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Master of Science Thesis CARBON CAPTURE AND UTILIZATION - SYNTHETIC FUELS

Making synthetic fuels for the residential sector via solid oxide electrolysis and catalytic upgrade using recovered carbon dioxide and residual biomass

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Abstract

Nowadays, an interest towards new fuels and new ways of storing energy has grown in the framework of the progressive independence from the more traditional fuels. The global warming and the terrible increase in the level of air pollutants require an immediate intervention and a change of course.

This study fits perfectly into this changing scenario, regarding actually the Power to Gas concept. In fact, the aim of this work is to substitute the fossil fuels traditionally exploited in the Italian residential sector with Synthetic Natural Gas (SNG) - produced via high temperature solid oxide co – electrolysis, followed by catalytic upgrade, i.e. a methanation step - and hydrogen produced via high temperature solid oxide steam electrolysis.

Different carbon sources, together with water available from the national public network, have been considered as feedstocks. Only energy from renewable energy sources has been considered to be fed to the various plants, in order to make the different pathways greener. Several scenarios have been outlined regarding the SNG production, because the upgrade of the different resources resulted in both pure carbon dioxide and raw syngas to be fed to the plants.

The results are presented comparing the demand covered with current resources' availability and the demand entirely satisfied with resources and electrical energy integration.

1. Introduction

In the last years, a clear necessity of moving from traditional fuels, intended as fossil ones, to alternative and synthetic fuels has arisen. Furthermore, the possibility of producing synthetic green fuels from "recycled" CO₂ can give a new direction to the global concern of mitigation of the greenhouse gases (GHG) emissions and help their management.

At the same time, the increasing production of electrical energy from renewable energy sources (RES) through the years has created new problems and new tasks to be answered. Usually, the electricity produced this way depends on the variability of the primary sources, so it is more difficult to dispatch and exploit with respect to the one produced in the traditional ways. This is directly linked to the second big problem around these new technologies: the energy storage. Due to the variable nature that characterizes the energy from RES, finding a way to store it and then use it in a second moment is mandatory. The most diffused technology nowadays is the pumped hydro, but this is only a partial solution, characterized also by finite capacity.

In this context, finding a way to alternatively exploit the energy from RES is recommended. One of these ways concerns the Power to Gas concept, that consists of using electrical energy to produce synthetic fuels, which can be hydrogen – rich gases or methane – rich gases.

The study that has been here conducted perfectly fits in this framework. Both hydrogen and Synthetic Natural Gas (SNG) have been considered as potential synthetic fuels to replace the fossil ones traditionally exploited in the residential sector. The reality chosen to be analysed is the Italian one, both on a regional basis and on national level.

The production of hydrogen can be achieved from simple water electrolysis using high temperature Solid Oxide Electrolytic Cells (SOEC). The same technology is exploited for the production of syngas via water and carbon dioxide co – electrolysis. This syngas is then catalytically upgraded via methanation process to obtain as final product SNG. Giglio et al. [1] compared together the results of two different plants for the SNG production, one considering simple steam electrolysis with respect to the other considering co – electrolysis, showing that the second setup is characterized by better performances.

The carbon sources considered in this study are:

• Carbon dioxide recovered from thermoelectric power plants, extracted via Acid gas removal process (Rectisol)

- Carbon dioxide from biogas upgrade via Amine scrubbing technique (aMDEA)
- Carbon rich syngas from residual biomass, gasified via Viking two stage gasifier.

The water is provided from the national public network, and can be considered nearly an infinite resource. Finally, the only way to keep these pathways green is to use only electrical energy from RES.

The technologies analysed in this study have reached at least pre – commercial status. Gasification technology is fully mature, even though the issue of tars is still a real concern. The same goes for Rectisol and aMDEA, established realities. Methanation technology is already at commercial status too, coupled to MW – scale H₂ electrolysis plants [2] [3]. A SOEC plant is actually at pre – commercial status, in the context of project GrInHy [4].

The aim of this work is the technical feasibility of these technologies based on input / output energy data. The fraction of satisfied demand with and without electrical integration will be analysed and investigated to verify the effective coverage that can guarantee each of these scenarios, starting from the work conducted by Monaco et al. [5] for the Italian transportation sector.

In the following of this chapter, a theoretical introduction has been done. It explains the concept of power to gas and briefly describes the electrolysis process and technologies.

In chapter 2, the main assumptions adopted for the fuel synthesis processes are listed. Three plant configurations have been modelled in Aspen Plus[®] for this study, two devoted to the production of SNG starting from different feedstocks, and one to the production of hydrogen. A detailed description of the various components of each plant is also performed.

In chapter 3, the composition of the energy demand referred to the Italian residential sector is described, with a further calculation of the energy consumption referred to the current year 2018. Afterwards, the resources' availability, together with the pathways to exploit them, is analysed

In chapter 4, the different scenarios and cases analysed are listed. For each case, the results are shown via graphs and tables, and then critically discussed, making also a final comparison among all of them.

The last chapter is the conclusion of the study.

1.1 Overview on Power to Gas concept

Power to Gas concept covers all the technologies capable of converting electrical energy to a gaseous fuel, which could be hydrogen – rich gases or methane – rich gases.

As can be seen in Figure 1, the first step is the electrolysis process, where the electric energy necessary to drive the process can be supplied either from renewable energy sources or from the grid. After that the produced hydrogen can be used for different purposes: it can be used to produce methane, or directly exploited in industry, in the transportation sector or for heating requirements. It is also possible to directly inject the hydrogen into the grid, even though actually there are no infrastructures dedicated to it.

In general, is preferable to exploit the hydrogen to produce methane via catalytic upgrade for several reasons:

- Methane has a higher energy density with respect to hydrogen, and its combustion is less problematic since it reaches lower flame temperatures.
- SNG has already an existing infrastructure that covers potentially the whole Europe, while hydrogen does not have any.
- It is almost a "carbon neutral" way to produce natural gas, since the carbon dioxide exploited to produce the syngas that afterwards will be turned into the natural gas itself is part of the CO₂ sequestrated from the one emitted because of the combustion of the natural gas produced this way.

The Synthetic Natural Gas can then be exploited in almost every sector, since it is one of the most flexible gases ever used.



Figure 1. Scheme about the Power to Gas concept [6]

1.2 Electro chemical cells

Chemical energy is a property that characterize a stream of mass of a specific substance. It can be seen as a potential form of energy. Chemical energy is the starting point of the production of electrical energy.

The classical ways to exploit chemical energy are:

- Thermo chemical transformation: production of high temperature heat usually via combustion.
- Thermo mechanical transformation: production of mechanical power at the shaft in a thermodynamic cycle fed by heat at high temperature.
- Electro mechanical transformation: production of electrical power in an alternator.

As it can be seen, these are very complex and inefficient ways to produce electrical energy starting from chemical energy, because several steps are needed, and each step involves its own efficiency. The overall efficiency is the product of the single ones.

In the last few years the research has made great strides in the field of direct conversion from chemical to electrical energy. These new technologies are the electro chemical cells, that are generally characterized by high efficiencies and low irreversibilities. They can be run in both "directions", intended as:

- Chemical to electrical energy transform: ΔG < 0 exploited in order to produce electric power.
- Electrical to chemical energy transform: ΔG > 0, so an external supply of electricity is needed to produce high valuable chemical species.

1.2.1 Working principles of electro chemical cells

The cell is composed of three main sections:

- Anode: electrode where the reaction of oxidation occurs, so a delivery of free electrons is involved. It will be established the equilibrium R₁ ↔ O_x + e⁻.
- Cathode: electrode where the reaction of reduction occurs, with a gain of free electrons.
 The equilibrium on this side is R₂ + O_x + e⁻ ↔ P.
- Electrolyte layer: layer that physically separates anode from cathode. Its function is to conduct ions and to be molecular – proof and electrons – proof. So, its main characteristics must be high ionic conductivity, low molecular diffusivity and low electronic conductivity.

 R_1 , R_2 are the reactants, P is the product, O_x is an ion, e^- represents one or more electrons.

The reaction that globally occurs is $R_1 + R_2 \rightarrow P$. Even if there is no direct contact between the two reactants, the reaction takes place because the ions can travel in the electrolytic layer, as said just before, while the electrons are conducted in an external circuit linking the anode and the cathode.

Due to the redox reaction, the phenomenon of charge separation occurs, and it causes the generation of electrical fields on both electrodes. This gives rise to a potential gradient ΔV between the two electrodes. By closing the external circuit, the equilibriums at the two electrodes are broken and a current I is generated by electrons flowing. The presence of both a current and a potential gradient will generate electric power, according to $W_{el} = \Delta V * I$.

A galvanic cell is an electro chemical cell in which the disequilibrium of reactants in terms of Gibbs free energy is directly transformed into electrical power. An example of global reaction occurring is $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$, with $H_2 \leftrightarrow 2H^+ + 2e^-$ as oxidation and $\frac{1}{2}O_2 + 2H^+ + 2e^- \leftrightarrow H_2O$ as reduction, in case of cationic electrolyte.

An electrolytic cell is an electro chemical cell in which a not spontaneous reaction, so characterized by a positive variation of Gibbs free energy $\Delta G > 0$, is driven by electrical power. The polarity of electrodes is inverted with respect to galvanic cells.

Cells can be classified in open and closed systems. In an open system, the reactant molecules are continuously supplied to the cell in form of stream of mass. Usually the electrodes don't take

part in the chemical reactions and their material remains unchanged. Fuel cells belong to this category. On the other hand, closed systems are fed by molecules which don't come from the external environment, but they are contained in the electrodes' structure. Therefore, electrodes physically participate in the chemical reaction and there is no external feeding. Typically, batteries are closed systems, with some exceptions like the promising technology of Lithium – air batteries that can be classified as half – opened cells.

Both systems can work in discharge regime, where the fuel is characterized by a $\Delta G < 0$ and the product is $W_{el} > 0$, power production, or in charge regime, where power is absorbed, $W_{el} < 0$, in order to produce chemical species, $\Delta G > 0$, or restore the electrodes in the batteries.

1.3 Electrolyzers

Electrolyzers are open electro chemical cells working in reverse mode.

The polarization curve for a specific electrolyzer is nearly symmetric, with respect to the line V_c = OCV, to the one of the associated fuel cell. For example, let's consider the Solid Oxide electro chemical cell:

- In direct operation (SOFC), the cathodic reaction is $H_2 + 0^{2-} \rightarrow H_2 0 + 2e^-$.
- In inverse operation (SOEC), the cathodic reaction is $H_2 0 + 2e^- \rightarrow H_2 + 0^{2-}$.

These two reactions have different rates of reaction and require different catalysts to improve their rate. For instance, if the catalyst is optimized for direct functioning, the rate of backward reaction is going to be penalized, and the polarization curve for inverse operation is going to be slightly above the perfectly symmetric one.

Electrolyzers are used to produce chemicals with high economic or thermodynamic value. The pathways commonly followed are the next two:

- H₂O splitting, with hydrogen production: $H_2O \rightarrow H_2 + \frac{1}{2}O_2$.
- CO₂ splitting, first step for syngas production: $CO_2 \rightarrow CO + \frac{1}{2}O_2$.

Both are exploited in the plants taken into account in this study, and that will be further on analyzed.

The three main commercial electrolyzers are:

 Proton Exchange Membrane Electrolytic Cell – PEMEC: Low temperature (50 ÷ 80 °C) application, used to produce hydrogen. High stability and controlled cost.

Anodic reaction: $H_2 O \rightarrow \frac{1}{2}O_2 + 2H^+ + 2e^-$ Cathodic reaction: $2H^+ + 2e^- \rightarrow H_2$

• Alkaline Electrolytic Cell – AEC:

Low temperature (50 ÷ 80 °C) application, used to produce hydrogen. Less commercially widespread than PEMECs. The electrolyte layer is usually composed of $KOH + H_2O$ or $NaOH + H_2O$, with the ionic conduction phase at around 30 %.

Anodic reaction: $2OH^- \rightarrow \frac{1}{2}O_2 + 2e^- + H_2O$

 $2H_2O+2e^- \rightarrow H_2+2OH^-$ Cathodic reaction:

Solid Oxide Electrolytic Cell – SOEC: •

High temperature (700 - 800 °C) application, allows fuel flexibility. The electrolyte is a solid ceramic layer, involving lower complexities with respect to a liquid one. This technology is the most competitive and widespread nowadays, and it's characterized by high overall efficiencies.

