

Possible circular use of CO₂ waste streams from geothermal power plants

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Abstract:

Geothermal fluid is usually characterized by the presence of water and minor percentages of non-condensable gases (NCG), including CO₂. Relevant CO₂ streams are currently released from the cooling towers of geothermal power plants operating in Tuscany. These emissions are largely of natural origin. The output streams of NCG are treated for removal of contaminants (Hg and H₂S) and consist in nearly-pure CO₂: that is the reason why it is worth to investigate about its potential circular use. Specifically, the possibility of transport and use as a long-distance heating or cooling fluid stream for local communities is investigated; integration with hydrogen production is also considered, with production of methanol to be used as synfuel or energy storage. Hydrogen can be harvested from several sources: a) from the captured H₂S stream b) from industrial facilities already existing along the transport path c) from integrating an electrolyser in the power plant premises thereby providing load flexibility (currently not present in geothermal power plants). The study is tailored on the local geographical, productive structure and population situation. The remaining part of the CO₂ stream is delivered to the sea where it can be finally destined to transportation (pipeline or ship) and sequestration. The results are encouraging in inspiring a potentially new sustainable economy structure.

Keywords:

Circular use; CO₂ stream; Geothermal power plant; Hydrogen; Methanol.

1. Introduction

A crucial environmental issue related to electricity generation using geothermal fluids is the emission of non-condensable gases. Vent stacks in geothermal plants emit carbon dioxide (CO₂) and methane (CH₄), raising serious concerns in terms of greenhouse gases. The amount of these emissions is quite small compared to carbon and fossil fuel plants, indicating that the contribution of these sources is practically negligible. Geothermal power plants (GPPs) also emit a higher amount of hydrogen sulphide (H₂S), as it is a main constituent of geothermal fluids. H₂S in air, water, soils, and vegetation is a vital environmental concern for geothermal fields [1].

Due to resource depletion, fossil fuels are not capable of compensating for the growing energy need. In addition, easily extractable fossil fuel is facing an increase in their prices. It is worth mentioning that greenhouse gases (mainly CO₂) have accumulated in the atmosphere by burning fossil fuels. Therefore, clean and sustainable energy has become relevant, with intensified research to make it more affordable and productive.

Currently, H₂ (hydrogen) and CH₃OH (methanol) are in the picture to fulfil the role of storable energy carriers [2]. Electricity surplus can be used to produce H₂ from the water via electrolysis, or further react H₂ with CO₂ obtained from the GPPs to synthesize CH₃OH (Power-to-Gas). This would mitigate greenhouse gas emissions and meet renewable energy directives. Methanol is a liquid that may give some advantages (e.g. it can be stored at ambient temperature and atmospheric pressure). Besides blending with gasoline in cars, an application that can be started directly as methanol is compatible with the current fuel infrastructure or using it as fuel in fuel cells, methanol can also be used as feedstock in the chemical industry.

This innovative renewable method for methanol synthesis may be applied in Tuscany, the Italian region with the highest use of renewable sources, thanks to the concentration of geothermal-electrical generation. Geothermal energy covers, in fact, about 33% of the electricity needs in Tuscany with a global nominal capacity of 914.5 MW and meets the electricity demand of about 2 million households [1].

From Tuscan geothermal plants, CO₂ can be easily stored and used for the synthesis of methanol. In addition, methanol can be produced more sustainably by synthesizing it from H₂ recovered from industries in the region as well as from H₂S reduction. The decomposition of hydrogen sulphide (H₂S) with simultaneous hydrogen (H₂) generation offers a sustainable energy production option and an environmental pollution abatement

strategy. Another way to use this carbon dioxide in order to provide additional services to the population is to exploit it for the production and distribution of heat and cold.

All in all, it is important to investigate both the potential exploitation of carbon dioxide emitted by GPPs and its mitigating implications using the Tuscany region as a case. In fact, this study tries to apply the possible circular uses of carbon dioxide just mentioned. Therefore, this document is part of the ecological transition trying to identify new forms of economy, a productive and industrial induced that can be strengthened and that is identified with the Tuscan territory.

