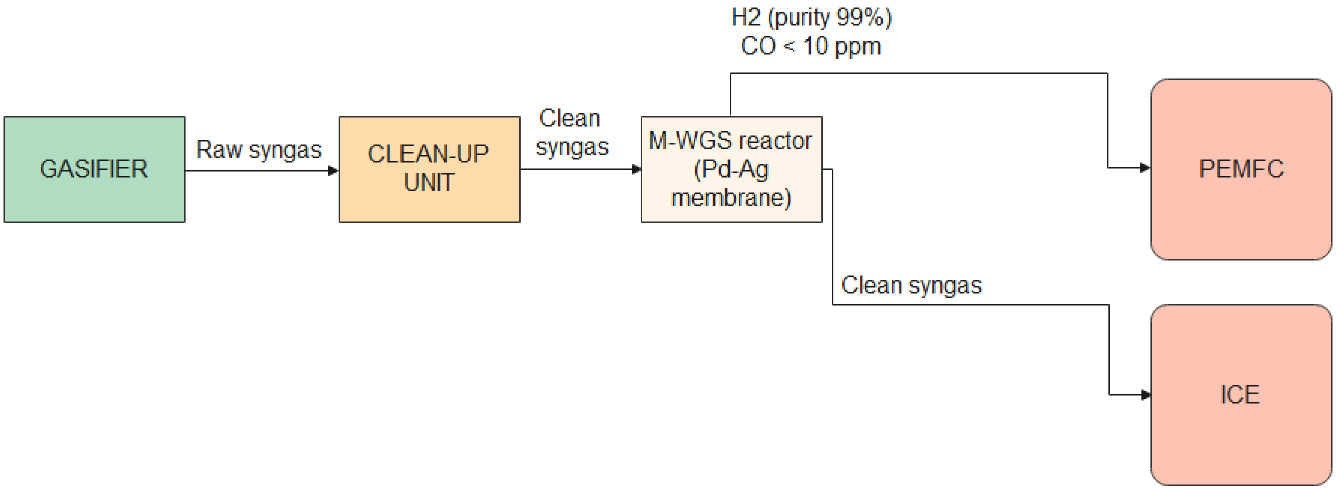
	Isentropic efficiency (%)	Mechanical efficiency (%)
Compressor	0.75	0.95
Fan	0.6	0.98
Expansion Turbine	0.84	0.85
Pump	0.6	0.9

4.3 From PEMFC fuel cells

In PATH 2, being syngas a mixture of hydrogen and carbon monoxide, sees the separation of H2 from the flow in order to use it as fuel for a PEMFC. The rest of the flow is conveyed to an internal combustion engine. The hydrogen as energy vector is a good solution to the growing necessity of new abundant, clean and safe energy sources. Fuel cells are in fact a great alternative to the conventional energy production systems, and they are great for transport and stationary production due to their characteristics as high efficiency (around 40%), modularity, the independency of the efficiency from load and plant dimension and the very reduced environmental impact. In fact, hydrogen burns in the air and the only product of its reaction with air is pure water. Beside all these positive aspects, it is important to underline that the only one very important requirement for this type of cells is that the feeding hydrogen has to be pure and almost CO-free, which imply a content of CO lower than 10 ppm. By getting in contact with some experts, reading literature and experimental results, membrane reactor is the best solution for hydrogen separation from the flow of syngas [23].

The solution adopted for the mathematical model is a membrane reactor with a single stadium for reaction/purification which consists into a membrane reactor for WGS with a Pd-alloy membrane (in particular Pd-Ag membrane). The permeated flow (pure hydrogen) is then conveyed to the fuel cell while the remaining gas exiting from the reactor goes to feed the internal combustion engine.

Figure 18. Schematic of PATH 2



4.3.1 **PEM Fuel Cell**

The Proton-Exchange Membrane fuel cells, as the other fuel cells, do not use a combustion reaction but they are electrochemical device with a very high efficiency (it can be over 50%) and very low environmental impact. They are composed by two porous electrodes with an electrolyte in between which lets the positive ions to pass from one electrode to the other one. They operate al low temperatures (70-90 °C) and the reactions at the electrodes are not helped by the heat but instead by some precious and expensive catalysts (Au, Pt, Ag), reason why the electrodes are porous and filled with catalysts. The electricity production of one single cell reaches low values of Watt, for this reason it is necessary to place the cells in series in a configuration called MEA, forming so the so-called stack of cells. From the poisoning side of the technology, the feeding fuel has to be pure and these types of cells suffer in particular from CO poisoning which risks to combine with the catalyst, blocking its functioning.

The semi-reactions happening at the electrode, being the ion through the electrolyte a positive ion H^+, are the following:

$$Anode: 2H_2 \rightarrow 4H^+ + 4e^- \qquad (hydrogen\ oxidation)$$

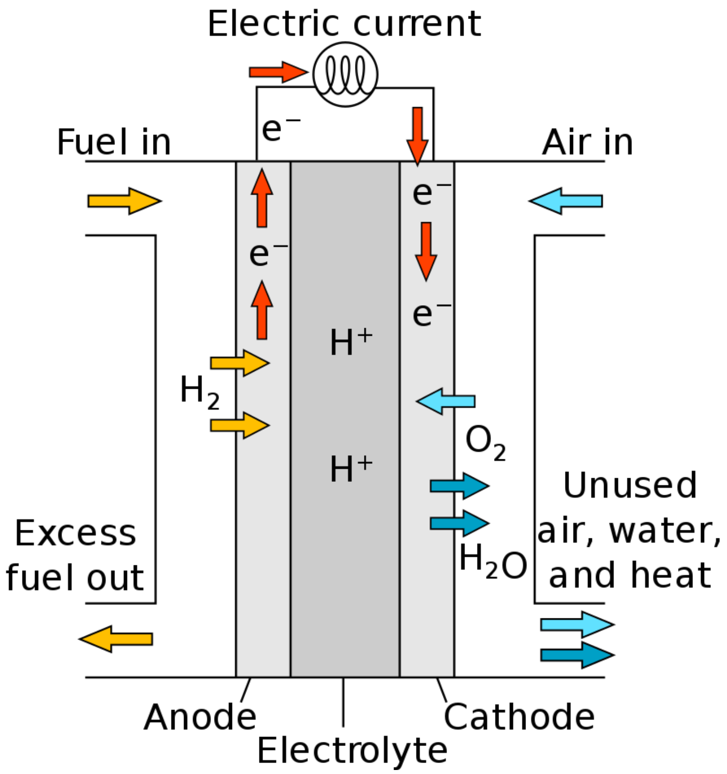
$$Cathode: O_2 + 4e^- + 4H^+ \rightarrow 2H_2O \qquad (oxigen\ reduction)$$

Finally the chemical reaction that is used in a PEMFC to produce electricity is the water syntesis:

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$$

The passage of current happens thanks to the difference in potential between the negative electrode (anode) and the positive one (cathode). The electrolyte permits instead a ionic current, so the passage of the positive ion in this PEM fuel cell. The difference between the thermal energy of reaction and the electricity production is released as heat at the operating cell temperature. For a good functioning of the cell, the temperature of the cell has to be kept constant and the surplus of heat released can be collected and used for cogeneration purposes.

Figure 19. Schematic of a PEM fuel cell

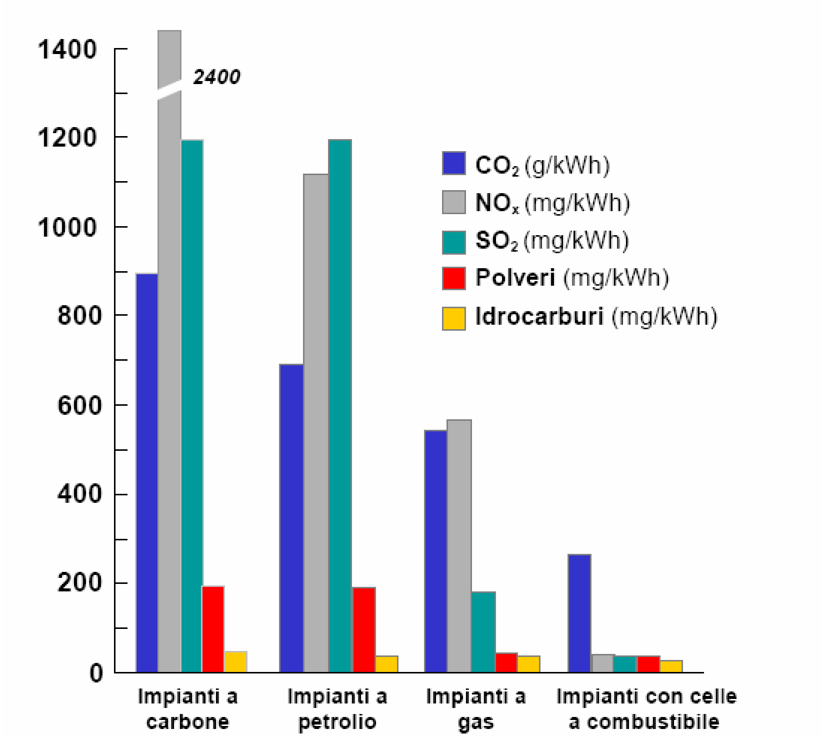


The application of PEM fuel cell is possible for vehicles and portable applications thanks to the fact that it does not use any corrosive fluid and can work oriented in any direction.

Working the cell al low temperatures, fuel flexibility is not feasible and the cell has to be fed with pure hydrogen (purity around 99.99%). Due to this reason, syngas cannot be used directly as fuel in this application but the hydrogen contained into it can be separated and used as feeding fuel for the fuel cell.

It is interesting to see the emission of PEM fuel cells compared to the traditional power generation plants.

Figure 20. Comparison of PEM fuel cells emissions to traditional power generation plants [26]



Since one of the goals of the future is the reduction of the greenhouse gases, from the figure above it can be clearly seen that the integration of fuel cells in the production of energy is of great interest.

4.3.2 Efficiency definitions

In this model, many technical efficiencies are calculated. Starting from the MR-WGS section, which is simulate in Aspen Plus, the conversion efficiency of CO is calculated as

$$CO\ conversion\ efficiency\ (\%) = \frac{100\% * CO\ outlet\ (kmol/s)}{CO\ inlet\ (kmol/s)}$$

where CO outlet is the molar flow of carbon monoxide exiting the reactor while CO in is the molar flow of carbon monoxide entering the reactor. This calculation is very important because this efficiency is the first parameters determines the quantity of hydrogen produced for the PEMFC. As seen before, in literature this values is around 85-90%.

The second efficiency definition is the separation efficiency of the Pd-Ag membrane and it is defined as

$$Membrane\ separation\ efficiency\ (\%) = \frac{H2\ permeated\ flow\ (kmol/s)}{H2\ feeding\ flow\ \ (kmol/s)} \tag{19}$$

In this model, seen the impossibility to perform the layout and so the experimental proof, this efficiency value is read from the literature and imposed to the model.

By proceeding to the fuel cell section, some other efficiencies are defined. First of all, a distinction has to be done between the efficiency at the stack level and the efficiency at the BoP level. Electrical efficiency at a stack level of a fuel cell is defined in equation (4) as the ratio of the electrical DC power produced Wel (MW) and molar flow rate of feeding fuel nfuel (kmol/s) multiplied by the LHV fuel (MJ/kmol) while thermal efficiency of the stack is calculated in equation (14) as the heat released from the cell Qreleased (MW) divided by the multiplication of LHV of the fuel by the mole flow rate of the fuel (kmol/s).

$$\mu_{el,FC} = \frac{Wel}{LHV_{fuel} \cdot n_{fuel}} \quad (20)$$

$$\mu_{th,FC} = \frac{Qreleased}{LHV_{fuel} \cdot n_{fuel}} \quad (21)$$

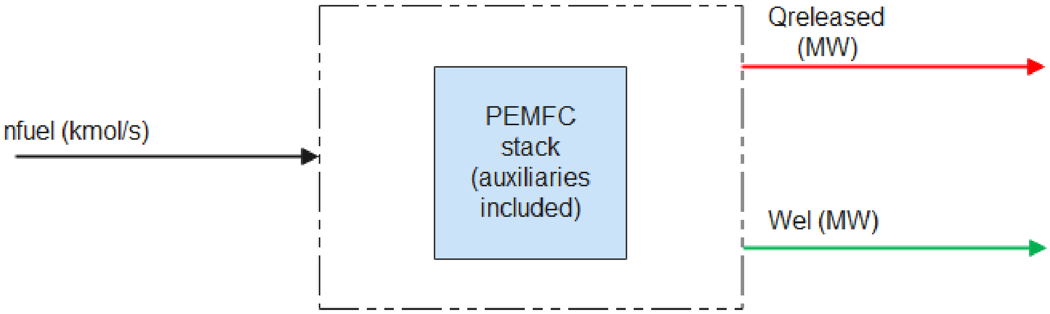
These two efficiencies are based on the gross electrical power that the fuel cell power and heat that the fuel cell can produce. Of particular interest for this thesis is the efficiency of the process in the whole, which means the combination of syngas production section, syngas treatment section and energy and heat production final section.

A new efficiency, called CHP efficiency or total efficiency, is calculated as the sum of thermal and electrical efficiency as follow

$$\mu_{total,FC} = \mu_{el,FC} + \mu_{th,FC} \quad (22)$$

Until this level, the control volume considered is the one of the stack as shown in the figure.

Figure 21. Balance at stack level for PEMFC



At this point, the parameters and efficiencies of the internal combustion engine are the same exposed in the mathematical model of the internal combustion engine of the section of the thesis before.