Anodic reaction:
$$0^{2-} \rightarrow \frac{1}{2}O_2 + 2e^-$$

Cathodic reaction: $H_2O + 2e^- \rightarrow H_2 + O^{2-}$

Cathodic reaction:



Figure 2. The operating principle of PEM electrolyzer [6]



Figure 3. The operating principle of SOEC cell [6]

1.3.1 Electrolyzers comparison

AEC always works in exothermic regime due to the fact that the endothermic regime is characterized by low voltages and currents. For this reason, a heat exchanger is mandatory in order to remove the heat produced by the system operation.

SOEC is the most performing due to its low Open Circuit Voltage, lower than the one of PEMEC and AEC because the temperature increase involves a decrease in the ΔG and thus in the OCV itself. SOEC is also characterized by lower activation and ohmic losses, meaning that at a given or fixed current of operation, it requires a lower voltage and thus a lower amount of power that has to be supplied.

Another point in favor of SOEC is the so called "fuel flexibility": SOEC can perform co – electrolysis of H_2O and CO_2 at the same time. Before the cell's inlet, a mixer merges the stream of mass of CO_2 with the one of H_2O .

$$H_20 + 2e^- \rightarrow H_2 + 0^{2-}$$

 $CO_2 + 2e^- \rightarrow CO + 0^{2-}$

Operating in co -electrolysis mode, a SOEC is able to produce at the outlet syngas, which is a mixture of H₂ and CO and the starting point of synthetic methane production via methanation.

$$3H_2 + CO \rightarrow CH_4 + H_2O$$

On the other hand, in a PEMEC the co – electrolysis can't take place. This is due to the fact that the two following reactions are in competition:

$$2H^+ + 2e^- \rightarrow H_2$$

$$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$$

For kinetic reasons, the first one is always prevailing and actually the second one never takes place. Furthermore, if CO could be produced, it would poison the Platinum contained in the electrodes. So, there are no conditions for CO production.

2. Plants setup

The solutions identified to substitute the tradition fuels nowadays used in the residential sector are two gaseous fuels, in the specific synthetic natural gas SNG and hydrogen H_2 . Three plants were designed in order to produce them: two for methane, because the several feedstocks available to produce it needed different feeding pathways, and one for hydrogen.

The plant for the SNG production fed with pure CO_2 will be identified with number 1, the one fed with syngas will be identified with number 2, and finally the plant for the hydrogen production will be identified as plant 3.

The plants have been modelled using the software Aspen Plus[®]. In the following sections, each component, together with the assumptions associated to it, is listed, in order to be able to reproduce the same plants if necessary.

2.1 Hypotheses and assumptions

Regarding the plant 1 and 2 heat balance, the heat necessary for the steam production is provided by the exothermicity associated to the synthesis process, i.e. the methanation process [7]. On the other hand, the heat necessary to pre – heat the SOEC's entering flows is recovered from the same SOEC outlet flows [8]. For these reasons, the thermal energy associated to the co – electrolysis process has not been taken into account in the external energy demand. For plant 3, the most conservative option in term of energy expenditure has been considered in the efficiency calculation, due to the lack of a pinch analysis performed on the plant (see section "4. Results").

For each plant, the SOEC is operated at the same conditions: 850 °C and at its corresponding thermo – neutral voltage, thus reaching the highest overall efficiency [9]. The thermo – neutral voltage is defined as

$$V_{tn} = \frac{\Delta h_{react}(T, p)}{z \cdot F}$$

where V_{tn} is the thermo – neutral voltage itself [V], $\Delta h_{react}(T,p)$ is the enthalpy variation at operating conditions [J/mol], *z* is the number of electrons transferred in the reaction and *F* is the Faraday constant, equal to 96485.33 C/mol.

For plant 1 and 2, whose task is the production of synthetic natural gas, the SOEC pressure, that coincides with the synthesis section's pressure, has been set to 33 bar, in order to take advantage of the methanation reaction occurring at the SOEC cathode and to further reduce the energy demand for compression [1]. For plant 3 the choice was the same, dictated however by the necessity of producing hydrogen in pressure, and then compressing liquid water is far less expensive then compressing gaseous hydrogen.

Furthermore, the Reactant Utilization RU has been fixed to 70 % [10]. It is defined as

$$RU = \frac{\dot{n}_{react,in} - \dot{n}_{react,out}}{\dot{n}_{react,in}}$$

where $\dot{n}_{react,in}$ and $\dot{n}_{react,out}$ are respectively the inlet and outlet molar flows [mol/sec].

Another assumption common to every plant is the imposition at the inlet of a minimum hydrogen molar concentration Y_{H2} of 10 %, in order to avoid nickel Ni oxidation at the cathode side and thus to preserve it healthy. This has been achieved recirculating part of the SOEC outlet

product, except in plant 2 where it was naturally respected, due to the nature of the syngas fed to the plant.

Only for plant 1 and 2, the operation of the cell has been modeled in order to achieve an outlet syngas with an optimal Feed Ratio FR, in order to maximize the subsequent synthesis section, i.e. the methanation. The Feed Ratio FR is defined as

$$FR = \frac{H_2 - CO_2}{CO + CO_2}$$

and has been set equal to 3, according to [1]. The water stream in those plants is modulated and co – fed at the cathode inlet in order to match the desired outlet FR.

Last note regarding the methanation section in plant 1 and 2. The total number of methanators is equal to two, and they are isothermal reactors working at 250 °C, with water separation in between. More detailed information in the future section "The methanation analysis".



Figure 4. SNG product quality with respect to Feed Ratio's values

2.2 Co – electrolysis plants - plant 1 and 2

The external resources needed to run both these plants are water and electrical energy, as for the plant for the steam electrolysis. On the other hand, in this case the goal is to perform the co – electrolysis followed by a methanation step to obtain synthetic methane. A carbon source is therefore needed. Three are the resources taken into account in this study:

- Carbon dioxide CO₂ from power plants' exhausts, extracted via Rectisol process.
- Carbon dioxide CO₂ derived from biogas upgrade via amine scrubbing process.
- Syngas from gasified residual biomass.

Nitrogen N_2 is also needed in the final section of the plant, in order to meet the Italian law requirements for injection into the gas grid [11].

The two plants for co – electrolysis considered are very similar with a lot of components in common. They are different because plant 1 is fed with pure carbon dioxide from the first two feedstocks, while plant 2 with syngas. The specific differences between the two configurations will be further highlighted in a while.

The plants are composed of:

• Water feeding section:



Figure 5. Water feeding section

 \circ Inlet: stream of mass of pure water H₂O at temperature of 25 °C and pressure of 1 bar. The quantity of water entering the system is regulated using a design specification which imposes the Feed Ratio FR equal to 3, with a precision of 1 e^{-3} . The FR is defined as

$$FR = \frac{H_2 - CO_2}{CO + CO_2} = 3$$

For the water amount it is imposed the lower limit equal to $CO_{2_{in}}/10$ and the upper one to $CO_{2_{in}}\cdot 10$. The value of 3 is imposed since it's the optimal ratio for the methanation process, which takes places after the co – electrolysis [1].

- Pump: $\varepsilon_{pump} = 0.8$, $\varepsilon_{driver} = 0.95$. It brings water pressure to 33 bar, it requires electrical energy to work.
- Economizer evaporator superheater: series of three components whose function is to heat the water up to 100 °C, make it evaporate and then overheat the steam up to 850 °C. Pressure losses are neglected in the model.
- Carbon dioxide feeding section (plant 1):



Figure 6. CO2 feeding section, plant 1

- Inlet: stream of mass of 1 kg/s of pure carbon dioxide CO₂ at temperature of 25
 °C and pressure of 1 bar.
- \circ Compressor: ε_{isentropic} = 0.85 and ε_{mechanical} = 0.95. It brings carbon dioxide pressure to 33 bar, it requires electrical energy to work.
- \circ $\;$ Heater: it raises carbon dioxide temperature to 850 °C.
- Syngas feeding section (plant 2):



Figure 7. Syngas feeding section, plant 2

 Inlet: stream of mass of 1 kg/s of syngas, with the molar composition listed below, at temperature of 25 °C and pressure of 1 bar.

Dry syngas molar composition			
Component:	Percentage:		
H ₂	49,07%		
СО	32,42%		
CH ₄	0,01%		
H ₂ O	1,37%		
CO ₂	17,02%		
N ₂	0,11%		

- $\circ \quad \text{Compressor: } \epsilon_{\text{isentropic}} = 0.85 \text{ and } \epsilon_{\text{mechanical}} = 0.95. \text{ It brings syngas pressure to 33}$ bar, it requires electrical energy to work.
- Heater: it raises syngas temperature to 850 °C.
- SOEC section:



Figure 8. SOEC section with recirculation, plant 1



Figure 9. SOEC section without recirculation, plant 2

- Mixer 1: it mixes the two inlet streams together, steam and carbon dioxide in the case of plant 1, steam and syngas in the case of plant 2.
- Mixer 2: it mixes the inlet stream with the fraction of product recirculated. This component is present only in plant 1, because plant 2 has no recirculation

pathway due to the fact that the inlet mixture has already a molar fraction of hydrogen Y_{H2} greater than 10 %.

- Heater: during the mixing process there is a loss of few degrees of temperature.
 This component heats the stream up to 850 °C again.
- SOEC: Solid Oxide Electrolytic Cell. It works at 850 °C without pressure losses. Electrical energy from an external source is needed. It works at thermoneutral conditions. The two reactions that take place are $H_2O \rightarrow H_2 + \frac{1}{2}O_2$ and $CO_2 \rightarrow CO + \frac{1}{2}O_2$. The reactant utilization RU has been set to 70 % [10].

SOEC electrical data				
Plant 1 Plant 2				
Total current [A]	17539098	12575905		
Thermoneutral voltage [V]	1,2227	1,1128		
Power input required [MWe]	21,446	13,994		

- Oxygen separator: fictitious component, it perfectly removes the oxygen from the SOEC's outlet. The pure oxygen is then cooled down and can be further utilized for example in oxyfuel combustion, in the medical field or in other applications. In the case of plant 2, this oxygen is exploited in the Viking two – stage gasifier to upgrade the residual biomass to the syngas which is entering the plant itself (see the section "Residual biomass" for more detailed information)
- Gibbs reactor: another fictitious component, whose function is to simulate the secondary chemical reactions between sub – products that take place in the SOEC, like the Water Gas Shift WGS one.
- Splitter: component that is present just in plant 1, as previously stated. It recirculates part of the product stream. The split fraction is regulated via a design specification which imposes a molar fraction of hydrogen Y_{H2} in the mixed stream equal to 0.1, with a precision of 1 e⁻⁴. This is necessary in order to preserve the nickel Ni catalyst layer and thus avoid any electrode mechanical stress. The presence of hydrogen favours the recombination of any nickel oxide through the chemical reaction $NiO + H_2 \rightarrow Ni + H_2O$.

• Methanation section:



Figure 10. Methanation section

- Cooler: it cools down the SOEC's outlet from 850 °C to 250 °C, in order to be able to perform isothermal methanation at the chosen temperature.
- Methanator 1: isothermal Gibbs reactor, it works at 250 °C without pressure losses. The two global reactions of methanation are:

$$CO + 3H_2 \rightarrow CH_4 + H_2O$$
$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$$

- Cooler: it cools down the stream from 250 °C to 35 °C, in order to be able to further separate water from the mixture.
- Water separator: it perfectly removes condensed water from the mixture. This step is fundamental in order to push carbon conversion to higher values, shifting the reaction's equilibrium towards the products, by removing the unwanted one of the two products.
- Heater: it heats the stream up to 250 °C, ready to be sent to the second methanator.
- Methanator 2: isothermal Gibbs reactor, it works at 250 °C without pressure losses.

CO ₂ conversion rate				
	Plant 1	Plant 2		
Step 1	97,420%	97,312%		
Step 2	99,794%	99,761%		

• Product refining section:



Figure 11. Product refining section

- Cooler: it cools down the stream from 250 °C to 35 °C, in order to be able to further separate water from the mixture.
- Water separator: it perfectly removes condensed water from the mixture. Now the stream is composed almost completely of methane, with traces of hydrogen and carbon dioxide.
- Compressor 1, intercooler, compressor 2: series of components whose function is to raise SNG pressure from 33 to 60 bar, as required by the Italian law [11]. The two compressors are isentropic compressors, with efficiencies $\varepsilon_{isentropic} =$ 0.75 and $\varepsilon_{mechanical} = 0.95$. The compression process is subdivided into two subprocesses, characterized by the same compression ratio β . This is generally defined as $\beta = \frac{p_{out}}{p_{in}}$. The specific β for the two compressors was calculated as $\beta_1 = \beta_2 = \beta = \sqrt{\frac{60}{33}} = 1.3484$. The first stage of compression reaches 44.4972 bar, while the second one reaches the final pressure of 60 bar. The compression is obviously an exothermic process, so between the two compressors there is

an intercooler, which has to cool down the SNG back to 35 °C before it enters

the second stage of compression.