2. Overall system configuration

The general configuration of the system includes a water electrolysis section, a unit for the direct splitting of hydrogen sulphide into hydrogen and sulphur, a methanol synthesis section (MSS), and the CO₂ district heating and cooling. Water electrolysis is performed with the commercially mature technology of alkaline electrolyzers. The system operates in the charge phase when electricity in excess is stored as chemical power into hydrogen. Figure 1 shows a simplified functional scheme of the general configuration of the overall system.

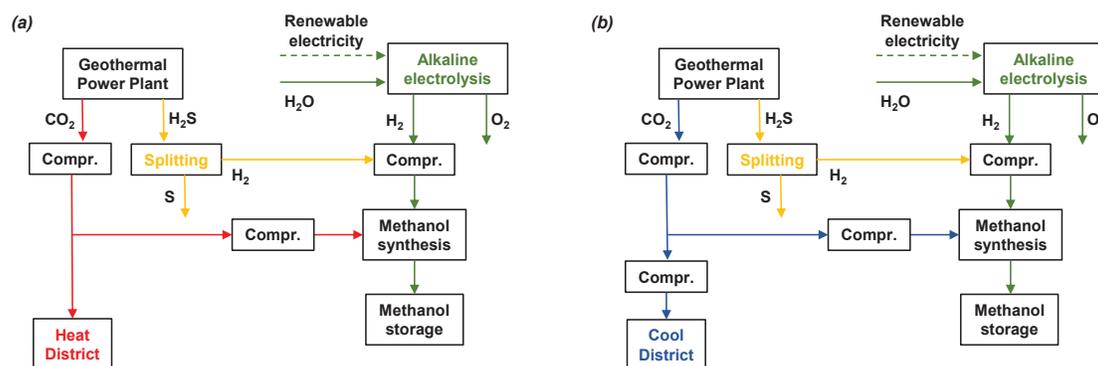


Figure 1. Scheme of the overall system: a) winter operation, b) summer operation.

Water and renewable electricity feed the electrolyser to produce hydrogen. Hydrogen sulphide from gaseous emissions in an AMIS system is separated into pure hydrogen and sulphur through the plasma catalytic reactor (PCR). Hydrogen and CO₂ are compressed at the operating pressure of the methanol synthesis reactor in two compressor trains. In the MSS, CO₂ hydrogenation to methanol is performed over a commercial catalyst (Cu/ZnO/Al₂O₃) and methanol is separated and purified in a distillation column. The non-synthesized CO₂ arrives in Livorno through a double pipeline: one transports liquid phase in summer operation, and the other, gaseous phase in winter operation. Along the way, the production and distribution of heat and cold is promoted.

3. CO₂ network

Carbon dioxide is practically the only gas that remains after the non-condensable gases have been cleaned with the mercury and hydrogen sulphide abatement system (AMIS®). In this study, one of the two 60 MWe Valle Secolo power plants was considered. The resulting CO₂ flow rate is 3.0 kg/s; with an operational period of 8760 hours/year, the total CO₂ emissions are 95371 t/year [3].

Two extreme seasonal functions were analysed, namely winter and summer operation, for each of which there is a dedicated pipeline. All CO₂ is first compressed up to 4 MPa and cooled to 40°C, in order to enter the steam pipe, which represents winter operation. Part of the stream is sent to the methanol production system. Then in order to enter the liquid pipeline, it is further compressed and cooled to reach winter operating conditions of 10MPa and 20°C. Indeed, the non-synthesized CO₂ will be transported from the GPP to the coast promoting along the way service uses: production and distribution of heat and cold.

Determining the pipeline route and length is the first thing to consider in the design of pipelines. The pipeline route will determine the total length of the pipeline and the bends on it. Even the pipeline pressure drop is dependent among other factors on the length of the pipeline.

The final terminal is identified in the SNAM refinery in Livorno, where there may be other possibilities for CO₂ transformation, or alternatively liquefaction and delivery in port areas for the purpose of confinement (for example, in deep water or underwater saline aquifers). Figure 2 shows the location and extent of the CO₂ pipelines, as well as the inhabited areas crossed. The road network was considered a general scheme for arranging CO₂ pipes. Existing brine ducts between the Saline di Volterra and Rosignano Solvay (dotted in green) have also been highlighted. The route starts from the Vallesecolo plant and passes through the Saline di Volterra, Cecina, Rosignano Solvay, and finally Livorno. It is proposed to implement another MSS along the route near Solvay Chimica S.p.A., located in Rosignano Solvay, where hydrogen is expected to be recovered.

