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TESI DI LAUREA MAGISTRALE

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Integrated Sorption Enhanced Gasification  
and SOFC stack system fed with organic  
waste

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*Relatore*

Massimo SANTARELLI

*Co-relatore*

Kas HEMMES

*Candidato*

Lorenzo MAISTRELLI

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# Abstract

The study here presented aims at designing an alternative system to conventional Waste-to-Energy technologies in order to provide a more efficient and clean solution to waste treatment and contribute to waste management. Such system, based on Sorption Enhanced Gasification (SEG) and a Solid Oxide Fuel Cell (SOFC), is also analyzed in terms of flexible operation. This will become particularly important in the future, when renewable energy sources will be deeply present in the power generation sector and balancing demand and supply in the grid will become critical. Moreover, this system could be well integrated in such scenario thanks to its ability to not only limit emissions but to even provide a carbon negative impact. In this study biodegradable wastes like organic fraction of municipal solid waste and wood are considered as suitable energy input based on considerations about their characteristics, amount produced and long-term availability. The concept is represented in CYCLETEMPO, which models the plant and provides the results of the thermodynamic analysis. These results show that the system is able to convert efficiently waste into electricity, hydrogen and heat, with total energy and exergy efficiencies up to 74% and 58% respectively, and to maintain such performance also in power regulation mode. Although the real efficiency is expected to be lower, the concept proposed is considered to be valid and worth further study.

# Sommario

Il presente studio è volto alla progettazione di un sistema alternativo ai convenzionali impianti Waste-to-Energy allo scopo di ottenere una soluzione più efficiente e pulita per il trattamento dei rifiuti e in grado di contribuire al loro smaltimento. Tale sistema, basato principalmente su Sorption Enhanced Gasification e celle a combustibile a ossidi solidi (SOFC), è stato analizzato anche in termini di funzionamento flessibile. La possibilità di regolazione sarà di particolare importanza in un futuro scenario in cui le fonti rinnovabili potranno costituire una componente prevalente nella generazione di elettricità e il bilanciamento della rete elettrica tra produzione e consumo si prospetterà complesso. Inoltre,

questo sistema è particolarmente adatto a questo nuovo panorama energetico grazie alla capacità di azzerare le emissioni di CO<sub>2</sub> e perfino produrre un'emissione "negativa", ovvero di rilasciare una quantità di gas serra inferiore a quella catturata dalla biomassa. Infatti, il sistema è alimentato con rifiuti biodegradabili quali la frazione organica dei rifiuti urbani o biomassa legnosa. Tale tipologia di rifiuto è stata individuata a seguito di considerazioni riguardanti le caratteristiche del rifiuto, la quantità prodotta e la disponibilità nel lungo periodo. L'impianto è stato modellato attraverso il software CYCLETEMPO con cui è stata svolta un'analisi termodinamica. I risultati prodotti mostrano la capacità del sistema di operare efficientemente e produrre contemporaneamente potenza elettrica, calore e idrogeno con efficienze energetica ed exergetica in grado di raggiungere valori pari al 74% e 58% rispettivamente. Il sistema è inoltre capace di mantenere tali prestazioni anche in regolazione. Nonostante i risultati ottenuti possano variare significativamente nel caso reale, si è dimostrato che il sistema qui analizzato può essere ritenuto una possibile alternativa alle tecnologie convenzionali.

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# Introduction

The generation of waste has been increasing steadily over the last decades. Although developed countries are trying to limit the amount of waste produced and to stabilize the trend, its management is still difficult. Especially in the developing world, the growth is more pronounced as the standard of living improves and economy grows. Many of these countries lack the adequate infrastructure for managing such waste stream and thus this could impact on the health of people and the environment. In particular, not only the world population increases but also the generation per capita undergoes a positive variation. Therefore, it can be easily seen how this trend is not compatible with the finite nature of the world. It is necessary to adopt policies aimed at reducing waste generation as well as implementing better waste management plans.

The European Union issued the Waste Framework Directive (Directive 2008/98/EC) in order to regulate waste management and lay down the principles and definitions that the member states should follow. The purpose of such directive is to prevent negative effects on human health and the environment, like contaminating soil and water or emitting greenhouse gases. In fact, wastes that are not disposed of adequately can be hazardous or release harmful substances in the soil or in the air. The basic guideline for such policy is the waste management hierarchy. This prioritizes certain actions over others. In order to reduce the amount generated, prevention is the main principle. However, for the waste already produced, recycling and recovery are better options than disposal. In fact, disposal in landfills is considered by the directive as the last alternative, since it can cause contamination and emission of substances like methane, which is a much stronger greenhouse gas than carbon dioxide. In particular, non recyclable wastes can be recovered as energy in Waste-to-Energy plants. Incineration converts the energy contained in the waste into useful energy like heat and electricity. However, the efficiency of incineration is low compared to other conventional technologies because of temperature constraints. This is due to the fact that the gas produced from the combustion of wastes is very corrosive at high temperature, which means that the steam produced in the boiler has a limited temperature and pressure. Since the maximum performance of such systems is defined by the Carnot efficiency, lower temperatures are a significant limitation. Combustion of wastes requires also a high excess air. Moreover, ashes and toxic substances must be captured in order to avoid emissions in the atmosphere, processes that causes a not negligible consumption. Therefore, an alternative, more efficient and clean technology is proposed in this study,

overcoming some of the limitations of incineration.

In the future, it is expected that systems using renewable energy sources to produce electric power will have a large share in the power generation portfolio. These will be favored over conventional technologies in order to address the challenge of climate change. However, most of the renewable energy sources are not available continuously and steadily. This can cause unbalance between the supply and the demand of electric power, meaning that there might be periods when the generation is larger than the consumption or when the demand cannot be covered. Several methods are being studied in order to match supply and demand, such as energy storing or smart energy systems. Flexible systems will be also important in this future scenario, balancing fluctuations in the electrical grid. Hence, the need for systems able to work efficiently in part-load conditions as well as in high power mode and with fast response to the changes in the operation. This study tries to deal with these challenges and provide a system at least able to work efficiently in most of the operating conditions.

Along with a larger penetration of renewable energy sources into the electricity generation sector, is likely that the hydrogen market will become more relevant. In fact, several technologies using  $H_2$  as a fuel are expected to be employed as replacement to the ones working on fossil fuels. Therefore, hydrogen demand is expected to increase significantly, although there is still uncertainty about this technological shift. Energy storage into chemicals could be the solution for both grid balancing and hydrogen production. Other alternatives include the generation of such chemical by directly using renewable sources like solar energy instead of converting these into electricity first.

The independence on fossil fuels is an important aspect in the European policies. Beside hydrogen, systems that work with alternative primary sources will be important in the future. Therefore, a system able to combine the disposal of waste with the generation of hydrogen could be well suited for such scenario. This will help to achieve energy self-sufficiency, reducing emissions and avoiding dependence on exporting countries. Moreover, the ability to avoid carbon dioxide emissions could be of particular interest for a future system. In fact, a carbon tax might be implemented to favor green technologies and therefore it could be convenient to limit the emissions when converting wastes into energy. Carbon capture could be a solution but conventional sequestration technologies are expensive and can decrease the efficiency of the power plant significantly. In particular, capturing  $CO_2$  from the flue gas is not efficient, therefore technologies able to capture it when it is present in larger concentration in the system might be more advantageous.

The system studied tries to merge the mentioned aspects and meet the challenges described. The purpose of this study is to identify a system able to provide a valid alternative to conventional Waste-to-Energy plants, generating multiple products efficiently as well as being compatible with a green future scenario. In particular, advanced and promising technologies like gasification and fuel cells are considered.

In the following chapters a suitable waste stream is identified, which is followed by the description and selection of the technologies used. The working assumptions are then

presented and the model of the system is explained. From these, the results are obtained and discussed afterwards.



# Chapter 1

## Waste streams

### 1.1 Waste generation

Every day, millions of tons of waste are produced in Europe. In 2014, the total amount of waste produced by EU-28 countries was equal to 2503 million tons, which translates into 4.9 tons per capita [24]. Many classification are possible in order to analyze wastes, for example in terms of sector, place of origin or hazardousness. Here an overview of the most common ones and those that are more pertinent to this project, as well as the respective quantities generated, will be presented. This will allow to identify a suitable stream for the system.

The main generation sources can be classified into six macro-categories: construction, mining and quarrying, manufacturing, waste and water services, households and other. The first two macro-categories contributed for more than 60% of the total generation, while on average 1758 kg of waste per inhabitant were produced in Europe in 2014, excluding major mineral waste <sup>1</sup> [20]. Solid wastes also include waste generated by the agricultural sector (agricultural and animal residues), public institutions, offices, shops, markets and restaurants [18]. In Figure 1.1, the contribution of each activity to the total generation in Europe is shown. It has to be noted that the amount of waste generated varies greatly among countries, mostly reflecting the economy and the standard of living, and that data provided by some countries may not be reliable enough due to insufficient implementation of waste management and monitoring regulation. In fact, some of the values provided by Eurostat are only estimations.

In 2015, the total waste generated in the Netherlands was 59.2 million tons, of which 77% were recycled. The three main activities contributed for more than 78% of the total amount: the building sector generated 23.826 Mt, industry 14.505 Mt and households 8.266 Mt [15].

In Italy, in 2016, 165.2 million tons of waste were generated [33, 34]. ISPRA (Istituto

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<sup>1</sup>Most of the waste generated by the construction sector and mining and quarrying is considered major mineral waste

Superiore per la Protezione e Ricerca Ambientale) classifies waste into two main categories: municipal waste (RU) and special waste (RS). Municipal waste accounted for 30.1 Mt while the remaining part was special waste [33, 34]. RS is classified, according to ISPRA, based on the hazardousness (hazardous or non-hazardous) or based on the activity this is produced from (for example agricultural waste, demolition, construction and mineral waste, industrial waste, waste from trade and service sectors and waste from waste treatment).

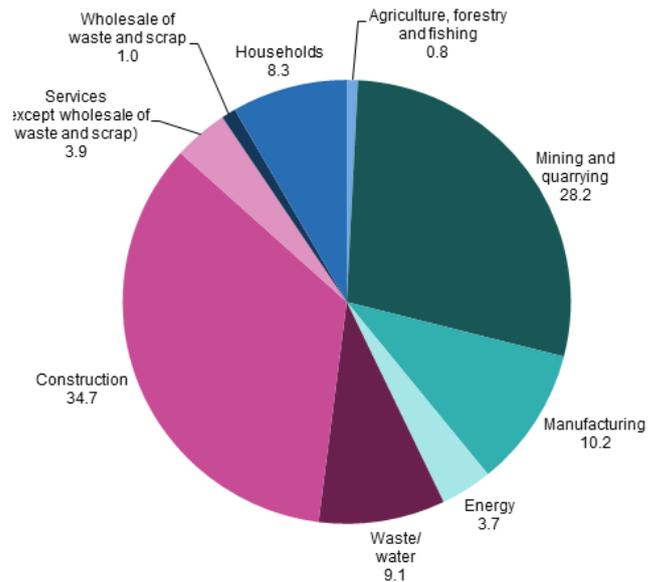


Figure 1.1: Waste generated by activity in Europe in 2014, in percentage of the total generation [24]

The European Waste Classification as defined by Eurostat identifies 51 waste categories [21]. The main categories of interest for the WtE sector are shown in the Table 1.1. It can be seen that household and similar wastes have the largest contribution in Europe, followed by animal and vegetal waste, sorting residues, wood wastes, paper wastes and mixed and undifferentiated materials. In particular, these categories are defined as <sup>2</sup>:

- Household and similar wastes: mixed municipal waste, bulky waste, street cleaning waste, kitchen waste, household equipment, except separately collected fractions. They include street-cleaning residues and wastes from markets and are mainly originated by private households. They do not include hazardous waste;
- Animal and vegetal waste (which are classified separately as animal and mixed food wastes and vegetal wastes). The former are animal waste of food preparation and

<sup>2</sup>These definitions are taken from the European Waste Classification [21]

Table 1.1: Waste generation in EU-28 in 2012 per category [44]

Category	Amount [Mt/yr]		
	EU-28	Netherlands	Italy
Wood wastes	57.489	2.572	3.901
Plastic waste	17.091	0.610	2.733
Paper wastes	46.945	2.313	5.148
Textile wastes	3.108	0.114	0.396
Waste tyres and waste rubber	2.631	0.062	0.354
Waste solvents	2.694	0.114	0.279
Waste oils	1.908	0.047	0.252
Chemical waste	17.048	1.221	2.197
Household and similar wastes	169.655	7.185	18.043
Mixed and undifferentiated materials	46.941	0.905	5.859
Sorting residues	65.417	1.412	13.536
Animal and vegetal waste	110.057	14.545	9.976
Dried municipal sewage sludge	9.860	0.346	n.a.

products, including sludges from washing and cleaning. Mixed wastes of food preparation and products include biodegradable kitchen and canteen wastes, and edible oils and fats. These are produced in food preparation and agriculture. The latter are defined as vegetal waste from food preparation and products, including sludges from washing and cleaning. These wastes are generated by agriculture and food production or derive from separate collection. Both are non-hazardous;

- Sorting residues: sorting residues from mechanical sorting processes for waste, like screening; fluff-light fraction combustible waste (refuse derived fuel); non composted fractions of biodegradable waste. They are generated mainly by waste treatment processes and might contain hazardous substances;
- Wood wastes: wooden packaging; sawdust, shavings, cuttings; waste bark, cork and wood from production of pulp and paper; Wood from construction and demolition of buildings. They are separately collected and originate from wood and paper processing and production. They might contain hazardous materials;
- Paper waste, classified as "paper and cardboard waste": paper and cardboard waste from sorting and separate collection. It is not hazardous;
- Mixed and undifferentiated materials: unspecific wastes and mixed waste, generated by nearly all industries and waste treatment. They might include hazardous materials.

Municipal waste, although not officially a category according to the classification above, comprises different types of wastes and is of particular interest because it is characterized

by a concentrated generation, which means that large amounts are produced over small areas. Moreover, increasingly more countries are implementing a good separation between different types of waste already at the source. Around 10% of the total waste produced in Europe is municipal waste [23], households accounting for 204 of the 246.38 million tons generated [22, 24]. Municipal solid waste is defined by Eurostat as "[...] waste collected by or on behalf of municipal authorities and disposed of through waste management systems. Municipal waste consists mainly of waste generated by households, although it also includes similar waste from sources such as shops, offices and public institutions". In 2015 Dutch households generated 8.4 million tons of waste, while 29.6 Mt were produced in 2017 in Italy in urban areas. About half of the municipal waste in Italy was source separated.

## 1.2 Waste treatment

The waste generated and collected can be reused, recycled through intermediate processes, recovered or disposed of. According to the waste management hierarchy (Directive 2008/98/EC), this is the order of priority that should be followed when considering waste management. Recovering is the treatment of interest for this study, since it refers to the use of waste as energy source.

Almost half of the total waste generated in 2014 in Europe was landfilled, while only 6.2% was incinerated - one fourth of it without energy recovery - and approximately 36% was recovered. In the same year, only 2.2% of the total waste generated in the Netherlands was landfilled, while 3.4% was sent to incineration. Almost all the remaining waste was reused [19]. In Figure 1.2, the amount of waste processed in 2015 can be seen. It has to be noted that the waste treated may not only be the one generated in the Netherlands but part of it could be imported. In particular, this can be observed for the amount incinerated, which is more than three times the one reported in the Environmental Data Compendium [19] for 2014, which shows that only 2020 million kg of waste generated in the country were incinerated. Moreover, the amount processed is usually lower than the one generated.

In Table 1.2, the quantities of waste processed in the Netherlands in 2012 for the treatments of interest are shown. The codes in the header are the ones used by the European Union: D1 to D7 and D12 indicate different types of disposal (landfilling and waste storage), D10 is incineration on land as thermal treatment in order to reduce the volume and hazardousness of waste, R1 is the use as fuel or other means to generate energy. As it can be seen in the table, mixed and undifferentiated materials, household and similar waste and sorting residues are the types of waste that offer more room for improvement in terms of processing, being the most landfilled categories. Moreover, along with wood waste and animal and vegetal waste, these are the categories that constitute most of the input in incineration plants with energy recovery. Since these systems usually have modest efficiencies, using these waste streams in more efficient technologies could be a suitable alternative.

In 2015, in Italy, around 19 Mt of waste were landfilled, which were composed by 7.8

Table 1.2: Waste treatment in the Netherlands in 2012 per category, in kt [44]

Category	Total treated	Landfill (D1-D7, D12)	Incineration (D10)	Incineration (R1)	Recovery
Wood wastes	2032	3	11	1043	975
Plastic waste	511	7	3	87	414
Paper wastes	2242	0	0	0	2242
Textile wastes	57	3	0	20	34
Waste tyres and waste rubber	60	0	n.a.	11	51
Waste solvents	91	0	13	34	44
Chemical waste	937	16	510	82	330
Household and similar wastes	5865	125	25	5705	10
Mixed and undifferentiated materials	865	144	33	117	571
Sorting residues	2073	75	13	1337	649
Animal and vegetal waste	14458	42	484	352	13580
Dried municipal sewage sludge	331	10	321	0	0

*Note:* For brevity, "recovery other than energy recovery" is indicated as "recovery".

million tons of municipal waste and 11.2 million tons of special waste. In 2016, 24.7% of the total municipal waste produced was landfilled [2]. Most of the waste sent to landfills was pretreated with bio-mechanical processes (TMB) that stabilize it before further processing and separates organic material from fractions with a high calorific content. In 2016, the amount of waste incinerated in Italy was 5.4 million of tons, more than half of which was undifferentiated municipal waste and the remaining part was mainly constituted by waste from waste treatment. In particular, only 990 thousand tons of special waste were incinerated. The amount of special waste recovered (R1 to R12) in 2016 in Italy was 93.8 million tons, accounting for almost 70% of the total production of special waste, while 14.4 Mt were found in storages, waiting for future recovery (R13). In the same year, 32 Mt of special waste were disposed of (D1 to D14) while 900 thousand tons were stored prior to disposal (D15) [31]. It has to be noted that the sum of these amounts is larger than the total quantity of special waste produced in 2016 because part of quantities waiting for treatment/disposal could have been originated in the previous years. In 2017, the mass of municipal waste processed by TMB plants was 10.7 million tons, including waste from waste treatment, while 5.6 Mt were incinerated, accounting also for co-incineration. In the same year, almost 7 Mt of municipal waste were landfilled, of which only 461 thousand tons were not treated beforehand. Although waste sent to composting (4 Mt) was still more than the one processed in anaerobic or integrated aerobic/anaerobic digesters (3.4 Mt), the latter increased almost by 15% from the previous year. However, organic waste disposal is still troublesome in Italy [32].

It has been estimated that 24% of the total municipal waste generated in 2016 in Europe was landfilled while 27.6% was incinerated [22] and around 16% was sent to composting [23]. In absolute values, 40 Mt were composted, 66 Mt incinerated and 59 Mt landfilled. In the Netherlands, about 0.3% of the waste generated by households was landfilled, less than 0.2% incinerated and more than 98% was recovered [19].

From the values reported, it can be seen that there is a considerable potential for en-

ergy conversion of waste in Europe. In particular, the amount landfilled that can undergo conversion processes could be used as a fuel for Waste-to-Energy plants, not only producing electricity and heat but also reducing the size of the waste significantly, allowing for an easier disposal. In fact, thermochemical processes (such as gasification) can reduce the mass of the waste by 70-80% and by 80-90% in volume [7]. Moreover, conversion to chemicals can also be obtained. For example, the compostable waste could be used, instead, for biogas production in an anaerobic digester. The residue would still have nutrients as in the compost. Alternatively, syngas could be produced in a gasifier. However, according also to the European policies, the choice of the types of waste that can be converted into energy should include only those that are not suitable for recycling. Therefore, waste treatment should give priority based on the waste management hierarchy, putting the emphasis on recycling, followed by recovery and disposal as the last choice.

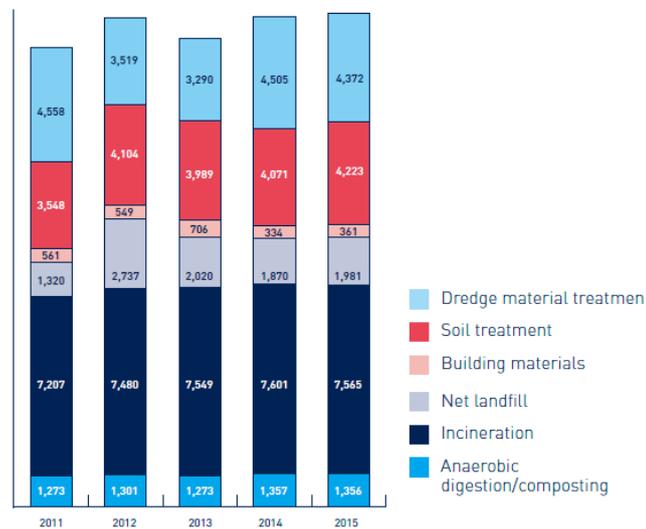


Figure 1.2: Amount of waste processed in the Netherlands in 2015, in kt [15]

### 1.3 Waste composition

Waste composition can be defined in different ways, depending on the level of detail required. A possible classification of municipal solid waste is the one based on its physical composition. The most general physical components are the following: organic fraction, paper and paperboard, plastics, glass, metals, textiles and others. In Europe, organic fraction (constituted mainly by kitchen and garden waste) usually ranges from 20% to 40% [18, 35]. As it can be observed also in Table 1.3, often data are not available or uncertain. According to the report of World Bank [29], organic fraction, paper and plastic account for 80% of the total MSW composition in the Netherlands. The other components are shown in Table 1.4. Waste from households is mainly composed of residual waste (46%),

Table 1.3: Waste physical composition in Europe (in percentage) [18]

Region	Food	Paper/ carboard	Wood	Textiles	Rubber/ leather	Plastic	Metal	Glass	Other
Eastern Europe	30.1	21.8	7.5	4.7	1.4	6.2	3.6	10.0	14.6
Northern Europe	23.8	30.6	10.0	2.0	n.a.	13.0	7.0	8.0	n.a.
Southern Europe	36.9	17.0	10.6	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Western Europe	24.2	27.5	11.0	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.

Table 1.4: Waste physical composition in the Netherlands (in percentage) [29]

Organic	Paper	Plastic	Glass	Metal	Other
35	26	19	4	4	12

vegetables, garden and fruit waste (both bulky and non, 22%), paper/board (11%) [15]. The composition of household waste in the Netherlands in 2015 is shown in detail in Figure 1.3.

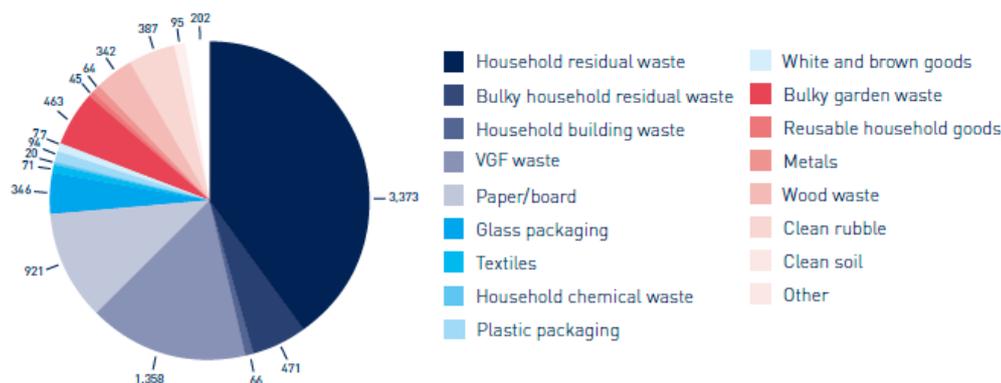


Figure 1.3: Composition of household waste in the Netherlands in 2015, in kt [15]

The average composition of municipal solid waste in Italy between 2008 and 2016 can be seen in Table 1.5, where the percentages of the physical components are shown. As common in developed countries, organic fraction is about one third of the total waste, and paper constitutes a large amount of the total. Also the fraction of plastics and glass are considerable, although in the future more attention will be paid on plastic generation, with the aim of limiting its production, being not environmentally friendly.