Nitrogen feeding section:



Figure 12. Nitrogen feeding section

• Inlet: stream of mass of pure nitrogen N_2 at temperature of 25 °C and pressure of 1 bar. The quantity of nitrogen entering the system is regulated using a design specification which imposes the Gas Gravity GG at least equal to 0.5548, with a precision of 1 e⁻³. The Gas Gravity is defined as

$$GG = \frac{\rho_{gas}}{\rho_{air}}$$

This ratio is imposed because of the Italian legislation [11], which will be explained more in detail in a further specific section (see "The requirements of the Italian law about the gas grid injection").

• Compressor 1, intercooler, compressor 2: series of components whose function is to raise nitrogen pressure from 1 to 60 bar, as required by the Italian law [11]. The two compressors are isentropic compressors, with efficiencies $\varepsilon_{isentropic} =$ 0.75 and $\varepsilon_{mechanical} = 0.95$. The compression process is subdivided into two subprocesses, characterized by the same compression ratio β . The specific β for the two compressors was calculated as $\beta_1 = \beta_2 = \beta = \sqrt{\frac{60}{1}} = 7.74597$. The first stage of compression reaches 7.7460 bar, while the second one reaches the final pressure of 60 bar. The compression is obviously an exothermic process, so between the two compressors there is an intercooler, which has to cool down the nitrogen back to 35 °C before the second stage of compression. • Final section:



Figure 13. Final section

- Mixer: it mixes together the stream of SNG and the stream of nitrogen. At this point, the law requirements [11] (Gas Gravity, Wobbe Index, Lower Heating Value and Hydrogen Percentage) must have been respected.
- Cooler: it cools down the outlet stream to 35 °C. Now the stream is finally ready to be injected into the gas grid.
- Outlet: stream of mass with molar composition listed in the table below at temperature of 35 °C and pressure of 60 bar.

Outlet stream			
	Plant 1	Plant 2	
Mass flow [kg/s]	0,365	0,447	
Molar composition:			
H ₂	0,198%	0,188%	
CO ₂	0,049%	0,051%	
CH ₄	99,749%	99,536%	
N ₂	0,004%	0,225%	
LHV [MJ/kg]	50,112	49,994	

2.3 Steam electrolysis plant – plant 3

The external resources needed to run this plant are water, taken from the water public network, and electricity, necessary to power the SOEC and for feeding auxiliary components like pumps and compressors. This plant is the number 3.

The plant is composed of:

• Water feeding section:





- $\circ~$ Inlet: stream of mass of 1 kg/s of pure water H_2O at temperature of 25 °C and pressure of 1 bar.
- Pump: $\varepsilon_{pump} = 0.8$, $\varepsilon_{driver} = 0.95$. It brings water pressure to 33 bar, it requires electrical energy to work.
- Economizer evaporator superheater: series of three components whose function is to heat the water up to 100 °C, make it evaporate and then overheat the steam up to 850 °C. No pressure losses are considered in their modelling.
- SOEC section:



Figure 15. SOEC section, plant 3

- Mixer: it mixes the water coming from the inlet with the fraction of product recirculated.
- Heater: during the mixing process there is a loss of few degrees of temperature.
 This component heats the mixture up to 850 °C again.
- SOEC: Solid Oxide Electrolytic Cell. It works at 850 °C without pressure losses. Electrical energy from an external source is needed. It works at thermoneutral conditions. The global reaction that takes place is $H_2O \rightarrow H_2 + \frac{1}{2}O_2$. The reactant utilization RU has been set to 70 % [10].

SOEC electrical data		
Total current [A] 7819364		
Thermoneutral voltage [V]	1,2906	
Power input required [MWe]	10,092	

- Oxygen separator: fictitious component, it perfectly removes the oxygen from the SOEC's outlet. The pure oxygen is then cooled down and can be further utilized in other applications or sectors.
- Splitter: it recirculates part of the product stream. The split fraction is regulated via a design specification which imposes a molar fraction of hydrogen Y_{H2} in the mixed stream equal to 0.1, with a precision of 1 e⁻⁴. This is necessary in order to preserve the nickel Ni catalyst layer and thus avoid any electrode mechanical stress. The presence of hydrogen favours the recombination of any nickel oxide through the chemical reaction $NiO + H_2 \rightarrow Ni + H_2O$.
- Product refining section:



Figure 16. Product refining section, plant 3

- Cooler: it cools down the SOEC's outlet, composed of water and hydrogen, from 850 °C to 35 °C, in order to be able to further separate water from the mixture.
- Water separator: it perfectly removes condensed water from the mixture.
- Compressor 1, intercooler, compressor 2: series of components whose function is to raise hydrogen pressure from 33 to 60 bar, as required by the Italian law [11]. The two compressors are isentropic compressors, with efficiencies $\varepsilon_{isentropic}$ = 0.75 and $\varepsilon_{mechanical}$ = 0.95. The compression process is subdivided into two subprocesses, characterized by the same compression ratio β . The specific β for the two compressors was calculated as $\beta_1 = \beta_2 = \beta = \sqrt{\frac{60}{33}} = 1.3484$. The first stage of compression reaches 44.4972 bar, while the second one reaches the final pressure of 60 bar. The compression is obviously an exothermic process, so between the two compressors there is an intercooler, which has to cool down the hydrogen back to 35 °C before it enters the second stage of compression.
- Outlet: stream of mass of 0.0817 kg/s of pure hydrogen H₂ at temperature of almost 72 °C and pressure of 60 bar, ready to be sent in a possible distribution grid or directly to a burner.

2.4 The requirements of the Italian law about the gas grid injection

The legal requirements taken as reference are drawn from "Codice di rete di Snam rete gas, revisione LXIV" [11].

The parameters that characterize the quality of the gas can be divided between chemical – physical parameters, necessary for the calculation of energy (Higher Heating Value, HHV), and parameters for the control of the natural gas quality.

The fundamental parameter for the calculation of energy is the Higher Heating Value, HHV, determined on the basis of the chemical composition of the gas.

The parameters controlling the quality of natural gas, to guarantee the safety of the transport system, as well as the interchangeability and transportability of natural gas, are several. The majority of these are intrinsically respected or not of interest in this study. On the other hand, the following ones are important and all the "product refining section" of the plants had to be set in order to meet those limits. The parameters to be considered are:

- Higher Heating Value, HHV
- Gas Gravity, GG
- Wobbe Index
- Temperature
- Pressure
- Hydrogen H₂ (formally should be considered only for the production of biomethane).

The reference conditions used here are the standard conditions (ref. ISO 13443), namely:

Pressure 101325 Pa

Temperature 288.15 K (15 °C)

The Higher Heating Value has as lower limit 34.95 MJ/Nm³ and as upper limit 45.28 MJ/Nm³. It is calculated as:

$$HHV_{CH4} = 55.662 \ \frac{MJ}{kg}$$

$$HHV_{CH4}^{NC} = HHV_{CH4} \cdot \frac{16^{kg}/kmol}{22.414^{m^3}/kmol} MJ/Nm^3$$

$$HHV_{CH4}^{SC} = HHV_{CH4}^{NC} \cdot \frac{273.15 K}{288.15 K} MJ /_{Sm^3}$$
$$HHV_{SNG}^{SC} = HHV_{CH4}^{SC} \cdot Y_{CH4} MJ /_{Sm^3}$$

With Y_{CH4} molar fraction of methane of the stream.

The Gas Gravity has to be between 0.5548 and 0.8. This index is responsible of the "Nitrogen feeding section" of plant 1 and 2, because to meet the lower limit is often necessary the addition of nitrogen to the stream, in order to increase its density. It's calculated as follows:

$$PM_{air} = PM_{N2} \cdot 0.79 + PM_{O2} \cdot 0.21$$
$$\rho_{air} = \frac{p}{T} \cdot \frac{PM_{air}}{8314}$$

 $PM_{SNG} = PM_{N2} \cdot Y_{N2} + PM_{CH} \cdot Y_{CH4} + PM_{CO2} \cdot Y_{CO2} + PM_{CO} \cdot Y_{CO} + PM_{H2} \cdot Y_{H2} + PM_{H2O} \cdot Y_{H2O}$

$$\rho_{SNG} = \frac{p}{T} \cdot \frac{PM_{SNG}}{8314}$$
$$GG = \frac{\rho_{SNG}}{\rho_{air}}$$

The Wobbe Index has values of acceptability from 47.31 MJ/Nm³ and 52.33 MJ/Nm³. It's defined as:

$$WI = \frac{HHV^{SC}}{\sqrt{GG}}$$

The molar fraction of hydrogen must be lower than or equal to 0.5 % Vol. This limit will be further analysed more in detail in the following sections "the methanation "issue" and "the methanation analysis".

The temperature of the outlet stream has to be in the range $3 \div 50$ °C, while the pressure has to be equal to 60 bars.

The final values measured for Plant 1 and 2 are shown in the following table:

Law limits				
	Plant 1	Plant 2		
Gas Gravity [-]	0,55431	0,55530		
Higher Heating Value [MJ/Nm ³]	37,571	37,490		
Wobbe Index [MJ/Nm ³]	50,463	50,310		
Hydrogen molar fraction [%]	0,19798%	0,18837%		

Last note, for the plant used to produce hydrogen, i.e. plant 3, there is still no law about the hydrogen displacement. This is due to the fact that there aren't an existing grid or infrastructures dedicated to this gaseous product. Hydrogen is highly explosive and volatile, and can cause steel embrittlement [12], in addition to other secondary possible problems.

My personal hypothesis for the future of this specific hydrogen technology is that the gas won't be displaced anywhere. In a possible future scenario, it will be produced on site in a district heating plant, that will cover the need of several neighbourhoods of a city. So, the only restraint put on this plant in this study was to have the hydrogen stream at a pressure of 60 bars.

2.5 The methanation "issue"

The first co – electrolysis plant modelized in this study had the methanation section composed of four adiabatic reactors with the inlet at 220 °C, with an intercooler between each one of them because of the high exothermicity of the reactions involved. A calculator was added to the *flowsheeting options* of Aspen Plus[®], with the function of monitoring the trend of the carbon conversion through the methanation pathway. It was structured in this way:

$$CO2CONV1 = \frac{NCO2IN - NCO2OUT1}{NCO2IN} \cdot 100$$
$$CO2CONV2 = \frac{NCO2IN - NCO2OUT2}{NCO2IN} \cdot 100$$
$$CO2CONV3 = \frac{NCO2IN - NCO2OUT3}{NCO2IN} \cdot 100$$
$$CO2CONV4 = \frac{NCO2IN - NCO2OUT4}{NCO2IN} \cdot 100$$

The carbon dioxide fraction after every methanator is compared with the one entering the first one, in percentage.

The final value of carbon conversion reached was equal to 97.92 %, a good result for sure. The final plant product had a molar composition of:

H ₂	1,9151%
CO ₂	0,4779%
CH ₄	96,4447%
N ₂	1,1623%

Analysing the Italian law about the injection in the grid of methane or natural gas [11], a new regulation about the percentage of hydrogen was pointed out. The presence of hydrogen can cause hydrogen embrittlement in the steel of the pipes [12] assigned to the gas displacement, with several structural problems associated. Furthermore, hydrogen raises the explosive rate of the mixture. For those reasons, a limit of the hydrogen molar concentration in the mixture was recently introduced, equal to 0.5 % Vol. of the stream [11]. In light of the above, a change to the plant was necessary. There were two possible solutions feasible:

• A membrane separator as last step of the plant, whose function is to remove the excess hydrogen from the mixture [13] [14].

 Pushing carbon conversion to higher values in order to have more methane and less hydrogen in the final product. This implies a change to the methanation section of the plant.

The first one came out to be just a partial and costly solution, and in addition it was required a temperature in the range 30 $^{\circ}$ C – 500 $^{\circ}$ C [15] [16], so the decision was to winnow several plant's solutions in order to reach the wanted hydrogen percentage. A study was made on this, taking plant 1 as case study and adopting isothermal and adiabatic reactors and water inter condensation between reactors.

2.5.1 The methanation analysis

The only section of the plant modified is the one dedicated to methanation. The cases analysed are several and they mix all the possible solutions that can be adopted.