In tracing the route, a possible development of district heating/cooling was considered, when passing through residential and commercial districts. Therefore, a doublet liquid/gas pipeline is proposed, with each pipe sized to transport the non-synthesized CO₂ flow rate. Friction and heat transfer correlations, implemented in the Engineering Equation Solver (EES) software, were used to model the CO₂ transport process.

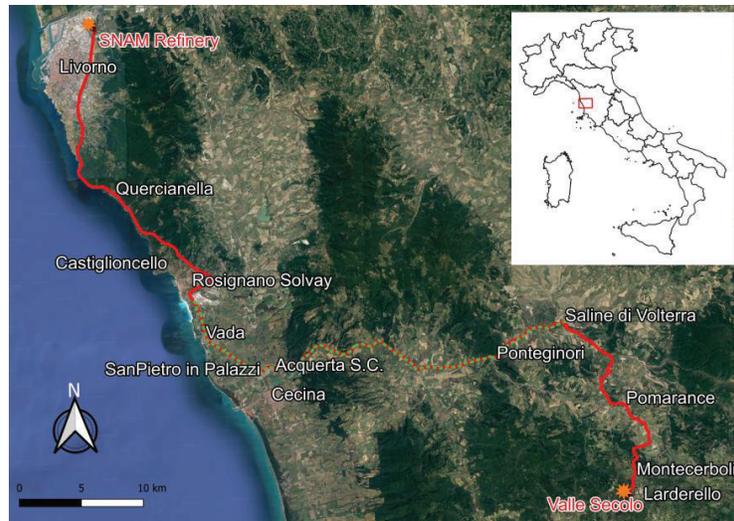


Figure 2. CO₂ pipeline and main residential area crossed.

3.1. Optimization of the CO₂ pipeline system

The flow rate data determine the fluid volume transportation from source to sink and, consequently, the adequate pipeline diameter for transportation. A pipeline diameter too small for the flow rate would cause high velocity of the fluid with attendant high losses in pressure and erosion of the pipe wall. Very large pipeline diameters would reduce pressure losses, have low velocities, and low or non-existent noise and erosion, but result more expensive. The optimum economic pipe diameter was estimated using the following formula [4]:

$$D_{i,opt} = 0.363m_v^{0.45} \rho^{0.13} \mu_c^{0.025}, \quad (1)$$

where $D_{i,opt}$ is the optimum inner diameter of the pipe, m_v is CO₂ volumetric flow rate in the pipeline, m³/s; ρ denotes CO₂ density at average temperature through the pipeline, kg/m³; and μ_c is average CO₂ viscosity.

Applying the above assumptions to Eq. (1) gives an optimum inner diameter of 0.15 m at a CO₂ flow rate of 2.86 kg/s with inlet conditions of 4 MPa and 40°C (vapour pipe); and an optimum inner diameter of 0.08 m at the same flow rate with inlet conditions of 10 MPa and 20°C (liquid pipe). These diameter values ensure that the losses are not too high even when the fluid is returned after the user in conditions of volume different from those designed for injection into the plant.

3.1.1. Pressure drop along the pipeline

An increase in pressure drop means higher operating costs and possibility the need to introduce recompression stations. Hence, it is necessary to estimate the pressure drop along the pipeline: the pressure drop is dependent on the flow rate as well as on the different geometric characteristics of the pipeline such as diameter, length, elevation changes, etc.

Since the CO₂ density is sensitive to pressure and temperature changes, the pressure drop along the pipeline will reduce the CO₂ density and increase the velocity, which will, in turn, increase the pressure drop.

In the simulation, the inlet conditions for CO₂ are fixed; it is transported to the point of arrival considering, as pressure drops, those distributed and those related to the contribution of the difference in height.