Waste composition can be also defined based on proximate and ultimate analysis. The proximate composition usually shows the composition in terms of moisture content, volatile

Table 1.5: Average physical composition of municipal solid waste in Italy between 2008 and 2016 (in percentage) [2]

Organic	Paper	Plastic	Glass	Metal	Wood	Textiles	Other
35	22.9	12.9	7.5	2.7	3	3.8	12.8

Table 1.6: Proximate and ultimate analysis of several waste components, on dry basis

	Moisture [%]	Proximate composition [%]			Ultimate composition [%]				
		Fixed carbon	Volatiles	Ash	C	H	O	N	S
Wood/ Yard waste <sup>a</sup>	72.57	21.26	73.46	5.28	48.75	5.93	39.32	0.60	0.12
Rigid plastic <sup>a</sup>	15.02	8.28	90.62	1.10	71.23	7.62	19.58	0.08	0.39
Plastic film/ styrofoam <sup>a</sup>	0.45	0.62	99.38	0.00	90.38	7.53	1.00	0.69	0.40
Food waste <sup>b</sup>	81.5	1.5	93	5.5	46.36	6.98	39.3	1.86	n.a.
Food waste <sup>c</sup>	50-80	n.a.	n.a.	2-8	48.0	6.4	37.6	2.6	0.4
Garden trimmings <sup>c</sup>	30-80	n.a.	n.a.	2-6	47.8	6.0	38.0	3.4	0.3
Paper <sup>d</sup>	4-10	n.a.	n.a.	6-20	43.5	6.0	44.0	0.3	0.2
Organic domestic waste <sup>d</sup>	54	n.a.	n.a.	18.9	42.09	5.43	31.14	1.78	0.41

<sup>a</sup> Shi et al. [45]

<sup>b</sup> Amuzu-Sefordzi et al. [4]

<sup>c</sup> Chandrappa and Das [10]

<sup>d</sup> ECN [17]

matter, fixed carbon and ash content. Ultimate analyses are more specific and are performed in order to determine the elemental composition. These values can then be used to evaluate the energy content and amount of contaminants (like heavy metals and hazardous chemicals), as also the required treatments for the removal of such contaminants. The ultimate composition allows also to predict the composition of the gas produced through chemical processes or incineration. From the data collected by Shi et al. [45], carbon content in municipal solid waste varies between 20.62 and 92 wt%, hydrogen content between 2.87 and 14.2 wt%, nitrogen between 0 and 10 wt%, sulphur content between 0 and 2.46 wt% and oxygen content between 0 and 49.4 wt%. These values are expressed on moisture free weight (db). In Table 1.6, the proximate and ultimate composition of some waste types are shown. Significant variations can be observed even among the same type.

## 1.4 Calorific content of wastes

Along with the chemical composition of the waste, its calorific content is another important characteristic. The lower heating value of a material expresses its specific energy content, often per unit of mass. Three definitions of LHV are commonly used for wastes according to the weight basis considered:

- as received (ar), which expresses the energy content per unit of weight of the waste as it is collected;
- dry (dry), which defines the heating value as the energy content per unit of weight of the moisture free waste;
- dry and ash free (daf), which represents the calorific value based on the moisture and ash free waste.

As it can be expected, the LHV increases from wet basis to dry and ash free. These values can be obtained through measurements using a bomb calorimeter or through empirical models, using for example the Dulong formula. Although tests with waste samples are able to provide more accurate results, experiments may not always be possible. Moreover, the composition is not constant. Empirical models usually allow to evaluate the lower heating value as a function of the ultimate composition. Several formulae can be used to estimate the LHV of the material considered and therefore the appropriate one has to be chosen in order to obtain acceptable results. Values of the energy content for the different physical components of waste are also available. These are strongly dependent on the characteristics of the fraction itself and thus vary considerably even among samples of the same fraction. It has to be noted that the standard deviation of the data representing heating value is significant. In fact, waste streams are composed by discrete components and therefore different samples will contain different materials, which consequently will affect the energy content. Moreover, the physical composition of waste streams may also vary over the year, determining a change of proximate and ultimate composition. In general, data for municipal solid waste are commonly available for each fraction while values for industrial waste are referred to specific type of wastes. However, since different and often not precise definitions are used by institutions and researchers, the error made when using the values found in the literature may not be negligible. In particular, often it is not explicitly indicated if the lower heating values are on wet, dry or dry and ash free basis. Moreover, despite the fact that the European Union has a standard classification of the waste types, categories used by institutions of different countries are usually defined in different ways, making it impossible to use a unified approach. This results in the difficulty of obtaining reliable and sufficiently precise data.

It is estimated that the lower heating value of European municipal waste ranges from 5.1 to 11.6 MJ/kg and has an average value of about 9 MJ/kg, while its moisture content is around 30-40% [44, 55]. In particular, the lower heating value of municipal solid waste is 9.2 MJ/kg in the Netherlands and 10 MJ/kg in Italy. In Table 1.7, the lower heating value for the main physical components is shown according to different authors and institutions. Although these data are in line with the ones found in the literature, they are average values since they are dependent on the actual composition of the waste. Especially for plastics, the energy content varies significantly with the type of plastic, ranging from more than 40 MJ/kg for HDPE to around 20 MJ/kg for PVC. The lower heating value of organic fraction, paper and wood may vary in a range of several MJ/kg, but significantly less than

Table 1.7: Lower heating value of the main components of municipal solid waste, according to three different sources

LHV [MJ/kg]						Source
Organic	Paper	Plastic	Textile	Wood	Residual waste (Household generated)	
12.5 ( <i>garden</i> ) 20.3 ( <i>kitchen</i> )	14.8	32.6	14.7	14.7	12	Waste2Go [55]
	16.7	35.7	17.4	13.4	13	Saveyn et al. [44]
16.86	14.57	39.18		15.84		ECN [17]

*Note:* The data shown are average values. Despite not being explicitly expressed, it is assumed that the values from Waste2Go [55] and Saveyn et al. [44] are on dry basis.

the one of plastic. The database Phyllis2, developed by ECN [17], provides data for some of the components of the Dutch waste. According to this database, the lower heating value (wet basis) of organic domestic waste is usually around 4.80 MJ/kg but can vary from almost 2 MJ/kg to around 11 MJ/kg and is approximately  $14 \div 16$  MJ/kg on dry basis while the most recent value for plastic is 35.02 MJ/kg (wb).

## 1.5 Energy available in waste streams

The energy available in the waste produced every year can be calculated by multiplying the total amount by its heating value. Although this approach is not able to provide accurate results, it can give an insight into the energy potential of the total amount of waste and the different streams. For a rough estimation of the primary energy contained in municipal solid waste in Europe, the heating value of 9 MJ/kg (as mentioned before) can be considered. For 2016, this results in 2.21 EJ. In order to obtain more accurate results, the contribution of each component could be evaluated and then summed. For the Netherlands, the primary energy related to household waste in 2015, considering a LHV of 9.2 MJ/kg, is 77.3 PJ. If all the household waste were incinerated in a WtE plant with an efficiency of 22% [44], the electricity produced would be equal to 4.7 TW h. Considering household residual waste (3.844 billion kg), the primary energy is 35.3 PJ, while the energy in vegetable, garden (not bulky) and fruit (4.80 MJ/kg) is around 6.52 PJ. Taking into account the amount of municipal solid waste generated in Italy in 2017 (29.583 million tons) and the lower heating value (10 MJ/kg), 295.84 PJ (82.18 TW h) of primary energy is available. With the same efficiency as before, WtE plants would be able to convert this energy into 18.08 TW h of electricity, which would account for 5.6% of 320.5 TW h of electrical energy consumed in Italy in 2017 [52]. Therefore, it can be seen that wastes offer good opportunities in the energy sector, since they could provide a non negligible contribution as primary energy sources.

The energy contained in the different streams can be also estimated with similar cal-

culations. For example, the primary energy in organic waste (6.62 Mt) in Italy in 2017 is 11.84 TW h, considering a moisture content of 54% and a lower heating value of 6.44 MJ/kg for the wet waste, the one in plastic waste (1.27 Mt) is 12.39 TW h (35.02 MJ/kg, lower heating value of plastic as received).

Table 1.8: Energy contained in waste types sent to incineration and landfill in EU-28 [44]

	<b>Incineration</b>		<b>Landfill</b>	
	(D10+R1)		(D1-D7-D12)	
	[PJ]	%	[PJ]	%
Wood wastes	375	21	7	0
Plastic wastes	31	3	51	4
Paper and cardboard wastes	6	0	3	0
Textile wastes	2	0	3	0
Waste tyres	35	2	2	0
Spent solvents	29	2	0	0
Waste oils	32	2	0	0
Chemical wastes	93	5	31	2
Household and similar wastes	470	26	616	44
Mixed and undifferentiated materials	149	8	120	9
Sorting residues	334	18	489	35
Animal and vegetal wastes	70	4	80	6
Dried municipal sewage sludge	22	1	7	0
Waste-derived biogas	108	6	0	0
Waste derived biodiesel	19	1	0	0
<b>Total</b>	<b>1805</b>	<b>100</b>	<b>1409</b>	<b>100</b>

*Note:* Energy recovered from anaerobic digestion is taken into account within waste-derived biogas

According to Saveyn et al. [44], few types contain most of the energy available in wastes in EU-28. These are wood wastes, household and similar wastes, mixed and undifferentiated materials, sorting residues, animal and vegetal wastes and waste-derived biogas. These account for 93% of the energy available in wastes sent to landfill and 83% of the energy of the one sent to incineration. In particular, household and similar wastes and sorting residues contribute for 79% of the total energy contained in landfilled waste, while if also wood wastes are included, these account for 26%, 18% and 21% respectively of the energy in the waste sent to incineration. These categories offer a significant potential for energy conversion thanks to the large available energy, which is mainly related to the amount of waste generated. In general, the types of waste that are commonly incinerated still offer room for improvement for energy conversion, being large amounts also landfilled. The values for the types of waste landfilled or incinerated are shown in Table 1.8.

## 1.6 Forecasts

In order to identify a suitable stream for the system, the future waste generation and management scenario must be considered. In this way, the concept could be implemented in the new energy sector. As it can be seen in Figure 1.4, the amount of municipal solid waste generated in Italy decreased in the last decade, although not monotonically. On the contrary, special waste increased from 2014 to 2016 (Figure 1.5). Therefore, the total amount of waste produced in Italy has increased in the last years, in agreement with the trends expected by World Bank [29], shown in Figure 1.6. In the same figure, the variations in composition between 2012 and 2025 of the solid waste generated is represented per level of income. For high income countries, relatively small changes in composition are expected, while these are more significant for poorer countries. In particular, it can be noticed that, although organic waste is the one that will see a decrease in percentage, in absolute terms there will be a large amount to manage in the future. In general, large differences in composition are not expected for European countries and therefore the current one will be considered in this report. However, variations in the same fraction are likely to happen because of new policies and regulations in the European Union. For example, plastic waste may see a decrease in amount generated and a shift towards different plastic materials which are more environmentally friendly and more easily recyclable.

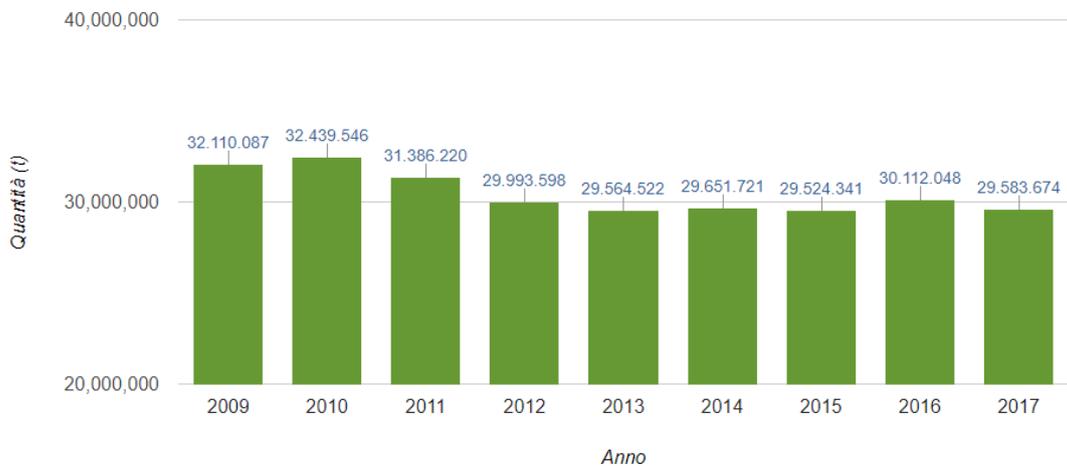


Figure 1.4: Trend of MSW generation in Italy between 2009 and 2017, in tons [34]

Stronger implementation of policies applying the waste management hierarchy principles could affect significantly the Waste-to-Energy sector. In fact, reuse and recycling are the primary steps to follow before considering disposal or energy recovery. In particular, the EU lays great stress on the importance of prevention and reuse as the main principles for decreasing the generation of new waste. Waste that is now landfilled should be used for energy recovery only if these two steps are not possible. Especially waste streams such as wood, plastic and textile wastes may see an increase in recycling in the future, thus

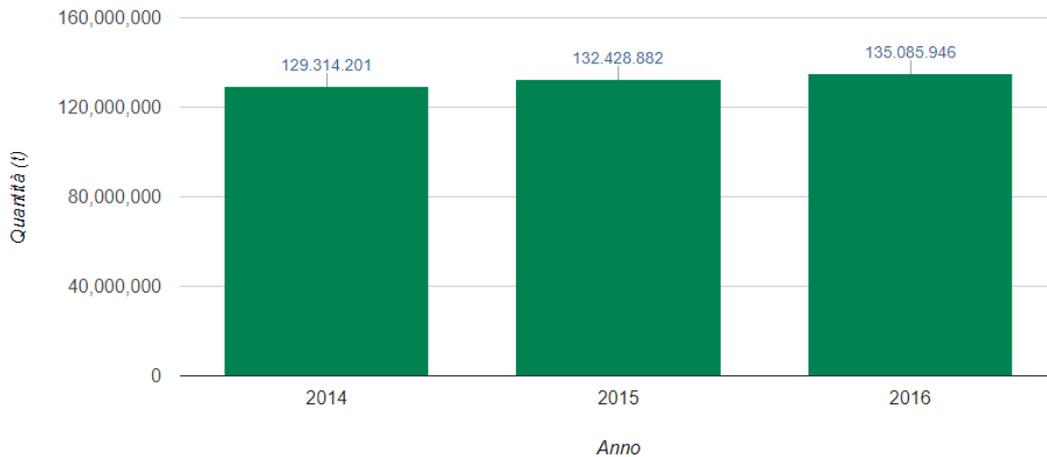


Figure 1.5: Trend of special waste generation in Italy between 2014 and 2016, in tons [33]

partially reducing the use in energy conversion plants. In addition to a policy aimed at reducing the amount of waste generated, it is likely that a better source-separated collection will be implemented. This will lead to a reduction of mixed waste and sorting residues [44]. In fact, mixed wastes are usually difficult to separate into individual components and are often landfilled. Fractions with a lower separated collection may see a larger share in energy recovery in order to avoid disposal in landfills. In particular, household and similar wastes have a low recyclability and energy recovery is the best alternative to landfilling.

Therefore, although a reduction of this type of waste is expected and probably a better source-separated collection will be applied, household and similar wastes are still likely to be used - or even see an increase - in the Waste-to-Energy sector. Nonetheless, streams that are already separated are easier to convert in power plants, therefore some of these could be specifically used for energy production.

In 2012, "recovery other than energy recovery" of animal and vegetal wastes was 86% of total amount managed [44]. This accounts also for use in anaerobic digestion plants, where energy and materials are recovered, in the forms of fuel and soil fertilizer. This type of waste processing may grow substantially in the future thanks to its advantages and the production of biogas could be significant, since the amount generated is large (see Table 1.1). However, modest efficiencies and quite long conversion times from waste to biogas are the drawbacks of such processes. Paper waste have been mainly reused and it is expected that this trend will continue in the future. On the contrary, waste tyres and household and similar waste are recovered as energy in a significant amount, as also mixed and undifferentiated materials and sorting residues.

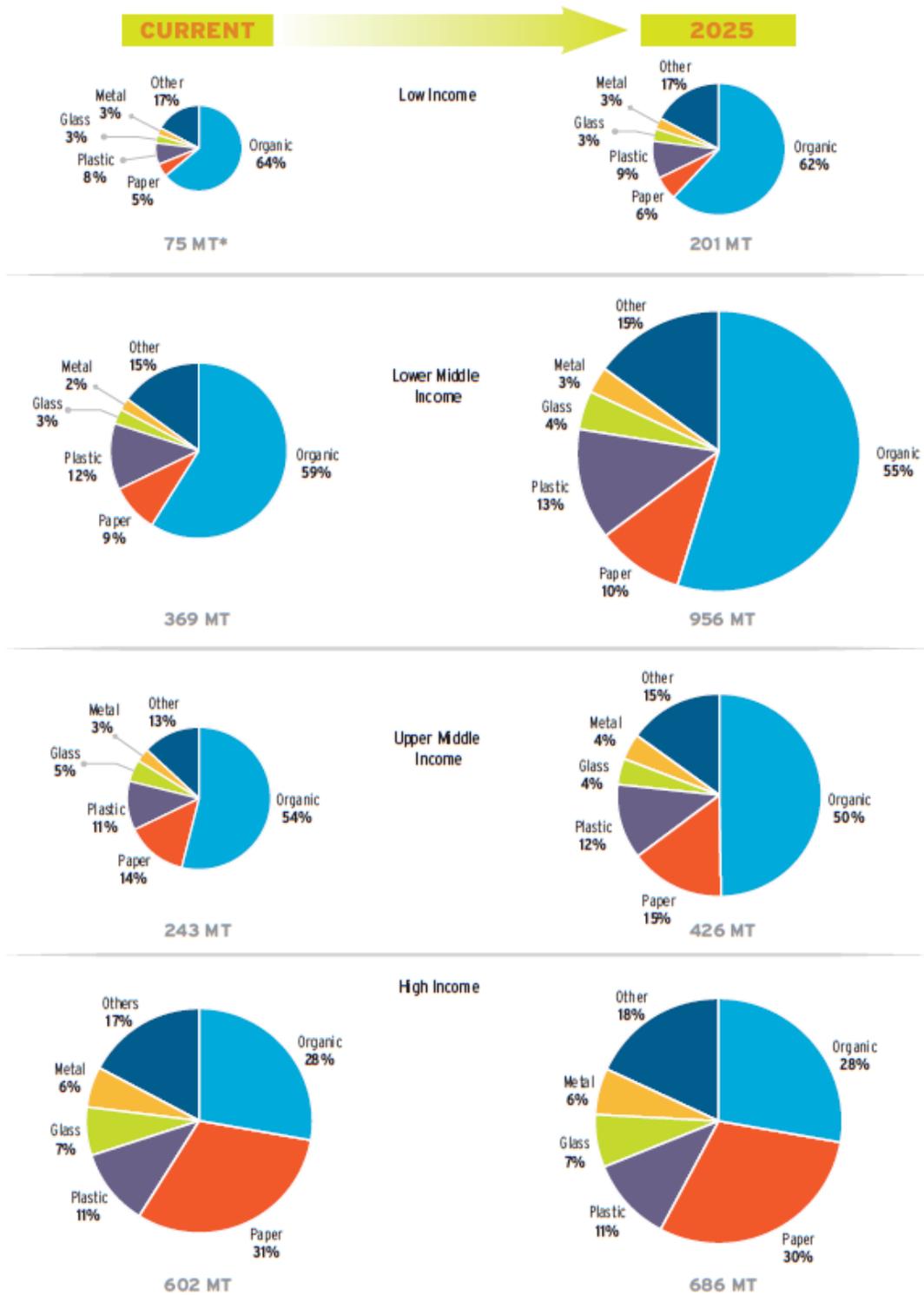


Figure 1.6: Projections of solid waste generation and composition from 2012 to 2025 for countries with different income level [29]

## 1.7 Selection of the waste stream

In this section the criteria used for selecting the type of waste stream to be used as energy source are discussed. Although it is difficult to find a type of waste that meets all of the desired characteristics, some of them are necessary for achieving the goals of the system. Here are the ones considered most important:

- long-term availability of the stream type(s);
- consistent generation and significant amount available;
- no reuse or recycling possible or less convenient if compared to energy conversion;
- critical streams (e.g. GHG emitting if landfilled or difficult to dispose of);
- suitable chemical properties (e.g. low amount of contaminants, suitable content of carbon and hydrogen, adequate lower heating value);
- area over which the stream is originated (concentrated or distributed generation/collection);
- presence of a collection infrastructure.

The criteria are here explained and it is evaluated which streams meet at least the most important ones. Long-term availability is one of the key principle for the identification of the suitable streams. In particular, the amount generated should be significant and at a steady production rate in order to guarantee its continuous use as an energy source. The availability of the waste types considered should be expected to be approximately constant in the future years. Therefore, the trends mentioned in the previous section are taken into account. Also continuous generation over the year is important, in order to allow the system to operate constantly. Moreover, the composition of such streams has possibly to be consistent over time or at least not undergo dramatic changes, so that the the system could still work close to the design point.

Since an important part of the scope of this project is to find a possible use for types of waste that have otherwise limited or less efficient alternative management, the focus should be on streams that are often landfilled. Therefore, also the present management of such streams has to be considered. In particular, the waste management hierarchy and its correlated policies can be used as a framework for the exclusion of those types of waste that has the potential to be recovered or recycled. In addition, it is expected that more actions will be taken in order the prevent the generation of some streams which production can be completely avoided or alternatively affected by modifying the characteristics of the waste. For example, plastic wastes could see a variation in composition and amount so that a more sustainable waste cycle can be implemented. Therefore, although a possible use in the WtE sector is not be completely excluded, plastic wastes were not considered, being also characterized by a large deviation in composition. Furthermore, streams that

could be used more efficiently can be also taken into consideration. Among these, the ones treated by incineration plants are included as possible choices, since this technology offers low conversion efficiency and has inherent limitations like the maximum working temperature, thus leaving room for improvement. Also anaerobic digestion has moderate efficiency, but it has to be noted that it is able to produce two useful substances.

Critical waste might also be considered. In fact, some of the current management and conversion strategies are not able to treat wastes limiting pollution or deal adequately with its hazardousness and thus greenhouse gas emissions or possible air or soil contamination could happen. For example, landfilling of biodegradable waste can lead to the release of methane and stock piling manure can cause water contamination. On the other hand, high temperature treatments like incineration can produce dioxins, NO<sub>x</sub>, SO<sub>x</sub> and other emissions. Hence, the need for a technology that can prevent such negative effects on the environment. However, at the same time, it is necessary to make a selective choice of the suitable waste for energy conversion which has not to be inherently polluting or that is too difficult to convert because of the large amount of contaminants. High temperature processes help to reduce its hazardousness, but other uses or prevention are better alternatives for streams which treatment would not be convenient. Chemical composition then plays a significant role in the choice: consistent composition, low content of sulphur, heavy metals and halides are necessary characteristics. Nonetheless, it has to be noted that sulphur and other possible contaminants can be removed efficiently by means of cleanup units. Moreover, a significant amount of hydrogen and carbon should be present in the waste in order to have suitable gasifier products to be used in a fuel cell. A sufficiently high LHV is also preferred in order to have gasifier off-gases with a good energy content and therefore the amount of oxygen in the waste should be limited.