Methanation setup:

- BASE: four adiabatic methanators (inlet at 220 °C), every time the outlet is cooled at 220 °C, without water separation.
- TEST 1: one adiabatic methanator (inlet at 220 °C), outlet cooled at 35 °C, water separated in a perfect separator (100 %), stream heated back at 220 °C, one isothermal methanator (working at 220 °C).
- TEST 2: one isothermal methanator (working at 220 °C), outlet cooled at 35 °C, water separated in a perfect separator (100 %), stream heated back at 220 °C, one isothermal methanator (working at 220 °C).
- TEST 3: one adiabatic methanator (inlet at 220 °C), outlet cooled at 220 °C, one adiabatic methanator (inlet at 220 °C), water separated in a perfect separator (100 %), stream heated back at 220 °C, isothermal methanator (working at 220 °C).
- TEST 4: three adiabatic methanators (inlet at 220 °C), every time the outlet is cooled at 220 °C, water separated in a perfect separator (100 %) before the last stage.
- TEST 5: four adiabatic methanators (inlet at 220 °C), every time the outlet is cooled at 220 °C, water separated in a perfect separator (100 %) before the last stage.

For every setup, a simulation was launched, and the carbon conversion values and final gas molar composition checked and compared together. The results obtained are shown in the next tables.

CO₂ conversion					
BASE	TEST 1	TEST 2	TEST 3	TEST 4	TEST 5
5,48%	5,48%	98,45%	5,48%	5,48%	5,48%
59,60%	99,32%	99,90%	59,60%	59,60%	59,60%
92,44%			99,59%	93,25%	92,44%
97,92%					99,50%

	Final product (molar fraction):						
	BASE	TEST 1	TEST 2	TEST 3	TEST 4	TEST 5	
H ₂	1,9151%	0,6375%	0,0991%	0,3923%	6,0353%	0,4711%	
CO ₂	0,4779%	0,1585%	0,0238%	0,0972%	1,4446%	0,1166%	
CH ₄	96,4447%	98,7644%	99,8727%	99,0698%	88,9153%	98,9716%	
N_2	1,1623%	0,4397%	0,0000%	0,4401%	3,5202%	0,4404%	

The conclusions made after these results are:

- TEST 1: partial solution. Though the carbon conversion value reached is high, over 99 %, the hydrogen fraction in the final gas is still slightly above the law limit, 0.64 %. To subject the law limit is necessary a further nitrogen dilution or a membrane separator.
- TEST 2: this solution is for sure the most performing. Both the value obtained are optimal.
- TEST 3: good solution, the hydrogen fraction is low enough to dispatch the gas produced.
- TEST 4: the worst solution, even worse than the base case. Three adiabatic reactors aren't enough to satisfy the request.
- TEST 5: another feasible solution, even if the hydrogen fraction reached is near the law limit.

The state of the art of the moment is to ideally reduce the total numbers of reactors in the plant and to adopt isothermal methanators over adiabatic ones. Considering this, the plant solution chosen is the "TEST 2", the one with two isothermal methanators with water separation in between. This solution has been further modified with the two reactors working at 250 °C instead of 220 °C because of the activation range of temperatures of the Nickel catalyst [1]. In real plants, an isothermal reactor needs a continuous removal of heat to work.

This is the definitive solution, adopted both in Plant 1 and Plant 2. The results obtained (plant 1) are the following ones:

CO ₂ conversion
97,42%
99,79%

Molar composition		
H_2	0,1980%	
CO2	0,0485%	
CH₄	99,7490%	
N_2	0,0000%	

3. Demand and resources' availability analysis

In this section, an analysis of the energetic demand in the Italian residential sector is made. Starting from the historical data available until 2008, the consumptions for the current year 2018 have been computed.

Afterwards, all the data related to the availability of the necessary feedstocks and resources have been collected. Most of them are not updated to 2018 but to previous years, because of the limited availability of data from the sources themselves. However, a significant modification of the order of magnitude of the data has not been seen, so for this study has been considered reasonable to use them.

Each region has been considered has an independent entity regarding demand and readiness of the necessary resources. This choice allows to perform a comparison among all the regions, in addition to keep the analysis coherent at the local scale. Furthermore, the analysis performed has been done only from a quantitative point of view: for each region, it has been considered a hypothetical plant exploiting just regional resources in order to satisfy just the regional demand itself.
3.1 Demand analysis

The first step of this study is to analyse the data about the energy consumption in the residential sector in Italy, on a regional scale. Those data were particularly difficult to find, because usually the residential sector is merged with "other sectors", with respect to the transportation sector or the industrial one. The only specific data found were the ones provided by ENEA (*Agenzia Nazionale Efficienza Energetica*, the Italian National Agency about the Energy Efficiency) [17]. They cover the period from 1990 to 2008.

The consumption's trend over the years is oscillating, without a periodic behaviour. The greatest peak of the period is located in the year 1999. In the last years the general trend is decreasing. An increase or decrease of the energy consumption from year to year is probably mainly due to the climatic trend of the year itself. For example, a particularly cold winter will make the annual energy consumption increase with respect to the previous year. Of course, also other secondary reasons contribute to the change of the trend. For example, the economy market situation, or an increase or a lowering of the price of the primary energy sources used, can affect the trend's behaviour.

For these reasons, no specific forecasting method, like the Holt – Winters one, can be adopted in this study. A forecast has been made up to the year 2018 through a simple trend line.

The national results and the trend line itself can be seen in figure 18. On the other hand, the data on a regional scale through the years are shown in Table 1.

The energy consumption varies from region to region due to the extension of the region itself, but above all because of the geographical position. The northern macroregion is more affected by the climatic winter conditions with respect to the central and southern ones.

ENEA also publishes every year an annual report on the energy efficiency. To cover the final period of the data found and the most recent period possible, the 2011 [18] and the 2018 [19] reports were analysed.

The analysis of the two previous reports and of the graph shown in Figure 17 can give us interesting information on how consumption is structured. The main energy source used is the natural gas, which covers more than the 50 % of the entire sector. Its consumption grows from year to year. The electric energy also plays a decisive role. The third major source of energy is disputed between diesel oil and wood. The first one has a decreasing trend over the last years.

On the other hand, the use of wood - that includes pellets, woodchips and firewood – is increasing.

The consumption of coal has been practically nil for several years. The Liquefied Petroleum Gas LPG is almost constant over the selected period. In the last few years, not shown in the graph, the share of renewable energy sources is growing, in particular solar thermal. However, they cover a minimal part of the total needs.

The increase in the natural gas consumption is partly attributable to the climatic trend, partly to the provision of heating systems in existing real estate units that did not have them, and partly to the replacement of electric boilers for the production of domestic hot water with natural gas systems. In addition, not to be underestimated the behavioural factor of the families that, formed by increasingly older members, demand from the heating plant higher operating temperatures with respect to the ones imposed by the Italian law's standards.



Energy Consumption in the Residential Sector

Figure 17. Energy consumption in the residential sector in Italy in the period 1990 – 2010 (adapted from

[18])

	Final energy consumption in the residential sector [PJ]																			
Region	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2018
Piedmont	107,8	115,8	108,6	110,1	100,6	107,8	110,8	112,1	126,0	128,1	104,3	107,8	101,5	105,3	105,3	110,9	104,8	99,3	97,4	98,9
Aosta Valley	7,6	7,7	6,9	6,8	5,4	6,5	5,3	6,7	6,8	6,2	5,6	5,8	6,4	6,5	7,5	7,3	6,6	5,7	5,2	5,7
Lombardy	263,3	295,2	273,7	267,8	241,7	263,2	272,1	271,2	294,8	296,6	215,3	222,1	212,3	221,1	219,4	225,5	210,7	197,4	204,7	157,6
Trentino - S. T.	26,7	28,7	26,9	26,3	26,1	30,3	29,3	30,7	31,0	35,0	34,8	35,9	34,2	35,9	32,1	39,1	39,4	35,4	33,0	44,0
Veneto	99,8	112,0	113,0	102,9	97,1	111,7	111,7	99,9	112,6	118,1	106,3	111,5	104,7	113,2	112,1	118,2	115,0	106,9	107,3	116,2
Friuli V. Giulia	28,9	31,9	31,8	30,1	30,4	33,1	32,5	34,0	33,3	32,8	29,0	29,7	28,6	29,0	29,2	31,6	32,2	28,2	26,1	27,7
Liguria	36,2	39,5	38,2	39,4	36,2	38,4	40,4	39,2	41,7	43,5	33,2	33,3	28,8	40,5	28,6	32,1	30,8	29,2	29,5	24,9
Emilia Romagna	113,0	126,5	113,7	117,3	103,0	111,6	111,4	112,5	126,1	130,8	102,1	106,8	105,0	113,1	115,9	120,6	114,3	109,9	110,6	110,1
Tuscany	78,9	92,1	97,2	91,8	82,8	89,7	92,6	87,7	101,3	107,7	88,6	83,1	89,6	92,1	99,2	98,0	89,7	83,0	80,2	90,3
Umbria	18,5	22,0	20,6	21,2	19,3	21,9	20,1	20,8	28,9	22,1	21,8	21,7	20,5	25,7	23,6	25,5	26,3	29,2	23,2	29,4
Marche	31,8	35,7	33,4	34,6	31,5	33,0	32,7	32,2	40,1	36,0	32,2	30,7	30,3	32,0	33,0	38,3	32,2	30,6	31,3	31,7
Lazio	94,4	100,9	88,9	99,6	93,0	101,1	92,5	96,1	114,3	109,5	91,3	100,4	94,9	99,9	100,5	104,6	103,9	93,3	96,6	102,8
Abruzzo	24,1	24,6	24,0	23,5	22,6	23,5	24,8	24,7	22,3	22,4	23,3	25,1	24,8	28,1	26,6	25,1	25,2	23,5	22,4	25,3
Molise	7,5	8,5	8,9	8,0	7,9	8,0	7,8	8,2	9,3	8,6	8,2	9,3	7,8	8,4	9,0	8,8	8,2	8,3	7,6	8,6
Campania	48,6	54,2	59,4	51,7	50,4	55,6	57,0	59,1	57,4	64,6	67,5	71,7	61,6	71,5	70,0	71,8	73,2	69,3	69,7	87,0
Apulia	37,8	41,7	42,4	43,4	41,4	45,4	46,5	41,9	39,7	40,0	42,1	43,7	43,7	46,1	45,3	48,1	47,7	44,4	41,8	48,1
Basilicata	7,6	10,3	9,4	10,0	8,2	8,5	8,9	9,0	8,7	7,9	8,1	8,3	9,3	10,1	11,1	10,3	10,2	9,5	8,9	10,3
Calabria	17,1	17,9	18,3	18,7	19,1	19,4	18,6	18,8	19,5	24,4	21,3	21,7	21,6	24,3	26,8	25,9	27,6	27,0	29,2	34,1
Sicily	33,2	35,8	38,6	37,6	35,7	38,5	38,9	38,1	37,7	42,1	37,4	40,0	39,3	38,1	45,3	40,7	40,0	40,5	37,9	44,1
Sardinia	17,2	19,7	21,6	20,8	21,7	24,2	16,5	15,8	17,3	20,9	20,0	21,2	22,0	21,8	20,7	23,2	24,7	26,1	22,1	25,8
ITALY	1100,2	1220,8	1175,5	1161,6	1074,3	1171,4	1170,5	1158,7	1268,9	1297,2	1092,3	1129,6	1086,9	1162,5	1161,3	1205,7	1162,6	1096,8	1084,6	1122,6

Table 1. Final energy consumption in the residential sector in Italy



Figure 18. Graph about the national energy consumption in the residential sector in Italy with trend line



Figure 19. Energy consumption in the residential sector in Italy, year 2018

3.2 Analysis of the available resources

3.2.1 Carbon sources

The carbon sources considered are the syngas obtained from residual biomass, the upgrade of biogas available from livestock manure, from the organic fraction of the municipal solid waste and from wastewater treatments plants and the carbon dioxide extracted from power plants' exhaust. All these resources will be further analysed in the following subchapters.

3.2.1.1 Residual biomass

The choice made at the base of this study was to proceed in the most sustainable way possible. To be consistent with this choice, the residual biomass considered is the one coming from food crops. Biomass from the cultivation of corn, sunflowers and olives has been considered, in addition to the one coming from orchards and vineyards. Residual biomass from dedicated crops wasn't taken into account, because it usually involves land exploitation.