By proceeding with the evaluation of efficiencies, for a practical application it is important to evaluate the efficiency of the whole process, which is defined as the total output of electricity or heat divided by the power of the fuel entering in PATH 2. At this point, the electricity produced is the summation of the quote produced from the PEMFC and the quote produced from the internal combustion engine.

$$W_{el,TOTAL}(kW) = W_{el,PEMFC}(kW) + Q_{el,ICE}\,(kW) \qquad (23)$$

$$Q_{TOTAL}(kW) = Q_{PEMFC}(kW) + Q_{ICE}\,(kW) \qquad (24)$$

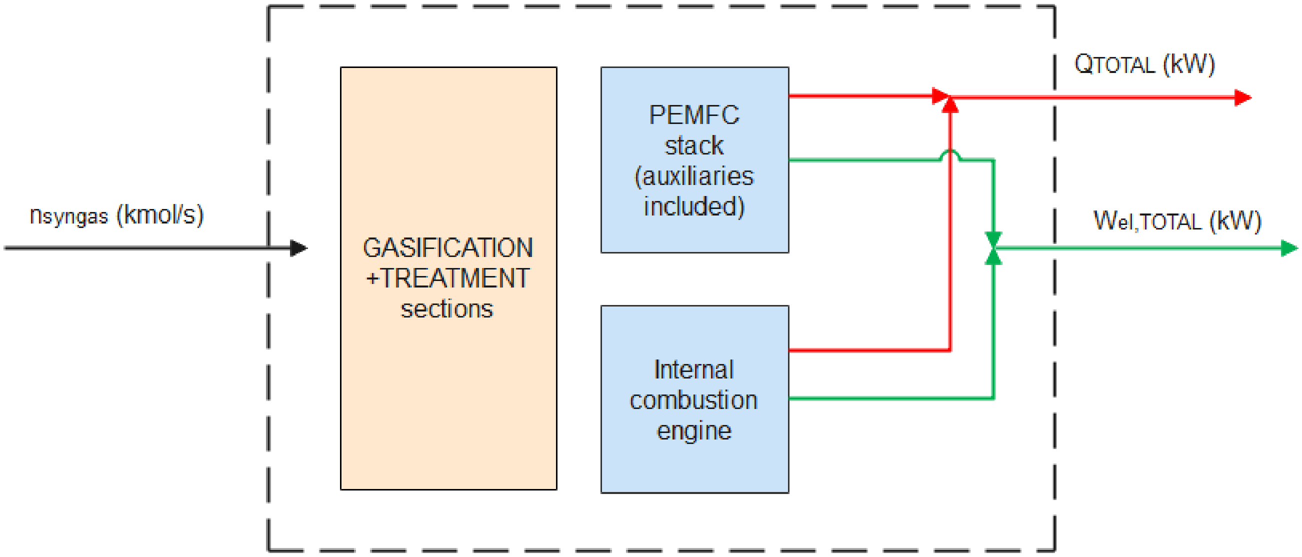
The total gross thermal and electrical efficiencies are evaluated as

$$System\ gross\ electrical\ efficiency\ (\%) = \frac{W_{el,TOTAL}}{\mathrm{LHV_{syngas}} \cdot \mathrm{n_{syngas}}} \quad (25)$$

$$System\ gross\ thermal\ efficiency\ (\%) = \frac{Q_{TOTAL}}{\mathrm{LHV_{syngas}} \cdot \mathrm{n_{syngas}}} \quad (26)$$

To help the understanding of the efficiencies, a schematic not detailed representation of these efficiencies calculation parameters is show below.

Figure 22. Balance at plant level PATH 2



A new parameter then is considered and it is named auto-consumption, both electrical and thermal. By evaluating from Aspen model the quantity of heat and electricity produced and consumed, the auto-consumption can be defined as

$$electricity\ autoconsumption\ (kW) = electricity\ absorbed\ (kW) \quad (27)$$

$$heat\ autoconsumption\ (kW) = heat\ absobed\ (kW) \quad (28)$$

For sake of simplicity, auto-consumption is usually expressed in percentage as

$$electricity\ autoconsumption\ (\%) = \frac{electricity\ absorbed\ (kW)}{W_{el,TOTAL}\ (kW)} \quad (29)$$

$$heat\ autoconsumption\ (\%) = \frac{heat\ absorbed\ (kW)}{Q_{TOTAL}\ (kW)} \quad (30)$$

At this point it is possible to evaluate net efficiencies and productions as

$$W_{el,NET-TOTAL}(kW) = W_{el,TOTAL} - \ electricity\ autoconsumption\ (\%) * W_{el,TOTAL} \qquad (31)$$

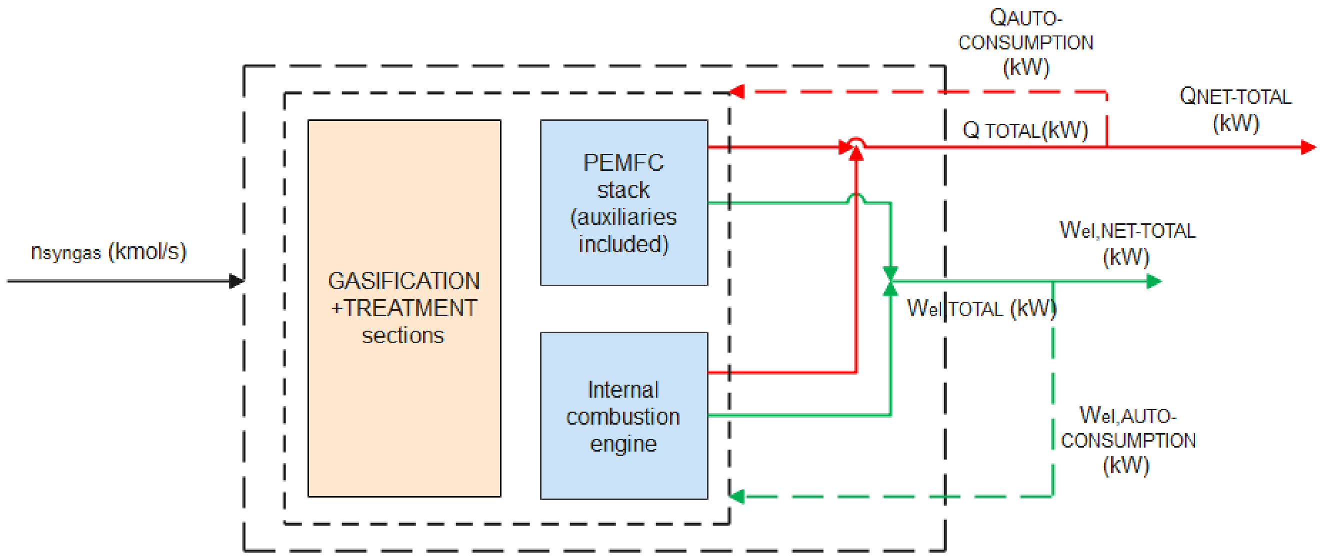
$$Q_{NET-TOTAL}(kW) = Q_{TOTAL}\ (kW) - heat\ autoconsumption\ (\%) * Q_{TOTAL}\ (kW) \qquad (32)$$

And relative efficiencies

$$System\ net\ electrical\ efficiency\ (\%) = \frac{W_{el,NET-TOTAL}}{\mathrm{LHV_{syngas}} \cdot \mathrm{n_{syngas}}} \qquad (33)$$

$$System\ net\ thermal\ efficiency\ (\%) = \frac{Q_{NET-TOTAL}}{\mathrm{LHV_{syngas}} \cdot \mathrm{n_{syngas}}} \qquad (34)$$

Figure 23. Schematic of balance of plant with auto-consumption PATH 2



4.3.3 Aspen Plus model

In Aspen's simulation, the starting point is then the syngas that comes, already cleaned in the treatment unit, from pyrolysis or gasification process. The flow of syngas in further sent to the WGS reactor equipped with Pd-alloy membrane where the shift reaction takes place:

WGS (Water Gas Shift) reaction $\mathrm{CO} + H_2 0 \rightarrow CO_2 + H_2$ $\Delta\mathrm{H} = -41 \frac{\mathrm{kJ}}{\mathrm{mol}}$ (35)

This step is necessary to convert carbon monoxide into hydrogen and so, to enrich the flow of syngas of hydrogen so that it possible to separate a greater quantity of hydrogen that goes to feed the PEMFC with a purity of 99.9%. The WGS reaction happens with a steam to carbon monoxide ratio between 2 and 4 [27] even though the reaction would take place also if the steam to carbon monoxide ratio would be 1 but by increasing the ratio it is possible to reduce the carbon deposition and so to preserve the reactor and the Pd-alloy membrane integrity. The model of the integrated WGS-Pd-alloy reactor is implemented in Aspen Plus.

Figure 24. Integrated WGS reactor

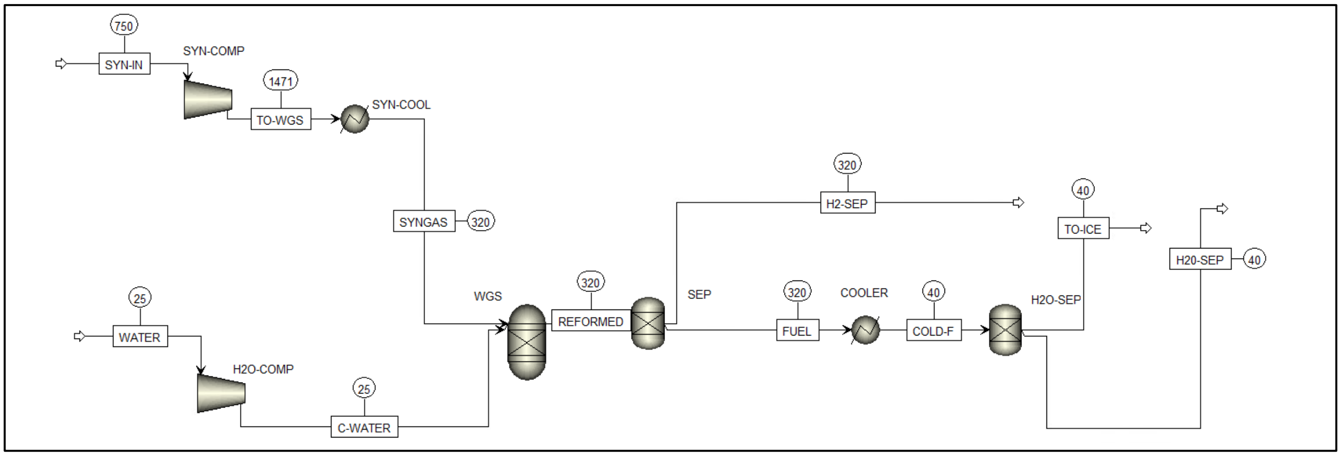


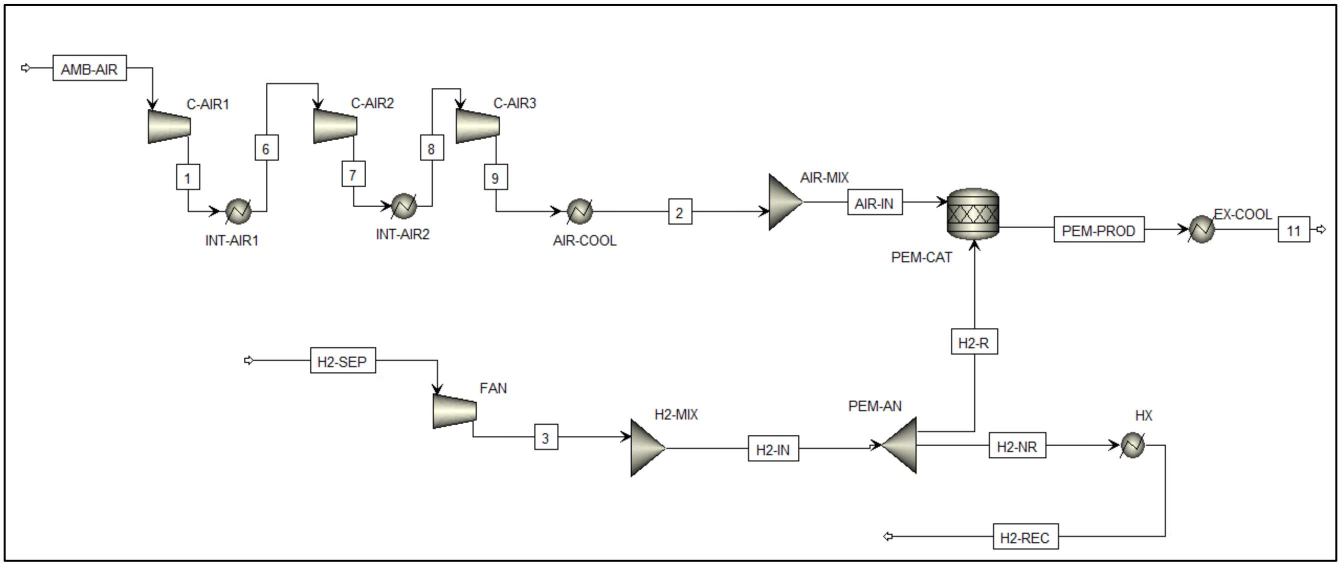
Table 8. Aspen plus model of WGS-reactor

Stream/Block	Specifications
SYN-IN	Syngas flow entering in the system after the upgrade and treatment unit
WATER	Clean and distilled water entering the WGS reactor
WGS	R-Gibbs where WGS reaction takes place
REFORMED	Syngas flow enriched in H2
SEP	H2 separator (Pd-alloy membrane)
SEP-H2	Pure H2 flow stream (>99.9% purity)
TO-ICE	Fuel flow to ICE

The syngas flow, either from plastic pyrolysis or from biomass gasification, enters the process at high temperature (around 750 °C). This high temperature is due to the heat required for the cleaning process of the gas before entering in the PEMFC and internal combustion engine. In this thesis, the cleaning unit is not analyzed step by step but the process is analyzed from there on. The assumption is then to start from a temperature of the syngas of 750 °C. The WGS reactor is fed from the SYNGAS flow and from the WATER (steam) flow. Both the streams are pressurized at a level of pressure of 6 bars to simulate the pressure of the WGS-reactor membrane of Pd-alloy which, as explained before, uses the difference in pressure to permeate the hydrogen from one to the other side of the membrane. The temperature of operation of the WGS reactor is set to 320 °C. It is important to notice that the water gas shift reaction almost not influenced by pressure while it is highly influenced by temperature. Being the reaction exothermic, it is better to keep the reactor temperature low. After the WGS reactor, the stream REFORMED is a stream richer in hydrogen and poorer in carbon monoxide compared to the entering composition of the SYN-IN. The conversion factor of CO at temperature 320 °C and pressure 6 bars is 0.92. The REFORMED stream enters in the SEP, which simulates the Ps-alloy membrane. In order to simulate its behavior, the exiting flow from the SEP is supposed to be at 1 bar, so finally the permeate side has a low pressure and the feeding side has the high pressure. In this way the proper work of the membrane is possible. To be consistent with the temperatures, since the reactor would ideally be concentrated in only one device, the temperature of the REFORMED gas is kept constant at 320 °C. After the separation, the H2-SEP flow is the flow of hydrogen at 99.99% of purity that feeds the PEMFC while the other part of the flow is conveyed to the internal combustion engine. Before sending the flow to the combustion engine, it is cooled into the COOLER, heat exchanger that lowers the temperature to 40 °C, being this temperature the entering one required by a gas engine. With this rapid cooling, heat is released and also water is condensed and separated (H2O-SEP). Finally the remaining fuel in the stream TO-ICE is conveyed to the internal combustion engine. It has to be noticed that, even though the components of the syngas are still the same, at this point of the process (TO-ICE stream), they assume new mole fraction values that are analyzed in details afterward. The changing of this values causes a change in the LHV of the feeding syngas to the engine and it certainly decreases. The analytic procedure is explained in the following paragraphs.