Existing waste collection infrastructure is also important in the selection of the appropriate waste streams. In fact, towns and cities have more potential because they offer the advantage of localized generation, which means that a significant amount of waste is available without the need to collect it over a large area and gather it in one location, causing more pollution in the transport. Moreover, the separation of the different components of waste is difficult and therefore source-separated waste is more promising as energy source, being the type of interest already isolated and requiring less processes. It has to be noted that many towns even struggle to handle all the amount of waste produced - especially in Italy - and therefore a system built in these locations able to provide help for the management could have many benefits. Such system could be very useful also in fast-growing cities in developing countries, since these are particularly critical, often lacking proper management infrastructure. Therefore, municipal waste is a promising category of waste to take into consideration.

Considering the criteria listed above, the type of waste selected is the organic fraction of municipal solid waste, and might include similar biodegradable streams like garden residues, animal and vegetal waste from the agroindustrial sector, wood waste and dried sewage sludge as well. It is not excluded that other types of waste could be used effectively.

These streams meet most of the above recommendations at least partially. In fact, a considerable amount of such waste is available, being usually the largest physical component in municipal solid waste, and this is even expected to increase worldwide. This means that the generation will unlikely see great negative shifts. The generation of organic fraction of municipal waste could be reduced only slightly since it is largely constituted by kitchen wastes. Its management usually involves composting, anaerobic digestion or landfilling. The use of organic waste in the system that will be presented could coexist with composting and anaerobic digestion or even be integrated with the latter, using the biogas produced. It has to be noted that composting does not provide benefits in energy terms but it only produces a soil conditioner, still emitting carbon dioxide (although maintaining carbon neutrality). On the other hand, landfilling of biodegradable waste has negative effects on the environment, being a source of greenhouse gases and potentially causing soil or water contamination. The disposal of pretreated (TMB) organic wastes in landfill in Italy is still significant. Although it is likely that wood waste will see a significant increase in recycling, products made of recycled wood will still need to be processed at the end of their life, therefore it is possible that some kind of wood derived waste will be produced. Similarly to the organic fraction, also sewage sludge will likely not see a decrease in the future, as also industrial animal and vegetal wastes.

The lower heating value of organic fraction of municipal waste may have not negligible variations in relative terms but these are relatively small and are only of some MJ/kg in absolute values. Wood waste has a LHV which varies much less than other waste types like plastic. On the other hand, however, moisture content can change quite significantly. The composition of the organic fraction of municipal waste may change over the year, but the average ultimate composition should not have great variations. Furthermore, these types of waste have similar chemical composition and LHV, therefore they can be used almost interchangeably in the system without - theoretically - causing great shifts in the operating point. However, the macrostructure of the wastes could affect the performance of the system, for example like the larger presence of lignin in wood biomass. Moreover, sulphur content is moderately low as also chlorine content.

The generation of the selected waste types takes place mostly in urban areas, meaning that a sufficient amount should be available for a plant to use it as a fuel. Moreover, a waste collection infrastructure is usually present and often waste types are already separated at the source.

Although it does not seem reasonable to use a carbon dioxide emitting plant as a future system to provide a balancing service in a renewable-dominated electric system, it has to be noted that if biomass is used, the CO<sub>2</sub> released in the atmosphere is equal to the one absorbed by the biomass itself, if transport of waste and other processes are not considered. Therefore, this type of waste fits well in the future "green" energy scenario, being able to (possibly) avoid greenhouse gases emissions. If not completely carbon neutral, using organic wastes as energy source should still cause reduced emissions compared to conventional fuels.



## Chapter 2

# System overview

### 2.1 Scope of the system

During the last years, the evidences that the environment is undergoing drastic and irreversible changes continued to increase. Climate change is possibly the main challenge that our age has to face and therefore actions have to be taken in order to mitigate the damage to the environment. International agreements have been stipulated in order to decrease greenhouse gas emissions and to try and establish a sustainable society. To realize such goals, it has become clear that the world has to renew several economic sectors and thus important technological challenges have to be overcome. Among these sectors, the electricity and heat production sector has to undergo important changes, in particular finding a substitute to fossil fuel powered plants, since this contributes significantly to total emission. In addition to the environmental aspect, fossil fuels are also limited in terms of amount available on the planet, which means that alternative energy sources have to be found. Therefore, it is easily understood why renewable energy sources (RES) have been increasing in relevance in the last years and many countries are reshaping their power generation portfolio to include more renewable energy plants. However, despite offering a solution to both environmental and availability concerns, most of RES are intrinsically intermittent. In particular, it is difficult for an electrical grid dominated by RES plants to follow the demand, since the generation depends on the momentary availability of the renewable sources. Although different grid management strategies are being studied, there will be still need for flexible systems. In order to be able to match the demand continuously, a considerably larger installed power of RES plants is required since the energy source is not always available. Therefore, in the future there will be then a surplus of power when there is a large availability of renewable energy and the generation exceeds the demand and a deficit when not enough is present and the generation cannot cover the demand. Energy storage is considered as a possible solution to this fluctuating behavior, accumulating energy during surplus periods and providing it when the generation cannot keep up with the demand. Electricity storage may be a candidate technology, but current ones are still not ready on large scale. However, the energy surplus could be stored into

useful chemicals. The system in this report draws partially inspiration from such concept and is designed to help with this balancing problem, providing an efficient generation.

Apparently unrelated, waste management is also a current challenge and it will particularly so in the future in developing countries. Due to the many types of waste and their different processing, waste management is a complex subject. In particular, it is difficult to treat the large amount generated in a sustainable way, without producing substances that may be harmful or still require special disposal. Moreover, many countries still make extensive use of landfills. Therefore, the technology presented is convenient since it is able to convert waste into useful products and to leave just a small amount of residue to dispose of. In fact, the mass and the volume of the residue after gasification is reduced greatly, being the waste almost completely transformed into useful gases that are then oxidized, producing species that are not harmful. In addition to flexible production of electric power, the continuous management of the waste produced is necessary, thus a base operation of the system is required. Moreover, some base load could still be expected in the future, and such system could help providing it. In brief, the design of the system here described has the scope of contributing to the management of waste and at the same to the one of the electricity grid, operating efficiently and constituting a possible alternative to current technologies.

## 2.2 Description of the system

The system consists of several units, to which corresponds different important processes. The main ones are: pre-processing of waste, gasification, gas cleanup, electrochemical oxidation. The components in which these steps take place are the shredder and dryer, gasifier, gas cleanup module and a high temperature fuel cell. Moreover, a heat recovery system is also used. In Figure 2.1 the schematic representation of the system is shown.

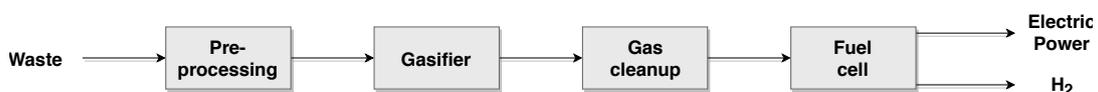


Figure 2.1: Main modules of the system

The feedstock in the form of biodegradable waste is pre-processed by firstly drying it up to the desired moisture content and shredding it into small particles in order to minimize internal heat transfer and mass diffusion resistances in the gasifier [43] and to homogenize the characteristics, as also to have a better control on the flow rate. These particles are fed to the gasifier, where the solid waste is converted at moderately high temperature into

a gaseous fuel, called syngas, with the aid of steam. The main advantages of gasifying wastes rather than direct combustion are related to the oxidation temperature and gas purification. In fact, in incineration plants, the combustion temperature (and thus the steam temperature) can only reach a certain value and therefore, according to Carnot's rule, the efficiency of the system, working on a thermodynamic cycle, is limited. In particular, the efficiency is limited because a large amount of excess air is used for the combustion in order to control the temperature. On the contrary, when the gasifier off-gas is used in a fuel cell, a higher efficiency can be achieved because it is not subjected to Carnot's efficiency. Moreover, several chemicals can be obtained from the syngas. In addition, incineration produces toxins and toxic metals, as well as NO<sub>x</sub> and SO<sub>x</sub>, that require a complex system to eliminate from the flue gas before dispersing them in the atmosphere. Gasification, instead, generates less critical contaminants, which can be removed from the produced gas before it enters the fuel cell and is oxidized electrochemically.

This gas is then sent to a cleanup unit, where substances not compatible with the fuel cell are removed. Through electrochemical reactions, the syngas is oxidized in the cells and electricity is produced. Since the gasifier output gas contains methane, this is reformed inside the fuel cells, providing a way to control the stack temperature together with the oxidant flow. In fact, reforming of methane is an endothermic reaction and therefore heat generated in the fuel cell can be used effectively. Beside electric power, also hydrogen is available at the output of the fuel cells because only a percentage of the total fuel can be oxidized in order to the voltage not to collapse. Part of the hydrogen is the one produced by internal reforming of methane and not converted while the remaining part is the one contained in the input flow. Depending on the fraction of fuel used inside the stack, a variable amount of power and hydrogen is available as output. Therefore, it is possible to change the operation of the system adjusting the fuel utilization, i.e. the ratio between the converted fuel and the one at the inlet, and the flow rate in order to vary the power output. The system can be controlled in order to help to avoid power surplus or deficit in the grid, producing less or more electricity varying fuel utilization or inlet flow. The variation of the operating point also induces a change in the amount of hydrogen that can be "generated", both in terms of outlet concentration and absolute flow. The operation of the fuel cell will be explained more in depth in section 2.4.

Since the gases at the outlet are still at high temperature, they can be used to preheat the inlet flows of the stack. Moreover, heat is required also by the gasifier and for drying the wastes, as well as for generating steam. Therefore, a heat recovery net is implemented in order to use the available heat minimizing the need from outside sources. Several heat exchangers are required, so that as much heat as conveniently possible is recovered.

The system can be sized based on the amount of waste available and the balancing power required by the local grid. As it can be expected, the actual size will depend on economic considerations. In the following sections, the components are described and their function explained, as well as the parameters that play an important role and the choices made. In particular, the technologies considered are presented and their advantages

explained.

## 2.3 Gasifier

In the gasifier, the shredded waste is converted into a gas mixture containing mostly hydrogen, carbon dioxide, carbon monoxide, methane and steam. Gasification consists of transforming, at high temperature and by means of one or more gasifying agents, the chemical energy of the solid fuel at the input into chemical energy and heat in the form of a gaseous product. The thermochemical decomposition of the fuel involves endothermic reactions and therefore heat is required. This can be achieved through partial oxidation of the fuel (*autothermal* gasification) or can be supplied by an outside source (*allothermal* gasification).

During gasification, multiple processes take place: firstly, water contained in the waste evaporates and volatile matter is released (*pyrolysis*), leaving behind a solid carbonaceous material, char; afterwards, char reacts with the gasifying agents (hence *gasification*) and several reactions occur in the gas phase. These steps activate at different temperature ranges and various gaseous products can be obtained depending on the gasification temperature. Although char reacts with the gasification medium, not all of it is converted and therefore a carbonaceous residue is present at the end of the process and also tar is usually produced. The three reactions below are char gasification (2.1), Boudouard reaction (2.2) and methanation (2.3) and are essential for char conversion since they directly involve carbon. Therefore, it can be seen how gasification is more convenient than pyrolysis, being more hydrogen and other gaseous fuels produced.



In order to minimize and possibly avoid solid carbon in the system, oxygen must be added. This can be in the form of air, pure oxygen, steam or carbon dioxide and should be in a sufficient amount so that the system is below the solid carbon boundary. In a C-H-O ternary diagram (Figure 2.2) this is represented by a line for a given gasification temperature. In Figure 2.2 an example of a ternary diagram for the composition of biomass can be seen. It can be noted how the A-C line would be much shorter than the one intersecting the carbon deposition boundary at the same temperature with air as gasifying medium. Moreover, the equilibrium composition has a higher hydrogen content and lower fractions of oxygen and carbon.

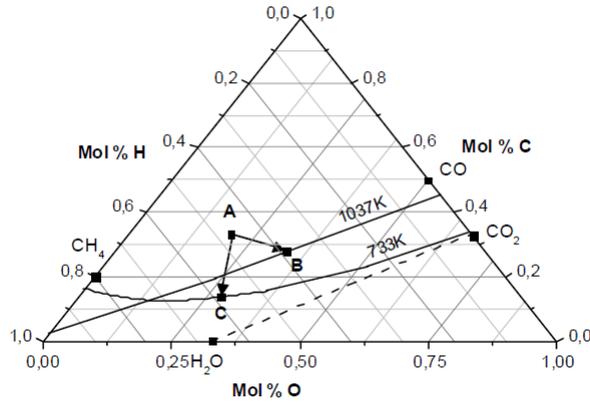
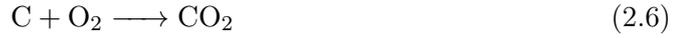


Figure 2.2: Example of a ternary diagram and carbon boundary lines. A represents the composition of the feed (biomass), B is the composition at equilibrium with air at the carbon boundary and C with steam at 500 K [42]

In this project, steam is considered as a gasifying agent because it provides a higher hydrogen yield [30] and a better conversion efficiency than air [42], pure oxygen or air/steam mixture. In addition, it enhances gas production and limits the amount of tar and char present in the system [54]. In particular, steam gasification is more convenient than having oxygen as gasifying agent because also hydrogen is fed into the system. This translates in a lower carbon boundary temperature for a given steam temperature due to the endothermic nature of the process and thus it promotes methane (and carbon dioxide) formation [42]. Moreover, no nitrogen is added to the system as opposed to air as a gasifying agent, which would dilute the mixture, causing a reduction in partial pressure of the useful products and of the lower heating value of the gas. However, the main reactions are endothermic, therefore it is necessary to supply heat for these to take place, as opposed to air or oxygen gasification, where the process is autothermal. Through steam reforming (2.4) and water-gas shift reaction (2.5), hydrogen is produced from methane and carbon monoxide reacting with steam, while char is consumed with steam in reaction (2.1).



It is important to note that some of the reactions above are exothermic and others are endothermic: char gasification (2.1), Boudouard reaction (2.2) and steam reforming (2.4) are strongly endothermic, while methanation (2.3) and WGSR (2.5) are mildly exothermic. It is clear then why steam gasification requires external heat. Other reactions do also take place, since the waste contains oxygen, sulphur, nitrogen and chlorine. Oxygen may consume char, carbon monoxide, hydrogen or methane with some of the following reactions.



These reactions cause a decrease of the lower heating value of the produced gas, but they also have the positive effect of providing heat for the endothermic reactions.

The presence of sulphur in the feed can cause the formation of hydrogen sulphide ( $\text{H}_2\text{S}$ ) and, in lower quantities, of  $\text{COS}$ ,  $\text{CS}_2$ , S-containing tars and S-solid char [28]. SOFCs are poisoned by  $\text{H}_2\text{S}$  and therefore its concentration must be reduced in order to stay within the tolerance limits. In the selected waste, nitrogen has a not negligible concentration, therefore molecular nitrogen ( $\text{N}_2$ ) and ammonia ( $\text{NH}_3$ ) are expected in the output gas of the gasifier. These are compatible with the fuel cell, since ammonia is a fuel in SOFCs, and are the primary chemicals that are produced with nitrogen. Very small amounts of other N-containing compounds like  $\text{NO}_x$  could also be produced [28]. Other undesired products may be particulates from char and ash, aromatic hydrocarbons, tars and hydrogen halides. These halides derive mainly from chlorine, which is the main halogen in biodegradable waste like kitchen waste and garden trimmings according to the Phyllis2 database [17], but can also come from fluorine if sewage sludge is used. Since the tolerance of SOFCs for these compounds is very low, particular attention must be paid to their concentration in the gas mixture produced. In Section 2.5 the measures adopted to avoid critical chemicals inside the fuel cells will be presented.

The composition and the amount of the product gas in the gasifier are dependent on thermodynamic variables like temperature, pressure and fuel composition and parameters like steam to carbon ratio (or alternatively steam to biomass ratio). Catalysts and other substances in the gasifier can also affect the process. It has to be noted that different values could potentially result in similar compositions depending on the type of gasifier chosen. Since informations on gasification of organic wastes are limited, in this report data and results for biomass (usually wood or types of crops) are considered. Although these may differ in the macrostructure, they often share similar ultimate compositions and therefore the results found in the literature are still considered sufficiently suitable for representing the selected wastes. In particular, this holds true because this project is thought as a preliminary study and is mainly focused on the concept of the system and its feasibility rather than the results, which will in any case differ for the actual system.

Many authors have chosen steam to biomass ratios (S/B) between 1.0 and 1.5 (in kg of steam over kg of biomass), since they tend to give a higher hydrogen production [30] and higher exergy of the output gas [42]. In particular, steam gasification produces a gas

mixture with the highest exergy at a steam to biomass mass ratio of about 1.3, according to Prins [42], although others have found lower values. It is necessary to provide sufficient steam to gasify char and avoid carbon deposition, i.e. presence of carbon in heterogeneous equilibrium with the gas, but not significantly more than the required amount so that the losses related to its generation are minimized. Moreover, if the concentration of steam in the products is large, the partial pressure of useful chemicals like hydrogen and carbon monoxide is low, causing a worse performance of the fuel cell. However, if methane or tars are present, a sufficient amount of steam is required in order to avoid carbon deposition in the fuel cell if internal reforming occurs. According to Wang et al. [54], methane yield depends strongly on steam to fuel ratio only up to the value at which all carbon is converted (stoichiometric amount), when it becomes less dependent on S/F mass ratio and temperature. At slightly larger values, reactions in the gas phase are enhanced, but theoretically methane yield should stay constant. If more steam is added, water-gas shift reaction (2.5) and steam reforming (2.4) are promoted, meaning that less methane and carbon monoxide and consequently more hydrogen and carbon dioxide are produced.

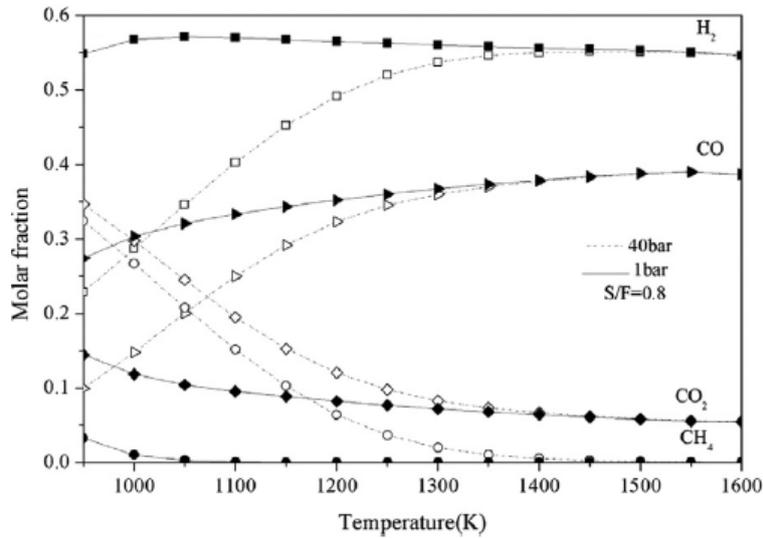


Figure 2.3: Example of composition of the dry gasification product gas for biomass, with complete carbon conversion, as a function of temperature [54]

Temperature and pressure affect the composition of the gas since equilibrium constants and the kinetics of reactions is dependent on their values. Methane and other light hydrocarbons are more easily broken down at higher temperatures (more than 600 °C) but tar can be decomposed effectively only at extremely high temperature. Therefore, tar removal may be still necessary after the gasifier. Reaction (2.1) is favored at high temperature and low pressure, similarly the Boudouard reaction (but more slowly) and the methanation reaction, which has optimal conditions above 1100 °C and at 6 ÷ 8 bar [8]. On the contrary, the water-gas shift reaction is more important at low temperatures. Furthermore, when the temperature is higher than 900 K, higher pressures favor carbon consumption, while at

lower temperatures pressure is less significant [54]. In general, carbon is more easily consumed at approximately 900 K or more. If carbon is completely converted,  $\text{CH}_4$  and  $\text{CO}_2$  concentrations increase with the increase of pressure while  $\text{H}_2$  and  $\text{CO}$  decrease. However, at high pressure, the concentration of several species tends to stabilize to a constant value when the temperature is further increased. This can be seen in Figure 2.3, where the theoretical concentrations of the dried products of biomass gasification at two pressure levels is shown. As it can be seen, the concentration of the species tends to become constant as the temperature is increased. On the contrary, the increase of pressure causes more significant variations.

The presence of catalysts in the gasifier can help the process considerably: they reduce the temperature required for the reactions to occur, improve reaction rate and increase the efficiency. In fact, the activation energy of the gasification decreases and thanks to their selectivity, it is possible to enhance the production of the desired species. Catalysts act mainly on char gasification that slowly takes place after pyrolysis. Different types of catalysts can be chosen. For lignin (biomass) gasification, alkali metal carbonates have been studied and used, in particular  $\text{Na}_2\text{CO}_3$ ,  $\text{K}_2\text{CO}_3$  and  $\text{Li}_2\text{CO}_3$ . These react with carbon in the char and  $\text{CO}_2$  through decomposition of the metal and recarbonation, releasing carbon monoxide, or with steam through decomposition and recombination in hydroxides and then carbonates or directly in carbonates, producing both carbon monoxide and hydrogen. Some researchers like Adinberg et al. [3] and Teixeira et al. [51] have proposed the use of these catalysts in the form of molten salt mixtures and they have found that these can improve gasification dramatically. In particular, reactors with eutectic mixtures of carbonates of potassium, sodium and lithium or sodium and potassium hydroxides have been studied for biomass pyrolysis and gasification. Also organic wastes have been used [41, 47]. It has been found that molten salts increase the surface interactions of the feed with the gasifying medium and catalyze several reactions as well as enhancing heat transfer and giving faster kinetics [3, 51]. In particular, a very high carbon conversion and significantly high fractions of hydrogen and carbon monoxide in the syngas can be obtained. However, the temperature of the gasifier must be chosen carefully because alkali metal have high vapor pressure or can even evaporate at high temperatures (around 800 °C), causing a loss of catalyst and the need for their removal before the gas enters the fuel cell. Nonetheless, molten salts have been found to be able to immobilize sulphur in the mixture, resulting in a gas mixture with low sulfur content [49]. Other important catalysts are alkaline earth metals, with calcium compounds (for example,  $\text{CaO}$  and  $\text{Ca}(\text{OH})_2$ ) being of particular interest. In fact, these can enhance hydrogen production in the gasifier. Calcium oxide also works as a sorbent for carbon dioxide absorption, resulting in the formation of  $\text{CaCO}_3$ , and thus removing  $\text{CO}_2$  in the gasifier. This translates in a reduction of the partial pressure of carbon dioxide and a shift of the equilibrium in the WGS towards right, yielding more hydrogen [39]. Therefore, Ca-based catalysts have a double action on the process. Moreover, these are easily available and inexpensive. Transition metal-based catalyst like nickel, iron and cobalt are also attractive because they improve steam gasification. For example, nickel is

usually found also on SOFC electrodes. Beside the type of catalyst, another important factor is catalyst loading. Higher loading leads to a higher activity, but only up to an optimal amount. It has to be noted that the waste selected may contain, according to ECN [17], some traces of these catalysts like potassium, sodium, iron and calcium, which could already improve gasification. In particular, interesting catalysts are those able to provide a higher yield of hydrogen and methane.