The regional data shown in Table 2 and the graphs shown in Figure 20 are taken from the ENAMA (*Ente Nazionale Meccanizzazione Agricola*, the Italian Institution for Agricultural Mechanization) study published in the 2011 [20].

The total amount of residual biomass comes from two big "sectors": tree crops and herbaceous crops.

The tree crops include:

- Olive
- Grapevines
- Pear
- Peach
- Nectarine
- Plum
- Apricot

- Citrus fruits
- Hazel
- Almond
- Actinidia (kiwi).

On the other hand, the herbaceous crops are inclusive of:

- Cereal straws (oats, barley, rye and rice)
- Corn stalks and cobs
- Sunflower stalks.

As we can notice, the amount of residual biomass is almost directly linked to the region extension. Of course, also the land use destination affects the amount of available resource.

The residual biomass is just the basis, the primary source of the entire process. The final product of interest is syngas. The residual biomass undergoes a gasification process via the Viking two – stage gasifier. This technology was developed by the Denmark Technical University [21] and it is particularly interesting because the two stages minimize the tar production during the gasification process [22], which is the main problem and obstacle of the gasification technology itself. The gasifier operates with steam in the pyrolysis section and with pure oxygen in the gasification section. The oxygen is directly recovered from the SOEC exhaust [23] (see "Plants setup" section), making this solution even more interesting and promising.

The gasification process wasn't directly investigated in this study, so two assumptions have been taken. The first one is a typical dry syngas composition, as taken from the work of Pozzo et al. [23]:

Dry syngas mo	ar composition
Component:	Percentage:
H ₂	49,07%
со	32,42%
CH₄	0,01%
H₂O	1,37%
CO ₂	17,02%
N ₂	0,11%
	100,00%



The second one is the gasification yield as taken from a second ENAMA report [24] of $1.7 \text{ m}^3/\text{kg}$ of dry syngas starting from dry residual biomass, in normal conditions.

The amount of obtainable syngas is shown in table #. This will be fed to Plant 2 as a source of carbon monoxide CO and hydrogen H_2 . It will undergo a co – electrolysis process and a further methanation.



Figure 20. Regional biomass availability -a) Orchards pruning -b) Olive pruning -c) Wine pruning -d) Sunflower stalks -e) Corns stalks and cobs (adapted from [20])



Figure 21. Viking two – stage gasifier [21]

	Residual Biomass (dry basis) - Year 2011									
Region	Tree crops [ton]	Herbaceous Crops [ton]	Total [kton]	Total Syngas [Mm ³]	Total Syngas [kton]					
Piedmont	59861	589820	649,68	1104,46	878,42					
Aosta Valley	726	55	0,78	1,33	1,06					
Lombardy	21222	676732	697,95	1186,52	943,69					
Trentino-S. T.	32025	771	32,80	55,75	44,34					
Veneto	70897	598536	669,43	1138,04	905,13					
Friuli V. Giulia	15422	194496	209,92	356,86	283,83					
Liguria	9327	1100	10,43	17,73	14,10					
Emilia Romagna	94745	455214	549,96	934,93	743,59					
Tuscany	108375	158031	266,41	452,89	360,20					
Umbria	28476	116598	145,07	246,63	196,15					
Marche	21022	168112	189,13	321,53	255,72					
Lazio	98959	99875	198,83	338,02	268,84					
Abruzzo	54137	46160	100,30	170,50	135,61					
Molise	15958	40206	56,16	95,48	75,94					
Campania	110392	64655	175,05	297,58	236,68					
Apulia	372389	203381	575,77	978,81	778,49					
Basilicata	34826	86922	121,75	206,97	164,61					
Calabria	155283	40877	196,16	333,47	265,22					
Sicily	288347	145345	433,69	737,28	586,39					
Sardinia	61495	55702	117,20	199,23	158,46					
ITALY	1653884	3742588	5396,47	9174,00	7296,47					

 Table 2. Residual biomass and obtainable syngas data

3.2.1.2 Biogas upgrade

The biogas for the upgrade taken into account in this study comes from three different sources.

The first one of them is livestock manure, in particular from pig farms, cattle farms and buffalo farms. The regional data are shown in Table 3.

The second source of biogas is the one from the sludges coming from wastewater (WW) treatment facilities. The data are shown in Table 5.

The data for livestock manure and wastewater treatment plants are taken from the 2009 report published by ENEA (*Agenzia nazionale per le nuove tecnologie, l'energia e lo sviluppo economico sostenibile*, National agency for new technologies, energy and sustainable economic development) [25].

The third and last source of biogas is the one coming from the anaerobic digestion of the Organic Fraction of the Municipal Solid Waste (OFMSW). The data are shown in Table 4, and are taken from the national report spread by ISPRA (*Istituto Superiore per la Protezione e la Ricerca Ambientale*, the Italian Institution for Environment Protection) in the 2015 about municipal wastes [26].

As we can notice, the largest share of biogas comes from the livestock manure, then from the municipal solid waste and finally from the sludges of wastewater treatment plants.

The process selected to upgrade the biogas is the amine scrubbing technique, also known as acid gas removal. The biogas undergoes a first clean – up section to remove the unwanted pollutants, then is ready to enter in a first reactor, called absorber or absorption column. The exploited process is the chemical absorption. The raw biogas enters in contact with a solution containing activated amine (aMDEA, a mixture of Methyl Diethanolamine), characterized by high capacity and high selectivity. Adopting the amine solution allows to have lower plant's pressure with respect to a plant of water scrubbing with the same capacity. A strongly selective chemical reaction takes part between the biogas and the solution, removing carbon dioxide CO_2 from the biogas itself. The solution, now rich in CO_2 , is then send to a stripper unit, whose function is to regenerate it. To make this happen, an amount of energy is necessary, in the form of process heat to heat up the solution. The amine mixture is then ready to be sent again to the absorber. At the exit of the absorber there is a stream of clean biomethane CH_4 , whereas the stream at the stripper outlet is pure CO_2 . The obtainable amount of the two gases is shown in table #.

Depending on the primary source of biogas, the latter will have a different dry composition:

- The one derived from OFMSW and livestock manure will have a composition of 60 % CH₄ and 40 % CO₂ [27].
- The one obtained from wastewater treatment plants will be composed of 65 % CH₄ and 35 % CO₂ [28].

As previously said, the amine scrubbing process requires an energetic contribution to work. This consists of an electrical consumption of 450 kJ and of a heat demand for the solution regeneration of 2 MJ per cubic meter of methane produced [29]. To take into account these two contributions in this study, a specific electrical equivalent consumption (SEEC) of 2.5 MJ has been introduced and has been considered in the final energy consumption for the synfuels production.



Figure 22. Amine Scrubbing Technique brief scheme [30]

	Biogas from Livestock Manure									
Region	Total Biogas [MNm ³]	CH ₄ producible [MNm ³]	CO ₂ recoverable [MNm ³]	CO ₂ recoverable [kton]						
Piedmont	243,21	145,93	97,28	190,97						
Aosta Valley	10,00	6,00	4,00	7,85						
Lombardy	531,19	318,71	212,48	417,10						
Trentino-S. T.	49,00	29,40	19,60	38,48						
Veneto	172,39	103,43	68,96	135,36						
Friuli V. Giulia	28,40	17,04	11,36	22,30						
Liguria	4,01	2,41	1,60	3,15						
Emilia Romagna	201,13	120,68	80,45	157,93						
Tuscany	24,31	14,59	9,72	19,09						
Umbria	18,32	10,99	7,33	14,39						
Marche	19,31	11,59	7,72	15,16						
Lazio	84,11	50,47	33,64	66,05						
Abruzzo	21,90	13,14	8,76	17,20						
Molise	12,79	7,67	5,12	10,04						
Campania	120,38	72,23	48,15	94,53						
Apulia	46,07	27,64	18,43	36,18						
Basilicata	25,54	15,32	10,22	20,05						
Calabria	42,88	25,73	17,15	33,67						
Sicily	86,41	51,85	34,56	67,85						
Sardinia	78,33	47,00	31,33	61,51						
ITALY	1819,68	1091,81	727,87	1428,86						

 Table 3. Biogas, CH4 and CO2 from livestock manure

	Biogas from OFMSW									
Region	Total Biogas [MNm ³]	CH ₄ producible [MNm ³]	CO ₂ recoverable [MNm ³]	CO ₂ recoverable [kton]						
Piedmont	56,77	34,06	22,71	44,58						
Aosta Valley	0,67	0,40	0,27	0,52						
Lombardy	155,42	93,25	62,17	122,04						
Trentino-S. T.	18,07	10,84	7,23	14,19						
Veneto	98,39	59,03	39,35	77,25						
Friuli V. Giulia	19,84	11,90	7,94	15,58						
Liguria	10,10	6,06	4,04	7,93						
Emilia Romagna	94,98	56,99	37,99	74,58						
Tuscany	57,66	34,59	23,06	45,27						
Umbria	13,79	8,27	5,51	10,82						
Marche	30,17	18,10	12,07	23,69						
Lazio	53,97	32,38	21,59	42,38						
Abruzzo	17,87	10,72	7,15	14,03						
Molise	1,46	0,88	0,58	1,15						
Campania	94,97	56,98	37,99	74,57						
Apulia	24,77	14,86	9,91	19,45						
Basilicata	2,36	1,41	0,94	1,85						
Calabria	6,80	4,08	2,72	5,34						
Sicily	17,67	10,60	7,07	13,87						
Sardinia	27,50	16,50	11,00	21,59						
ITALY	803,20	481,92	321,28	630,69						

Table 4. Biogas, CH4 and CO2 from OFMSW

	Biogas from WW									
Region	Total Biogas [MNm ³]	CH ₄ producible [MNm ³]	CO ₂ recoverable [MNm ³]	CO ₂ recoverable [kton]						
Piedmont	41,23	26,80	14,43	28,33						
Aosta Valley	1,99	1,30	0,70	1,37						
Lombardy	68,08	44,25	23,83	46,78						
Trentino-S. T.	12,35	8,03	4,32	8,48						
Veneto	48,29	31,39	16,90	33,18						
Friuli V. Giulia	10,02	6,51	3,51	6,88						
Liguria	9,47	6,15	3,31	6,50						
Emilia Romagna	40,84	26,54	14,29	28,06						
Tuscany	44,11	28,67	15,44	30,31						
Umbria	4,10	2,66	1,43	2,82						
Marche	9,99	6,50	3,50	6,87						
Lazio	40,65	26,42	14,23	27,93						
Abruzzo	10,75	6,99	3,76	7,39						
Molise	5,39	3,50	1,89	3,70						
Campania	43,22	28,09	15,13	29,69						
Apulia	34,76	22,59	12,17	23,88						
Basilicata	3,39	2,20	1,18	2,33						
Calabria	10,39	6,75	3,64	7,14						
Sicily	22,79	14,81	7,98	15,66						
Sardinia	15,95	10,36	5,58	10,96						
ITALY	477,74	310,53	167,21	328,24						

 Table 5. Biogas, CH4 and CO2 from WW

	Total biogas										
Region	Total Biogas [MNm ³]	CH ₄ producible [MNm ³]	CO ₂ recoverable [MNm ³]	CH ₄ producible [kton]	CO ₂ recoverable [kton]						
Piedmont	341,21	206,79	134,42	147,61	263,88						
Aosta Valley	12,66	7,70	4,96	5,49	9,75						
Lombardy	754,69	456,22	298,47	325,67	585,92						
Trentino-S. T.	79,42	48,27	31,15	34,46	61,15						
Veneto	319,06	193,85	125,21	138,38	245,80						
Friuli V. Giulia	58,26	35,46	22,80	25,31	44,76						
Liguria	23,58	14,62	8,96	10,44	17,58						
Emilia Romagna	336,95	204,21	132,74	145,77	260,57						
Tuscany	126,08	77,85	48,22	55,57	94,67						
Umbria	36,20	21,93	14,28	15,65	28,03						
Marche	59,47	36,18	23,29	25,83	45,72						
Lazio	178,73	109,27	69,46	78,00	136,36						
Abruzzo	50,52	30,85	19,67	22,02	38,61						
Molise	19,64	12,06	7,59	8,61	14,89						
Campania	258,56	157,30	101,27	112,29	198,79						
Apulia	105,59	65,09	40,50	46,47	79,50						
Basilicata	31,28	18,94	12,34	13,52	24,23						
Calabria	60,07	36,56	23,51	26,10	46,15						
Sicily	126,86	77,26	49,61	55,15	97,38						
Sardinia	121,78	73,86	47,91	52,73	94,06						
ITALY	3100,63	1884,26	1216,36	1345,06	2387,79						

 Table 6. Biogas, CH4 and CO2 from all the three sources

3.2.1.3 Power plants' exhaust

The main task about power plants' exhaust was to define the emissions factors. This was done analysing the mix of electrical production of fossil – fuelled power plants at regional scale during the previous years [31].