At this point, the model used for the internal combustion engine is the one that has been explained in the section before. The model of the PEMFC is implemented in Aspen with the following scheme.

Figure 25. Aspen Plus model of PEMFC in air-feed configuration



AMB-AIR and H2-SEP enters the section at 25 °C and 1 bar and 320 °C and 1 bar. The stream H2-SEP is the separated oxygen coming from the previous WGS process and separation. This arrives at high temperature and pressure of the permeated side to provide the continuity of the chain and guarantee the validity of the simulation. Both the fuel (H2) and the oxidant (air) exit the cell at a temperature of 50 °C. The cell is cooled down by a circuit that is later discussed.

The atmospheric air is compressed before entering the fuel stack being the operating pressure of the stack of around 20 bars. The calculation of the air necessary to feed stack starts from the calculation of the stoichiometric amount of air necessary for the hydrogen reaction.

Being the reaction of the hydrogen

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$$

from the proportion between the mole flow of hydrogen (kmol/s) and the stoichiometry of the reaction the stoichiometric mole flow of air is calculated as

$$\dot{n}_{air,stoic} = \dot{n}_{H2} * \frac{1}{2} * \frac{100}{21} \qquad (36)$$

Once obtained the stoichiometric mole flow of air, the real flow rate is calculated by considering the concept of AU (Air utilization) which is the ratio of stoichiometric mole flow of air on real mole flow of air

$$AU = \frac{\dot{n}_{air,stoic}}{\dot{n}_{air,real}} \qquad (37)$$

This indicator assumes usually values in the range from 0.10 to 0.3, depending on the application.

Now, the real mole flow of air necessary to feed the PEMFC is calculated as

$$\dot{n}_{air,real} = AU * \dot{n}_{air,stoic} \qquad (38)$$

The greater is the mole flow of hydrogen entering in the system, the greater will be the real mole flow of air and so the work to compress it.

For small scale PEMFC an air blower would be sufficient to send the air to the fuel stack while for bigger applications compressors are needed [28] since they have to guarantee higher pressures. The stack is represented by the stoichiometric reactor PEM-CAT which is the cathode and the splitter PEM-AN which is the anode. The cathode receives the positive ions H3O+ from the anode and in this way, the fuel (hydrogen) oxidizes. The splitter is the component that defines the fuel utilization of the stack that, according to literature, is set to 0.8 while the HX simulates the internal heat up of the unused fraction of hydrogen. The fuel exhaust can be partially recirculated and mixed with fresh H2. In order to increase the efficiency of the cell the anode outlet could be closed so that the unconsumed hydrogen does not exit the cell (dead-end configuration), but this configuration cannot be adopted for real configurations because it would lead to accumulation of impurities such as nitrogen that crosses over from the cathode and fuel impurities and would make water management of the cell difficult. This happens because the water produced from the semi-reaction is recirculated with the anode gas and wets the inlet fuel.

The full reaction is the standard water formation reaction

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2\mathrm{O} \qquad (39)$$

and the semi-reactions happening at the electrodes are

$$H_2 \rightarrow 2\mathrm{H}^+ + 2\mathrm{e}^- \qquad (40)$$

$$\frac{1}{2}O_2 + 2\mathrm{H}^+ + 2\mathrm{e}^- \rightarrow H_2\mathrm{O} \qquad (41)$$

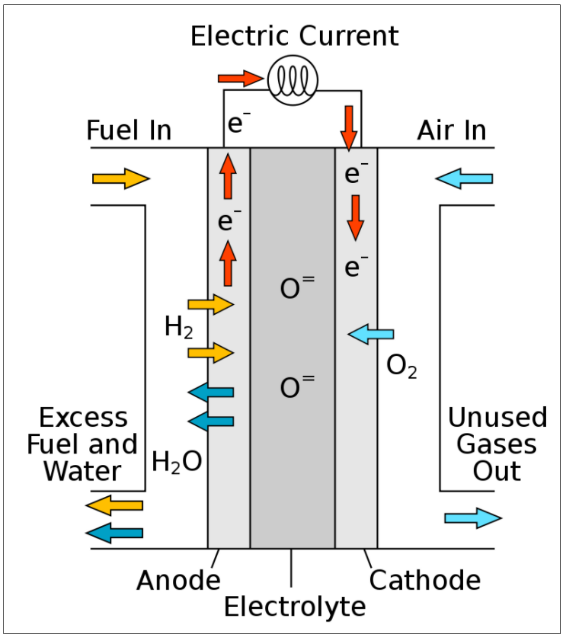
The sizing of the whole process is studied to guarantee 50 kW of electric net power as the sum of the power produced from the PEMFC and the power produced from the IC.

4.4 From SOFC (Solid oxide fuel cell)

4.4.1 SOFC fuel cell

Solid oxide fuel cells are a clean, pollution-free technology for the production of electricity at high efficiency. There are many advantages in the use of these cells, in particular the high efficiency of the cell itself, the modularity, the great fuel flexibility, the low emission of NOx and SOx and the possibility of internal reforming of natural gas into the stack. Fuel flexibility is the condition that allows the integration of the cells with other systems as steam turbine cycles in cogeneration systems. Cells work at high temperatures (750-800 °C) and for this reason they are composed by a solid electrolyte. This electrolyte is a ceramic material which is able to conduct O2- ions. The anode of the cell is made of cermet, composite ceramic material ceramic (ZrO2)- metallic (Ni). Nickel is a good conductor material and, in addition to that, it acts as catalyzer for the internal reforming of methane. Cathode is made by a composite ceramic material that contains conductor oxides of electrons and from ceramic materials able to conduct ions.

Figure 26.Scheme of a SOFC [29]



For a traditional SOFC fed by hydrogen, the reaction happening at the stack is

$$2H_2 + O_2 \rightarrow 2H_2O \tag{42}$$

and the semi-reactions happening at the electrodes are

$$2H_2 + 2O_2{}^{-} \rightarrow 2H_2O + 4e^{-} \tag{43}$$

$$O_2 + 4e^{-} \rightarrow 2O_2{}^{-} \tag{44}$$

Due to the high temperatures of operation, heat and electricity are both useful products of the fuel cell and the produced heat of the stack can be used to maintain the high operating temperature of the cell and to pre-heat the cathodic flux to the cell. The disadvantages of SOFC are the elevated temperatures which is a big challenge for the stability of the materials of the cell and their chemistry. Moreover the degradation of the material is greater and more expensive materials have to be employed. The dynamic of operation is slower and they have very long start-up time, for this reason they cannot be employed for transportation applications but instead for base-load applications so that they can rely on the absence of thermal cycles. The fact that the high temperature favors the kinetic charge transfer, there is no need of precious catalysts for SOFC. In fact, Nickel is an industrial product and it is the most used in these applications. Another advantage of the temperature is given by the fact that the cell produces heat at high temperature which is translated, in thermodynamics, into more precious quality heat and higher exergy content.

The use of syngas as direct fuel for the SOFC is possible thanks to the high temperatures of operation of this type of cell. The mechanism of reaction into the cell becomes more complex when the fuel is not pure hydrogen because many species and reactions take place. The reaction with the fastest kinetic at the anode is the oxidation of hydrogen but other species can directly react at the anode according to its composition. For example, carbon monoxide reacts directly at the anode of Ni/YSZ with a slower kinetics compared to the hydrogen's one.

$$\mathrm{CO} + \mathrm{H_2O} \rightarrow \mathrm{CO_2} + \mathrm{H_2} \qquad (45)$$

The other most important reaction happening is the so-called steam reforming which is activated by Nickel

$$\mathrm{CH_4} + \mathrm{H_2O} \rightarrow 3\mathrm{H_2} + \mathrm{CO} \qquad (46)$$

which is able to convert natural gas into precious hydrogen. This reaction is highly exothermic endothermic and it needs heat to happen.

Also the dry reforming can happen when the gas mixture is directly fed to the SOFC

$$\mathrm{CH_4} + \mathrm{CO_2} \rightarrow 2\mathrm{H_2} + 2\mathrm{CO} \qquad (47)$$

And the direct electrochemical oxidation of CH4

$$\mathrm{CH_4} + 4\mathrm{O_2}^{-} \rightarrow 2\mathrm{H_2O} + CO_2 + 8\mathrm{e}^{-} \qquad (48)$$

What happens exactly in the cell depends on kinetic and thermodynamics.

4.4.2 **Efficiency definitions**

For what concerns fuel cell section a distinction has to be done between the efficiency at the stack level and the efficiency at the BoP level (as it is done in PEMFC section). Electrical efficiency at a stack level of a fuel cell is defined in equation (4) as the ratio of the electrical DC power produced Wel (MW) and molar flow rate of feeding fuel nfuel (kmol/s) multiplied by the LHV fuel (MJ/kmol) while thermal efficiency of the stack is calculated in equation (14) as the heat released from the cell Qreleased (MW) divided by the multiplication of LHV of the fuel by the mole flow rate of the fuel (kmol/s).

$$\mu_{el,FC} = \frac{Wel}{LHV_{fuel} \cdot n_{fuel}} \quad (49)$$

$$\mu_{th,FC} = \frac{Qreleased}{LHV_{fuel} \cdot n_{fuel}} \quad (50)$$

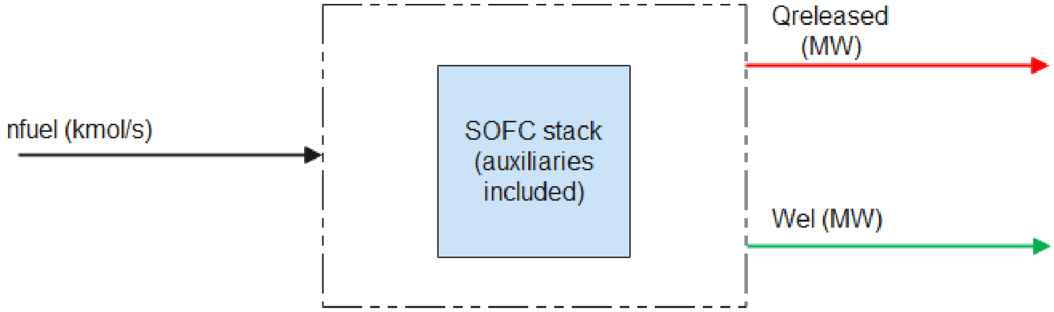
These two efficiencies are based on the gross electrical power that the fuel cell power and heat that the fuel cell can produce. Of particular interest for this thesis is the efficiency of the process in the whole, which means the combination of syngas production section, syngas treatment section and energy and heat production final section.

A new efficiency, called CHP efficiency or total efficiency, is calculated as the sum of thermal and electrical efficiency as follow

$$\mathrm{\mu_{total,FC}} = \mathrm{\mu_{el,FC}} + \mathrm{\mu_{th,FC}} \quad (\ 51\ )$$

Until this level, the control volume considered is the one of the stack as shown in the figure.

Table 9.Balance at stack level for SOFC



By proceeding with the evaluation of efficiencies, for a practical application it is important to evaluate the efficiency of the whole process, which is defined as the total output of electricity or heat divided by the power of the fuel entering in PATH 3.

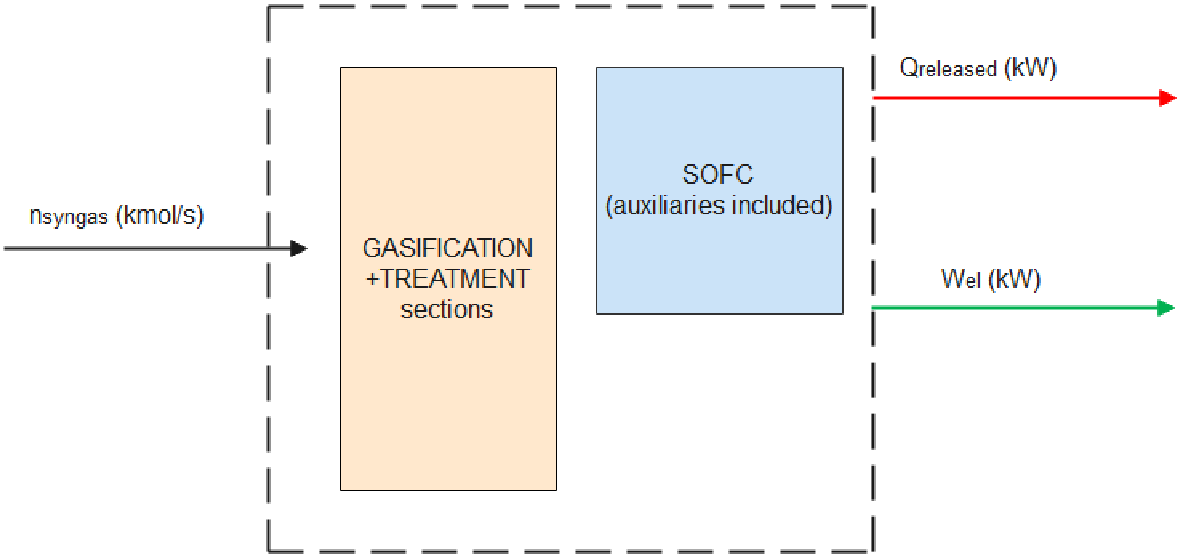
The total gross thermal and electrical efficiencies are evaluated as

$$System\ gross\ electrical\ efficiency\ (\%) = \frac{W_{el}}{\mathrm{LHV_{syngas}} \cdot \mathrm{n_{syngas}}} \quad (52)$$

$$System\ gross\ thermal\ efficiency\ (\%) = \frac{Q_{released}}{\mathrm{LHV_{syngas}} \cdot \mathrm{n_{syngas}}} \quad (53)$$

To help the understanding of the efficiencies, a schematic not detailed representation of these efficiencies calculation parameters is show below.