Once the main parameters of gasification are understood, the performance of the process can be addressed. In order to evaluate the conversion of the waste into the fuel gas, a suitable definition of efficiency must be chosen. Many possible expressions are available but only some of them can accurately describe the performance of the gasifier. For example, cold-gas efficiency (CGE) is commonly used and is defined as

$$\text{CGE} = \frac{\dot{m}_{\text{gas}} \cdot \text{LHV}_{\text{gas}}}{\dot{m}_{\text{feed}} \cdot \text{LHV}_{\text{feed}}} \quad (2.9)$$

where the subscripts "feed" indicates the waste fed to the gasifier and "gas" the gaseous mixture produced and  $\dot{m}$  is the mass flow rate. Alternatively, lower heating values and flow rates can be referred to molar quantities. Often, higher heating values are also used. In Figure 2.4, the cold-gas efficiency calculated by Wang et al. [54] as a function of steam to biomass ratio and gasification temperature can be seen. Although not explicitly stated, the definition of cold-gas efficiency used was probably with higher heating values. They obtained these results with constant inlet conditions for steam and biomass and gasification pressure. The graph shows a knee, where the slope of the curves decreases significantly because adding more steam causes a rise in the external heat needed larger than the increase of calorific value of the produced gas [54], as well as "diluting" the gas mixture.

It has to be noted that it is unclear if in the definition of cold-gas efficiency the lower heating values or higher heating values must be used and therefore confusion might arise if it is not specified. Moreover, this definition of efficiency does not take into account the sensible heat of the streams, especially the output one, which can give a significant contribution to the total energy of the flows. A hot-gas efficiency could be used, considering the sensible heat of the the flows, but it would still not account for the "quality" of the energy. Therefore, a definition based on the exergies of such streams seems more adequate for representing the performance of the process, since the energy available is weighted on the actual useful work that the flows can produce, which means that the "quality" of the energy is taken into consideration. Also for the exergy efficiency several definitions are possible. Prins [42] and others authors proposed two possible expressions ((2.10) and (2.11)), shown below.

$$\Psi_{\text{I}} = \frac{E_{\text{gas}}}{E_{\text{feed}} + E_{\text{steam}}} \quad (2.10)$$

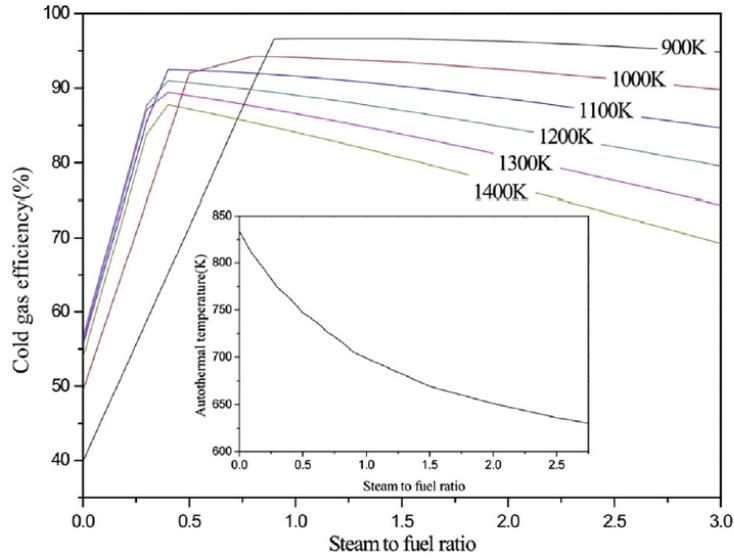


Figure 2.4: Cold-gas efficiency for steam gasification of biomass as a function of steam to biomass ratio and gasification temperature [54]

$$\Psi_{II} = \frac{E_{\text{gas}} - E_{\text{steam}} - E_{\text{air}}}{E_{\text{feed}} - E_{\text{char}}} \quad (2.11)$$

where the  $E_{\text{gas}}$ ,  $E_{\text{feed}}$ ,  $E_{\text{steam}}$  and  $E_{\text{char}}$  are the exergy of the output gas, feed, steam and char. Expression (2.10) is the ratio between the gas product and the fuel input but if remaining char is present and is considered as useful product, this can be included in the numerator. This definition is also often referred to as universal efficiency. Expression (2.11) is called rational efficiency or functional efficiency and is defined as the ratio of exergy gains to exergy losses or, alternatively, as the ratio between useful products and sources. Prins [42] found that the maximum rational efficiency for biomass steam gasification is approximately 87%. Wang et al. [54] found similar values, but the optimal steam to biomass ratio was less than 1.0 as opposed to 1.3. Moreover, the trend of the exergy efficiency as a function of steam to biomass ratio and temperature was found similar to Figure 2.4, showing that lower ratios and temperatures provide better results, although steam to fuel ratio is less important when it is larger than the optimal value. In fact, for S/F above the optimal value, the exergy efficiency is almost constant and varies slightly with the temperature. Therefore, it is expected to find similar trends for the efficiency in the case of biodegradable waste. From these considerations, temperatures around 900 K and steam to fuel ratios between 0.5 and 1.3 are considered more suitable for gasification of organic waste.

Once the desired products of the gasifier are chosen (in terms of composition and within

the limits of feasibility) the most suitable type of gasifier must be selected. Different technologies are possible, some of which commercially available while others only in laboratory scale. It is important to note that the gasifier type depends also on the size of the plant, i.e. the rated power, and therefore it might change if the system is upscaled or downsized. For example, fluidized bed gasifiers are more suitable for larger applications than fixed bed ones, which can be used for smaller plants. Furthermore, fixed bed ones usually produce more tar and char and therefore a better cleaning of the output gas is required, while fluidized bed gasifiers provide better mixing between solids and gases, resulting in a more pure fuel gas, and are generally more efficient [1]. Parameters like temperature and steam to fuel ratio have different effects depending on the gasification technology and thus the optimal value of these quantities may vary between gasifiers. However, also non-optimal parameters for the gasifier might be chosen, since the system includes also other components, which operation must be taken into consideration.

Although molten salt gasifiers (MSG) and sorption enhanced gasification (SEG) are far from being established technologies, these seem to be among the most promising ones, in terms of efficiency, process requirements and desired products. Moreover, this report aims at finding an innovative concept for a system that will be implemented in the future energy scenario, which means that the current readiness level of the technology is less important than its prospective benefits. In the case of the former technology, a molten salt mixture is used as a catalyst and heat transfer "enhancer", while for the latter CaO is usually used both as catalyst and a sorbent as explained before [30, 1]. Some authors like Adinberg et al. [3] have proposed to use solar energy for the gasification with molten salts, which can provide heat for the salts to stay in the liquid phase and for the endothermic reactions. However, harvesting solar energy usually requires large areas and is expensive. Since modelling such technology is beyond the scope of this project, sorption enhanced gasification is considered instead. Moreover, the ability of this gasification technology to capture carbon dioxide can be seen as suitable characteristic for integration in a renewable scenario. The reaction between calcium oxide and carbon dioxide is exothermic, which is convenient in steam gasification. The use of calcium oxide in the gasifier improves the water-gas shift reaction, since it removes CO<sub>2</sub>, which means that also carbon monoxide is consumed, producing a gas rich in hydrogen and with a significant amount of methane. This gas composition is convenient in the system considered, because a high H<sub>2</sub> concentration in the gas results in a higher voltage across the SOFC and the conversion of methane inside the fuel cell allows a better temperature control and current distribution. Below, the carbon absorption reaction is shown. The carbonation reaction (2.12) is significantly exothermic, releasing 178.3 kJ/mol of heat. Other reactions can take place, like reactions with tar and sulphur to form coke and calcium sulphide, respectively. These can be favourable, since they would remove part of the species that are critical for the fuel cell, although it is expected to be only small quantities. However, this implies also a loss of CaO in the gasifier. Therefore, Acharya [1] suggested to use temperatures above 600 °C in order to limit tar formation and favor reaction (2.12). Calcium oxide works also as a catalyst

for tar decomposition nonetheless, meaning that even at low temperatures the amount of tar formed should be somewhat limited compared to gasification without the sorbent. Furthermore, reaction with steam to form calcium hydroxide is also possible and it favors carbonation.



SEG would be usually performed in fluidized bed gasifiers although fixed bed ones has mainly been used in experiments [56]. In addition, this could also take place in a separate reactor. Sorption enhanced gasification has several advantages compared to conventional gasification, some of which already discussed, that derive from the catalytic effect of CaO and its reaction with CO<sub>2</sub>:

- higher hydrogen yield than conventional gasification;
- lower operating temperatures (500÷700 °C) still result in higher hydrogen production compared to gasification without sorbent;
- carbon absorption is exothermic, therefore less heat than conventional gasification is required;
- tar reforming is enhanced;
- the voltage in the fuel cell is higher since there is a lower dilution of the fuel gases in carbon dioxide;
- possibility of achieving a "carbon negative" system.

In the case of biodegradable waste, carbon capture through SEG could lead not only to a carbon neutral but even to a carbon negative system. In fact, the carbon dioxide captured is the one absorbed by the organic material during its life and if this is not further released, potentially less CO<sub>2</sub> than the amount removed from the atmosphere by the biomass could be emitted. Considering also the scope of this system, it can be easily seen how this technology could provide benefits other than that of an efficient balancing plant. Moreover, such system could fit well in the future renewable scenario.

The possibility of having a lower gasification temperature allows to carry out the conversion into hydrogen in two steps. One occurs in the gasifier, where a high H<sub>2</sub> and CH<sub>4</sub> containing gas is produced, and the second in the high temperature fuel cell, inside which methane is reformed. In this way, no extra heat is required by the gasifier because steam reforming takes place in the fuel cell, where high temperature and usually a Ni catalyst are present. Moreover, WGSR has a larger equilibrium constant at lower temperatures, although also a lower reaction rate. Direct heat transfer in the fuel cell is also expected

to be more efficient than the one between the gasifier and the heating source. This also leads to a decrease of the excess amount of oxidant required by the fuel cell for cooling, which then translates into less electric power consumed by the compressor. In general, a higher electrical efficiency is therefore expected. Moreover, according to Hongrapipat [28], at lower temperature less hydrogen sulphide should be present in the gas phase, remaining in the solid char.

However, gasification with carbon capture through calcium oxide has the drawback of resulting in a limited carbon conversion, since it is more convenient to work at lower temperatures. Carbon captured through carbonation in the form of solid carbonate must also be accounted for as converted carbon though, as stated by Zhang et al. [56]. To reduce the amount of unconverted carbon, they proposed to add alkali metal catalyst, for example in the form of  $K_2CO_3$ , since it enhances carbon conversion. Zhang et al. [56] found also that the addition of potassium-based species can also improve the hydrogen concentration in the output gas and in particular increase the yield. This means that more gas is produced, i.e. a higher carbon conversion is achieved. Especially in the system under study, this could be promising because it could result in a higher Nernst voltage in the fuel cell, being the concentration of oxidizable species higher. Other authors like Tang et al. [50] proposed to use a Fe-Cr catalyst in order to enhance water-gas shift reaction even more, increasing the reaction rate. During their experiments, they found that the catalytic effect of  $Fe_2O_3$  and  $Cr_2O_3$  catalysts can give good gasification results even at temperatures below  $550\text{ }^\circ\text{C}$ . Moreover, during their experiments it was found that higher temperatures result in larger hydrogen (and methane) concentration and thus lower carbon monoxide and dioxide ones. This can be explained if steam reforming and carbon gasification reactions are considered. In fact, these are endothermic and both have carbon monoxide on the product side. Since this is consumed by the WGSR, reactions (2.1) and (2.4) have the equilibrium point shifted to the right. Furthermore, also the increase of steam to fuel and calcium carbonate to carbon (CaO/C) ratios enhanced hydrogen and methane formation up to an optimum point (for biomass, 2 and 1.5 respectively). In addition to the effect of calcium carbonate, the  $Fe_2O_3$ – $Cr_2O_3$  catalyst accelerates the water-gas shift reaction, causing an increase in hydrogen yield and a reduction of the concentration of carbon monoxide with the rise of the temperature. Therefore, its effect is well coupled with the one of CaO. In Figure 2.5 the composition of the product gas as a function of temperature (as found by Tang et al. [50]) can be seen. The graph shows a concentration of carbon dioxide at  $550\text{ }^\circ\text{C}$  of about 5% while the sum of  $H_2$  and  $CH_4$  concentrations is more than 90%.

Once calcium oxide reacts with carbon dioxide, it can be recuperated and regenerated in order to be able to use it again. A circulation system can then be employed. Acharya [1] proposed to use a regenerator, in this case a fast fluidized bed, in which calcium carbonate releases carbon dioxide in the calcination reaction, which is the reverse reaction of carbonation. A loop is created between the gasifier and the regenerator, in which the sorbent circulates and is regenerated. The circulating fluidized bed based chemical looping gasification system studied by the author involved a bubbling fluidized bed gasifier, where

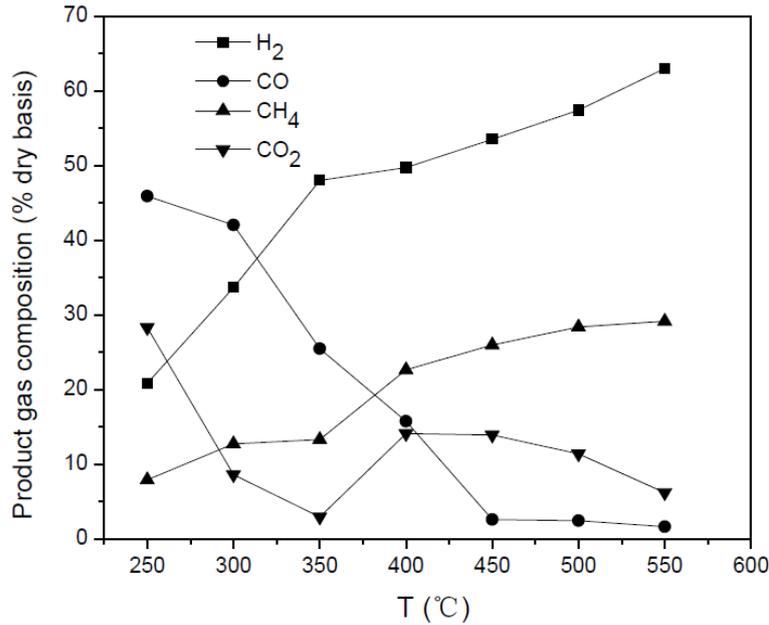


Figure 2.5: Gas composition at  $\text{Ca}/\text{C} = 1.5$  (molar ratio) and a  $\text{S}/\text{B}=2$  (mass ratio), with the addition of Fe–Cr catalyst, as a function of temperature [50]

the fuel is converted into syngas and the solid bed is recirculated, and a fast fluidized bed regenerator, where the calcium carbonate is calcined. Another reactor between the gasifier and the regenerator should prevent the char to enter the latter. The gas and solid coming from the regenerator are then sent to a cyclone, where they are separated and CaO is recycled in the gasifier. Despite the more complex system, this configuration allows to reuse the calcium oxide carbonated in the gasifier and the sensible heat that it absorbs in the regenerator. However, calcination is strongly endothermic and requires heat. This is equal to the one released during carbonation and can be supplied in several ways. Acharya [1] proposed to fluidize the solids from the gasifier (CaO, CaCO<sub>3</sub> and the escaped char) with steam since it allows to have lower temperature for the calcination reaction and can be condensed after so that pure carbon dioxide can be obtained. It was found that the conversion during calcination is significant even at temperatures around 700 °C, although residence times of about 30 minutes are required in the regenerator. Moreover also the kinetics of the conversion is better for steam than other fluidizing media like nitrogen or carbon dioxide. Nevertheless, absorption with CaO through carbonation reduces progressively with the increase of regeneration cycles, because of sintering of the particles in the regenerator, that leads to a lower gas diffusion rate and thus lower conversion [1]. The lower temperature of regeneration with steam results in lower sintering but fresh sorbent is still required. An alternative to the chemical looping system would be the continuous supply of fresh sorbent. This may not be economically convenient, although a cost analysis should be performed in order to evaluate the effect of selling calcium carbonate to recover the cost of calcium oxide. In fact, calcium carbonate is widely used in many industries.

However, million of tons of calcium oxide would be required every year for a small-sized plant with a power output of some megawatts. In the system here presented, this aspect is not considered, not being clear yet which is the most suitable solution.

## 2.4 Fuel cell

The fuel cell type selected for this system is a high temperature one. Specifically, a Solid Oxide Fuel Cell (SOFC) is chosen as opposed to a Molten Carbonate Fuel Cell (MCFC) because carbon dioxide is expected to have very low concentration in the gas entering at the anode and it usually operates at higher temperatures. The cell is constituted by an anode, a cathode, an electrolyte, an interconnect and a sealing. It is so called because it uses a solid ceramic electrolyte, which conducts oxide ions from the cathode to the anode, where water is produced from the reaction of hydrogen with the ions. The electrolyte is usually made of zirconia stabilised with yttria, because it is able to conduct oxide ions. However, this takes place only at high temperature, hence the elevated operating temperatures of SOFCs (700 ÷ 1100 °C). Therefore, a very thin electrolyte is used, so that the resistance is reduced. The anode is composed of a zirconia cermet, a mixture of ceramic and a metal, usually nickel, and is where oxidation (usually of hydrogen) and the resulting release of electrons occur. Nickel works as a catalyst and allows to carry out reforming of methane directly inside the fuel cell, which is referred to as direct internal reforming (DIR). The cathode is also made of a ceramic material, able to easily conduct oxide ions. The interconnect is the part of the cell that connects adjacent fuel cells and allows the electrons to flow from one to the other when multiple fuel cells are used. In order to avoid leakage of gas between the cathode and the anode, which would reduce the performance of the fuel cell, a sealing is used. SOFCs can be tubular or planar, meaning that a cylindrical or flat configuration respectively is used. Despite not being strictly necessary for the modelling of the system, a planar design is considered, having higher power density and superior stack performance [37].

Compared to low temperature fuel cells, SOFCs have lower reversible voltage because Gibbs free energy of formation of water is less negative at high temperature, being

$$V_{\text{rev}} = -\frac{\Delta\bar{g}_f}{zF} \quad (2.13)$$

where  $V_{\text{rev}}$  is the reversible potential,  $z$  is the number of electrons exchanged during oxidation (two in the case of hydrogen),  $F$  is Faraday's constant (96485 C/mol) and  $\bar{g}_f$  is the molar specific Gibbs free energy of formation. The reversible open circuit voltage for a cell working at 850 °C is about 0.9 V. Also Nernst voltage undergoes a larger decrease for the same increase in temperature compared to a low temperature cell, being dependent on the temperature itself.

$$V_{\text{Nernst}} = -\frac{\Delta\bar{g}_f}{zF} + \frac{RT}{zF} \ln \left( \frac{\prod (p_{\text{reactant}}/p^0)^{\nu_i}}{\prod (p_{\text{product}}/p^0)^{\nu_j}} \right) \quad (2.14)$$

where  $R$  is the ideal gas constant,  $p_{\text{reactant}}$  and  $p_{\text{product}}$  are the pressures of the reactants and products,  $p^0$  is the standard pressure,  $\nu_i$  and  $\nu_j$  are the stoichiometric coefficients for each reactant and product. However, irreversible losses are lower. In fact activation losses have less impact on the performance, as also cathode polarisation, while ohmic losses contribute the most. From equation (2.14), it can be seen that the voltage should vary along the cell because reactants are consumed and converted into products. Nevertheless, different parts of the same electrode are at the same voltage thanks to the small resistance of the interconnect, thus it is the current density to vary. In particular, this decreases going towards the exit of the cell. Equation (2.16) shows the real voltage of the cell when also the irreversible losses are considered.

$$V = V_{\text{Nernst},x} - \Delta V_x \quad (2.15)$$

where  $V$  is the actual cell voltage,  $V_{\text{Nernst},x}$  is the local Nernst voltage over the cell and  $\Delta V_x$  is the local voltage loss. The real voltage is considered to be constant as already mentioned. Several ways are possible to calculate the voltage loss. The software used in this study uses a simplified approach, expressing it as  $\Delta V_x = R_{\text{eq}} i_x$ , with  $R_{\text{eq}}$  the equivalent cell resistance and  $i_x$  the local current density. Other authors have proposed other formulae, like the one of Standaert et al. [46], where a third term is added and the real voltage of the cell is expressed as

$$V = V_{\text{Nernst}} - \frac{1}{2} \alpha u_f - i R_{\text{eq}} \quad (2.16)$$

Since the  $i$ - $V$  curve of a SOFC can be considered linear with a good approximation, such models predict the voltage of the cell with a sufficient accuracy.

If all the energy in the fuel is converted into work, the voltage would be

$$V_{\text{max}} = -\frac{\Delta\bar{h}_f}{zF} \quad (2.17)$$

where  $\bar{h}_f$  is the molar specific enthalpy of formation of water. Therefore this voltage would be higher because it is the one related to a 100% efficient system, where all the energy of the fuel is converted into useful work and not also into heat. From this, the maximum

achievable efficiency (equation (2.18)) is obtained when the cell operated reversibly, being the power produced the product between the voltage and the current.

$$\eta_{\max} = \frac{\Delta\bar{g}_f}{\Delta\bar{h}_f} \quad (2.18)$$

In reality, as already seen, the voltage of the cell is lower than the maximum and the reversible one due to the production of "reversible" and "irreversible" heat and because only part of the fuel fed to the inlet is used in the cell and reacts with the oxidant. In fact, from equation (2.14), it can be seen that the cell would not produce power if all the fuel were consumed inside it because the voltage would collapse. Therefore, the fuel utilization (equation (??)) is used as the quantity that represents the amount of fuel converted. In a similar way, also the oxidant utilization is defined, since only a fraction of the inlet oxidant flow reacts with the fuel. Generally, the oxidant flow rate is larger than the one strictly required, because it provides cooling to the fuel cell. In addition, the cooling required by the cell depends on fuel utilization, since less heat is produced when a smaller amount of fuel reacts.

$$u_f = \frac{\dot{n}_{\text{reacted}}}{\dot{n}_{\text{in}}} = \frac{I}{\dot{n}_{\text{in}}zF} \quad (2.19)$$

$$\dot{n}_{\text{in}} = \dot{n}_{\text{H}_2} + \dot{n}_{\text{CO}} + 4\dot{n}_{\text{CH}_4}$$

where  $\dot{n}_{\text{reacted}}$  is the molar flow rate of fuel reacted inside the cell,  $\dot{n}_{\text{in}}$  is the equivalent molar flow rate available at the inlet (in the case under study it is composed by H<sub>2</sub>, CO and CH<sub>4</sub>) and  $I$  is the electric current flowing from the anode to the cathode. Hence, the definition of electrical efficiency of a single cell

$$\eta_{\text{cell}} = \frac{V_c}{V_{\max}} u_f \quad (2.20)$$

where  $V_c$  is the actual cell voltage. Equation (2.20) represents the ratio between the actual power generated by the cell and the maximum power that could be produced if all the energy contained in the fuel were converted, i.e. the whole inlet flow had reacted. In order to provide electric power to the grid, the voltage has to be increased and the direct current of the stack has to be transformed into alternate current, therefore part of the power generated by the fuel cells is lost in the conversion. This can be taken into account with the efficiencies of the components that convert the voltage.

In the present system, the stack is fed with a gas mixture, comprising not only hydrogen, but also steam, methane, carbon monoxide and carbon dioxide. Therefore, evaluating the performance of the stack is more complex than for a hydrogen-fuelled cell because many

reactions take place inside the cell. In fact, the fuel cell operates also as a steam reformer (direct internal reforming), where methane is converted into carbon monoxide and hydrogen according to reaction (2.4), and also the water-gas shift reaction occurs, producing more hydrogen from carbon monoxide, although CO could be directly oxidized. Therefore, the hydrogen concentration inside the cell varies because is not only consumed via the electrochemical reaction with the oxide ions from the cathode, but it is also produced by the reactions mentioned. Since the voltage cannot vary, the current density will have a distribution over the electrode that is considerably different from the one of a H<sub>2</sub>-fed cell. Moreover, also the temperature distribution and the resistance of the cell change along the path of the fuel.