3.1.2. Effect of ambient temperature

Optimization of CO₂ transport via pipeline must account for the effect of ambient temperature because of heat transfer along the pipeline between the CO₂ in the pipe and the surroundings. For environmental conditions, atmospheric pressure and a temperature of 10°C and 27°C for winter and summer operations respectively were considered. The pipes are assumed to be carbon steel [5] and placed above the ground. The insulation is made of polyurethane foam (conductivity 0.027 W/mK) with a thickness of 25 mm. To evaluate the heat exchanger between CO₂ and the environment the following phenomena are considered.

Forced convection is present between CO₂ and the internal duct surface, and natural convection between the insulation external metallic surface and the environment (with air temperatures varying from summer to winter operation). Conduction is present in the duct thickness and in the insulation (including the outlet covering).

3.2. Operating conditions of pipes

Two methods were used for CO₂ transport and exploitation, each working under certain operating conditions. The superstructure of the system is represented in Fig 3.

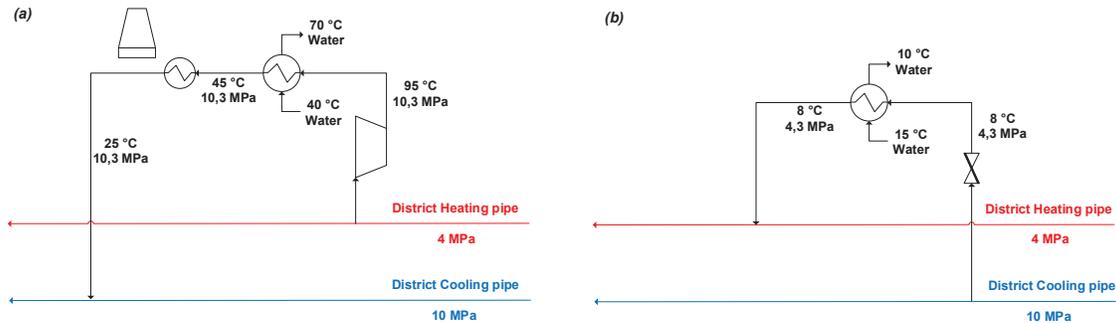


Figure 3. General scheme: a) Heating mode, b) Cooling mode.

In winter operation CO₂ is drawn from the vapour phase pipeline. By setting through a valve the delivery pressure at subcritical values ($p_c = 7.38$ MPa), the fluid reaches the user at conditions similar to those at the condenser of a closed cycle heat pump. The condenser heat recovery is exploited to heat water for household or commercial building heating. The layout corresponds to a trans-critical heat pump operating directly with CO₂: typical pressures of these applications are 9-10 MPa at the condenser and 3.5-4.5 MPa at the evaporator. The trans-critical CO₂ heat pump solution is attractive because it is possible to operate with common radiator temperatures; also, the heat transfer match with the resource is good (30 °C temperature glide on the cold utility side; 50 °C on the resource (CO₂) side). The CO₂ leaving the heat recovery exchanger is still in vapour phase, therefore it is necessary to further cool it at least down to 25 °C to bring it to liquid conditions (recovery of the CO₂ stream in the liquid transport pipe, at supercritical pressure). The liquid CO₂ stream will not thus undergo phase changes along the way but will remain liquid despite the pressure drops along the pipeline.

For the steam pipe, the inlet temperature is set at 40 °C to avoid two-phase formation due to the lowering of the temperature ($T_s = 5$ °C at 4 MPa). The pressure value of 4 MPa was selected considering the operation conditions of the heat pump. At higher pressures the saturation temperatures, T_s , are higher and thermal dispersion could determine a temperature below the saturation value (at 5 MPa $T_s = 14.5$ °C and at 6 MPa $T_s = 22$ °C) leading to the formation of liquid droplets along the pipe.

The same assumptions were made for summer operation: CO₂ is delivered to the user (needing cooling) in the liquid phase. The liquid pipeline is operated at high pressure in summer (10 MPa); a partial flowrate is laminated to low pressure and brought to the right saturation temperature for cooling (at 4.3 MPa $T_s = 8$ °C). The pressure of 10 MPa ensures that pressure drops do not lead to steam formation along the pipeline, with an inlet temperature of 20 °C. Expansion of the fluid to 4.3 MPa allows to cool a water stream from 15 to 10 °C, which is used for cooling the rooms. After use as a coolant, the CO₂ stream can be recovered without pumps in the vapour phase pipe which is operated at 4 MPa.