Figure 27. Balance at plant level PATH 3



A new parameter then is considered and it is named auto-consumption, both electrical and thermal. By evaluating from Aspen model the quantity of heat and electricity produced and consumed, the auto-consumption can be defined as

$$electricity\ autoconsumption\ (kW) = electricity\ absorbed\ (kW) \qquad (54)$$

$$heat\ autoconsumption\ (kW) = heat\ absobed\ (kW) \qquad (55)$$

For sake of simplicity, auto-consumption is usually expressed in percentage as

$$electricity\ autoconsumption\ (\%) = \frac{electricity\ absorbed\ (kW)}{W_{el,TOTAL}\ (kW)} \qquad (56)$$

$$heat\ autoconsumption\ (\%) = \frac{heat\ absorbed\ (kW)}{Q_{TOTAL}\ (kW)} \qquad (57)$$

At this point it is possible to evaluate net efficiencies and productions as

$$W_{el,NET-TOTAL}(kW) = W_{el,TOTAL} - \ electricity\ autoconsumption\ (\%) * W_{el,TOTAL} \qquad (58)$$

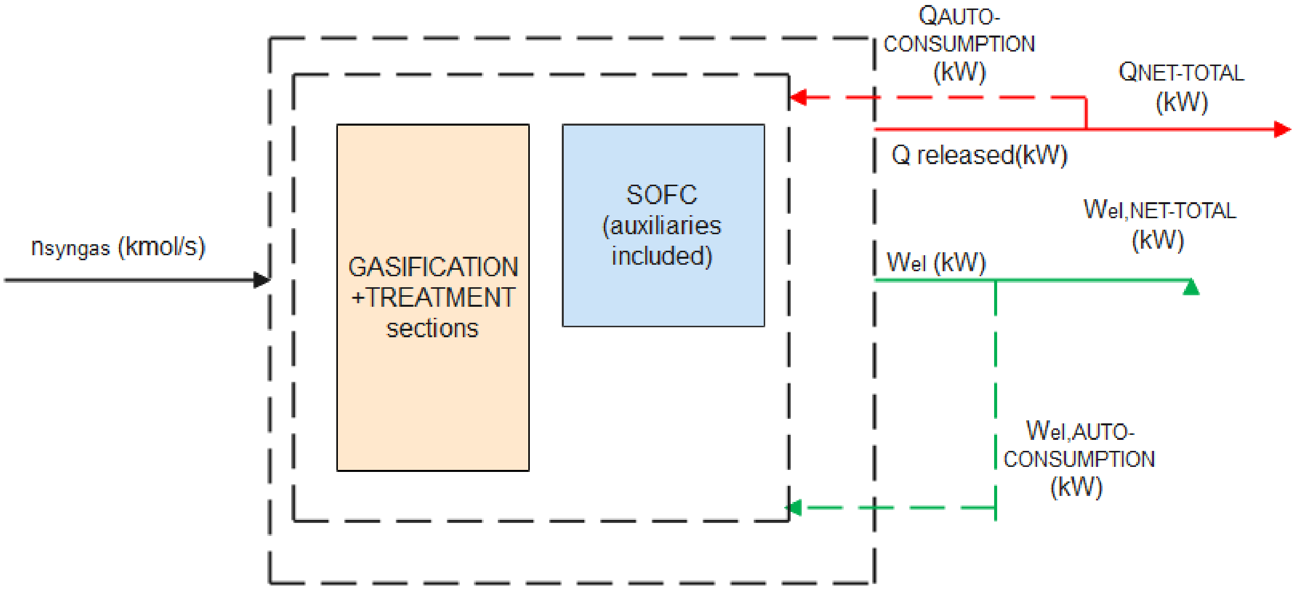
$$Q_{NET-TOTAL}(kW) = Q_{TOTAL}\ (kW) - heat\ autoconsumption\ (\%) * Q_{TOTAL}\ (kW) \qquad (59)$$

And relative efficiencies

$$System\ net\ electrical\ efficiency\ (\%) = \frac{W_{el,NET-TOTAL}}{\mathrm{LHV_{syngas}} \cdot \mathrm{n_{syngas}}} \qquad (60)$$

$$System\ net\ thermal\ efficiency\ (\%) = \frac{Q_{NET-TOTAL}}{\mathrm{LHV_{syngas}} \cdot \mathrm{n_{syngas}}} \qquad (61)$$

Figure 28. Schematic of balance of plant with auto-consumption PATH 2

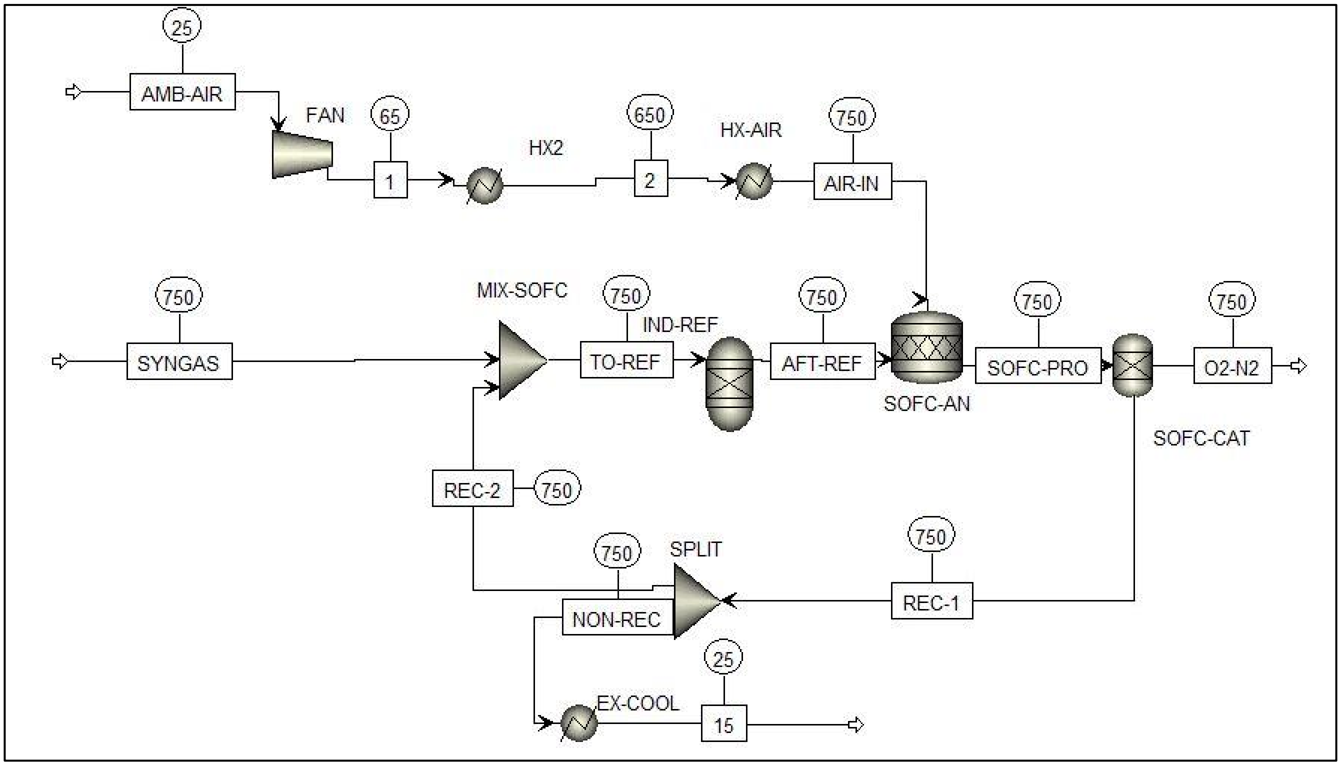


4.4.3 Aspen Plus model

The SOFC model in Aspen Plus in implemented in air-feed configuration because oxygen feed-configuration is still not tolerated from the materials that are used now for commercial stacks. In fact, the presence of a too high oxygen partial pressure on the cathode electrode would cause the degradation of the cell and the oxidant works also as coolant fuel so it is needed in big amount and a great and free quantity of oxygen for it would be difficult and expensive to be produced.

Syngas and ambient air enter the system at 750 °C and 25 °C respectively. Syngas comes from the cleaning unit which brings the levels of contaminants of the tolerated value from the cell. The exiting temperature from the cleaning unit is 750 °C. The SOFC does not work in pressure so the syngas coming from the treatment unit does not need to be compressed before being used. The fuel, before entering in the stack, is mixed with the recirculated fraction of non-reacted fuel exiting from the stack. The recirculated fraction of non-reacted fuel is 0.75. Recirculation of the anode exhausts is implemented and usually adopted by commercial stack because it can bring many great advantages as the reduction of the number of the cells of the stack due to the lower in-cell utilization and the pre-heating of the fuel since the flue gases are at high temperature and, mixing with the incoming gas they heat it up. In this model the ejectors mean the recirculating of the exhaust gases. They are represented as passive components since they do not need mechanical power. The primary fuel at high pressure is accelerated through the nozzle before entering in the chamber where it will be mixed with the secondary fuel where the momentum exchange between the two creates a moving effect causing the movement of the entrained fuel.

Figure 29. Aspen Model of SOFC fed by syngas



Syngas is subjected, after the mixing, to a reforming into IND-REF. It is a Gibbs reactor set at the equilibrium condition at a temperature of 750 °C. In this way, thanks to the recirculated amount of water from the anode-exhausts, steam reforming happens and natural gas is converted into hydrogen and carbon monoxide, both useful fuels for the SOFC.

$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad (62)$$

The HX-FUEL is the heat exchanger that controls the temperature of the gas just before that it enters and has the duty to keep it constant so that temperature change does not occur at the cell stack. By varying the recirculation fraction, the electrical efficiency of the stack and the volume flow rate change. The fuel cell stack is modeled as a stoichiometric reactor (SOFC-AN) and a separator (O2-SEP). The stoichiometric reactor has as input the two main reactions that happens in the cell. Even though many other reactions take place, to guarantee a result close to the reality, it is valid the hypothesis of considering as only current-giving reaction the oxidation of hydrogen and carbon monoxide

$$H_2 + {O_2}^- \rightarrow H_2O + 2e^- \qquad (63)$$

$$CO + {O_2}^- \rightarrow CO_2 + 2e^- \qquad (64)$$

The O2-SEP has the function of electrolyte that maintains the separation air/oxygen stream and the unreacted fuel with produced water. Anode exhausts are then cooled to a temperature of 85 °C and water is separated by condensation before that the anode off-gas recirculation (AOR) takes place.

By travelling along the ambient air path, it is taken from the environment and pre-heated in HX2 and HX-AIR before entering the stack. This pre-heating is performed in two steps for thermal integration reasons. Air is pushed to the cell thanks to a FAN that absorbs electrical power.

5 Green plasma and CLAIM project

5.1 Iris and internship

Iris s.r.l., the office where the internship was developed, is working on the realization of small-scale system for pyrolysis of marine litter (plastic). At the moment the office develops two small scale pyrolysis systems (PYR1, PYR2) obtained during laboratory test (TRL6) and tests in operating conditions (TRL7) in Genoa's port and on board of a vessel in Ancona. The project full title is "CLAIM: Cleaning litter by developing and applying innovative methods in European seas" and it is a EU project.

The pyrolysis systems are developed to guarantee an off-grid operation and they are studied to be installed in port areas and the idea is that they can be either connected to the grid or guarantee a service as electric mobility for example through electric bikes or electric cars charging stations. The idea rises from the meeting of the necessity to clean the seas from one side and the production of electricity from the other side and, in this way, the marine litter can be used as fuel bringing efficiently combining a useful product (electricity) and a useful action (cleaning of the sea).

5.2 3.2 CLAIM project and Green Plasma (PYR1, PYR2)

5.2.1 PYR1

PYR1 is an evolution of the Plasma Pyrolizer. It uses plasma-assisted high temperature to transform solid waste into syngas. The small-scale prototype can receive 5 kg/h of waste (around 100 kg per day) and fits into a 20' container. The size makes it suitable for its application in the port area. The reaction chamber of the pyrolizer is cylindrical and made of stainless steel insulated with ceramic material. The piece is kept at high temperature by the plasma generator. This small scale system maximum absorption is 7.5 kW.