Converting methane into hydrogen inside the fuel cell is particularly convenient if the heat balance is considered. In fact, the electrochemical reactions are exothermic, producing an amount of "reversible" heat equal to  $T\Delta S$ , to which adds the heat that is also generated by the irreversible losses, while steam reforming is endothermic. Therefore, methane reforming allows to cool down the cell without requiring large oxidant flow rates, reducing the losses of the system and improving the efficiency. Since hydrogen is consumed by the oxidation reaction, steam reforming and water-gas shift reaction keep taking place, converting more reactants. Moreover, steam that is required by the steam reforming and water-gas shift reactions is readily available as it is produced by oxidation with hydrogen. It is important, however, to supply enough steam in order to avoid carbon deposition, which occurs because of the reverse reaction of char gasification, Boudouard reaction and methane cracking. In fact, a higher partial pressure of steam leads to an equilibrium point shifted to the right in reaction (2.1) and consumes more carbon monoxide in the water-gas shift reaction limiting carbon dioxide formation, which in turn limits the amount of carbon that could be formed with the Boudouard reaction. In order to avoid carbon deposition, it is usually recommended to not have values of steam to carbon ratio too low. In particular, according to Tsai [53], soot is not formed at the usual SOFC temperatures (above 750 °C) if S/C is approximately higher than 1, as it can be seen in Figure 2.6. The deposition of carbon on the Ni catalyst of the anode would inhibit the reactions taking place over it, resulting in a worse performance of the cell. However, carbon formation should be somewhat limited by the very low amount of carbon monoxide and dioxide in the system under study, in addition to the already not negligible steam concentration in the output flow from the gasifier due to excess steam in the gasification. Also the significant concentration of hydrogen in the feed should provide enough steam through electrochemical reaction with the oxide ions. Thus, it should be evaluated if a recycle of the outlet flow from the anode is convenient, because a sufficient amount of steam may already be available.

Other contaminants might compromise the performance of the cell, like particulates, tars, sulphur-based and chlorine-based compounds. The tolerance of Solid Oxide Fuel Cells for such substances is not well defined, since different authors have found different results. Moreover, it depends also on the fuel fed to the cell and the materials which the cell is made of. Some indicative values are shown in Table 2.1. Especially for tar which is the

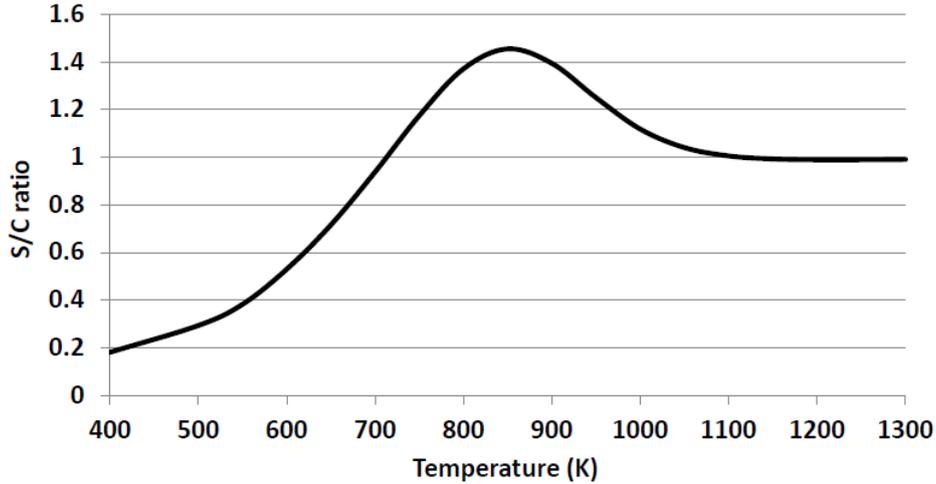


Figure 2.6: Minimum steam to carbon ratio (S/C) in order to avoid carbon deposition as a function of the temperature [53]

Table 2.1: Tolerance of SOFC for different contaminants [5, 14]

Contaminant	Tolerance
Particulate	few ppmw
Tars	$< 10 \div 100$ ppmv
Alkali metals	few ppmw
H <sub>2</sub> S	$\ll 10$ ppmv
HCl	$< 10$ ppmv

main responsible of carbon deposition, the range of values found in the literature is large. This derives from the fact that tar can be consumed in the cell but the actual tolerance depends strongly on the feed characteristics, cell temperature and steam to carbon ratio.

As stated by Hemmes et al. [26], electrochemical oxidation in a fuel cell is convenient especially in a multi-product point of view, since not only the system could be capable of providing heat and power (cogeneration), but also useful material streams like hydrogen. In fact, hydrogen is present at the output of the fuel cell and thus it can be accounted for as another product of the cell. When the load is changed in order to balance the electrical grid, a variable amount of hydrogen will be consumed inside the stack, leading to a different concentration in the output flow. At high power and high fuel utilizations, less hydrogen will be available at the output, while at lower load, the decrease in power could be compensated by the increase in available hydrogen. Therefore, the cell is always able to produce a valuable product. In the next chapter the concept will be further explained, in particular regarding the operation of the system here presented.

## 2.5 Gas cleanup

In order to be able to guarantee the operation of the SOFC within its tolerance limits for contaminants, the gas produced in the gasifier must be cleaned before entering the cell. In particular, the contaminants that can cause poisoning or deposits on the electrodes are particulate, tar, hydrogen sulphide and hydrogen chloride. These can also cause corrosion and clogging. Particulates are solid particles that are carried by the gas produced in the gasifier and consist mainly of ash, unreacted char, alkali compounds and bed material. Due to the limited gasification temperature, not all the char is converted and therefore part of it exits the gasifier with the gas streams. Potentially, this could be fed again to the gasifier, increasing conversion efficiency [28]. Particulate can cause pore blocking and decrease the active surface of components, meaning that it must be removed from the gas flow in order to guarantee the correct operation of the components.

Tar consists of organic compounds with high molecular weight like hydrocarbons and are condensable at temperatures above the atmospheric one. Therefore, these can cause obstruction of filters and pipes and reduce the heat transfer coefficient if condensed on a surface [13]. However, tars are expected to get reformed in the fuel cell if fed with sufficient steam and working at suitably high current loads, according to Aravind et al. [5]. If these conditions are not satisfied, carbon deposition on the cell anode may occur with the reactions already explained previously, compromising the performance of the SOFC and possibly damaging it, or causing blocking in the pipes.

Due to the presence of sulphur and chlorine in the waste composition, hydrogen sulphide and chloride form in the gasifier, although very small amounts of other compounds containing these elements or other hydrogen halides may be present. These acid gases can deactivate the electrode catalyst in the cell, reducing its activity. Thus their concentration in the gas feed needs to be brought down to small values (few ppm) before entering the SOFC stack. Moreover, these can cause corrosion at low temperature due to condensation.

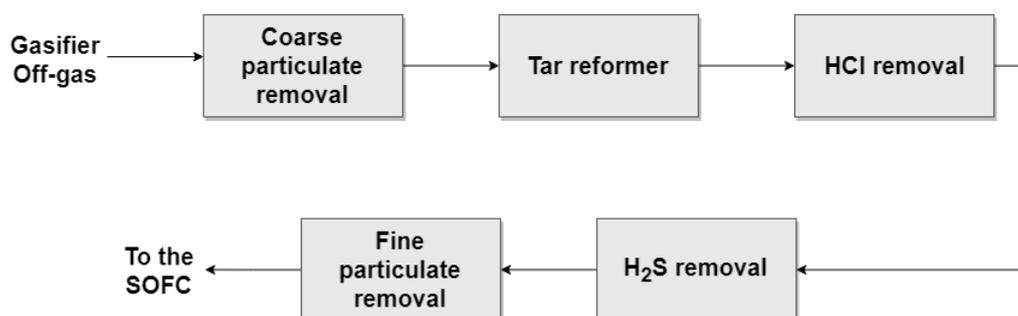


Figure 2.7: General schematic of a gas cleaning system

Several processes are required in order to remove such contaminants. A generic scheme of the steps needed is shown in Figure 2.7. Particulates are removed with the aid of cyclones

and filters, in order to separate large particles first and smaller ones next. Cyclones are usually employed after the gasifier and are followed by a tar removal unit. If the gas is always kept at temperatures above the dew point of the tars (above 350 °C), these may not require to be reformed and could potentially be directly fed to the SOFC [40]. In fact other authors like Aravind et al. [5] and Martini et al. [40] hypothesize tars to be able to get reformed on the anode electrode of the fuel cell. However, it must be assessed if the presence of tar might compromise the correct operation of the other cleanup components. Generally, tars are reformed in specific units where catalyst enhances the reaction, generating more useful species like CH<sub>4</sub>, CO and H<sub>2</sub>. In the system studied by Liu et al. [38], a dolomite/nickel catalyst is used in order to almost completely decompose tar. Such unit works at temperatures above 700 °C [13], therefore heat would be required in the system here presented to bring the gas flow from the gasifier to the reforming temperature. In other system like the intermediate temperature gas cleaning system studied by Aravind et al. [5], the tar cracking unit is placed after the other cleanup units, which would be convenient in terms of heat management.

After removing tar (if necessary), other contaminants like smaller particulate and alkali metals are eliminated. According to Liu et al. [38], when the temperature of the flow is decreased to 450 °C, alkalis are expected to condense on the particulate, which is then removed with a filter. The gas flow is mostly cleaned from particles and is sent to the units where the acid gases are adsorbed.

Hydrogen chloride can be removed by means of several substances, but the most common one is Na<sub>2</sub>CO<sub>3</sub>. This reacts with HCl according to the following reaction



In their study, Liu et al. [38] proposed to perform the reaction between sodium carbonate and hydrogen chloride at about 450 °C, so that heat losses in the system are reduced. Alternatively, NaOH or NaHCO<sub>3</sub> and calcium-based sorbents (CaO) can be used to remove HCl [5, 12, 27]. Calcium oxide could be convenient because it is also used in the gasifier, thus providing a simpler system. According to De Filippis et al. [13], it has better performances at around 500 °C and can also act as hydrogen sulphide removal agent. This reacts with HCl according to reaction (2.22).



NaHCO<sub>3</sub> seems also a promising sorbent since it works well between 400 °C and 500 °C

and can reduce the concentration of hydrogen chloride up to few ppm.

Desulphurisation usually involves a metal oxide, which reacts according to the sulphidation reaction (2.23).



where Me is the metal. The most common metal oxides used in the reaction are based on Fe, Zn, Ca, Mn and Cu [12, 28, 40]. The main characteristics of these oxide are [27, 28]:

- high adsorption capacity;
- high equilibrium constant;
- fast kinetics of the reaction;
- chemical stability in the working conditions;
- simplicity of regeneration;
- suitable reaction temperatures.

Zinc oxide sorbents are particularly common since they offer good performances and are inexpensive [28]. ZnO is stable below 550 °C although the reaction with H<sub>2</sub>S is favourable at higher temperatures. Alternatives to zinc oxide are zinc ferrite (ZnFe<sub>2</sub>O<sub>4</sub>) and zinc titanate. The former has a large capacity and is able to undergo several adsorption-regeneration cycles. Moreover, it can operate at a slightly higher temperature than ZnO. However, it must be noted that these oxides consume also hydrogen in the reaction, contrary to ZnO. Also calcium-based sorbent can be used for sulphur removal. As reported in Section 2.3, calcium oxide can also reacts with hydrogen sulphide, therefore part of the sulphur is removed in the gasifier, although it implicates a loss of sorbent. Since this specie is already used in the gasifier, it could be convenient to employ it also for sulphur removal. However, the performance of H<sub>2</sub>S adsorption with CaO is not as well documented as for zinc-based compounds and some authors (Hofbauer et al. [27], Hongrapipat [28]) reported that it has modest efficiency and requires high operating temperatures (no reaction takes place below 600 °C).

After the metal oxide reacts with H<sub>2</sub>S it is then regenerated. Regeneration is usually carried out at temperatures higher than the sulphidation one. The products of the adsorption process are reactivated through oxidation with steam, air or even SO<sub>2</sub> [28]. Since higher temperatures are required, regeneration with air seems suitable for the system, being a hot air flow available at the outlet of the cathode of the SOFC. Moreover, oxidation with air is exothermic and therefore low oxygen concentration in the air stream is convenient for temperature control of the reaction. After the elimination of such contaminants, another

filter is usually employed to remove the remaining particulate and the one generated in such processes.

Since a gas cleaning system similar to the ones proposed by Liu et al. [38] and Aravind et al. [5] is considered and an intermediate gasification temperature is chosen, the sorbent based on manganese or calcium are not used for sulphur removal, but zinc oxides are considered instead, with a possible second stage at higher temperature using CuO. The selection of the sorbent for HCl elimination has less impact on the design of the system since the reaction temperatures of such species are compatible with an intermediate temperature gas cleaning system. However, CaO could be a convenient choice.

The temperature level of the cleanup system considered is around 450 °C, which results in better overall efficiency according to Aravind et al. [5]. In fact less heat losses occur, allowing for better energy management. Moreover, tar should be less critical for this system since it is supposed to constitute a limited amount thanks to the sorption enhanced gasification and the ability of the fuel cell to use it as a fuel. On the contrary, despite the catalytic effect of CaO in breaking char and the fact that this type of gasification should provide better conversion even at lower temperature than without sorbent at higher temperatures, a not negligible amount of char could remain unconverted and consequently cause more particulate in the gasifier off-gas. Therefore, a cyclone and filters are required in order to remove such contaminants. Moreover, the waste types considered may contain significant amount of other contaminants, causing the need for an effective cleanup system. Another possible challenge for the cleanup system is being able to efficiently remove contaminants in different concentrations. In fact, the feedstock composition is not constant over time and the possible blend of different types of waste could change, resulting in a continuous variation of contaminants concentration in the gas produced in the gasifier.

## 2.6 Pre-processing

Before sending the waste to the gasifier, it must be properly treated in order to improve gasification performance and the subsequent processes. Moreover, incompatible wastes like glass and metals must be removed from the raw waste. In fact, waste arrives at the plant with a wide distribution of sizes and characteristics and has a high moisture content. In particular, the primary pretreatments are shredding and drying. A smaller particle size results in more homogenized characteristics of the feed and enhances heat and mass transfer during gasification. This is important especially for wastes, since the properties may vary considerably within the same batch. Moreover, shredding allows to increase the density and uniform it over the volume of the waste and thus have a better control over the flow rate, as well as improving the surface area to volume ratio [48]. Pulverization is convenient for a better performance of the gasifier. Very fine particles should also result in lower solid residue after gasification because the inside of the particles is less "insulated" from the reactants and the temperature profile in the particle is better distributed. Similarly, drying is helpful in achieving a more controlled moisture content in the waste, which translates in a

better monitoring of the product gas of the gasifier. Moreover, the decrease in water content causes an increase in calorific value of the waste, which is usually considered favorable for gasification [42], and increases flowability of the feed. Drying is also convenient in terms of waste storage before processing, limiting decomposition and the reduction in calorific content.

Possible pre-treatments of the waste and equipments are here briefly described. Common equipment used in MSW shredding are hammermills, shear shredders and crushers [48, 25]. Before choosing the type of size reduction machinery, the limitations of each of these devices must be considered. In particular, hammermills and crushers cannot work with high moisture content, while shear shredders are not able to finely break down the feed. Moreover, hammermills have a quite large energy consumption. Therefore, more than one shredder might be required. In addition to the need for multiple stages in shredding, it might be necessary to dry the waste before reducing its size because of the high deformability of the raw waste. This can also reduce the power consumption of such equipment. However, drying small particles is more efficient and the compatibility of shredders with a hot feed must be assessed. Since hot exhaust gases will likely be available in the system under study, it is more convenient to remove moisture using this type of heat source. Moreover, flue gas temperatures usually match drying ones, since temperatures lower than 100 °C are favorable in order to minimize the release of organic compounds. At these temperatures it is possible to obtain moisture as low as 10% [36]. Lower moisture content is usually more difficult to obtain and can increase the heat demand considerably. Several types of dryer can be used, such like perforated floor dryers, fluid dryers or band conveyor dryers. These have different requirements in terms of particle size and power consumption but all three can operate with flue gases.

The suitable equipment has to be chosen depending on the analysis of the actual waste that will be fed to the system. Moisture content and average size of the waste delivered are among the main parameters to take into consideration and that will influence the selection.

## Chapter 3

# Model and operation of the system

### 3.1 Assumptions and parameters

In order to evaluate the performance of the system and its feasibility, operating assumptions have to be made and the working parameters of each component defined. Firstly, it is assumed for simplicity that the composition of the waste is the one present in the Phyllis2 database [17] for organic waste, therefore the change in composition due to mixing with other streams is not considered. Moreover, it is assumed that after drying, the waste still contains an amount of moisture equal to 10% of the total mass. According to the report of E4tech [16], obtaining a moisture content below 10% is not convenient due to the significant increase of consumption of the dryer. In addition, since gasification with steam as gasifying agent is performed, the presence of water in the feed contributes to the steam to fuel ratio, although more heat has to be provided in the gasifier in order to evaporate the moisture. The sum of the mass fractions representing the ultimate composition provided by the database results in 100% only with halides (which are not specified), otherwise this would reach only 80.85%, according to ECN [17]. Therefore the percentages are recalculated in order to give unity neglecting the non specified amount constituting the waste but including the moisture content taken into account (Table 3.1). Also the lower heating value is obtained again, considering also the negative contribution of the evaporation of water.

$$\text{LHV}_M = (\text{LHV}_d - 0.1 \cdot \Delta h_{\text{H}_2\text{O}}^{\text{eva}})/1.1 \quad (3.1)$$

where  $\text{LHV}_M$  is the lower heating value for the waste with 10% moisture,  $\text{LHV}_d$  is the lower heating value for the dry sample and  $\Delta h_{\text{H}_2\text{O}}^{\text{eva}}$  is the latent heat of vaporization of water at atmospheric pressure (2.257 MJ/kg).

The feed is available at ambient conditions (25 °C, 1.01325 bar) and is dried at 90 °C, as it is convenient to keep a low temperature in order to minimize the release of organic volatile components [36]. The gasification technology considered is sorption enhanced gasification,

Table 3.1: Characteristics of the selected waste in terms of mass fractions according to Phyllis2 database [17] for the dry waste and for the waste with 10% moisture

Characteristic	Units	Dry	M=10%
<b>H<sub>2</sub>O</b>	%	0.00	10.00
<b>C</b>	%	42.09	46.71
<b>H</b>	%	5.43	6.03
<b>O</b>	%	31.14	34.56
<b>N</b>	%	1.78	1.98
<b>S</b>	%	0.41	0.46
<b>Cl</b>	%	0.24	0.27
<b>LHV</b>	<i>MJ/kg</i>	16.86	15.12

using calcium oxide as a sorbent. Based on the results found by Acharya [1] and Tang et al. [50], the gasification temperature chosen is 600 °C. Due to pressure losses in the pipes, heat exchangers and cleaning unit, the gasification pressure is set to 3.2 bar. At these conditions, a considerable concentration of hydrogen in the product gases is expected and the regeneration temperature of the sorbent is close to the gasification one. The steam used as gasifying agent is fed at the gasification pressure and at the corresponding evaporation temperature (135.7 °C). The ratio between the steam flow and the fuel flow is 0.9 since several authors found that the optimal value is around 1.0 and water is present also in the processed waste.

Due to the intermediate temperature for the gasification reactions, a moderate amount of char and particulate is expected. However, thanks to the sorbent that also catalyzes the gasification, this should be somewhat limited compared to the case without the calcium oxide bed. Nonetheless, the cleanup system has to be able to remove such contaminants effectively. Elimination of sulphur and chlorine containing compounds is also required so that the the produced gas can be sent to the fuel cell to be oxidized without compromising its functioning. In the cleaning unit, the gas flow to the SOFC stack encounters a cyclone first, it is then cooled down to 450 °C and is passed through a filter. After the filter, two units are used in order to remove chlorine-based compounds and sulphur-based chemicals. The flow is then heated up to 750 °C and, if necessary, goes through a tar cracking module. The gas is therefore ready for being used in the fuel cells. Both flows entering the SOFC stack (anodic and cathodic ones) are heated up to 750 °C. This means that the air flow needs to be brought up to this temperature from ambient conditions, requiring a large amount of heat. The anodic and cathodic flows are supposed to undergo a temperature increase of 100 °C inside the cell. The temperature of the cell is assumed to be equal to the average temperature between the inlet and outlet. The SOFC stack works at a pressure slightly higher than the ambient one in order to compensate the successive pressure losses and avoids possible air infiltration, providing also a better performance. A resistance of the cell equal to 0.65  $\Omega \text{ cm}^2$  is assumed [5, 38, 6] The anode and cathode off-gas flows are

used to heat up the flows required at high temperature. A combustor is used in order to obtain more thermal energy and heat up the flows to the process temperature. Only part of the anode off-gas is used in the combustor while the remaining stream is purified so that only hydrogen is obtained. For simplicity, the heat of evaporation of water is provided by the combustion of natural gas, since the combustion of hydrogen is expected to not always be able to provide enough heat, depending on the fuel utilization.

The model of the system with the software CYCLETEMPO is performed based on the assumptions listed below. The main parameters are also summed up in Table 3.2, while the main assumptions of the model are here presented:

- steady state operation;
- all processes are considered adiabatic;
- no pressure losses inside pipes;
- pressure losses considered only in heat exchangers and cleanup unit;
- pressure loss in the whole cleanup unit equal to 1.6 bar;
- complete removal of contaminants;
- waste composition constant and equal to the one in Table 3.1. Presence of metals and other species is not considered;
- compressors, blowers and pumps performance constant at different flow rates;
- constant pressure losses in the components;
- consumption of auxiliary equipment (like shredders and hydrogen purification) is not considered;
- hydrogen produced at ambient conditions.

## 3.2 Model with CYCLETEMPO

The concept here proposed is modelled with the software CYCLETEMPO, developed by Delft University of Technology in conjunction with TNO. With the software, it is possible to create a flow sheet of the process and to obtain the results of the thermodynamic analysis of such system in terms of energy and exergy.

In Figure 3.1, the flow sheet of the model is shown. The waste flow is modelled with a fuel stream having the same composition and lower heating value as shown before. This flow enters the gasifier where the gasification process is modelled at the conditions in Table 3.2. In the gasifier also a steam flow is added, while the heat of the reactions is provided by the exhaust flow. Such reactions are calculated at the equilibrium conditions. Since sorption enhanced gasification cannot be represented in the software, the process is

Table 3.2: Working parameters of the system

<b>Parameter</b>	<b>Value</b>
Dried waste temperature	90 °C
Steam temperature	135.7 °C
Steam pressure	3.2 bar
Gasification temperature	600 °C
Gasification pressure	3.2 bar
Steam to fuel ratio	0.9 (kg/kg)
Gas cleanup temperature	450 °C
Fuel cell inlet temperature	750 °C
Fuel cell pressure	1.2 bar
Fuel cell exhaust gas temperature	850 °C
Equivalent cell resistance	0.65 $\Omega \text{ cm}^2$
SOFC stack area	5000 $\text{m}^2$
DC/AC converter efficiency	96%
Exhaust gas stack temperature	100 °C
Pumps, blowers and compressors isentropic efficiency	75%
Pumps, blowers and compressors mechanical efficiency	98%

modelled with two gasifiers. In the second gasifier, the carbon dioxide produced in the first one is removed, causing a shift of reactions such as WGSR and affecting other reactions as already explained, representing the effect of calcium oxide. It is therefore assumed that gasification occurs in two steps: in the first one the syngas is produced at the gasification conditions, in the second step carbon dioxide is removed and the reaction shift to the new equilibrium at the same conditions. However, the sorbent has also a catalytic effect and reacts with other species, but such characteristics cannot be represented in the software. Nonetheless, as it will be presented in the following chapter, sorption enhanced gasification is modelled well enough if the output concentration is considered and compared to the results found in the literature.