Once the emissions factors have been defined, they have been used to evaluate the carbon dioxide emissions and potential CO_2 that can be recovered from them in the year 2014. The emissions' data were taken from TERNA – Rete Elettrica Nazionale, an operator that manages electricity transmission networks in Italy [32].

The process to which the exhausts are subjected in order to separate the carbon dioxide from them is the Rectisol Acid Gas Removal. Rectisol was developed by Lurgi and Linde around sixty years ago, and it is a physical wash process, very flexible. It exploits methanol, cheap and chemically stable, as a physical solvent, so no chemical reactions are involved, as opposed to the amine scrubbing technique previously analysed.

The methanol has to be chilled to around -40 °C. The low temperature will ensure an optimal and selective absorption, as it can be noticed from the graph in figure 24, where the trend with varying temperatures of the absorption coefficient α for several gases in methanol is shown. Both the gas and the methanol are pressurized to enhance the removal itself as well.

The process works with the raw gas and the methanol entering a scrubber unit in counterflow configuration. The acid gas, in this case CO₂, is solved in methanol and thus removed. The solvent, rich in carbon dioxide, is then depressurized in a second reactor, causing the release of the CO₂.

Electrical energy is required for methanol refrigeration and to pressurize the gases, so a SEEC of 925 kJ per kg of CO₂ recovered has been established [33]. This has been considered in the energy consumption for the synfuels production. The percentage of CO₂ extracted is equal to 95 %.



Figure 23. Rectisol Acid Gas Removal simplified scheme.



Figure 24. Absorption coefficient α for various gases in methanol [34]

Emissions and CO ₂ recovered from thermoelectric production									
Region	Thermoelectric production 2014 [GWh]	Emissions factors [kton/GWh]	CO ₂ produced [kton]	CO ₂ recovered [kton]					
Piedmont	12784,0	0,4161	5319,77	5053,78					
Aosta Valley	11,9	0,7742	9,21	8,75					
Lombardy	26295,2	0,4090	10754,08	10216,38					
Trentino-S. T.	1400,7	0,3983	557,96	530,06					
Veneto	11205,2	0,6413	7186,26	6826,94					
Friuli V. Giulia	6123,3	0,6740	4126,87	3920,52					
Liguria	6888,6	1,0187	7017,41	6666,54					
Emilia Romagna	13797,9	0,3644	5027,48	4776,10					
Tuscany	7264,1	0,8030	5833,22	5541,56					
Umbria	814,1	0,5144	418,79	397,85					
Marche	495,2	0,3407	168,74	160,30					
Lazio	17280,1	0,5163	8922,39	8476,27					
Abruzzo	1282,3	0,3971	509,22	483,76					
Molise	1264,4	0,3969	501,81	476,72					
Campania	4835,3	0,5066	2449,57	2327,10					
Apulia	30188,3	0,9319	28133,82	26727,13					
Basilicata	531,3	0,4655	247,30	234,93					
Calabria	5592,8	0,3909	2186,39	2077,07					
Sicily	17249,2	0,6185	10667,85	10134,46					
Sardinia	10867,2	0,6253	6795,54	6455,76					
ITALY	176171,1	0,5105	106833,67	101491,98					

Table 7. Emissions and	CO ₂ recovered in Italy.
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3.2.2 RES availability

One of the goals behind the whole project is to reduce GHG emissions in the atmosphere and the only way to reach this target is to use electrical energy produced only using renewable energy sources (RES) to feed the conversion plants for electrolysis and co-electrolysis. The amount of energy taken into account in this analysis comes from hydroelectric, wind, photovoltaic and geothermal power plants. The exclusion of the amount related to biomass, biogases and bioliquids is due to the fact that it wasn't considered sustainable enough since the pathway to exploit those energy is not completely green and environmental – friendly.

The data are taken from the GSE (*Gestore dei Servizi Energetici*, the Italian Institution for the Management of the Energetic Services) report drafted in 2015 about the Italian situation in the year 2014 [35]. The various data are subdivided for each type of energy source and they are given on a regional scale. They are shown in Table 8.

As it can be noticed after a brief analysis, the hydroelectric is the most impacting sector, since it heavily affects the total amount of energy available. The hydroelectric is more widespread in the northern regions, due to the presence of the alpine arch, while the photovoltaic and the solar are widespread more southern. In fact, the increasing longitude enhances the quantity of solar radiation available. Usually, the wind in Italy is constantly present more likely on the coasts and on the two main islands, Sardinia and Sicily. Finally, the geothermal is nearly absent in almost every Italian region, except for the Tuscany where it accounts for over 70 % of the total regional production.

Overall, the amount of energy available for each region is directly linked to the total area of the region itself, and in principle the northern regions have a higher amount of energy accessible.

	Electric energy production from Renewable Energy Sources -Year 2014 [GWh]										
Region	Hydroelectric	Wind	Photovoltaic	Geothermal	Biomass	Bioliquids	Biogases	Total	Total considered		
Piedmont	8369,9	26,1	1646,5	-	539,8	179,0	1012,5	11773,8	10042,5		
Aosta Valley	3431,0	3,7	22,7	-	-	0,6	11,3	3469,3	3457,4		
Lombardy	13623,6	-	2046,1	-	1378,4	168,7	2702,2	19919,0	15669,7		
Trentino - S. T.	13249,3	1,2	407,1	-	110,4	144,5	85,5	13998,0	13657,6		
Veneto	5558,5	17,9	1784,1	-	535,2	205,2	1158,3	9259,2	7360,5		
Friuli V. Giulia	2524,7	-	509,3	-	73,4	266,4	366,3	3740,1	3034,0		
Liguria	350,4	117,3	96,1	-	0,3	-	125,1	689,2	563,8		
Emilia Romagna	1277,1	27,2	2093,1	-	847,4	639,3	1272,3	6156,4	3397,4		
Tuscany	1060,7	220,6	847,8	5916,3	140,5	167,9	295,6	8649,4	8045,4		
Umbria	1819,1	3,0	526,6	-	90,6	28,2	104,8	2572,3	2348,7		
Marche	608,4	1,8	1243,9	-	1,5	7,7	177,2	2040,5	1854,1		
Lazio	1316,9	87,1	1572,2	-	267,5	154,7	282,1	3680,5	2976,2		
Abruzzo	2094,9	335,8	861,4	-	11,1	62,2	87,7	3453,1	3292,1		
Molise	240,7	681,1	217,9	-	139,6	5,7	19,5	1304,5	1139,7		
Campania	673,3	2046,8	855,8	-	371,3	572,5	84,6	4604,3	3575,9		
Apulia	4,4	4297,5	3612,2	-	180,3	1367,1	103,0	9564,5	7914,1		
Basilicata	314,5	825,6	481,3	-	20,5	173,7	19,8	1835,4	1621,4		
Calabria	1521,0	1906,3	636,3	-	944,8	-	79,5	5087,9	4063,6		
Sicily	146,4	2922,4	1893,3	-	142,1	3,5	113,6	5221,3	4962,1		
Sardinia	360,5	1657,0	952,5	-	397,9	194,2	97,5	3659,6	2970,0		
ITALY	58545,3	15178,4	22306,2	5916,3	6192,6	4341,1	8198,4	120678,3	101946,2		

 Table 8. Electric energy production from RES in Italy

3.2.3 Water availability

For both the two plant typologies, one of the resources for the production of synthetic fuels is the water.

Water is naturally distributed along all the country, and it can be considered as an "infinite" resource. Anyway, it was taken into account the ISTAT (*Istituto Nazionale di Statistica*) report about the Italian water network in the year 2015, on a regional basis [36]. The data are divided in water entered in the network and water supplied to users.

The only regions where a problematic situation can be present, usually due to summer drought, are the southern ones and the two islands.

The data are shown in Table 9.

Natural water resources - Year 2015							
Region	Water supplied by the network [Mm ³]	Water entered in the network [Mm ³]					
Piedmont	378,20	584,05					
Aosta Valley	21,20	26,09					
Lombardy	992,97	1391,86					
Trentino - S. T.	112,24	159,81					
Veneto	388,27	647,57					
Friuli V. Giulia	102,05	195,59					
Liguria	160,36	238,69					
Emilia Romagna	326,21	471,05					
Tuscany	241,39	426,73					
Umbria	54,24	101,98					
Marche	110,10	167,14					
Lazio	458,34	972,54					
Abruzzo	120,16	230,77					
Molise	28,12	53,49					
Campania	437,44	820,10					
Apulia	231,01	426,65					
Basilicata	42,67	97,75					
Calabria	206,15	350,05					
Sicily	341,57	683,15					
Sardinia	121,99	275,00					
ITALY	4874,67	8320,06					

Table 9. Water availability in Italy

4. Results

Four main scenarios have been analysed in this study. They are summarized in the following Table 10:

	Pathways for synfuels production										
#	Source	Process	Upgrade technology	Synthesis	Plant #	Final product					
1	Exhaust gas of fossil power plants	CO2 separation via Acid Gas Removal process (Rectisol)	SOEC co - electrolysis	Methanation	1	SNG					
2	Biogas off - gas after upgrading to biomethane	CO2 separation via Amine Scrubbing	SOEC co - electrolysis	Methanation	1	SNG					
3	Residual biomass sources	Biomass gasification (Viking two - stage gasifier)	SOEC co - electrolysis	Methanation	2	SNG					
4	Water from public network	-	SOEC electrolysis	-	3	Hydrogen					

Table 10. Recap on pathways for synfuels production

Each scenario differs from the others mainly on the resource exploited to produce the final product. The cases that will be analysed in the following sections are:

- 1. SNG production from carbon dioxide recovered from thermoelectric power plants' exhaust
- 2. SNG production from carbon dioxide recovered from biogas upgrade, taking into account also the amount of biomethane produced from the biogas upgrade
- 3. SNG production from carbon dioxide in plant 1, a cumulative of the two previous cases, united by the same carbon source
- 4. SNG production from gasified residual biomass
- 5. Hydrogen H₂ production using water from the public network.

The three plants are supposed to work for 90 % of the total hours of the year, so they are in function for 7884 hours per year.

The inlet stream of the carbon source in plant 1 and 2 and the water stream in plant 3 were imposed equal to 1 kg/s. The outlet stream and all the other physical quantities were then weighted on the specific demand needed.

For each pathway, a specific conversion efficiency has been computed, according to the following equations:

$$\eta_{SNG\ from\ CO2} = \frac{M_{SNG} \cdot LHV_{SNG}}{E_{SOEC} + E_{aux} + E_{sep\ CO}}$$

 $\eta_{SNG from residual biomass} = \frac{M_{SNG} \cdot LHV_{SNG}}{E_{SOEC} + E_{aux} + M_{bio} \cdot LHV_{bio}}$ $\eta_{H2} = \frac{M_{H2} \cdot LHV_{H2}}{E_{SOEC} + E_{aux} + Q}$

Where M_{SNG} and LHV_{SNG} are respectively the synthetic natural gas' mass and Lower Heating Value. This one is calculated by weighing the H₂ and CH₄ LHVs (respectively equal to 120 MJ/kg and 50 MJ/kg) with their molar fraction. E_{SOEC} and E_{aux} are the amount of electrical energy needed for the SOEC and for the auxiliary systems like pumps and compressors. $E_{sep \ CO2}$ is the specific electrical equivalent consumption of the CO₂ separation process: Rectisol in the power plants' exhaust case, Amine scrubbing for the biogas. M_{bio} and LHV_{bio} are respectively the residual biomass' mass and Lower Heating Value. The latter is equal to 17.9 MJ/kg, and it has been evaluated as the average of the LHVs of several biomass sources, as shown in the following table. The data are taken from [20].

Lower Heating Values [MJ/kg dry bas	sis]	
	MIN	MAX
Herbaceous crops:		
Cereal straws (wheat, barley, oats, rye)	17,5	19,5
Rice straws	17,0	18,4
Corn stalks and cobs	16,8	18,0
Sunflower stalks	-	-
Tree crops:		
Vine shoots	16,0	19,0
Olive pruning	17,0	19,0
Orchards pruning	18,0	18,5
Average LHV [MJ/kg d.b.]	17	7,9

Finally, M_{H2} and LHV_{H2} are respectively the Hydrogen mass and Lower Heating Value, equal to 120 MJ/kg.