Figure 30. PYR1 illustration on port installation

5.2.2 PYR2

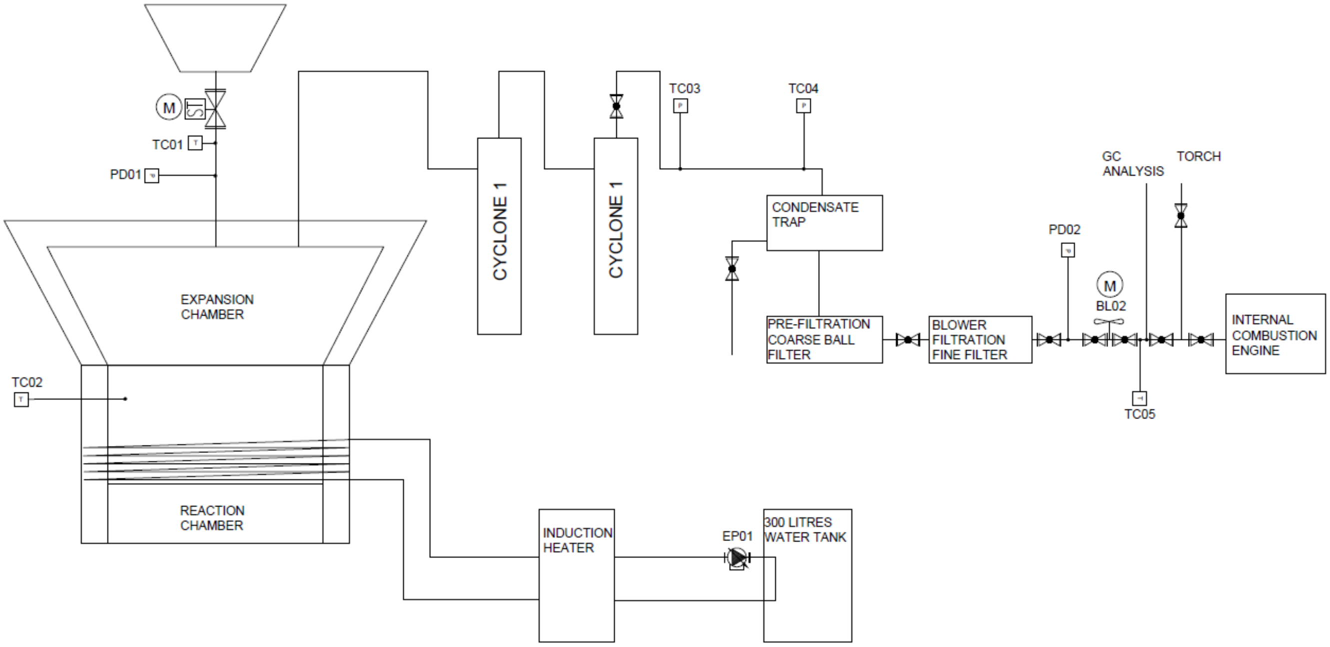
PYR2 is an Induction assisted vessel Pyrolyser, evolution of PYR1. It uses induction-assisted high temperatures to transform the solid waste into syngas, gas that, after a treatment procedure, can be directly used on-site. Also this is a small-scale model and it is able to treat up to 100 kg of waste per-day (5 kg/h). Due to the fact that marine litter cannot be recycled, this system is the opportunity to produce energy while you clean the environment. The system is made by a cylindrical steel reactor insulated with rock wool. Thermocouples are installed along the prototype in order to control and check the temperatures. Thermocouples are then connected to a smart box that is able to bring the system to reach the correct values of temperature in order to guarantee the correct functioning of the system. maximum absorbed energy measured during the test is 6.5 kWe. This means that if the prototype has to be inserted off-grid, as for example on a boat, a set of lithium batteries of 30 kWh has to be installed to guarantee the 6.5 kWe. In the laboratory, during the test, batteries are connected to the prototype to simulate the off-grid operation.

Table 1. General description on PYR2 [30]

General description	
Device	PYR2
Operation site	Vessels (offshore)
Weight	550 kg
Footprint	1m x 2.4 m
Reaction type	Induction
Average Energy Consumption	5 kWh
Construction Material	~ 90% inox

A simplified diagram P&ID diagram of the prototype is presented in Figure 8.

Figure 31. PYR2 – Simplified P&ID diagram [31]



During the internship, test were performed and composition of syngas at the exit was performed with proper instruments.

After that the thermal insulation is checked, the device is switched on, so the induction machine starts to heat the reaction chamber. When the temperature in the reaction chamber reaches the value of 500 up to 600 C, one man starts to insert the feedstock into the device. Feedstock enters the prototype with a mass flow of 5 kg/h and is pyrolyzed in the reaction chamber. At the beginning, gas is not conveyed to the internal combustion engine but it is sent to the torch. It can be seen that in the first minutes of operation of the device the flame of the torch is yellowish which is the sign of a not very clean gas. This is due to the heating up time of the device and the fact that, if the temperature still does not reach the optimal value, contaminants and tars are produced in greater value. After some minutes of running, the flame becomes more blue/purple and, being it a clue of the cleanliness of the syngas, the flow of it is now conveyed to the internal combustion engine. The gas engine is switched on and the production of electricity starts. An important parameter that is always doublecheck with some pressure valves is the depression of around 30 mbar at the entrance of the internal combustion engine. In this way it is guaranteed that the syngas flow goes in the right direction. After some hours of operation, device is switched off. At this point, two actions are performed.

From one side, once cooled, filters are opened and measurements on the dirtiness of them are performed in order to evaluate their functioning. In particular, residues collected by cyclone 1 and cyclone 2, ashes contained into the reaction chamber, condensate collected in the consensus trap, viscous residue collected in the coarse filter, viscous residue collected in the fine filter. It is observed that the higher is the operating temperature, the lower is the quantity of condensate found in the filters.

From the other side, the syngas produced from the pyrolizer is collected and examined. Tests on its composition are performed in the laboratory and, by changing each time mainly the feedstock composition and the operating temperature, different quality of syngas are obtained. In particular, lower pyrolysis temperature means less electricity consumption but higher contaminants and tars in the syngas.

For this simulation, feedstock is the marine litter material and it is pyrolyzed at 750 C. The total pyrolyzed mass of marine litter is 1 kg. Rate of introduction of marine litter into the pyrolizer is approximately 25 grams/minute. The average composition of syngas obtained is shown in Table XX and the LHV of syngas calculated in Table XX as:

$$LHV_{syngas} = \sum_{i=1}^{n} \%vol_i \cdot LHV_i \qquad (65)$$

Where n is equal to the number of species and LHV_i is the lower heating value of the i-specie of the syngas.

Table 10. Composition of the syngas. Concentrations are reported in parts per million by volume (ppmV). To obtain the percentages by volume, divide by 10000.

Gas	Formula	Volume %
Hydrogen	H_2	14.2
Carbon monoxide	CO	5
Methane	CH_4	5.6
Ethane	C_2H_6	1
Ethylene	C_2H_4	3.9
Propane	C_3H_8	2.1
Fuels gas		31.7
Nitrogen	N_2	59
Oxygen	O_2	6.3
Carbon dioxide	CO_2	3.3
Total syngas		100.2

Table 11. Syngas from marine litter LHV from MicroGC analysis

Element		% V	V	Lower Heating Value (LHV)	LHV syngas
		[%]	[Nm^3]	[kWh/Nm^3]	[kWh/Nm^3]
Hydrogen	H_2	14.22	0.14	2.84	0.4
Carbon monoxide	CO	5	0.05	3.34	0.17
Methane	CH_4	5.6	0.06	9.95	0.56
Ethane	C_2H_6	1	0.01	7.6	0.08
Ethylene	C_2H_4	3.9	0.04	15.83	0.62
Propane	C_3H_8	2.1	0.02	6.41	0.13
TOTAL					1.96

6 Modelling and analysis

6.1 Input data

After presenting all the type of gasifiers, a commercial type of gasifier is used in this thesis. The biomass gasifier taken in consideration is the ESPE CHiP50 that uses wood chips for gasification. In particular, it is a parallel flow fixed bed gasifier (or Downdraft). It can guarantee a M10 chip supply flow of 49 kg/h and an average generated syngas flow of 0.036 kg/s. The average syngas LHV is 5.5:6 MJ/kg and the gasification efficiency is greater than 75%. The operating temperature is greater then 1000 C. The advantages of this type of reactor are the structural simplicity of the device and the purity of gas obtained. This happens thanks to the high operating temperature that helps in thermal cracking of the heavy hydrocarbons. The typical thermochemical reactions that have been observed by the supplier are the following.

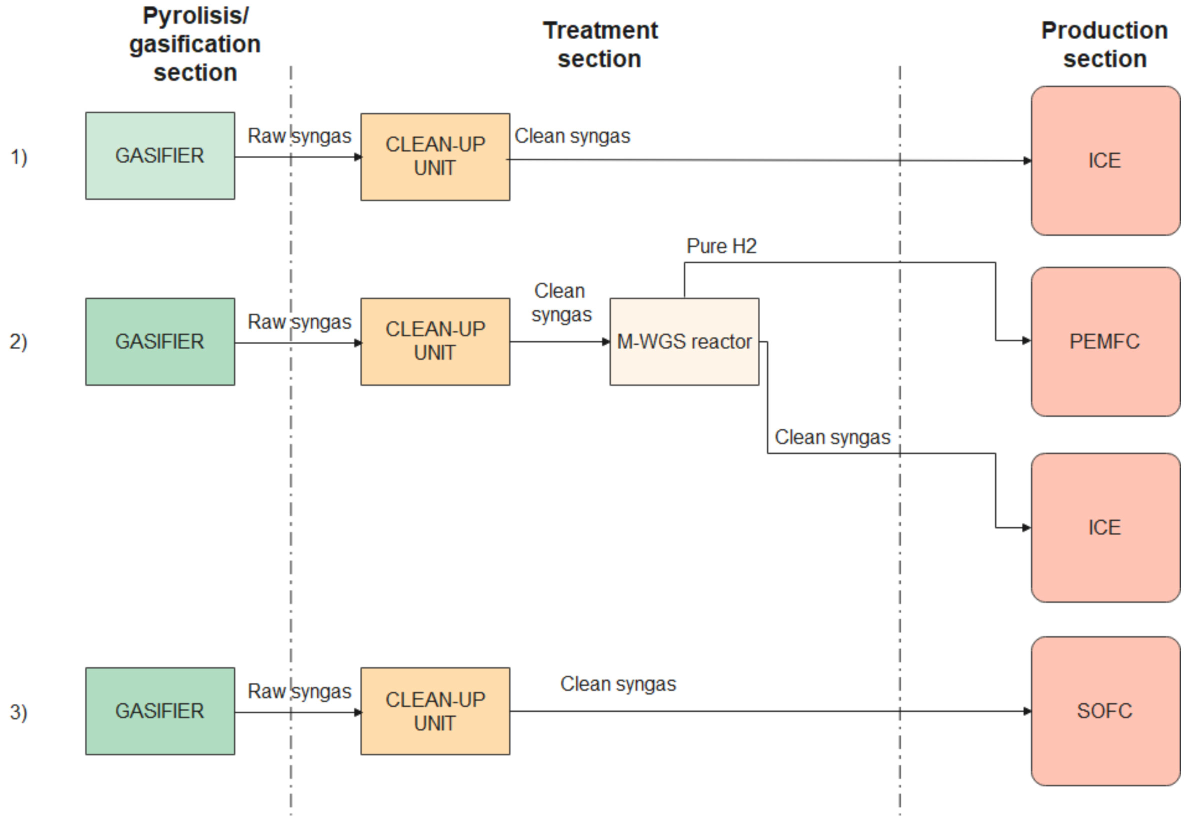
Table 12. Typical thermochemical reactions within the gasification process

	Oxidation area	Reduction area
Boudouard reaction	C+O2 -- CO2	C+CO2 -- 2CO
Hydrogen reaction	C+1/2O2 -- CO	C+H2O -- CO + H2
Methane reaction	H2 + 1/2 O2 -- H2O	C + 2H2 -- CH4

As shown before, some contaminants are present in the final product, syngas, but research is going on and it is studying new methods and devices able to increase the purity of the syngas.

This commercial syngas so is used to feed three different configurations for electricity production and heat production (cogeneration). In fact three different usage of the syngas are analyzed: in the first path it goes directly to an internal combustion gas engine (PATH 1), in the second path syngas' flow is first enriched in hydrogen thanks to a WGS reactor (which converts part of the carbon monoxide into hydrogen through the following reaction: $CO + H_2O \rightarrow CO_2 + H_2$) and after this step hydrogen is separated thanks to the use of a Pd-alloy membrane to feed a PEMFC while the remaining gas flow is conveyed to an internal combustion gas engine (PATH 2). At last, the third path consists in the use of the syngas as direct fuel for a SOFC (PATH 3).

Figure 32. Investigated syngas path 1, 2 and 3



To size the models and to make a valid comparison, it is assumed that the net electrical power to the end-user that has to be guaranteed is 50 kW. The choice of providing 50 kW as a final product is not casual but it relies on the fact that CHP systems up to that value of power belong to the Micro-CHP category. This category, in other words, is the "Residential application" of cogeneration. The best application for this size of Micro-CHP installation are the facilities that have high annual hours of operation and continuous thermal load [32]. Then the decision to sell a certain size of the CHP installation is done by considering a real situation where the producer sells to the consumer a certain amount of electrical power. In this way, the comparison between the three paths relies on an equal output and on a real situation which is what happens when a firm sells its products to a buyer. The following paragraphs describe the model used to simulate the phenomenon and considers both products (heat and electricity) and auto-consumption (heat and electricity). For each model, auxiliaries are considered in the economic analysis so that the estimation of capex and opex is as detailed as possible and the results are as close as possible to a real investment.

In addition to that, to make the comparison of the three paths as real as possible, the necessary cleaning unit with its own cost is considered. Different cleaning technology configurations for synthesis gas can be used according to the clean up requirements for each different production technology (ICE, PEMFC, SOFC).

6.2 Simulation with biomass

6.2.1 PATH 1

The mathematical model is applied to the syngas (dry basis) of a commercial gasifier whose composition in volume is 14% H2, 53% N2, 4% CH4, 17% CO, 12% CO2 and the LHV is 1.15 kWh/Nm3. The power of the fuel that feeds the engine is 165 kW and the volumetric flow rate of syngas, calculated as shown in equation (XX), is equal to 143.5 Nm3/h. The operating hours are estimated to be 7000 per year and electric energy produced is 346500 kWh and thermal energy produced is 693000 kWh, being the thermal efficiency of the engine 60.8% and the electrical efficiency 30.4 %.