The produced gas is then cooled down to the cleaning temperature. The cleanup unit is represented by three separators, where solid residues, chlorine-based compound and sulphur-based compounds are removed respectively. Regeneration of reactants for the removal of contaminants is not modelled, due also to the limited capability of CYCLETEMPO, as well as the actual reactions of the removal of contaminants. Tar removal is not represented, as also alkali and other solid materials, since it is absent in the calculated composition of the gasifier off-gas and only carbon residue is present (char). Moreover, as already stated tar may not be critical for SOFCs if enough steam is provided.



oxidation of hydrogen take place. As it will be explained in the following section, the waste flow rate is calculated from the desired electric power at the design conditions. The flow rate of cathodic air is obtained by the software considering the required cooling and the oxidant utilization is then calculated. This flow is compressed to the desired pressure taking into account the pressure drop in the heat exchangers and is then heated up to the SOFC inlet temperature.

The outlet gases from the fuel cell are at high temperature and therefore the heat can be used for increasing the temperature of the cold flows. The anode off-gas flow is used to heat up the correspondent entering one. Part of the anode off-gas must be combusted in order to provide a sufficient amount of heat for the gasifier and the incoming air flow. The remaining part contains hydrogen - the fuel utilization is always less than 100% - which can be extracted with technologies like pressure swing adsorption (PSA) or more modern membrane systems. The separation of hydrogen is represented in the software without considering a specific technology and its energy consumption. Moreover, at high fuel utilization only a small concentration of hydrogen is present in the output gas, therefore the useful amount is limited, being a larger fraction of the anode off-gas burnt. The combusted part provides heat to the gasifier and to the cathodic flow. Since not enough heat is available in the system, natural gas is used in the evaporator to produce steam. The water flow is compressed and brought to the evaporation temperature by using the heat of the gas produced in the gasifier, which need to be cooled down to 450 °C. Since CYLCETEMPO requires a flow of the "gas type" for representing the steam injected in the gasifier, steam in the steam generation is modelled as a separate flow. The flue gas from the combustion of natural gas are also used to preheat the comburent air. No optimization of the system is performed. Flue gases are then discharged in the atmosphere through a stack.

### 3.3 Base operation

The system is designed to efficiently convert waste into energy with possibly no environmental impact and to provide flexibility as a service to the electric grid management, accommodating changes in the load. In order to vary the system load, the fuel utilization is varied within a determined range of values. Moreover, the produced gas flow in the gasifier can be modified moderately within the limits of the gasifier. The main advantage of such system is that it should be always able to provide an useful product, being mostly power when the demand is high or power and hydrogen when the load is low, depending also on the operation of the system. The freedom of operation is given by both variation of fuel utilization and flow. Higher fuel utilizations result in more power produced and less hydrogen available at the anode outlet while lower  $u_f$  in less power and larger hydrogen concentration in the anode off-gas. In addition to this variable parameter, the flow can be changed in order to maintain a certain fuel utilization if for example very low or high power is required or if it is more economically convenient to maximize the power generation from

a given input flow. It has to be noted that such changes in the operation of the cell occur continuously also due to the variation of the composition of the feed, which means that a suitable control system has to be implemented. The system should therefore be able to always provide an useful output regardless of the operation. However, the actual operation of the system will be obtained when the results are examined, in the next chapter. The amount of hydrogen produced by the system depends on the fuel utilization, to which corresponds a concentration in the anode off-gas, and the flow rate of waste, both affecting the fraction of the flow at the anode outlet that needs to be combusted in order to provide the heat required by the inlet streams. Such fraction is dependent on the fuel utilization because a higher hydrogen concentration in the anode outlet gas flow is present at low  $u_f$  (thus having a larger lower heating value), resulting in a lower input requirement in the combustor, and the opposite for high  $u_f$ . In both cases, the combustion temperature is limited due to the limited concentration of oxidizable chemicals, therefore contaminants usually forming at high temperature are not present. Moreover, thanks to the gas cleaning unit, the concentration of acid gases should be negligible, thus allowing for lower flue gas stack temperature.

In order to be able to carry out the evaluations of the performance of the system at different conditions, a base load design must be considered. This allows also to have a reference when other operating points are considered, thus acting as a benchmark for such conditions. This is done by taking into account the considerations above. The size of the plant is chosen arbitrarily, with a nominal output of 10 MW. This is already a considerable capacity for a SOFC plant, but fuel cell systems are expected to become more common in the future and thus to increase in average size. Moreover, such capacity is expected to guarantee the treatment of a considerable amount of waste, which could eliminate the problem of organic waste disposal. CYCLETEMPO calculates the flow rate required at the input of the system in order to obtain such power, having set the fuel utilization. The fuel utilization at the design point (base load) is 80%, giving freedom of operation when the plant is in balancing mode. Moreover, at such fuel utilization the electrical efficiency is not expected to be optimal but still high and close enough to the maximum value, especially if compared to conventional technologies. In fact, this should correspond to a good compromise between voltage and conversion of the energy flow at the inlet. In particular, the system is expected to transform a considerable fraction into electricity, while less hydrogen or heat are available. Once the base load flow rate is known, this becomes the input of the system and the fuel utilization is varied in order to obtain the different points of operation at constant input or it can be changed so that the optimal load variation strategy can be assessed.

### 3.4 Balancing operation

The system works in balancing mode when a surplus or deficit of electric power is present in the grid. Since in the future renewable energy will have a large share in the European

power generation, there will be the need for systems able to balance the electric grid. As already mentioned, the present study is more focused on offering a valid alternative to conventional Waste-to-Energy technologies in terms of conversion efficiency and emissions, but at the same time it is important to design a system that can reduce its power output efficiently.

In order to change the power produced by the plant, the power of the SOFC stack has to be varied. As already stated, this can be done by varying the fuel utilization of the cell or the waste flow. The range of fuel utilization and energy input depends on the ability of the components to permit variations in the operating conditions, especially in terms of flow rates, with the air flow being one of the most critical. In fact, in order to avoid thermal stress in the cell, which reduces its lifetime, the temperature of the SOFC should undergo only slight changes or possibly be constant. This is obtained with the air flow that provides the main cooling [9]. For simplicity, the temperature of the cell is considered constant, as also the ones of the anodic and cathodic inlet flows, so that no excessive thermal gradients occur. In order to achieve such regulation strategy, the air flow rate is changed accordingly. This could penalize the system because at certain conditions it might be necessary to burn a larger fraction of the anode outlet flow in order to keep constant the temperature of the air, although the temperature difference could have been acceptable, in addition to cause a higher consumption of the compressor.

Only part of the cathodic flow is required for the oxidation of the fuel while most of it works as a cooling medium. Therefore, although also the amount of reacting air changes depending on the fuel utilization and flow rate, the "surplus" air is the one that undergoes the largest variation. Components like pipes, heat exchangers, the compressor, as also the cathode side of the cells, must be able to permit these significant variations in flow rate. In fact, the diameter of the pipes and the cross sections of the components is constant, causing an increase or decrease in the velocity of the gas, which can become too low or too high depending on the fuel utilization. Moreover, also the heat exchanger area and active area of the cells are fixed, therefore these components may not work properly when the flow rate is subjected to great changes with respect to the design one. In order to avoid too large variations in flow rate, the fuel utilization values considered in the calculations range from 0.6 to 0.95, while the flow rate may increase by 15% with respect to the base case [11]. A larger negative variation (-25%) of the flow rate is considered, since lower velocities are expected to be less critical. In order to evaluate the feasibility of such operations, tests should be carried out on a real system. In fact, the performance and hence the efficiency of the components varies with the flow rate, while in the present study such changes are not considered.

It has to be noted that systems integrating gasification and SOFCs are inherently difficult to regulate and to design in order to make them flexible. As mentioned before, in fact, high temperature fuel cells are delicate in terms of thermal cycles and thus they should not undergo drastic and fast variations in temperature. Moreover, the limits of the overall system and the inertia of the components when going from one operating point to another

should be considered when designing for flexible operation. Therefore, also the time taken by the system to move from a load condition to a new one must be taken into account and evaluated in order to determine the feasibility of such operation. In this case, the system is not thought as a base load one with the ability to work efficiently in part load but rather as multi-product system which can provide different outputs depending on the operation and the economical convenience. Therefore, large variations in power delivered as other systems are not possible, but this must be also compared to the alternative technologies for waste treatment.



# Chapter 4

## Results and discussion

### 4.1 Base case results

In this section the results for the base case are presented and discussed. In Table 4.1, the parameters and results of the base case are shown, while in Table 4.2 the different concentrations of the cleaned gas entering the SOFC stack are presented. It can be seen that the performance of the cell is acceptable, having a suitable voltage and current density for a base load operation. However, there is a great difference between the flow rate at the anode inlet (1.065 kg/s) and the air flow rate (in Table 4.1). This causes the large power requirement of the compressor, which reduces the output of the system considerably. In fact, approximately 12% of the power generated by the SOFC stack is consumed internally, reducing the electrical efficiency greatly. Moreover, also the need for external heat causes a reduction in efficiency. In this case, this is provided with natural gas and it is used in the evaporator where steam is produced and then fed to the gasifier. In fact, through a brief and simplified pinch analysis, it was seen that an external heat source is required since not enough heat is available at the temperatures at which it is demanded, not permitting to employ only internal exchanges. In particular, the streams that have to be cooled in the system cannot provide the evaporation heat required by the water, thus an external source is used. However, the heat exchanger network is not optimised and improvements to the overall system can almost certainly be made. Moreover, alternative sources for the evaporation heat can possibly be found. If also the energy absorbed by other equipment like the waste shredder were to be considered, the available output of the system would decrease even more. However, this study aims mainly at exploring the feasibility of such system, that can be further examined if it is considered convenient in energy and economical terms.

In Table 4.1, the obtained efficiencies at the base conditions are shown. These are calculated with the following formulae.

$$\eta_{el} = \frac{P_{net}}{\dot{m}_{waste}LHV_M + \dot{m}_{NG}LHV_{NG}} \quad (4.1)$$

Table 4.1: Base load conditions and results

Parameter	Symbol	Value
Waste flow rate	$\dot{m}_{\text{waste}}$	1.033 kg/s
Steam flow rate	$\dot{m}_{\text{steam}}$	0.930 kg/s
Air flow rate	$\dot{m}_{\text{air,c}}$	38.274 kg/s
Natural gas flow rate	$\dot{m}_{\text{NG}}$	0.056 kg/s
SOFC power	$P_{\text{SOFC}}$	10 MW
Current density	$i$	2739.78 A/m <sup>2</sup>
Cell voltage	$V$	0.7604 V
Fuel utilization	$u_f$	80%
Air compressor power	$P_{\text{Comp}}$	1.155 MW
Air blower power	$P_{\text{Blower}}$	9.03 kW
Water pump power	$P_{\text{Pump}}$	0.29 kW
Net power	$P_{\text{net}}$	8.835 MW
Thermal power	$\dot{Q}$	1.903 MW
H <sub>2</sub> produced	$P_{\text{H}_2}$	1.120 MW
Electrical efficiency	$\eta_{\text{el}}$	50.0%
CHP efficiency	$\eta_{\text{CHP}}$	60.8%
Total energy efficiency	$\eta_{\text{tot}}$	67.6%
Electrical exergy efficiency	$\eta_{\text{ex,el}}$	44.9%
CHP exergy efficiency	$\eta_{\text{ex,CHP}}$	47.7%
Total exergy efficiency	$\eta_{\text{ex,tot}}$	53.6%

$$\eta_{\text{CHP}} = \frac{P_{\text{net}} + \dot{Q}}{\dot{m}_{\text{waste}}\text{LHV}_M + \dot{m}_{\text{NG}}\text{LHV}_{\text{NG}}} \quad (4.2)$$

$$\eta_{\text{tot}} = \frac{P_{\text{net}} + \dot{Q} + P_{\text{H}_2}}{\dot{m}_{\text{waste}}\text{LHV}_M + \dot{m}_{\text{NG}}\text{LHV}_{\text{NG}}} \quad (4.3)$$

$$\eta_{\text{ex,el}} = \frac{P_{\text{net}}}{E_{\text{waste}} + E_{\text{NG}}} \quad (4.4)$$

$$\eta_{\text{ex,CHP}} = \frac{P_{\text{net}} + E_{\text{heat}}}{E_{\text{waste}} + E_{\text{NG}}} \quad (4.5)$$

$$\eta_{\text{ex,tot}} = \frac{P_{\text{net}} + E_{\text{heat}} + E_{\text{H}_2}}{E_{\text{waste}} + E_{\text{NG}}} \quad (4.6)$$

where  $\eta_{\text{el}}$ ,  $\eta_{\text{CHP}}$ ,  $\eta_{\text{tot}}$ ,  $\eta_{\text{ex,el}}$ ,  $\eta_{\text{ex,CHP}}$  and  $\eta_{\text{ex,tot}}$  are the electrical efficiency, heat and power efficiency, total energy efficiency, electrical exergy efficiency, heat and power exergy efficiency and total exergy efficiency, respectively.  $\dot{m}_{\text{waste}}$  and  $\dot{m}_{\text{NG}}$  are the flow rates of the dried waste and the natural gas, while  $E_{\text{waste}}$  and  $E_{\text{NG}}$  are the relative exergy flows.  $P_{\text{net}}$

is the net power produced by the system, i.e. the power produced by the SOFC stack to which the consumption of the pump, the compressor and the blower is subtracted.  $\dot{Q}$  is the thermal power produced while  $E_{\text{heat}}$  is the exergy associated to the heat flow.  $P_{\text{H}_2}$  is the energy flow of the hydrogen produced, calculated taking into account its lower heating value, while  $E_{\text{H}_2}$  is its exergy flow. The exergy of all the streams is calculated by CYCLETEMPO, considering as environment the one of Baehr (at 25 °C and atmospheric pressure). Although air has not the same composition of such environment, the exergy of air is neglected, being available at ambient temperature and pressure and having air only minimal composition differences. Since the power of the shredder and the heat required for drying are not considered, the waste at the input of the system is considered already dried and shredded, hence the use of the dried waste flow rate and its lower heating value in the calculations. In Table 4.1, it can be seen how the difference between the efficiencies considering only electrical power, only heat and power (CHP) or accounting also for the hydrogen produced (total) are significant. Approximately 66% of the anode off-gas is combusted, while the remaining fraction is cooled and purified in order to obtain hydrogen. At this fuel utilization, the thermal power available is larger than the energy flow of the hydrogen produced, therefore the difference between the CHP efficiency and the total efficiency is smaller than the one between the former and the electrical efficiency. However, since the heat is not available at significantly high temperatures, the exergy associated to it is modest, resulting in only a limited increase in terms of exergy efficiency. On the contrary, the contribution of the exergy flow of hydrogen is more substantial. It can be noted that the electrical efficiency of the system is high compared to conventional WtE plants or even to plants fed with traditional fuels. The efficiency as a combined heat and power plant is significantly smaller to most of the established CHP systems, though, since a great part of the available heat is used to bring the flows to the operating temperatures.

From Table 4.2, the similarity in composition of the cleaned gas with the ones found by Acharya [1] and Tang et al. [50] can be seen. Although the catalytic effect is not represented, the model with two gasifiers and the removal of carbon dioxide can be considered realistic enough for the purpose of this study. Moreover, S/C ratio can be calculated so that it can be seen whether a recycle loop is necessary to provide enough steam and avoid carbon deposition. Considering the concentrations in Table 4.2, the ratio can be obtained as

$$S/C = \frac{y_{\text{H}_2\text{O}}}{y_{\text{CO}_2} + y_{\text{CH}_4} + y_{\text{CO}}} \quad (4.7)$$

and is equal to 1.34, sufficiently high if compared to the values of the graph of Figure 2.6 at the operating temperature of the SOFC stack.

In order to identify the size of the system in terms of area and population which it would serve, it is possible to estimate the mass of wastes at the input. Assuming a constant operation at the base conditions and a capacity factor of 80% (being still uncertain the

Table 4.2: Molar composition of the cleaned gas (anode inlet), with the concentration represented as fraction of the total

<b>Specie</b>	<b>Concentration (<math>y</math>)</b>
H <sub>2</sub>	0.4331
H <sub>2</sub> O	0.3200
N <sub>2</sub>	0.0087
CO <sub>2</sub>	0.0591
CH <sub>4</sub>	0.1492
CO	0.0299
NH <sub>3</sub>	0.0001

actual capacity factor for such systems), the yearly amount of waste processed can be obtained considering the data in Table 4.1. This results in about 26.06 thousand tons of dried waste that are fed to the gasifier yearly, which are almost 51 thousand tons in terms of wet unprocessed waste, i.e. waste as it is collected. Such amount of organic waste corresponds in Italy to the the generation of a relatively large city or a small province. This is due to the low LHV compared to conventional fuels, which means that a large amount at the input of the system is needed. It has to be noted that if also sewage sludge or agricultural residues and wood waste are considered, such quantity of waste is produced by a lower number of people and thus the system can work also in moderately small towns. Nonetheless, larger systems may not be convenient due to the need of transporting the waste over long distances, unless other more energetic types of wastes are considered.

In the following sections the results in balancing mode with different fuel utilizations and flow rates are presented.

## 4.2 Balancing operation results

### 4.2.1 Operation at constant input flow

The system can vary its output by changing the fuel utilization or the input flow rate. As already mentioned, in order to obtain the net power produced by the system also the consumption of the water pump, air compressor and blower has to be considered. If only the fuel utilization is varied, the waste flow rate is constant and thus also the steam required, being the steam to fuel ratio fixed. Consequently, also the power needed by the water pump is constant, as also the amount of fuel required for the evaporation. It has to be noted that the pump consumes a negligible quantity of the power generated nonetheless. On the contrary, compressing air requires much more energy. Hence, as seen before, most of the internal consumption of electric power is caused by the compressor. In particular, since a constant SOFC temperature operation is considered and the power required by the compressor depends approximately linearly on the flow rate of air, at higher

fuel utilization more power produced by the SOFC stack is consumed to operate it while at lower fuel utilization less is needed. From this result, it can be already seen that this behavior affects the flexibility of the system, not allowing large net power variations. In fact, the SOFC stack can vary its output by almost 3 MW, while the overall system only by 1.6 MW. In Figure 4.1, this is shown by the orange line, representing the net power of the system (excluding auxiliary power consumption) as a function of only fuel utilization. The curves correspondent to the power delivered by the SOFC and the one consumed are almost parallel, resulting in a net power that varies only moderately. In particular, keeping the inlet flow constant, the system can decrease its output by about 14% with respect to the base case, while the maximum output of the system is approximately 9.25 MW, only 4.7% higher than the base load. Therefore, varying only  $u_f$  does not provide enough flexibility in comparison to conventional technologies like gas turbine power plants, that are able to halve their power.

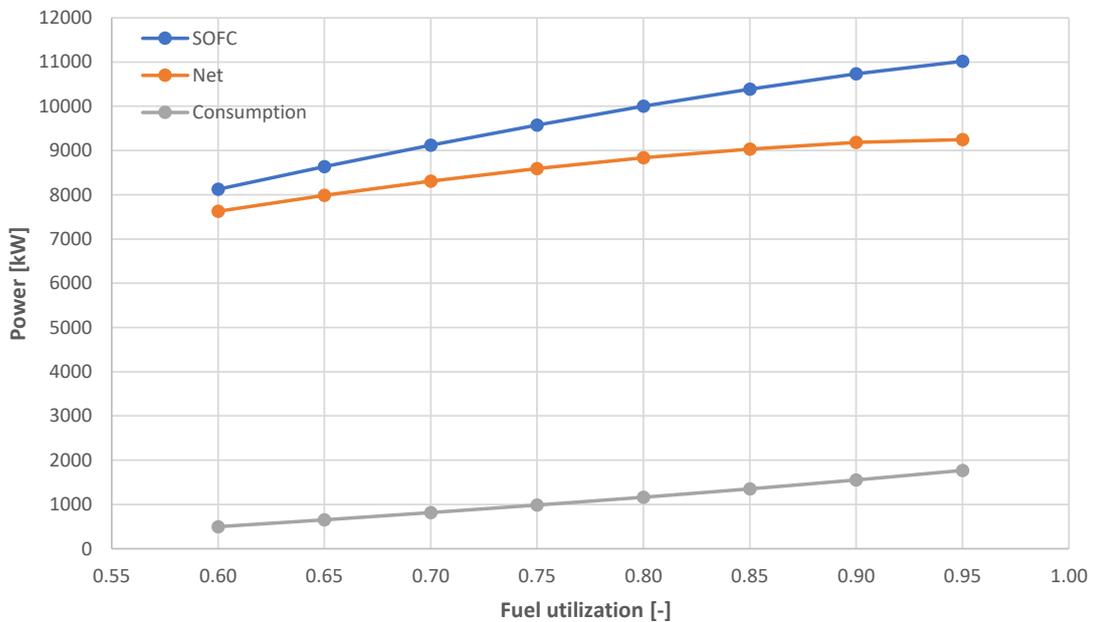


Figure 4.1: Generated, consumed and net power varying only fuel utilization, with constant energy input

In Figure 4.3 the efficiencies of the system for this operation are shown. The electrical efficiency varies between 43.1% at a fuel utilization of 0.6 and 52.3% at 0.9. This is due to the fact that more energy contained in the fuel is converted into electricity at high fuel utilization, while at low ones the gas exits the SOFC stack still with exploitable energy. However, it can be seen that the behavior of the electrical efficiency is sublinear because Nernst voltage is higher at low  $u_f$  due to the lower conversion and thus larger reactant concentrations. Moreover, since a higher fuel utilization implies a larger current density, ohmic losses do also get larger with  $u_f$ , causing a reduction in voltage and efficiency

gain at high conversions. Therefore, the power produced by the cells grows with the fuel utilization but the increase is hindered by the lower Nernst voltage and the irreversible losses resulting only in slight improvements, as it can be seen in Figure 4.1. In addition, at low fuel utilization, the anode off-gas contains more chemical energy and thus less anode off-gas must be combusted in order to heat up the air flow. This explains the behavior of the CHP efficiency and the total efficiency trend. In fact, since at low fuel utilizations more hydrogen is present in the anode outlet gas than required in the combustor, part of it is extracted and it is considered as a useful product. The part of the anode off-gas that is not burnt is cooled down before the hydrogen is separated, generating also heat. Therefore, the production of hydrogen implies also availability of heat at intermediate temperature. This can be also seen in Figure 4.2, which shows that the heat produced increases when lowering  $u_f$ . However, it must be noted that at  $u_f < 0.7$ , the fraction of combusted anode outlet gas does not decrease as much as at higher utilizations. This is due to the fact that less irreversible heat is produced in the cell and therefore more gas is burnt in order to maintain the minimum temperature difference in the air heat exchanger (set to 10 °C), as opposed to just guarantee a flue gas temperature of 100 °C. Therefore, the heat available tends to become approximately constant when lowering  $u_f$ . From this consideration, the change of concavity of the curve of the hydrogen flow in Figure 4.2 is then understandable.