In the last efficiency there is *Q* in the denominator, which is the amount of heat needed for the steam production and overheating. In the other two efficiencies, which are referred to plant 1 and 2, this term isn't counted because the various sources of heat (the SOEC outlet flows, the entire methanation process) provide enough heat, due to the high exothermicity of the reactions involved, to have a positive thermal energy balance [7] [8]. For this reason, the thermal energy related to the co – electrolysis processes, which are steam production and pre – heating

of the several inlet flows, has not been considered in the external energy demand of plant 1 and 2.

For each of the five cases analysed a table is provided. This table is subdivided in two main sections:

- "Demand covered with resources' availability": it shows the amount of energy [PJ] and the fraction of the demand covered [%] with the current resources' availability. The limiting resource, which often coincides with the RES limited availability, is shown in the third column.
- "Resources needed to cover 100 % of demand": for cases 1 to 4, it shows the amount of RES electrical energy and carbon source needed to fulfil the entire demand with respect to the actual resources' availability. The amount of water isn't shown because it's never a limit. Its utilization is about 1 – 2 % of the total availability. As regards case 5, it shows the amount of RES electrical energy and water needed to fulfil the entire demand.

In addition to the table, two graphs per each case are provided. They are referred to the two sections of the table. The one regarding the "Demand covered with the current resources' availability" has the axis of the ordinates fixed to 0 - 100 % in every case, for an easier comparison between each scenario.

After all the various cases' analysis, there is a final section in which they are compared to each other.



4.1 Case 1 – SNG production from carbon dioxide recovered from power plants' exhaust

Figure 25. Demand covered with the current resources' availability, case 1



Figure 26. Resources necessary to fulfil the entire demand, case 1

	Case	1: SNG prod	luction from CO ₂ recover	ed from power plants' exhaust	
Parala a	Demand	covered wit	h resources' availability	Resources needed to co	over 100 % of demand
Region	[PJ]	[%]	Limiting resource	Fraction of CO₂ used	Fraction of RES used
Piedmont	29,10	29,43%	RES	106,98%	339,75%
Aosta Valley	0,16	2,81%	CO ₂	3552,62%	54,66%
Lombardy	44,95	28,52%	RES	84,34%	350,58%
Trentino - S. T.	9,69	22,01%	CO ₂	454,25%	108,02%
Veneto	21,21	18,26%	RES	93,03%	547,62%
Friuli V. Giulia	8,24	29,70%	RES	38,68%	336,66%
Liguria	1,41	5,65%	RES	20,41%	1768,73%
Emilia Romagna	9,90	9,00%	RES	125,98%	1111,28%
Tuscany	23,14	25,62%	RES	89,10%	390,26%
Umbria	7,00	23,82%	RES	404,04%	419,83%
Marche	2,93	9,24%	CO ₂	1082,63%	570,43%
Lazio	8,43	8,20%	RES	66,31%	1219,58%
Abruzzo	8,85	34,94%	CO ₂	286,23%	259,10%
Molise	3,29	38,35%	RES	98,46%	260,75%
Campania	10,55	12,13%	RES	204,38%	824,12%
Apulia	16,68	34,65%	RES	9,85%	288,64%
Basilicata	4,30	41,66%	CO ₂	240,04%	214,86%
Calabria	11,69	34,27%	RES	89,81%	291,81%
Sicily	12,69	28,80%	RES	23,77%	347,16%
Sardinia	7,50	29,05%	RES	21,86%	344,27%
ITALY	287,05	25,57%	RES	60,48%	391,07%

This scenario is the one with the greatest availability of resources among the carbon – based scenarios. In fact, thermoelectric power plants are spread all over the country and the Italian electrical production is based mainly on them.

In no region the demand is fully satisfied with the actual resources' availability. In some regions, like Basilicata and Molise, the plants' production is able to cover around the 40 % of the total demand, an interesting result for sure.

In only five regions the limiting resource is the carbon dioxide. These regions have small or medium territorial extension with respect to the others. In the other fifteen regions, the limiting resource is the electrical energy availability from renewable energy sources.

In eleven regions, which can be identified by the fraction of carbon dioxide needed below 100 %, theoretically an electrical integration is sufficient to satisfy the actual demand, and the availability of resource can also lead to an over production, which can be exploited in other sectors like the industrial one for example.

The electrical integration consists in adding a further amount of electrical energy to the actual share coming from RES. It can be achieved in three ways:

- In a hypothetical future scenario, the actual share of RES can be increased installing more plants which can exploit renewable energy, like photovoltaic or hydroelectric ones. They can ideally be dedicated specifically to this use. This solution is probably the most unlikely to happen, because at national level the availability needed is almost four times the actual one and this is a huge amount to cover just with renewable energy.
- The missing amount can be covered buying electrical energy from other foreign countries. This amount hypothetically is produced via renewable energy sources, but more likely it would come from nuclear power plants like the French ones.
- Integration using electrical energy produced exploiting fossil fuels in thermoelectric plants. This is the most feasible solution, but it goes against one of the principles behind this study. The intention is to substitute fossil fuels in favour of a greener pathway, so the entire idea of "electrical integration" go beyond the goal set.

Taking a look at the overall national results, the amount of carbon dioxide needed to satisfy the Italian demand is just the 60 % of the total availability. On the other hand, almost four times the RES actual availability is required. So, if the amount of electrical energy is integrated, the

demand would be satisfied and there would be a huge overproduction exploitable in other sectors.



4.2 Case 2 – SNG production from carbon dioxide recovered from biogas upgrade

Figure 27. Demand covered with the current resources' availability, case 2



Figure 28. Resources necessary to fulfil the entire demand, case 2

	C	ase 2: SN	G production from CO2 recov	vered from biogas upgrade	
Region	Deman	d covered	with resources' availability	Resources needed to a	cover 100 % of demand
Region	[PJ]	[%]	Limiting resource	Fraction of CO ₂ used	Fraction of RES used
Piedmont	4,83	5,27%	CO ₂	1895,93%	303,85%
Aosta Valley	0,18	3,29%	CO ₂	3036,45%	52,11%
Lombardy	10,72	7,58%	CO ₂	1318,70%	301,35%
Trentino - S. T.	1,12	2,64%	CO ₂	3783,55%	103,08%
Veneto	4,50	4,12%	CO ₂	2429,92%	494,42%
Friuli V. Giulia	0,82	3,09%	CO ₂	3233,61%	290,42%
Liguria	0,32	1,32%	CO ₂	7574,84%	1435,99%
Emilia Romagna	4,77	4,64%	CO ₂	2156,26%	1008,13%
Tuscany	1,73	1,98%	CO ₂	5055,27%	361,77%
Umbria	0,51	1,79%	CO ₂	5583,09%	405,07%
Marche	0,84	2,75%	CO ₂	3641,49%	546,44%
Lazio	2,49	2,52%	CO ₂	3965,52%	1105,46%
Abruzzo	0,71	2,92%	CO ₂	3430,20%	244,88%
Molise	0,27	3,34%	CO ₂	2993,22%	238,20%
Campania	3,64	4,47%	CO ₂	2238,08%	758,34%
Apulia	1,45	3,17%	CO ₂	3150,40%	192,69%
Basilicata	0,44	4,60%	CO ₂	2174,88%	198,11%
Calabria	0,84	2,57%	CO ₂	3887,61%	268,65%
Sicily	1,78	4,31%	CO ₂	2318,75%	277,32%
Sardinia	1,72	7,42%	CO ₂	1347,02%	260,69%
ITALY	43,67	4,14%	CO ₂	2416,55%	344,88%

This scenario is the one with the least availability of resources among all the scenarios. In fact, as it can be easily noticed, the limiting resource is always the carbon dioxide availability.

From the biogas upgrade both carbon dioxide CO₂ and methane CH₄ are obtained. The hypothesis made for this case is to take into account also the amount of biomethane produced via upgrade, since it's nearly the same product that the one we are willing to produce at the outlet of the plant. So, the CH₄ derived from the biogas upgrade will be dedicated to the residential sector itself, thus going to lower the demand.

In no region the demand is fully satisfied with the actual biogas availability. In all regions, the total demand covered is below the 10 %. The global national result is even worse: the demand fulfilled is just the 4.14 %.

The amount of electrical energy from RES necessary to upgrade the biogas and then convert it into SNG is minimal. So, in no region an electrical integration is sufficient to satisfy the actual demand.

As regards instead the resources required to cover the entire demand, an insane amount of biogas is needed. In one region, i.e. the Liguria, the amount required is even seventy - five times the actual one. At the Italian level, the amount needed is slightly more than 2400 %.

These are the reasons that led to the idea of coupling this case with the first case, since they are united by the fact of having the same resource, i.e. CO_2 , even if it is extracted from two different sources. The plant is obviously the same, plant 1, so it's a feasible solution.



4.3 Case 3 – SNG production from carbon dioxide in plant 1: a cumulative of case 1 and 2

Figure 29. Demand covered with the current resources' availability, case 3



Figure 30. Resources necessary to fulfil the entire demand, case 3

	Case 3	3: SNG prod	luction from CO₂ in plant	1, a cumulative of case 1 and 2	2
Profes	Demand	covered wit	h resources' availability	Resources needed to co	over 100 % of demand
Region	[PJ]	[%]	Limiting resource	Fraction of CO₂ used	Fraction of RES used
Piedmont	28,88	31,57%	RES	94,08%	316,78%
Aosta Valley	0,34	6,25%	CO ₂	1599,74%	52,18%
Lombardy	44,42	31,44%	RES	71,53%	318,11%
Trentino - S. T.	10,81	25,55%	CO ₂	391,34%	104,08%
Veneto	21,08	19,30%	RES	84,45%	518,25%
Friuli V. Giulia	8,18	30,90%	RES	36,50%	323,63%
Liguria	1,40	5,75%	RES	19,93%	1739,81%
Emilia Romagna	9,84	9,58%	RES	111,55%	1044,25%
Tuscany	23,07	26,35%	RES	84,91%	379,47%
Umbria	6,99	24,42%	RES	367,41%	409,42%
Marche	3,77	12,37%	CO ₂	808,11%	548,66%
Lazio	8,39	8,48%	RES	62,78%	1178,64%
Abruzzo	9,55	39,44%	CO ₂	253,55%	248,65%
Molise	3,28	40,17%	RES	90,69%	248,95%
Campania	10,50	12,90%	RES	176,14%	775,06%
Apulia	16,39	35,78%	RES	9,34%	279,47%
Basilicata	4,74	49,18%	CO ₂	203,34%	201,84%
Calabria	11,65	35,49%	RES	84,50%	281,78%
Sicily	12,52	30,32%	RES	22,07%	329,80%
Sardinia	7,32	31,59%	RES	19,34%	316,54%
ITALY	284,87	26,99%	RES	55,55%	370,46%

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This case is the cumulative of the previous two. It's a hypothetical scenario, where the carbon dioxide fed to plant 1 is extracted both from power plants' exhaust and from biogas upgrade, taking also into account, as it was said for case 2, the amount of methane derived from the upgrade itself.

In no region the demand is fully satisfied with the actual resources' availability. In ten of the twenty regions, the plants' production is able to cover more than the 30 % of the total demand. In Basilicata the amount of covered needs reached is even equal to almost the 50 %.

In only five regions the limiting resource is the carbon dioxide, the same as case 1. This data highlights how the contribution given by the carbon dioxide coming from biogas upgrade is minimal with respect to the one coming from power plants' exhaust. In the other fifteen regions, the limiting resource is the electrical energy availability from renewable energy sources.

In twelve regions, one more, i.e. the Piedmont, with respect to case 1, an electrical integration is sufficient to fulfil the actual demand, and the availability of resource can also lead to an over production, which can be exploited in other sectors.

Having a look at the national results, they are just slightly better than case 1. The amount of carbon dioxide needed to satisfy the Italian demand is just the 55 % of the total availability, while the 370 % of the energy from RES actual availability is required. So, if the amount of electrical energy is integrated, the demand would be satisfied and there would be a huge overproduction exploitable in other sectors.

This means that an extra carbon source, like the one coming from biogas upgrade, is not really required with respect to the huge need of electrical energy. On the other hand, the amount of methane deriving from the upgrade can be useful to lower the total demand.