Table 13. Internal combustion engine assumptions and results with syngas from biomass

Internal combustion engine specifications (CHP)	
Engine installed gross power (kWe)	50
Engine electrical efficiency (%)	30%
Engine thermal efficiency (%)	61%
Fuel power (kW)	165
Operation hours (h)	7000
LHV syngas (kWh/Nm3)	1.15
Internal combustion engine outputs (CHP)	
Volume syngas flow (Nm3/h)	143.4
Gross electricity (kW)	50.16
Gross heat (kW)	100.32
Gross electrical energy (kWh)	346500
Gross thermal energy (kWh)	693000

The electricity self-consumption is estimated equal to the 15 % of the electricity produced and around 7.5 kW. Net electrical power output, considering the whole system, is 42 kW.

6.2.2 PATH 2

The input parameters of this simulation start from the syngas composition of a commercial biomass gasifier that correspond to the stream SYN-IN.

Table 14. Syngas composition of a commercial biomass gasifier

Syngas composition (% vol)	
H2	14%
N2	53%
CH4	4%
CO	17%
CO2	12%

Syngas enters at a temperature of 25 °C and pressure or 1 bar. Then it is mixed with steam in WGS reactor and changes its molar fraction. Here in the table below is shown the composition before and after the WGS (REFORMED).

Table 15. Syngas molar fraction (%) before and after WGS reactor

Component	SYNG molar fraction (%)	REFORMED molar fraction (%)
H2	14%	22%
H2O	0%	14%
O2	0%	0%
N2	53%	39%
CH4	4%	3%
CO	17%	1%
CO2	12%	21%

Table 16. Syngas molar flow (kmol/s) before and after WGS reactor

Component	SYNG molar flow (kmol/s)	REFORMED molar flow (kmol/s)
H2	0.406	0.858361
H2O	0	0.547639
O2	0	4.57E-39
N2	2	2
CH4	0.116	0.116
CO	0.493	0.040639
CO2	0.348	0.800361
total	2.9	3.9

CO conversion factor is 0.90 and the REFORMED stream exits from the WGS reactor depleted in CO and richer in H2. Respectively, the molar fraction of hydrogen in the REFORMED increases and the molar fraction of the CO decreases.

At this point, the separator (Pd-alloy membrane) separates pure hydrogen with membrane permeation efficiency of 0.75 which means that only the 75% of the hydrogen contained in the incoming gas can pass through the membrane. The 35 % of the hydrogen that does not pass through the membrane is conveyed in the gas that goes to the internal combustion engine. Of great importance is the investigation of the LHV of the remaining gas. Due to the fact that it loses great quantity of carbon monoxide and oxygen this means that the lower heating value of it decreases. The molar fraction of the gas going to the engine is calculated with Aspen:

Table 17. Molar fraction (%) composition of gas to internal combustion engine

Component	Molar fraction (%)
H2	8%
N2	57%
CH4	4%
CO	2%
CO2	30%

It is already observed that the percentage of H2 and CO in the gas is very low and so is the LHV that is calculated and equal to 0.713 kWh/Nm3.

To obtain a total installed power of around 50 kWe the syngas entering volumetric flow is 96 Nm3/h. The total separated pure hydrogen flow to the PEMFC is 21 Nm3/h and the gas volumetric flow going to the internal combustion engine is 89 Nm3/h. The electric power produced from the PEMFC is 33 kWe (from Aspen simulation), by considering the inverter efficiency from AC to DC 96%. The power produced from the engine is 19 kW, by considering the electrical efficiency of the engine 30% (commercial engine specification).

Table 18. Input parameters for PEMFC model

PEMFC input parameters	
Power net (kW)	33
Temperature of the stack (°C)	50
Temperature inlet fuel (°C)	25
Temperature inlet air (°C)	25
FU	0.8
ASR (Ω cm2)	0.29
Acell (cm2)	125
Vop (V)	0.82
Jcell (A/cm2)	1.07
Atotal stack (cm2)	37500
ncell (#)	300
inverter efficiency (%)	96

Table 19. Input parameters for internal combustion engine

Engine input parameters	
Syngas flow (Nm3/h)	89
LHV syngas (MJ/kmol)	57.5
Engine electrical efficiency (%)	30
Engine thermal efficiency (%)	60
Engine electric power (kW)	19
Engine thermal power (kW)	38

The tab below shows the results and the efficiencies that have been previously defined.

Table 20. Efficiencies

Index	Value	Unit
Total electricity self-consumption	16	kW
Electricity self-consumption percentage	32	%
Heat self-consumption	0	kW
Heat self-consumption percentage	0	%
Gross electrical efficiency	40	%
Net electrical efficiency	27	%
Gross thermal efficiency	38	%
Net thermal efficiency	38	%
Total gross CHP efficiency	78	%
Net total CHP efficiency	65	%

6.2.3 PATH 3

The input parameters of the simulation of SOFC is performed with syngas composition of a commercial biomass gasifier.

Table 21. Syngas composition of a commercial biomass gasifier

Syngas composition (% vol)	
H2	14%
N2	53%
CH4	4%
CO	17%
CO2	12%

Syngas enters in the system at a temperature of 750 °C and arrives from the clean-up system. SOFC works at high temperatures and the fact that the syngas enters the system already at high temperature is an advantage in terms of heat duty required to heat it up if only it would be at ambient temperature. For this reason the gas is sent from the cleaning unit to the SOFC directly. The other entering flow is the air at ambient temperature and pressure. Pure oxygen fed SOFC is not considered to simulate the process due to the fact that, in reality, it would be too expensive to obtain pure oxygen and feed it at large amount to the fuel cell. Air-feed configuration is chosen for the purposes of the simulation. The syngas flow, SYNGAS, after being mixed with the recirculating flux of the anode-exhaust in MIX-SOFC, enters in the IND-REF which is a Gibbs reactor. The steam reforming of methane contained in the entering flux happens at 750 C. The composition of the gas before (TO-REF) and after (AFT-REF) the internal reformer is showed below.

Table 22. Molar fraction (%) of syngas before and after internal-reforming

Component	TO-REF molar fraction (%)	AFT-REF molar fraction (%)
H2	14%	12%
H2O	0%	23%
O2	0%	0%
N2	53%	20%
CO	4%	13%
CO2	17%	32%
CH4	12%	0%

Table 23. Mole flow (kmol/s) of syngas before and after internal-reforming

Component	TO-REF mole flow (kmol/s)	AFT-REF mole flow (kmol/s)
H2	0.000192	0.000248
H2O	0.000479	0.000486
O2	0	2.36E-22
N2	0.000417	0.000417
CO	0.000194	0.000264
CO2	0.000718	0.00068
CH4	3.15E-05	3.85E-08
total	0.0020315	0.002095039

The exiting syngas from IND-REF sees a flux of H2 and CO increased and of CH4 decreased. This is the proof that, bringing the syngas at the equilibrium at a temperature of 750 C in the reactor the steam reforming happens and syngas is enriched in H2 and CO, useful fuels for the fuel cell. Once out from the SOFC-AN, the SOFC-CAT is simulated and the anode-exhaust REC-1 goes to the splitter to be recirculated. The splitting fraction is 0.75 (from literature this value ranges from 0.7 to 0.9). REC-2, which is the net recirculated anode-exhaust flow, is mixed with the new incoming flow of syngas from the cleaning-unit. The part of exhausts NON-REC is cooled up to ambient temperature of 25 C. This heat is collected through EX-COOL to a heat exchanger.

The input parameters used for the model of the SOFC are

Table 24. SOFC input parameters

SOFC input parameters	
Power net (kW)	50.6
Temperature of the stack (°C)	750
Temperature inlet fuel (°C)	750
Temperature inlet air (°C)	25
FU	0.8
ASR (Ω cm2)	0.23
Acell (cm2)	215
Vop (V)	0.805
Jcell (A/cm2)	1.0171
Atotal stack (cm2)	64500
ncell (#)	300
inverter efficiency (%)	96

To size the SOFC, a net output power of around 50 kW is required considering also the inverter efficiency 96%, common value for commercial devices. From Aspen model, a volumetric flow of 69.2 Nm3/h of pure syngas is required. The LHV of syngas is 113.438 MJ/kmol. The power of the fuel is 97.307 kW and the gross electric power produced from the cell is 52 kW. The net electric power produced is 50.6 kW.

Table 25. SOFC simulation results

SOFC Index	Value	Unit
Electricity auto-consumption	1.5	kW
Electricity auto-consumption percentage	30	%
Heat auto-consumption	25	kW
Heat auto-consumption percentage	63	%
Net electricity produced	49.1	kW
Net heat produced	15	kW
Electrical efficiency	52	%
Net electrical efficiency	51	%
Thermal efficiency	41	%
Net thermal efficiency	15	%
Total CHP efficiency	93	%
Net total CHP efficiency (net thermal + net electrical)	66	%

7 Techno-economic analysis

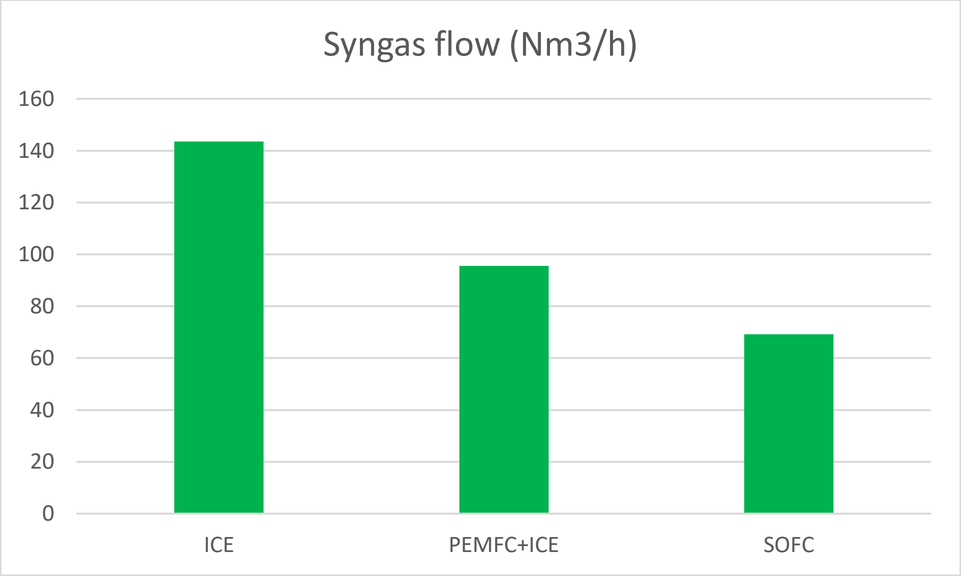
Techno economic analysis (TEA) is a very important tool in engineering and gives the opportunity to provide a thorough understating of the impact that technology have on the financial viability of the conversion strategy. It integrates previous stages analysis to gather info in order to calculate the KPI of interest.

The goal of this study is to the quantity of syngas required from each path to produce a deliverable power of around 50 kW. For all the three paths this data is evaluated with the use of the models explained before.

Table 26. Comparison of volume flow rate (Nm3/h) of syngas for each path

Quantity investigated	ICE		PEMFC+ICE		SOFC	
	Path 1		Path 2		Path 3	
Syngas flow	144	Nm3/h	96	Nm3/h	69	Nm3/h
Syngas power	165	kW	125.4	kW	97	kW

Graph 1. Syngas flow (Nm3/h) required from each path to produce 50 kWe output



ICE is the path the requires the higher value of syngas flow (Nm3/h) and this is addressed to a lower efficiency. For this purpose, being the electrical energy in this thesis the output of interest, technical efficiency of the process coincides with the electrical efficiency. This is calculated as

$$Global\ electrical\ efficiency_{PATH1}\ (\%) = \frac{Electrical\ power}{Syngas\ power} = \frac{Electrical\ power}{LHV_{syngas} * G_{syngas}} \quad (66)$$

$$Global\ electrical\ efficiency_{PATH2}\ (\%) = \frac{Electrical\ power}{Syngas\ power} = \frac{Electrical\ power}{LHV_{syngas} * G_{syngas}} \quad (67)$$

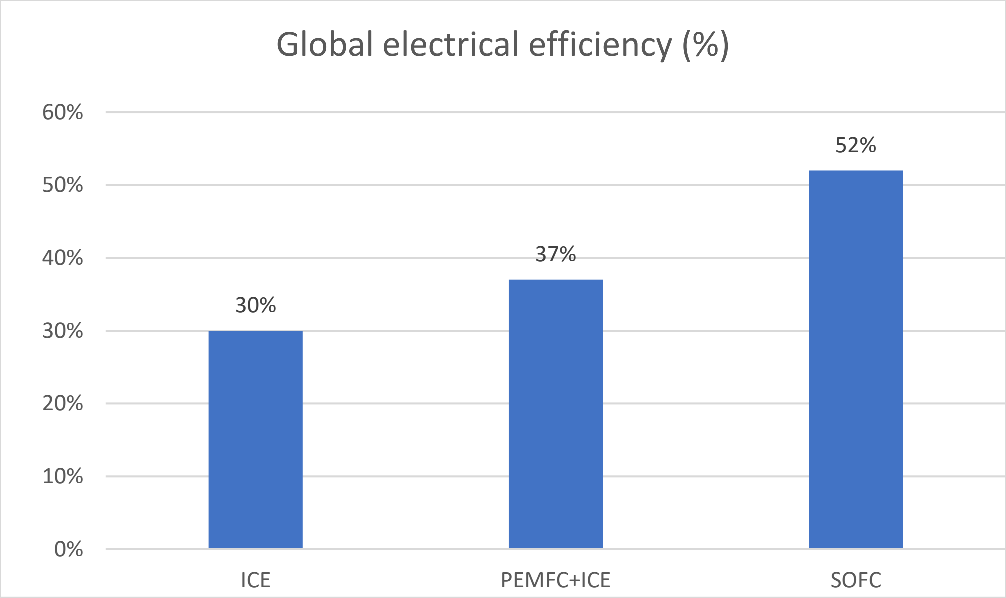
$$Global\ electrical\ efficiency_{PATH3}\ (\%) = \frac{Electrical\ power}{Syngas\ power} = \frac{Electrical\ power}{LHV_{syngas} * G_{syngas}} \quad (68)$$

The resulting efficiencies are summarized in the table below.