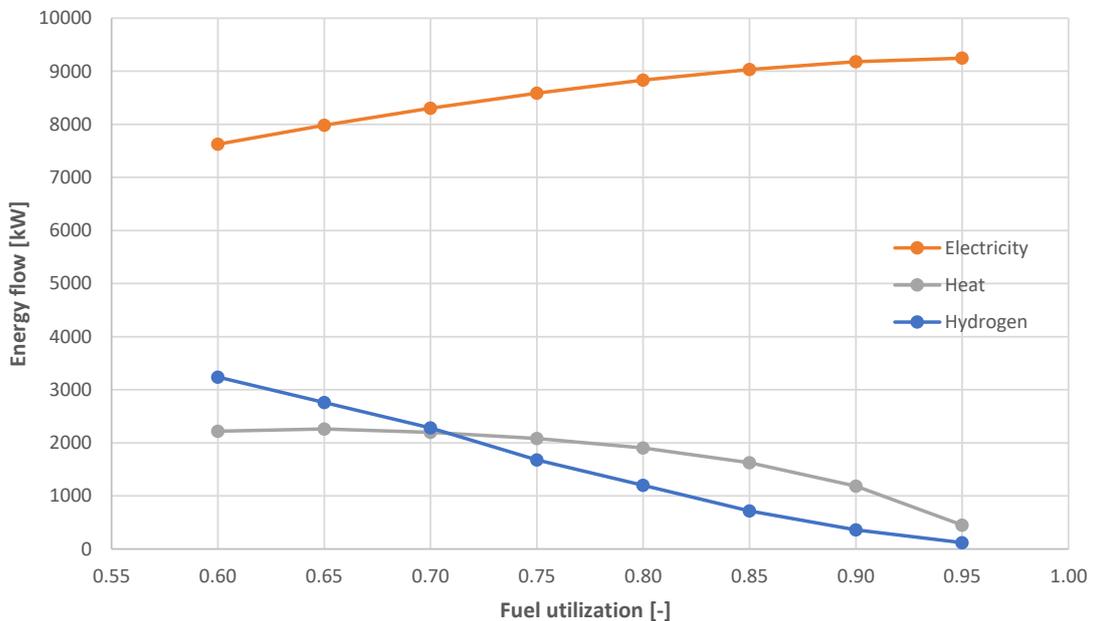


Figure 4.2: Produced energy flows of the system as a function of only fuel utilization, with constant energy input

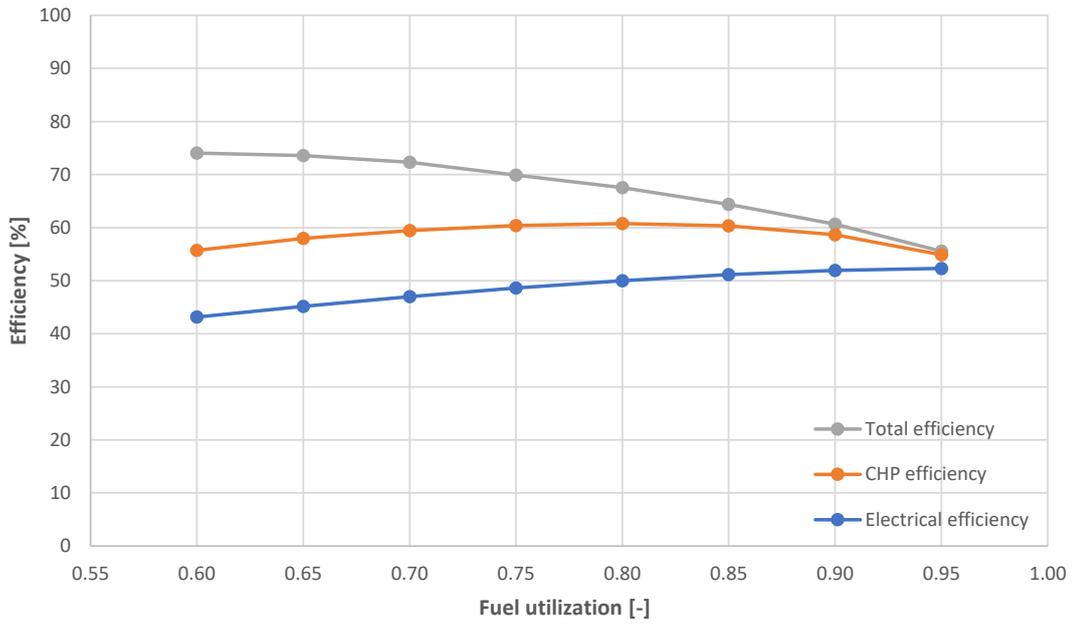


Figure 4.3: Energy efficiencies of the system as a function of only fuel utilization, with constant energy input

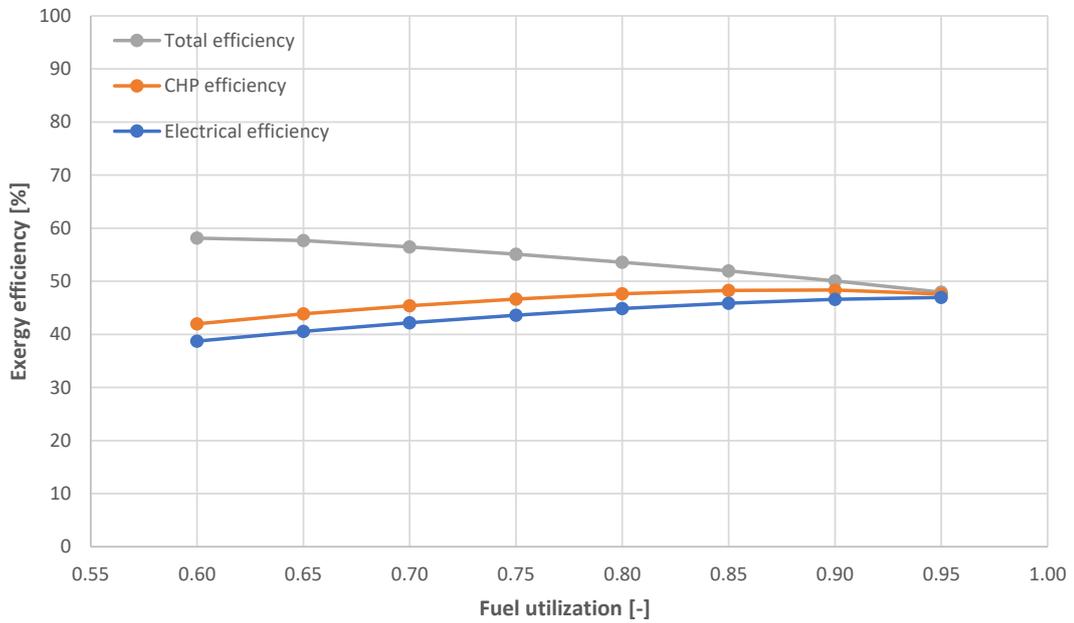


Figure 4.4: Exergy efficiencies of the system as a function of only fuel utilization, with constant energy input

If also the energy flow associated to the hydrogen produced is considered, not only

the efficiency is higher but it becomes monotonically decreasing with the fuel utilization. Moreover, the three efficiencies tend to converge into one at higher fuel utilizations, since a small amount of hydrogen is produced and the heat available is low, as it can be seen in Figure 4.2. When  $u_f = 0.95$  the curves differ only by few percentage points.

In Figure 4.4, the exergy efficiency of the system is shown. As for the energy efficiency, three curves accounting for only electrical power, power and exergy of the available heat and the latter with the addition of the exergy flow of hydrogen are represented. These present similar behaviors to the energy efficiencies. The major differences are the smaller increase in efficiency when also the exergy flow relative to the thermal power is considered (due to the lower exergetic content of heat) and the absence of an absolute maximum in the range examined. Similarly to the total energy efficiency, the exergy one is monotonically decreasing and the contribution of the exergy flow of the hydrogen produced to the total efficiency is also analogous.

#### 4.2.2 Operation varying the input flow

As also stated above, the degree of freedom that the operation at constant energy input offers is quite small. In order to evaluate the ability of the system under study to vary more significantly the power produced, the flow rate is also altered. The variation range considered for the waste flow rate is between  $-25\%$  and  $+15\%$  of the base value. Five different input flows are considered (75%, 85%, 95%, 105% and 115% of the base flow), to which the results obtained previously for the base case are added. For simplicity, only four fuel utilizations (between 0.6 and 0.9) for each case are considered. From the previous results it was found that the operation at  $u_f > 0.9$  is generally less convenient (unless only electrical power is wanted) thus the calculations are carried out only for lower conversions, since similar results are expected for the different inputs. Moreover, only small variations are presumed between  $u_f = 0.9$  and  $u_f = 0.95$  and it is possible that not enough thermal energy is available in the system at low energy inputs to heat up the cathodic flow to the desired temperature.

The trend of the power as a function of the fuel utilization for the six cases can be seen in Figure 4.5. In Figure 4.5a, the power at the output of the SOFC stack is shown, while in Figure 4.5b the available power after deducting the consumption of the pump, compressor and blower is represented. Similarly to what already found in the previous case, it can be seen how the net power is not decreased by a constant amount but it does also undergo a reduction in slope. This means that at higher fuel utilizations a large increase in fuel conversion produces only a limited variation in power. As already mentioned, this is due to the worsening of the performance of the fuel cell while the power of the compressor keeps increasing as the power produced grows. Although less evident, at lower system inputs the slope of the curves tends to be larger while at higher waste flow rates these are flatter. This is expected to happen due to the lower current density in the cells, which translates in less irreversible losses and higher voltage. Compared to the previous case, a larger range of operation is possible. While the operation at constant inlet allows to work only between

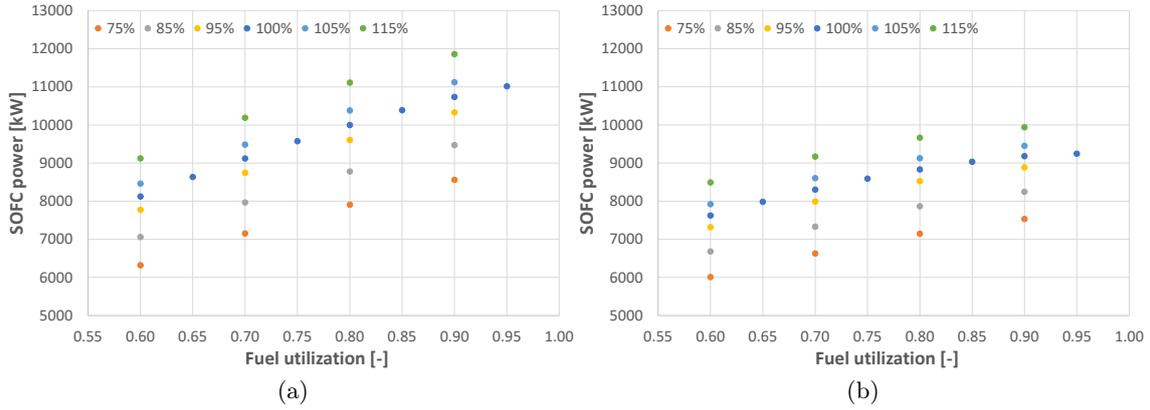


Figure 4.5: Power produced as a function of the fuel utilization for different inputs: (a) SOFC stack power, (b) net power

7.6 MW (86.3% of the base case) and 9.2 MW (104.7% of the base case), the variation of the waste flow permits greater variations. In fact, the minimum power within the conditions considered is 6.0 MW while the maximum is 9.9 MW. Although it may seem a small improvement, in relative terms the system is able to operate between 68% and 112.5% of the base load. This means that the maximum net power based on the previous assumptions is almost 1.7 times greater than the minimum one. Moreover, in Figure 4.5b, it can be seen that the same power can be produced at various conditions, i.e. different  $\dot{m}_{\text{waste}}$  and  $u_f$  can result in the same output. However, as it might already be expected, these conditions will correspond to different efficiencies, therefore some will be more convenient than others. This can be seen in Figure 4.6, which shows the electrical efficiency (in energy terms) with respect to the net load. In the figure the curves are monotonically increasing, although the increase in efficiency is different for each one. Therefore, if maximum conversion of a given input into electric power is wanted, it is convenient to operate the system at a flow rate such that the fuel utilization is as high as possible. This means that for the same load, lower waste flow rates at the inlet of the system result in better performances than higher ones with a lower fuel utilization. Moreover, at lower waste flows, these maxima reach higher values in comparison to higher system inputs. This trend is the same for all the curves, meaning that lower flow rates at the input of the system give better performances. In Figure 4.6, it can be also seen better how the increase in fuel utilization from 0.8 to 0.9 (last two right points in the curves) results in only a modest increase in power, especially for larger flows. In fact, the segment connecting these points becomes shorter as the input gets larger and the slope is lower. This derives from the considerations above, related to worse SOFC performance.

In addition to the electrical power, heat and hydrogen are also produced. The amount of these quantities is represented for the fuel utilizations considered and for each input in Figure 4.8a and Figure 4.7, respectively. In the figures it can be seen that the system produces hydrogen almost linearly with the decrease of  $u_f$ , while the heat tends to become

constant a low fuel utilization, as already found previously. For high inputs, due to more irreversible heat produced in the SOFC, less energy is required in the combustor and therefore more is available as product. This results in a higher amount of hydrogen available at the output of the system at larger flow rates. Similarly, the heat flow produced is larger at low fuel utilizations and high waste flow rates. This behavior derives directly from the amount of hydrogen produced. In Figure 4.8b the exergy flow of the heat generated is represented. This is significantly smaller than energy flow, but it still accounts for a not negligible amount.

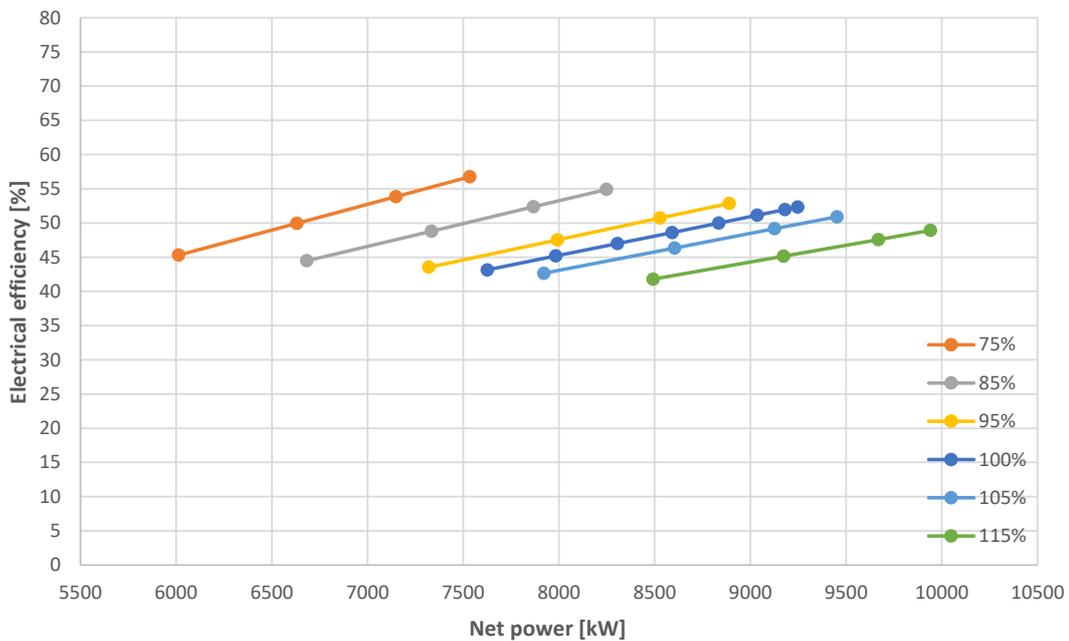


Figure 4.6: Electrical efficiency as a function of the net power

The trends of hydrogen and heat production explain the difference in shape of the curves for electrical efficiency, CHP and total energy efficiency. Comparing Figure 4.9a to Figure 4.6, it can be seen that the point of maximum efficiency shifts from a fuel utilization equal to 0.9 (or higher) to 0.8 (or more likely between 0.8 and 0.9) due to the addition of the heat term to the numerator of the expression of the efficiency. Considering also the energy flow related to the hydrogen produced, the maximum moves to  $u_f = 0.6$  and the curves become monotonically decreasing (Figure 4.9b). At this fuel utilization, the electrical power produced at a given energy input is minimum in the range considered because the conversion to electricity in the SOFC stack is limited, while the generation of the other two products combined is maximum. In Figure 4.9, it can be also seen how the total energy efficiency tends to equal the heat and power efficiency at high fuel utilizations. This derives from the fact that a smaller flow of hydrogen is produced at high  $u_f$ . Also the difference between the CHP efficiency and the electrical efficiency decreases at high

fuel conversion, being the hydrogen and the heat produced strictly related. Moreover, in Figure 4.10 the graph shows the significant improvement of the system efficiency at low fuel utilization compared to the case accounting only for electric power. For example, at  $u_f = 0.6$  and  $\dot{m}_{\text{waste}}$  equal to 85% of the base one, the efficiency moves from 44.5% to 74.0% going from the electrical efficiency to the the total efficiency. Compared to an efficiency of 61.2% at a fuel utilization of 0.9, it can be seen that the operation of the system at low fuel utilization is more convenient.

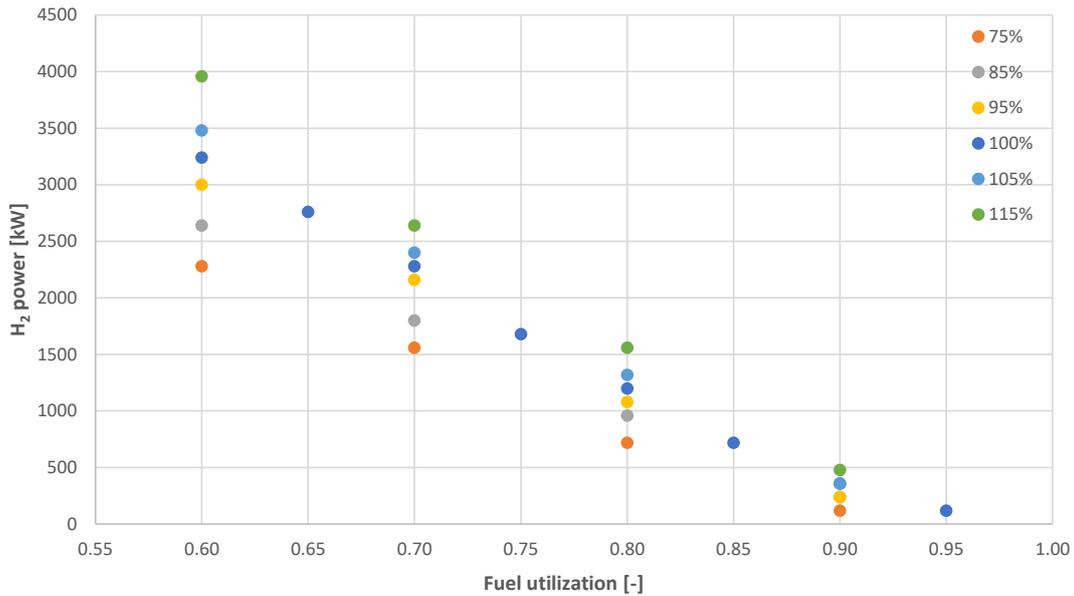


Figure 4.7: Hydrogen produced (in terms of energy flow) with different system input flows as a function of the fuel utilization

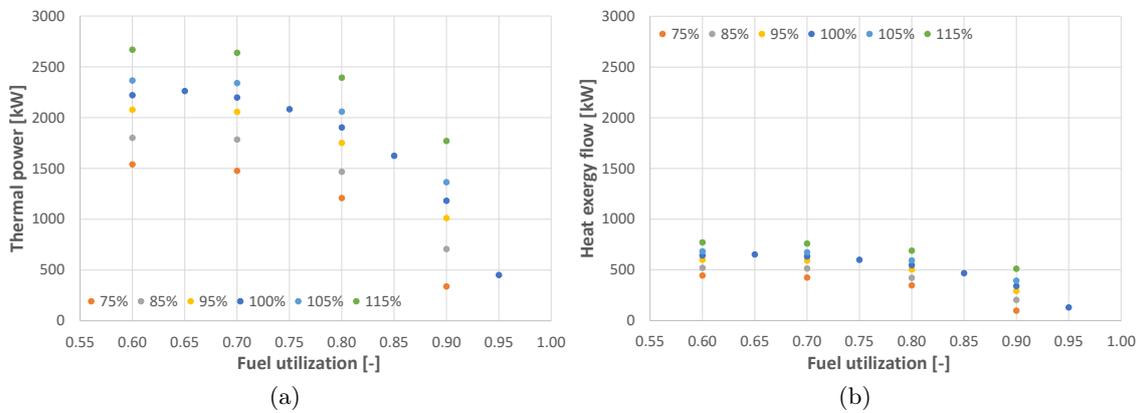


Figure 4.8: Heat produced by the system as a function of the fuel utilization for different inputs: (a) thermal power, (b) exergy flow associated with the heat

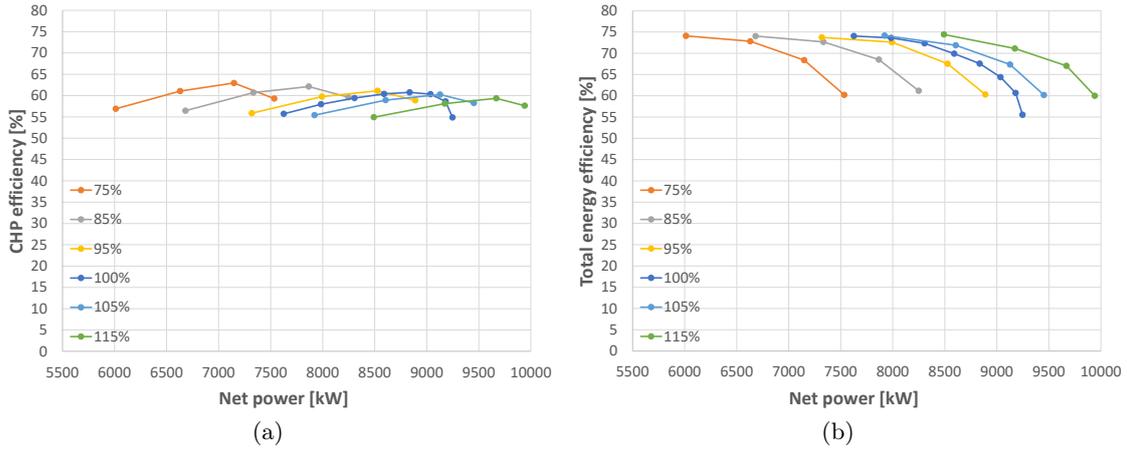
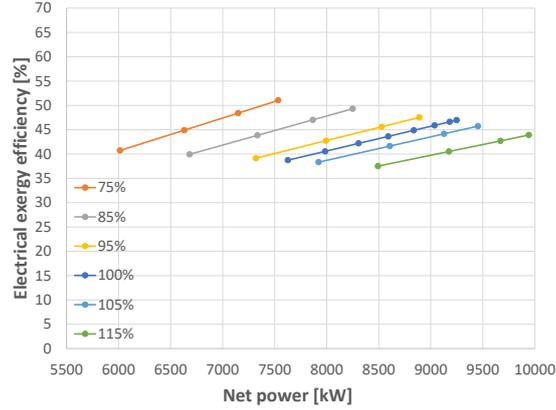


Figure 4.9: Energy efficiency of the system as a function of the net power output for different inputs: (a) CHP efficiency, (b) total energy efficiency

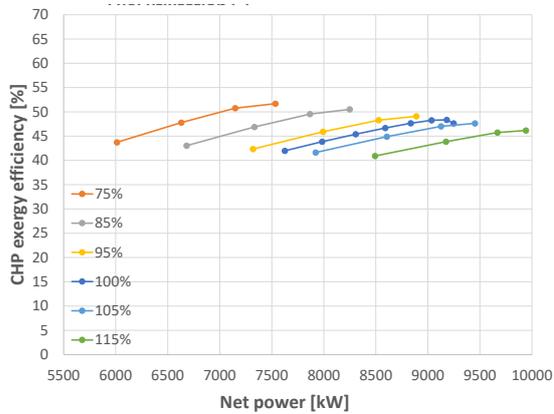
However, in order to evaluate the actual performance of the system compared to the reversible case, its exergy efficiency is considered. This allows to assess objectively the potentiality of the system and if possible improvements can be made. In Figure 4.10, the exergy efficiencies of the system are represented. Compared to the energy efficiencies, it can be seen that the difference between Figure 4.10a and Figure 4.10b is smaller. In fact, as already seen in Figure 4.8b, the exergy flow associated to the heat produced is small, therefore the improvement is able to shift the maximum from 0.9 to only 0.8 (or more likely 0.85). On the other hand, the total exergy efficiency is considerably higher for low conversions, thanks to the hydrogen flow, which exergy is close to its energy since it is of high quality. It can also be noted that the total exergy efficiency for the different input flows does not vary greatly from  $u_f = 0.6$  to  $u_f = 0.8$ . Therefore, the performance of the system would not drop dramatically if the load were controlled only by varying the fuel utilization in this range since a lower power is compensated by a larger amount of hydrogen produced, which has high exergetic content. If a fast response to load changes is required, such operation in this range of fuel utilization could be considered, although not optimal. However, this might not be convenient. In fact, the maximum of the curves decreases in a negligible way when the waste flow is increased. This means that the system could be operated in balancing mode maintaining almost a constant total exergy (and energy) efficiency if only the waste flow is varied.