4.4 Case 4 – SNG production from gasified residual biomass

Figure 31. Demand covered with the current resources' availability, case 4



Figure 32. Resources necessary to fulfil the entire demand, case 4
Case 4: SNG production from gasified residual biomass					
Design	Demand covered v		ith resources' availability	Resources needed to cover 100 % of demand	
[PJ] [%]		Limiting resource	Fraction of GAS IN used	Fraction of RES used	
Piedmont	19,63	19,85%	GAS IN	503,79%	184,22%
Aosta Valley	0,02	0,41%	GAS IN	24101,60%	30,77%
Lombardy	21,09	13,38%	GAS IN	747,39%	188,17%
Trentino - S. T.	0,99	2,25%	GAS IN	4444,57%	60,33%
Veneto	20,22	17,41%	GAS IN	574,33%	295,25%
Friuli V. Giulia	6,34	22,86%	GAS IN	437,38%	171,05%
Liguria	0,32	1,27%	GAS IN	7899,07%	825,75%
Emilia Romagna	16,62	15,10%	GAS IN	662,35%	606,05%
Tuscany	8,05	8,91%	GAS IN	1122,03%	210,01%
Umbria	4,38	14,91%	GAS IN	670,79%	234,20%
Marche	5,71	18,00%	GAS IN	555,48%	320,29%
Lazio	6,01	5,84%	GAS IN	1711,23%	646,21%
Abruzzo	3,03	11,97%	GAS IN	835,76%	143,92%
Molise	1,70	19,77%	GAS IN	505,91%	140,92%
Campania	5,29	6,08%	GAS IN	1644,82%	455,12%
Apulia	17,39	36,14%	GAS IN	276,70%	113,79%
Basilicata	3,68	35,66%	GAS IN	280,41%	119,02%
Calabria	5,93	17,37%	GAS IN	575,71%	157,09%
Sicily	13,10	29,74%	GAS IN	336,23%	166,11%
Sardinia	3,54	13,72%	GAS IN	728,90%	162,58%
ITALY	163,04	14,52%	GAS IN	688,56%	206,02%

Table 14. That data regularing case 4	Table	14.	Final	data	regarding	case	4
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This scenario is similar to the one with carbon dioxide coming from biogas upgrade. They both share the problem of fuel starvation, with fuel intended as the carbon source for the plant. Of course, this is also the only point that unites them.

In no region the demand is fully satisfied with the actual syngas availability. In two regions, Apulia and Basilicata, the production is able to cover more than the 35 % of the total demand. On the other hand, in most regions the amount covered is around the 15 %, which coincides roughly with the fraction of the total demand satisfied at Italian level.

In all regions the limiting resource is the entering syngas. In no region the limiting resource is the electrical energy coming from renewable energy sources. In fact, the amount of electrical energy necessary to convert the actual availability of syngas into SNG is minimal. So, in no region an electrical integration is sufficient to satisfy the demand.

As regards instead the resources required to cover the entire demand, an insane amount of syngas is needed. In several regions the amount required is even ten times or more the actual one. At the Italian level, the amount needed is slightly less than 700 %.



4.5 Case 5 – Hydrogen production using water from the public network

Figure 33. Demand covered with the current resources' availability, case 5



Figure 34. Resources necessary to fulfil the entire demand, case 5

Case 5: Hydrogen production using water from the public network						
D estina	Demand covered with resources' availability			Resources needed to cover 100 % of demand		
Region	[PJ]	[%]	Limiting resource	Fraction of H₂O used	Fraction of RES used	
Piedmont	34,78	35,17%	RES	2,71%	284,30%	
Aosta Valley	11,97	210,56%	-	2,71%	47,49%	
Lombardy	54,27	34,44%	RES	1,53%	290,39%	
Trentino - S. T.	47,30	107,41%	-	4,11%	93,10%	
Veneto	25,49	21,95%	RES	2,91%	455,65%	
Friuli V. Giulia	10,51	37,88%	RES	2,51%	263,98%	
Liguria	1,95	7,85%	RES	1,53%	1274,33%	
Emilia Romagna	11,77	10,69%	RES	3,12%	935,28%	
Tuscany	27,86	30,86%	RES	3,52%	324,10%	
Umbria	8,13	27,67%	RES	4,62%	361,42%	
Marche	6,42	20,23%	RES	2,76%	494,28%	
Lazio	10,31	10,03%	RES	2,03%	997,26%	
Abruzzo	11,40	45,02%	RES	1,93%	222,11%	
Molise	3,95	45,98%	RES	3,05%	217,47%	
Campania	12,38	14,24%	RES	1,98%	702,36%	
Apulia	27,41	56,95%	RES	1,68%	175,60%	
Basilicata	5,62	54,45%	RES	2,42%	183,67%	
Calabria	14,07	41,25%	RES	1,64%	242,42%	
Sicily	17,19	39,01%	RES	1,19%	256,35%	
Sardinia	10,29	39,86%	RES	1,99%	250,90%	
ITALY	353,08	31,45%	RES	2,19%	317,94%	

Table	15.	Final	data	reaardina	case	5
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This scenario is different from the others, since the product is hydrogen H_2 instead of SNG and the only stream of mass entering the plant is water, no carbon source is needed.

A due premise concerns the water availability: it is never a limit. Water can be considered almost an infinite resource for this case study, since its fraction exploited is always below 5 % for every region, also in the hypothetical case of covering the entire demand with electrical integration. The limiting resource is always the electrical energy availability from renewable energy sources.

In two regions, Aosta Valley and Trentino – S. T., the demand is fully satisfied with the actual resources' availability. There is even an overproduction, that for example in the Aosta Valley reaches two times the actual energy demand, that can be exploited in other sectors. In several regions the plants' production exceeds the 30 % of the total demand, with some peaks over 50 %. At national level, with the actual energy from RES availability, the demand satisfied is over 30 %, an interesting result for sure and the best one got among all cases and scenarios.

In all the regions an electrical integration is sufficient to satisfy the actual demand. The availability of resource can also lead to a huge over production, to be exploited in other sectors, but this is not the case, since the amount of electrical energy is the limiting factor, and over - produce means that an even higher amount of it would be required.

Taking a look at the national results, slightly more than three times the RES actual availability is required to completely fulfil the demand. On the other hand, regarding the fraction of water exploited, it is just the 2.19 % of the total Italian availability.

4.6 Comparison between the previous cases



Figure 35. Number of regions for each scenario where the demand is covered either with current availability or with electric integration



Figure 36. Demand covered with the current resources' availability, comparison between the various scenarios

After the analysis carried out for each single case, a final comparison among all the scenarios has been done.

In Figure 35 and 36 two graphs are shown, which can help to visually compare the various scenarios.

Having a look mainly at the second one, the most interesting cases regarding the demand covered with the actual resources' availability are for sure the hydrogen and the SNG produced exploiting the carbon dioxide coming from power plants' exhaust, or its subcase, i.e. the cumulative of case 1 and 2. The hydrogen case, highlighted in green colour on the graph, is the only scenario in which the production is able to completely cover the demand in two regions, while in most of the remaining regions it exceeds the 30 %, or even the 50 % in few cases. At the national level, the coverage amounts to 31 %.

Regarding the SNG produced from CO_2 from plants' exhaust and its subcase, respectively highlighted on the graph in blue and grey, in slightly less than half of the regions the production is able to cover around the 30 % of the actual demand. In no region the demand fulfilled reaches the value of 50 %. At national level, the demand satisfied is around 25 – 27 %.

The SNG produced via biogas upgrade, highlighted in orange, isn't viable as a stand – alone solution, since the primary resource availability is too few. Its coverage is around the 5 % for all the regions. It can be possibly coupled with the first case to increase the carbon dioxide globally available.

Lastly, the SNG produced via gasified residual biomass, displayed in yellow on the graph. Also in this case, the availability of primary resource, even if it is more abundant than the biogas' one, is the main problem. The average value of coverage reached is around the 15 %, with some peaks over the 35 %. As a side note, in three regions, the amount of demand satisfied overcomes the amount covered via plants' exhaust and biogas upgrade, i.e. case 3.

Figure # instead shows the number of regions per each case where the demand is covered either with the current resources' availability or with electric integration.

As previously stated, the only scenario where the demand is entirely covered with the actual availability is the hydrogen production in two regions.

More interesting, even if more unrealistic or less congruent with the aim of this study, are the cases with electric integration. In the scenario of SNG produced via thermoelectric power plants'

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exhaust, the entire demand of eleven regions (and of Italy, globally) can be satisfied with electric integration. Adding the biogas upgrade to the sources exploitable, one more region, i.e. the Piedmont, can be totally covered.

The cases of SNG from biogas upgrade or from gasified residual biomass don't include any region fully covered, because of primary resource availability lack.

On the other hand, the hydrogen production can cover every region's demand, because of the huge availability of water in Italy, thus requiring an equally heavy amount of electrical energy to be provided to the steam electrolysis plants.

The last comparison parameter to be taken into account is the efficiency associated to each pathway, as previously defined (see the section "4. Results"). For easier and faster viewing of the results, the efficiencies calculated are summarized in the following table:

Pathways' efficiencies						
Case #	Source	Final product	η			
1	Power plants' exhaust	SNG	80,29%			
2	Biogas upgrade	SNG	76,76%			
3	Previous two	SNG	80,21%			
4	Residual biomass	SNG	78,99%			
5	Water	Hydrogen	67,86%			

As it can be seen, the pathway with the greatest efficiency is the SNG production from power plants' exhaust, with a high and promising value of 80.29 %. Of course, the value associated to case 3 is very similar because it is mainly derived from case 1.

SNG from gasified residual biomass is the second one in term of efficiency, even if the gathering of the biomass itself isn't taken into account. This would further increase the overall energy expenditure, and thus decrease the pathway efficiency.

Detached by a few percentage points there is the efficiency of SNG from biogas upgrade. This and the previous ones are all above the 75 %, a very good result for global pathways.

Finally, there is the hydrogen production from water via steam electrolysis. Its efficiency is still high, but significantly lower with respect to the others. This is due to the fact that the entire energy expenditure for heating water from 25 °C to 100 °C, making it evaporate and heating the steam up to 850 °C, was taken into account in the denominator, even if there is a huge amount of heat recoverable from two heat exchangers regarding the hydrogen stream plus the heat

recoverable from the oxygen produced. Therefore, the most conservative option for the efficiency calculation has been taken into account.

5. Conclusions

The aim of this study was to evaluate the feasibility of substituting the fuels traditionally exploited in the Italian residential sector with synthetic natural gas and hydrogen produced via solid oxide electrolysis and further catalytic upgrade. Several feedstocks and consequently scenarios have been analysed, and only electrical energy from renewable energy sources has been used.

In few scenarios, i.e. SNG from biogas upgrade and SNG from gasified residual biomass, the lack of primary resource was the real limiting factor. On the other hand, in most of the other scenarios the limit was represented by the electrical energy availability. Cases with electrical integration from the grid were also analysed, but they are not very congruent with the study itself. In addition, the hypothesis of using the entire amount of available electrical energy from RES was not very consistent, since most part of this amount is actually used in other sectors in Italy.

The most promising cases were two:

- Hydrogen produced from water: considering the actual resources' availability, this is the scenario with the highest coverage, equal to 31.45 % of the total Italian demand. In addition, in two regions (Aosta Valley and Trentino S. T.) the demand can be entirely satisfied with even an overproduction, which could be exploited in other sectors. Its efficiency is equal to 67.86 %, but it was calculated under conservative hypotheses. The feedstock is nearly unlimited, and the hydrogen is a completely zero carbon fuel, since from its combustion only water is generated. This scenario qualifies probably as the best, even though the current infrastructures are not ready to dispatch hydrogen, and its combustion in large quantities could create several difficulties.
- SNG produced from carbon dioxide recovered from thermoelectric power plants' exhaust: this pathway has the greatest efficiency among all the others, equal to 80.29 %. The national demand coverage reaches the 25.57 %, which is a good result too. The 60 % of the current carbon availability from this feedstock is sufficient to cover the entire Italian demand, even though electric integration would be required to make this happen. Concerning this scenario, an interesting aspect consists in the carbon capture from the exhausts and its reutilization in the form of another fuel instead of being immediately released to the environment.

The other scenarios, mainly due to the lack of feedstocks, are not viable as stand – alone solutions, because the amount of covered demand is not high enough to be considered satisfying for the purposes of this study. However, they can be coupled to other solutions, like the case 3 analysed or more traditional solutions.

In conclusion, some of the scenarios analysed seem very promising for the near future. The global warming and the increasing level of air pollutants require a change in the way energy is produced and then exploited. A switch to greener pathways is mandatory in every sector, not just in Italy but in the entire world. The proposed solutions seem viable in the Italian reality, as long as the plants for renewable energy source are substantially upgraded. These scenarios can be probably adopted also in other sectors in addition to the residential one.

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