Table 27. Global electrical efficiency

Quantity investigated	ICE		PEMFC+ICE		SOFC	
	Path 1		Path 2		Path 3	
Syngas flow	144	Nm3/h	96	Nm3/h	69	Nm3/h
Syngas power	165	kW	13.444.282	kW	9.730.712	kW
Global electrical efficiency	30%		37%		52%	

Graph 2. KPI-1: Global electrical efficiency (%) of PATH1, PATH2, PATH3



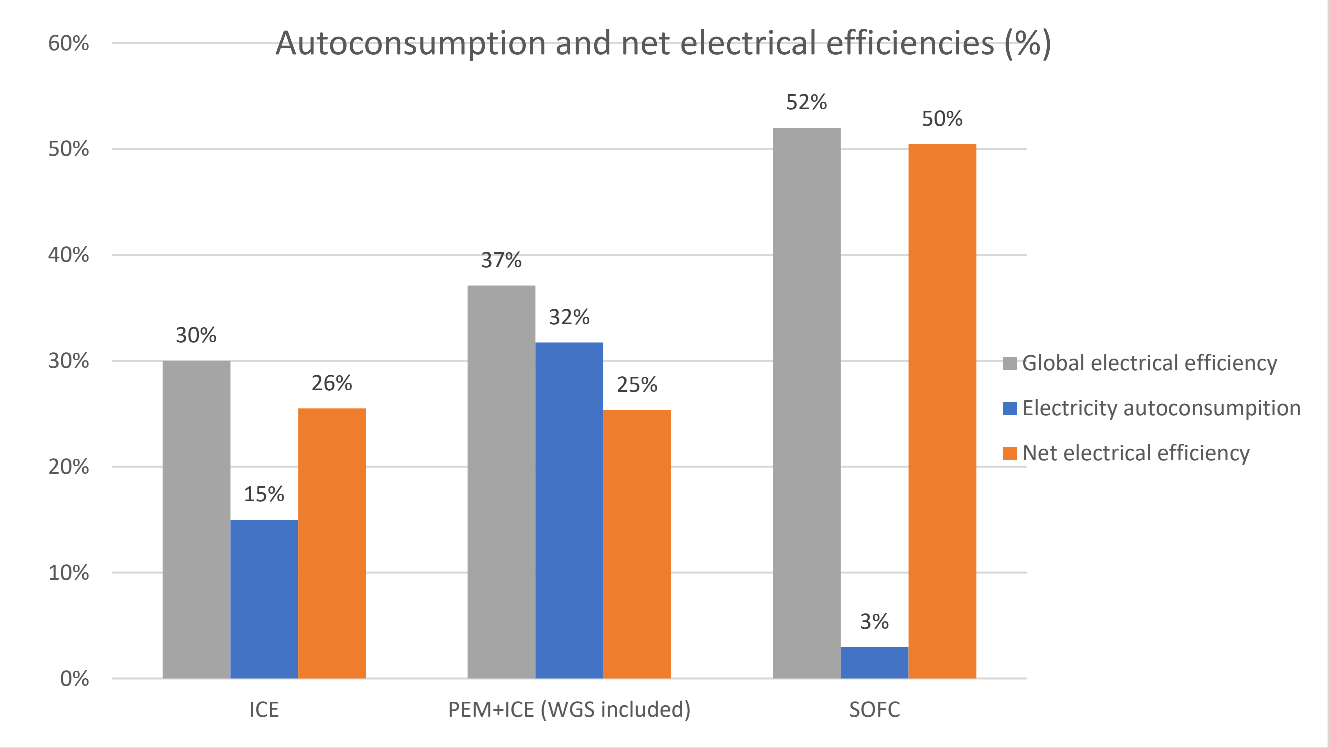
Greatest global efficiency is obtained by SOFC technology and reaches a value of 52%. The process with the lower global efficiency is the ICE technology while the PEMF+ICE configuration assumes an intermediate efficiency value of 37%. These values find a good compatibility with the ones expressed in literature.

Until now, the electric power output has been considered as all ‘usable’. An further KPI evaluates the quote of consumption, both thermal and electrical, that each path requires (for path it is considered the system composed by gasification section, treatment section and production section). Net total efficiency and net thermal efficiency indicates the efficiency of each process by considering that the quote of auto-consumption is withdrawn from the global electric power produced.

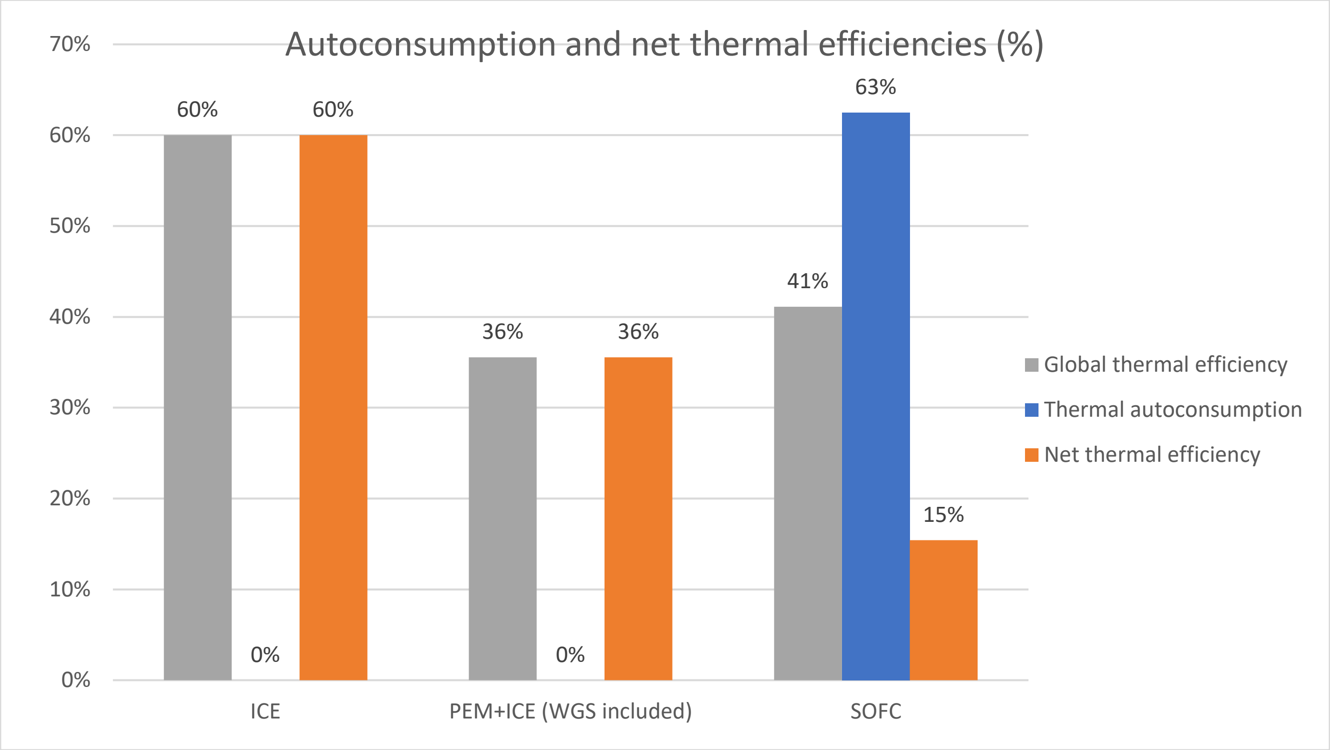
Table 28. Efficiencies considering auto-consumption

Quantity investigated	ICE		PEMFC+ICE		SOFC	
	Path 1		Path 2		Path 3	
Global electrical efficiency	0.3		37%		52%	
Electricity auto-consumption	15%		32%		3%	
	7.425	kWp	15.835	kWp	1.5	kWp
Net electrical efficiency	26%		25%		50%	
Net electrical power	42.075	kW	34.065	kW	49.1	kW
Global thermal efficiency	60%		36%		41%	
Thermal power	99	kWth	47.8	kWth	40	kWth
Thermal auto-consumption	0%		0%		63%	
	0	kWth	0	kWth	25	kWth
Net thermal efficiency	60%		36%		15%	
Net thermal power	99	kWth	47.8	kWth	15	kWth

Graph 3. KPI-2: Electricity autoconsumption and net electrical efficiency



Graph 4. KIP-3: Thermal auto-consumption and net thermal efficiency



From KPI-2 and KPI-3 it can be observed that for what concerns electrical efficiency, the greatest electric auto-consumption happens in PATH 2 and this is addressed to the use of the WGS-reactor which absorbs power. The lower electric auto-consumption from the other side is linked to PATH 3 since the technology works at high temperature and the higher request comes at level of heat and not electricity as it can be doublechecked by looking at the heat autoconsumption. At last, to conclude the technical KPIs, cogeneration efficiencies which are the ones that take into account hat and electricity together are calculated as

$$Global\ CHP\ efficiency\ (\%) = Global\ electric\ efficiency\ (\%) + Global\ thermal\ efficiency\ (\%) \qquad (69)$$

$$Net\ CHP\ efficiency\ (\%) = Net\ electric\ efficiency\ (\%) + Net\ thermal\ efficiency\ (\%) \qquad (70)$$

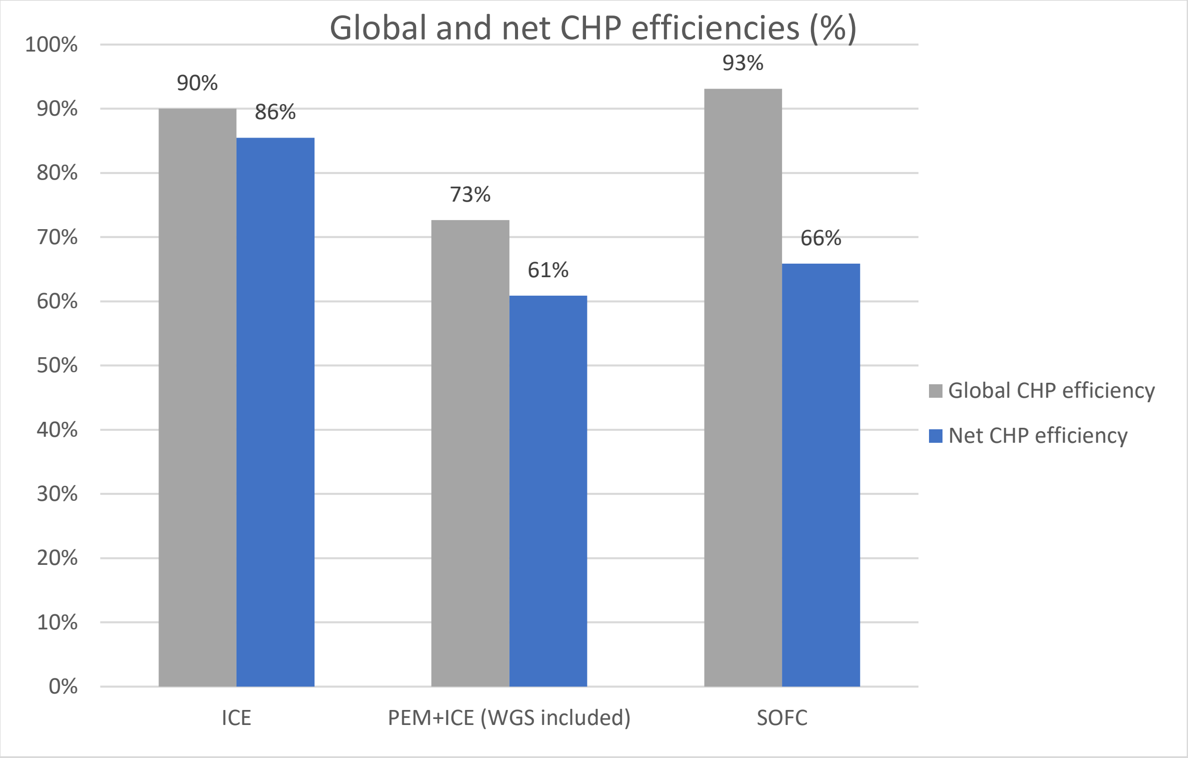
Obtained values are reported in the table below

Table 29. Global CHP efficiencies

Quantity investigated	ICE	PEMFC+ICE	SOFC
	Path 1	Path 2	Path 3
Global CHP efficiency	90%	73%	93%

Net CHP efficiency	86%	61%	66%

Graph 5. KPI-4: Global and net CHP efficiencies



To conclude the technical analysis, the greater net CHP efficiency results to be higher for PATH 3 without considering auto-consumption while this primate is lost in favor of PATH 1 if auto-consumption is considered. This is easy to be explained since the engine, once on, does not require a lot of energy to stay on since the combustion is given from the fuel and gives the power while both the solutions with fuel cells require special conditions and in particular in some case high pressure while in other high temperatures which are highly energy consuming conditions to be obtained.

From the economical point of view, CAPEX and OPEX are calculated with current market costs. CAPEX and OPEX are divided into different categories of costs for each path and the division is slightly different from one path to the other due to the difference in the layout of the plant and so the needed equipment for each installation. Cost of biomass has been kept constant for all the layouts and the current market value of biomass M10 is 0.1 €/kg. In particular, for PATH 1, the ICE, CAPEX and OPEX costs are divided as represented the pie charts below.