### 4.3 Exergy analysis

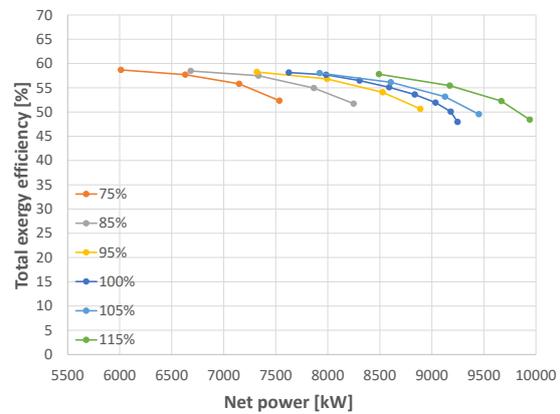
After having obtained the exergy efficiency of the system, the exergy losses in the system are calculated. In order to find room for improvement in further possible evaluations, the performance of the different units is assessed. This can be done by finding the losses in the units of the system through an exergy analysis. In this way the contribution to the



(a)



(b)



(c)

Figure 4.10: Exergy efficiency of the system as a function of the net power output for different inputs: (a) electrical exergy efficiency, (b) CHP exergy efficiency, (c) total exergy efficiency

total loss of each module can be estimated. The main irreversibilities of the system can be found in Table 4.3 for the base case (base waste flow and  $u_f = 0.8$ ). Instead of obtaining the losses of each component, the irreversibility of processes is calculated, i.e. the overall loss for groups of components performing a major step in the system. As it is shown in the table, the main contributions to the total exergy loss are given by steam generation and heating and compressing of the cathodic flow. These derive from the large temperature difference between the heating medium and the water and the limited efficiency of the air compressor. In fact, water is firstly heated up to the evaporation temperature using the heat of the outlet gas from the gasifier, which is at 600 °C and has to be cooled down to 450 °C, and is then evaporated with the heat provided by the combustion of natural gas. This can be observed in Figure 4.11, where the shaded area represents the exergy loss in the evaporation. The irreversibility generated during the combustion of natural gas accounts only for one third of the total one in the production of steam. Similarly, air is compressed and brought to the inlet cell temperature. Due to the limited efficiency of the compressor and, in a lesser extent, to the heat exchange between air and the flue gas, the

irreversibility contribution of the preparation of air to the desired conditions is significant. In general, it can be noted that most of the units are characterized by comparable losses. It is expected that not having modelled in a detailed way some of the processes, as well as not having considered regeneration of the sorbents, have affected such results considerably. Moreover, the exergy related to the carbon dioxide flow separated in the gasifier is not considered, which accounts for almost 4% of the total exergy input of the system. In fact, it must be evaluated if this can be usefully used. Since the CO<sub>2</sub> flow is not released to the environment, the system presents a beneficial characteristic that has to be taken into consideration. However, it might be complex to define a quantity in terms of exergy in order to also account for such property of the system. Moreover, the calcination reaction is not represented in the software, which would affect the conditions of the carbon dioxide produced.

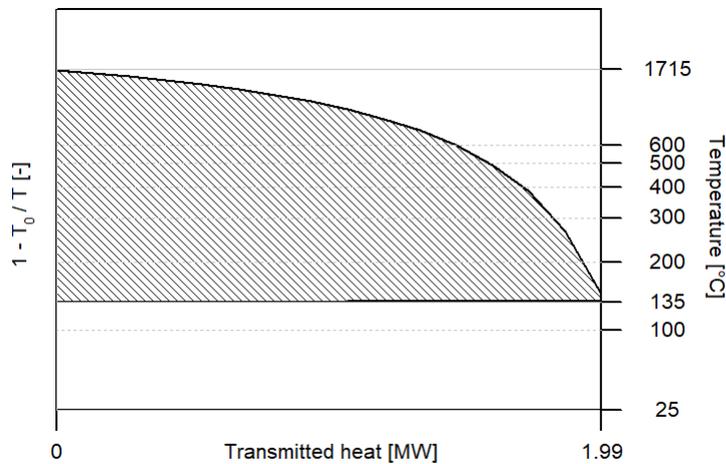


Figure 4.11: Value diagram of the evaporator

In Table 4.3 also the total exergy of the flue gases is shown. This is low because it is assumed that these flows exit the system at 100 °C, having already exchanged most of their energy. Among these also the remaining flow after separation of hydrogen is considered. However, it must be noted that this is assumed to be at 25 °C after separation. Nonetheless, the contribution should vary moderately if another temperature for the purification is chosen because of the low flow rate of the separated fraction.

Although gasification is expected to have a high exergy efficiency, the losses found are probably too low. This almost certainly derives from the modelling of SEG with two gasifiers in CYCLETEMPO. Nonetheless, Prins [42] found also high values for wood biomass, even though still lower than the one here obtained.

It was observed that the exergy efficiency changes when the fuel utilization is varied at constant input. Therefore, also the losses in some of the components undergo variations, some of them significantly while others are constant. In Figure 4.12, the exergy losses as a function of fuel utilization for the base flow rate are shown. For simplicity, only four fuel utilizations are considered. As already observed with the total exergy efficiency, it can be

Table 4.3: Irreversibility for the main units at the base conditions

Unit	Irreversibility [kW]	Irreversibility/Exergy input [%]
Gasifier	1465.7	7.4
Steam generation	1791.6	9.1
SOFC	1247.6	6.3
Cathodic flow preparation	1664.6	8.5
Anode off-gas burner	1079.2	5.5
Flue gases	893.3	4.5
Total	8141.9	41.3

seen in the figure that at low fuel utilizations the overall loss is lower. In fact, the amount of steam required is constant with  $u_f$ , and thus the irreversibility of the process does not change. Similarly, the losses in the gasifier are also constant. On the contrary, some of the processes are characterized by significant variations, like the preparation of air to the inlet cell conditions and the electrochemical oxidation in the SOFC stack. These are easily explained since in the fuel cell larger irreversible losses occur at high fuel conversion due to a higher current density and more air is required in order to maintain the temperature constant. With an opposite trend, the exergy loss in the combustion of the anode off-gas and the exergy associated to the flue gases decreases with the fuel utilization. This happens because of the higher temperature of the exit gas from the burner, achieved with a larger fraction of the anode off-gas that is combusted. At low fuel utilization, more gas is combusted than strictly required since the minimum temperature difference in the heat exchangers has to be satisfied. Therefore, the flue gases have a higher exergy, resulting in larger stack losses.

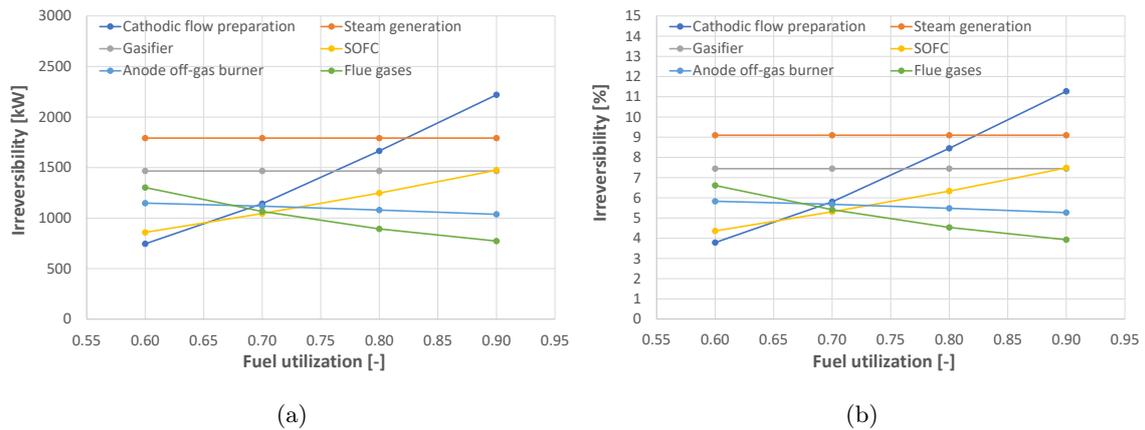


Figure 4.12: Exergy losses of the main units of the system: (a) in absolute terms, (b) in relative terms to the total exergy input of the system

The trends of the exergy losses are expected to be similar with different waste flows.

Moreover, from the considerations on the total exergy efficiency, it can be already foreseen that larger inputs result in larger irreversibilities due to the larger air flow rate required and the worse SOFC stack performance at higher current density.

It has to be noted that this exergy analysis is not able to give a detailed view of the system due to the assumptions previously taken. In fact, the system is considered to be adiabatic and no regeneration of the sorbents is considered, which will affect the heat balance of the system and thus possibly the external heat required. In general, the software assumes equilibrium conditions, thus the losses calculated are certainly lower than the ones of a real system, where non-equilibrium processes occur. However, the analysis can provide a first overview of the losses in the components and the expected variations that might occur.

## 4.4 Considerations

In the previous sections the results obtained were presented. However, it must now be assessed if these show that the system is feasible and if so, whether all the operating points found are conditions at which the system can work. Moreover, the convenience of such system has to be evaluated.

From the analysis carried out, it can be shown that the system under study could be feasible, although major changes might be necessary. In fact, the model is based on some important assumptions that affect the results greatly. In reality, worse performances are expected. Moreover, it might be challenging to operate the plant flexibly because of the many constraints and variables that affect its output. Among these, the composition of the waste and the temperature of the fuel cell, as well as the off-design operation of most components. In fact, the performance of the units depends on the conditions of the flows and the mass flow rate, thus a study on the control system is required. The composition of the waste is an important factor in the control of the system because it affects the characteristics of the gas produced in the gasifier and consequently the operation of the cleaning unit and the SOFC stack. Moreover, the gasification technology proposed is still under study and its potential has to be properly evaluated with more small scale experiments and further scale up. In particular, the possible regeneration of the CaO sorbent is not considered and it might impact on the overall thermal balance in a significant way. Similarly, the heat released during the absorption reaction is not taken into account. Despite these challenges that need to be addressed, the study here presented identifies the system studied as a possible alternative to conventional technologies although further research is required in order to determine its actual performance.

Considering the base operation as the reference case, it was seen that the system is able to work efficiently with an output of approximately 8.8 MW. Such base case was used as a benchmark which the performance of the system at different conditions were referred to. Considering the amount of waste at the input of the system, it must be noted that the power produced is quite modest. However, the low LHV causes the need for

a high flow rate in order to obtain a reasonable power. Nevertheless, a large portion of the energy at the input of the system is converted into electricity. For all the operations considered, the electrical efficiency is always higher than 42%, which is considerably high if compared to conventional WtE plants. Even in comparison to traditional power-producing systems, the electrical efficiency is considered to be satisfactory. However, the consumption of auxiliary equipment and other processes like shredding and hydrogen separation was not considered, thus the efficiency could decrease considerably. Even if the other consumptions are taken into account, the electrical efficiency is still expected to be higher than the one of incineration plants, which usually is lower than 25%. It must also be taken into account that not only electrical power is produced but also heat and hydrogen are generated. These contribute to the efficiency in a significant way, resulting in some cases almost in a 30% increase. Most of the established cogeneration technologies are able to convert about 70% or more of the fuel at their input into electricity and heat. If the system under study is evaluated only as a combined heat and power plant, the thermal efficiency is considerably lower than the one of these power plants since it is around or below 60% in most cases. However, if the exergy efficiency is taken into account it can be seen how the system proposed has significantly better performances than most of the common CHP technologies, being always larger than 40%. This is mainly due to the high electrical exergy efficiency, since the heat produced can reach just 30% of the electrical power at most and only when the system is characterized by larger irreversibilities. Nonetheless, the heat available is at higher temperature than conventional CHP plants, which means that it is of better quality and its exergy is higher.

The ability to generate also hydrogen is of particular interest. In fact, most of the hydrogen that is produced with current technologies derives from fossil fuels. With the studied system, hydrogen is generated from a "waste" flow, since at the same time it originates from organic waste and it is extracted from the anode outlet gas, which could be seen as a "spent" flow. Considering the base input flow and the most efficient conditions for such input, which are at a fuel utilization equal to 0.6, 2334 kg (28577 m<sup>3</sup>) of hydrogen can be produced daily. This becomes only 259 kg at  $u_f = 0.9$  and the same waste flow rate. If the system input is decreased or increased, the amount of hydrogen generated varies accordingly. Therefore, the flow of hydrogen available can vary largely depending on the operating conditions. In particular, it is interesting to note the variation in hydrogen produced per unity decrease in electrical power. In energetic terms, an average of 2 kW of hydrogen are produced for each kW of electrical power not produced. This means that the increase in generation of H<sub>2</sub> is about 200% the variation in power. Such value changes depending on the system input and the fuel utilization. At low input and fuel utilization, a unity decrease in power can cause an increase in hydrogen flow as low as 16%, while at high waste flow and  $u_f$  such value can almost reach 400%. This derives from the previous considerations, i.e. the larger irreversible heat available at high current density and the larger amount of hydrogen burnt in order to satisfy the minimum temperature difference at low fuel utilization. However, the amount of hydrogen produced is considerably lower

than the one of plants working specifically for hydrogen generation. Nonetheless, several useful products are available at the output of the system studied.

The system works at optimal exergy and energy efficiency when the fuel utilization is low, thus a consistent hydrogen flow could be produced when the system is operated changing only the input flow rather than the fuel utilization. Although electrolysis using renewable energy could represent a more efficient approach, the system here presented is also able to provide power and heat along with hydrogen. Compared to electrolysis as a grid balancing option, this system is not only able to reduce its output but also to increase it when the demand is higher than the supply. Moreover, the efficiency of the system is almost constant if it works at constant fuel utilization while the quantity of the products changes. This is an important characteristic for a balancing plant, since it allows an almost always optimal operation. On the contrary, when the fuel utilization is varied, the ratio between the products changes, shifting to a larger power generated and low heat and hydrogen at high fuel utilization and the opposite at low  $u_f$ . However, the range of loads at which it can work is not large, even though the maximum power considered is 165% higher than the lowest one. Moreover, it must be assessed if all the operating points are feasible. As already mentioned, the main constraints on the balancing operation are the flow rate at the input of the gasifier and the air flow rate required by the SOFC stack. In fact, other parameters like temperature and pressure were kept constant for every flow most of the time.

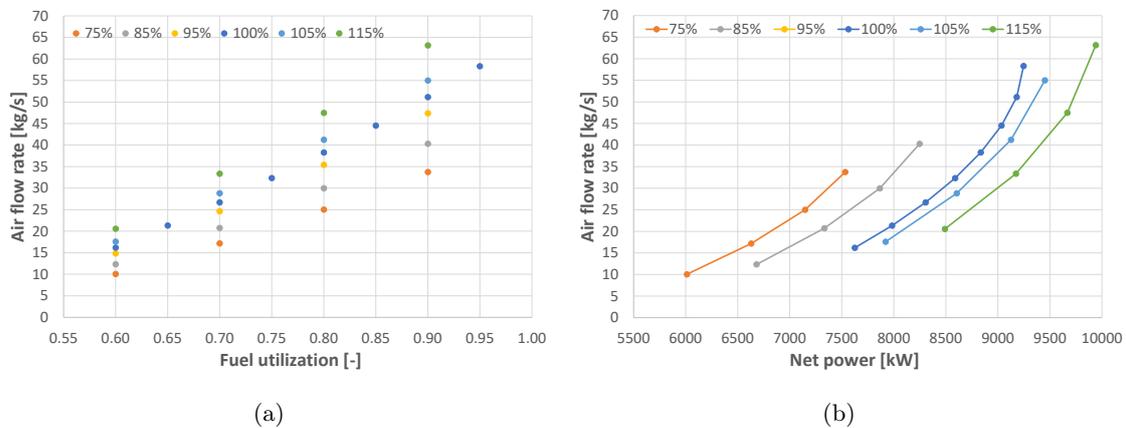


Figure 4.13: Air flow rate for different system inputs as a function of: (a) fuel utilization, (b) net power

In Figure 4.13 the air flow rates for the different waste flows and fuel utilizations are represented. It can be observed that large variations occur when the system input or  $u_f$  are modified. In particular, considering the waste flow rate - which varies only slightly with respect to the one in Table 4.1 - the air flow rate is significantly larger, especially for higher fuel utilizations. This is due to the fact that the oxidant utilization is low because the cell is operated at constant temperature and at constant inlet and outlet temperature

difference. As a matter of fact, the oxidant utilization does reach values as low as 10.1% when the fuel utilization and the waste flow rate are maximum and in general is always lower than 30%. Such low values affect positively the performance of the fuel cell in terms of voltage but imply larger air flow rates than strictly required, resulting in a substantial electrical consumption. Moreover, components must also be sized accordingly, which causes an increase in the investment cost. Such components must also be able to permit the flow rate variation when the load is changed. As shown in Figure 4.14, the air flow rate varies between 26.3% and 165% of the base flow rate going from the minimum to the maximum power considered. If it is assumed that the maximum flow rate variation that the system is capable of accommodating is 50%, considered for both positive and negative variation, the power range at which the system can work reduces considerably. This would have about 6.74 MW as lower limit and approximately 9.85 MW as upper limit. Therefore, the decrease in the operation range would be significant. However, it must be noticed that these variations are expressed with respect to the reference case, which would not be the design point according to the considerations of the efficiency already seen.

Another important characteristic of the system under study is its environmental impact in terms of emissions. If the same amount of waste were burnt in an incineration plant, assuming all the carbon present in the fuel converted into CO<sub>2</sub>, 1.77 kg/s of carbon dioxide would be released in the environment, considering the base conditions. This would not impact negatively on the environment, being the carbon absorbed by the biomass in the first place. However, the system under study is not only able to operate at constant CO<sub>2</sub> balance, but even generating a carbon negative impact. In fact, part of the carbon dioxide generated in the gasifier is captured by the calcium oxide, avoiding further discharge in the atmosphere. Although such gasification technology is modelled in a simplistic way for the purpose of assessing the feasibility and general performance of the system, the avoided emission can approximately be estimated. In particular, it can be observed that the carbon dioxide flow exiting the plant is not dependent on the fuel utilization but only on the flow rate at the input of the gasifier. Therefore, the amount of CO<sub>2</sub> emitted can be evaluated. For the base system input, the flow rate of carbon dioxide present at the outlet is 0.96 kg/s, resulting in 0.81 kg/s not emitted. This accounts for approximately 46% of the emission that would have occurred if the waste were combusted. In general, the avoided discharge is always between 0.61 kg/s and 0.93 kg/s for every input considered and always results in about 46% of emissions avoided. In other terms, about 0.78 kg of CO<sub>2</sub> for each kilogram of waste are not discharged. Compared to conventional carbon capture methods, sorption enhanced gasification provides considerably better results. In fact, no power consuming and expensive processes are required for capturing CO<sub>2</sub> from flue gases before the discharge. Moreover, carbon dioxide is separated when it has the highest concentration in the system. Nonetheless, thermal energy is required for the regeneration of the CaO sorbent, although the overall performance of the system is expected to be superior compared to conventional technologies which a carbon sequestration unit is added to. However, the challenge of disposing of the captured carbon dioxide has still to be addressed.

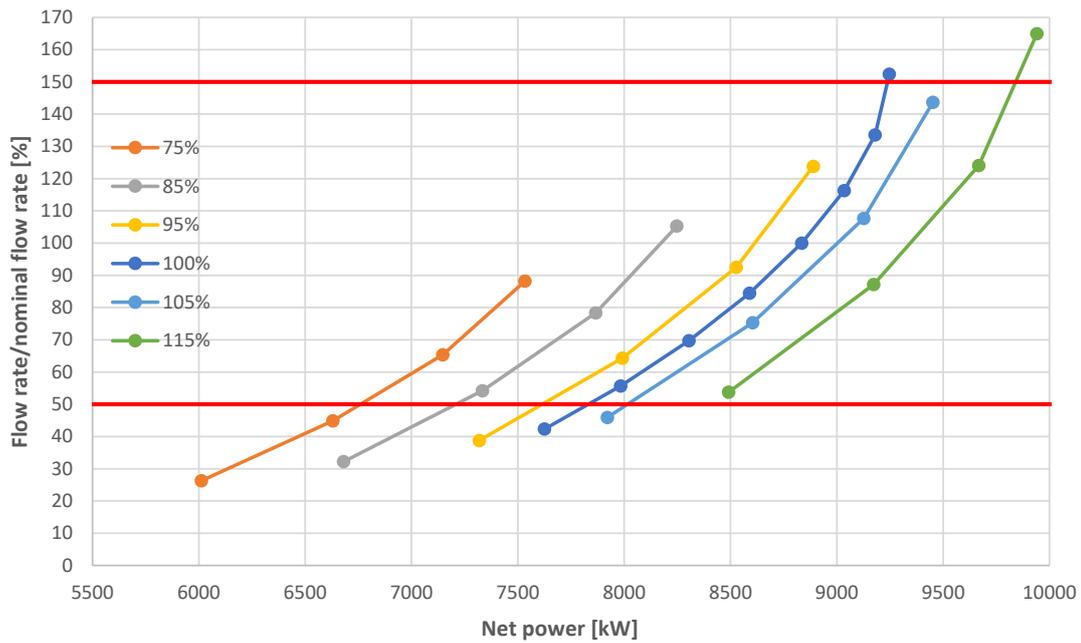


Figure 4.14: Air flow rate variation with respect to the base case as a function of the net power. The red lines show the upper and lower limit considered

The results obtained show that the concept of the system studied in this report could fit well in a future renewable scenario. In addition to generating power, heat and hydrogen and processing waste, the plant could also contribute to reducing the carbon dioxide present in the atmosphere. In particular, considering an average between the minimum and maximum release of carbon dioxide that is avoided and a plant capacity factor of 80%, about 19.4 thousand tons of CO<sub>2</sub> could be "extracted" from the environment yearly. At the same time, the system is able to convert the waste at the input with high efficiency. Therefore, further evaluations of the concept proposed might be of interest in order to provide a good solution for both waste disposing and integration services for the operation of the electrical grid.

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