Table 30. CAPEX for PATH 1

Downdraft gasifier with ICE CHP		
Technical Description	**Repl. time [years]**	**€/year**
CAPEX		
Multi stage downdraft gasifier for syngas production (700°C - 50kg/h)	20	4.250
Electric components, syngas pipeline system, valves, pumps, monitoring system etc..	20	430
Ashes conveyor and storage	20	88
Syngas filter (tar, and cooling system)	20	806
Syngas production/conditioning CAPEX		**5.574**
ICE internal combustion engine 4000 cc with electic system integration	3	7.500
Selective Catalytic Reduction (SCR), particulate filters etc..	20	600
Standard skid with: burner, heat exchanger, exhaust engine gas, electric components, syngas pipeline system, valves, pumps, monitoring system etc..	20	1.075
Simple monitoring platform with simple control system	20	93
Total CAPEX		**14.841**

Table 31. CAPEX for PATH 2

Downdraft gasifier with PEM + ICE		
Technical Description	**Repl. time [years]**	**€/year**
CAPEX		
Multi stage downdraft gasifier for syngas production (700°C - 30kg/h)	20	3.500
Electric components, syngas pipeline system, valves, pumps, monitoring system etc..	20	589
Ashes conveyor and storage	20	213
Syngas filter (tar, and cooling system)	20	806
Syngas separation station (WGS reactor, Pd-membrane)	5	2.275
Syngas production/conditioning CAPEX		**7.383**
PEMFC	7	20.571
ICE	3	4.500
Selective Catalytic Reduction (SCR), particulate filters etc..	12.000	20
Standard skid with: steam generator, anode off-gas recirculation device, burner, heat exchangers, blowers, electric components, syngas pipeline system, valves, pumps, monitoring platform (MP), advanced plant Controllers (C)	20	2.609
Energy management system (sP-EMS) including: Central Controller and Cloud service, Graphical User Interface (see Concept 1.3)	20	93
Total CAPEX		**35.175**

Table 32.CAPEX for PATH 3

Downdraft gasifier with SOFC		
Technical Description	**Repl. time [years]**	**€/year**
CAPEX		
Multi stage downdraft gasifier for syngas production (700°C - 25kg/h)	20	3.500
Electric components, syngas pipeline system, valves, pumps, monitoring system etc..	20	949
Ashes conveyor and storage	20	213
Syngas treatment and cleaning (plasma oxydation system, Vessels and sorbents and catalyst)	20	2.000
Syngas production/conditioning CAPEX		**6.661**
SOFC solid oxide fuel cell by solid power 50 kWe (considering the current launched SOFC mass production)	7	39.286
Not present		
Standard skid with: steam generator, anode off-gas recirculation device, burner, heat exchangers, blowers, electric components, syngas pipeline system, valves, pumps, monitoring platform (MP), advanced plant Controllers (C)	20	3.624
Energy management system (sP-EMS) including: Central Controller and Cloud service, Graphical User Interface (see Concept 1.3)	20	93
Total CAPEX		**49.663**

Table 33. OPEX for PATH 1

OPEX (excluding feedstock cost)		
O&M (€ for 7000 hours operation) costs for feedstock treatment, gasifier, ICE ahses treatment	1	1.750
Consumables materials (oil, filters, seals, etc..)	1	1.000
Landfilling costs (disposal costs €/t)	1	784
General (administration, insurance etc)	1	557
Syngas production/conditioning OPEX		**4.091**
O&M (€ for 7000 hours operation) costs for ICE, electronic system, device(€/7000 hours)	1	2.100
Consumables materials (oil, filters, seals, etc..)	1	2.500
General (administration, insurance etc)	1	289
Total OPEX		**8.981**

Table 34. OPEX for PATH 2

OPEX (excluding feedstock cost)		
O&M (€ for 7000 hours operation) costs for biomass treatment, gasifier, cleaning system, ahses treatment, advanced remote monitoring and control for a predictive maintenance -	1	1.750
Consumables materials (filters, sorbents, etc..)	1	2.200
Non-reusable ashes will be completely vitrified with thermal plasma	1	0
General (administration, insurance etc)	1	568
Syngas production/conditioning OPEX		**4.518**
O&M (€ for 7000 hours operation) costs for SOFC, electronic device, monitoring system considering a semi automatic, software maintenance - advanced remote monitoring and control	1	1.400
Consumables materials (oil, filters, etc..)	1	2.750
General (administration, insurance etc)	1	990
Total OPEX		**9.658**

Table 35. OPEX for PATH 3

OPEX (excluding feedstock cost)		
O&M (€ for 7000 hours operation) costs for biomass treatment, gasifier, cleaning system, ahses treatment, advanced remote monitoring and control for a predictive maintenance -	1	1.750
Consumables materials (filters, sorbents, etc..)	1	2.200
Non-reusable ashes will be completely vitrified with thermal plasma	1	0
General (administration, insurance etc)	1	666
Syngas production/conditioning OPEX		**4.616**
O&M (€ for 7000 hours operation) costs for SOFC, electronic device, monitoring system considering a semi automatic, software maintenance - advanced remote monitoring and control	1	1.400
Consumables materials (oil, filters, etc..)	1	2.750
General (administration, insurance etc)	1	1.747
Total OPEX		**10.513**

The total capex is calculated as the summation of the capex for each year as shown in the formula below. Th estimated total capex is 14841 €/year for PATH 1, 35175 €/year for PATH 2 and 49663 €/year for PATH 3.

$$TOTAL\ CAPEX\ \left(\frac{€}{year}\right) = \sum_{i=1}^{n} CAPEX\ costs_i \left(\frac{€}{year}\right) \quad (71)$$

The total opex is calculated with the formula below and is 14841 €/year for PATH 1, 9658 €/year for PATH 2 and 10513 €/year for PATH 3.

$$TOTAL\ OPEX\ \left(\frac{€}{year}\right) = \sum_{i=1}^{n} OPEX\ costs_i \left(\frac{€}{year}\right) \quad (72)$$

For the economic evaluation of the layouts, specific KPI can be useful to understand the feasibility of the plant not only from technical performances results which sometimes are not compatible with economic evaluations. The technical performance analysis is at this point evaluated in combination with the economic analysis.

CAPEX and OPEX are evaluated as cost per year and as cost per energy produced as follow

$$KPI_{CAPEX}\left(\frac{€}{kWh}\right)=\frac{CAPEX\left(\frac{€}{year}\right)}{Electric\ energy\ produced\left(\frac{kWh}{year}\right)} \tag{73}$$

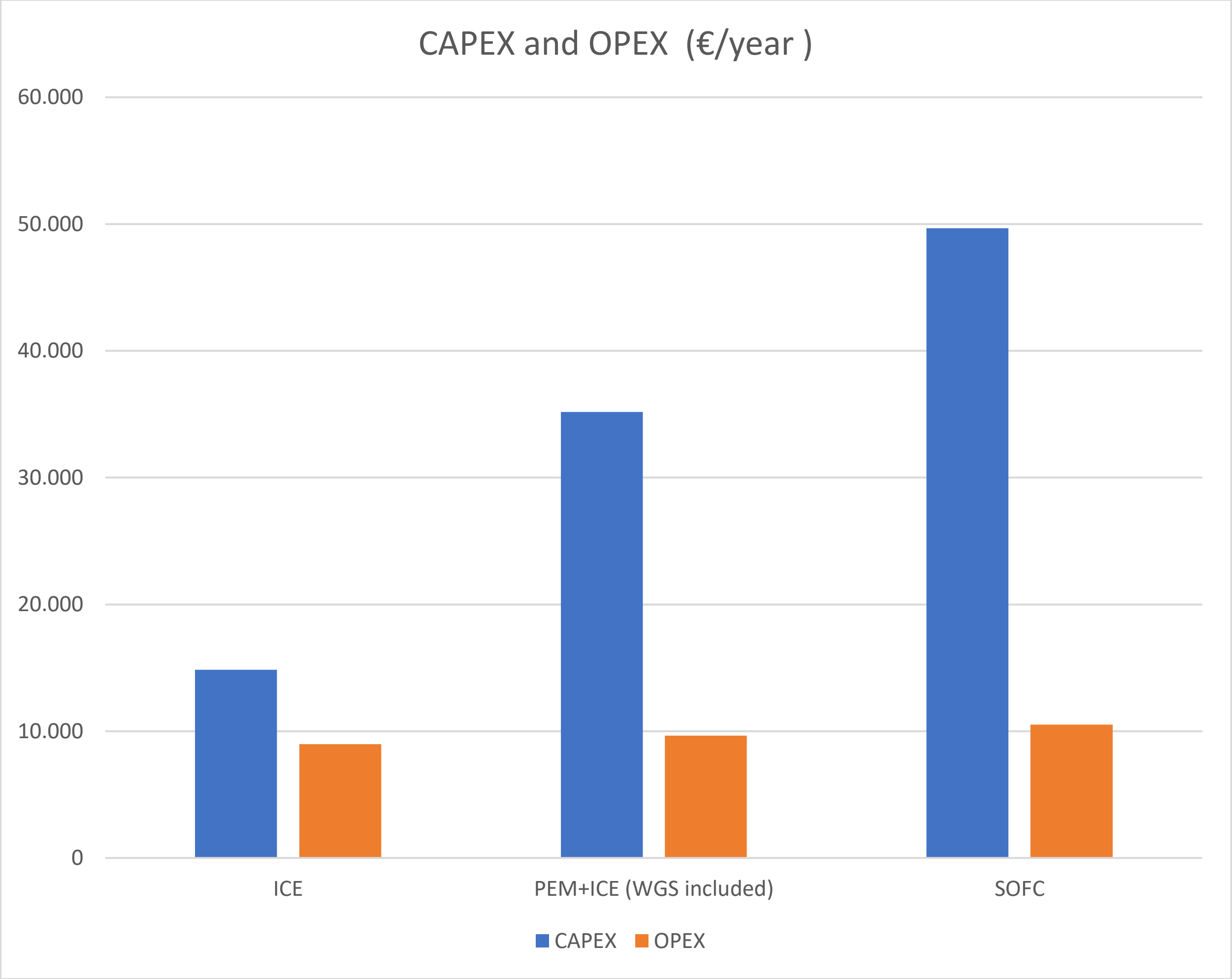
$$KPI_{OPEX}\left(\frac{€}{kWh}\right)=\frac{OPEX\left(\frac{€}{year}\right)}{Electric\ energy\ produced\left(\frac{kWh}{year}\right)} \tag{74}$$

The values obtained are reported in table below.

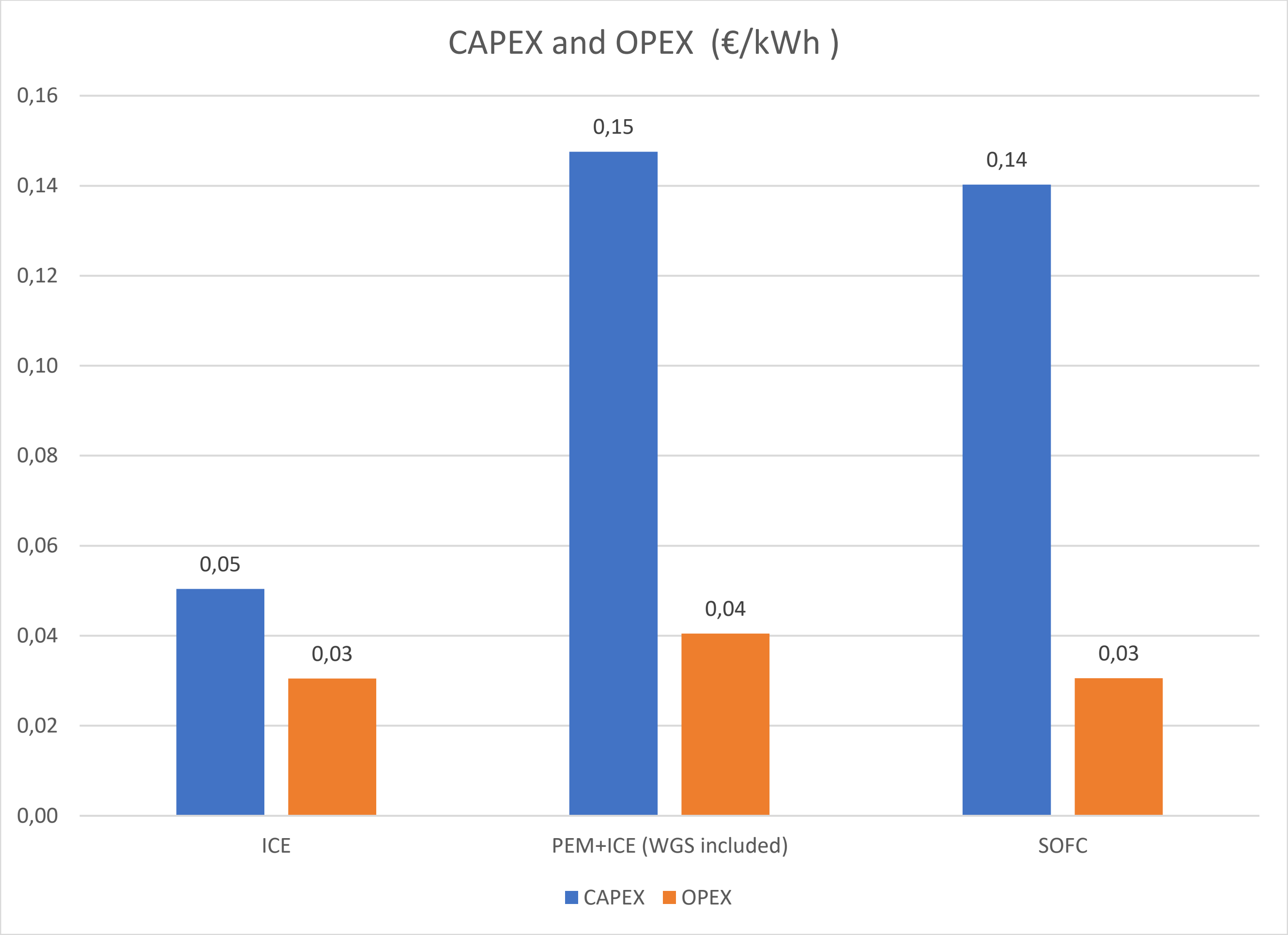
Table 36. CAPEX/OPEX values

KPI	Path 1	Unit	Path 2	Unit	Path 3	Unit
CAPEX/year	14841	€/year	35175,15	€/year	49663,21	€/year
OPEX/year	8980,6	€/year	9657,71	€/year	10512,75	€/year
CAPEX/kWh	0,05	€/kWh	0,15	€/kWh	0,14	€/kWh
OPEX/kWh	0,03	€/kWh	0,04	€/kWh	0,03	€/kWh

Graph 6. KPI-5: CAPEX and OPEX per year



Graph 7. KPI-6: CAPEX and OPEX per energy produced



From this analysis it is evident that, even if ICE has the lower technical efficiency followed by PEMFC+ICE and SOFC, at the end of the economic analysis it results cheaper than the other two technologies that are highly disadvantageous.

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