4. Thermal energy needs

The main urban centres crossed along the pipeline were analysed to consider them as possible users for heating and cooling. Among the main ones, we find Cecina, Rosignano Solvay, and the final terminal located in Livorno. Referring to these towns, the winter and summer thermal loads have been estimated precisely to consider them as possible users. A shopping centre was also included - the only one that is present on the path to Livorno: is the Acquerta shopping centre, located near Cecina. Considering the available flow rate, we will discuss as an example the shopping centre of Acquerta and the thermal needs of part of the neighbouring residential area of San Pietro in Palazzi, which were evaluated as users.

The CO₂ infrastructure was considered to be possibly connected to representative buildings located in the San Pietro in Palazzi area, to study their different operating modes and performances. The Acquerta shopping centre and the San Pietro in Palazzi area are presently heated by natural gas, with an efficiency assumed as 0.9. For the energy performance index for cooling, no efficiency was considered because it is not supplied in terms of primary energy. In fact, that parameter does not take into account the efficiency of the installation providing the service and is therefore not primary energy.

From the climate conditions and the characteristics of the typical dwelling in this zone, heating (primary energy) and cooling demands throughout the year can be obtained. The characteristics of the representative buildings can be seen in Table 1. The Heating Degree Days (HDD) values are obtained using a base temperature of 20°C. For the calculation of the Cooling Degree Days (CDD), a base temperature of 24°C is assumed. It has to be mentioned that in Italy and unlike for heating, no national standard defines how to compute CDD.

Table 1. Representative block of flats characteristics.

San Pietro in Palazzi population	3141
Surface per dwelling [m ²]	100
Number of inhabitants per dwelling	3
Number of dwellings	1047
Heating efficiency with natural gas	0.9
Volume Acquerta S.C. [m ³]	48000

The area here studied falls within climate zone D, so heating systems can be operated from November until April 15 for 12 hours a day, or 1992 hours a year. 610 hours of annual cooling operation were assumed (no legislation limits exist in Italy for this), i.e. about 5 hours per day for four months, while for the shopping centre, 1342 hours per year were assumed, i.e. 11 hours per day for four months. For the two and a half months in which there is no need for thermal energy, it is assumed that the transport of CO₂ takes place with the methanol synthesis along the path.

5. Hydrogen recovery and production

A notable opportunity for circular economy based on CO₂ recovery is the production of synfuels using hydrogen. Here, the production of methanol through hydrogen reaction is considered attractive, as it produces a liquid synthetic fuel already used in the formulation of vehicle fuels. The hydrogen required for this reaction is partly recovered from geothermal and industrial activities, and partly produced. A recovery option is indeed possible at the GPP: considering the entire 120 MW plant operated by ENEL GP in Vallesecolo, it was assumed to produce hydrogen from the hydrogen sulphide present in the geothermal fluid. At the plant premises, it was hypothesized to produce hydrogen through electrolyzers when substantial input to the grid from photovoltaics was present: this makes the GPP effectively operate as a substitute storage capacity, as the plant would be operated full load at night (when no PV input is available), and effectively decrease its nominal power feeding a large electrolyser at daytime. The most important industrial recovery option for H₂ takes place at Rosignano Solvay, where in the Solvay Chimica S.p.A. alkali plant hydrogen is a by-product in the soda-chlorine process. This section assesses the potential for recovering and producing hydrogen.

5.1. Plasma catalytic reactor section

The hydrogen sulphide emissions of both groups of Valle Secolo (120MW) are here considered as possible circular economy resources for the production of H₂ and S. The production of H₂S from the plant – currently captured by the AMIS plant - was taken from public monitoring reports [3], a value of 199 kg/h. The power plant emission treatment abatement system was ideally modified by adding a PCR (Fig 4) [6]. The stream to be processed is from the extraction compressor of non-condensable gas, which is currently being sent to the AMIS treatment (with oxidation and alkaline scrubbing for removal of sulphur species), finally delivering a nearly-pure CO₂ stream at the cooling towers (where dispersion profits from the highly buoyant plume).

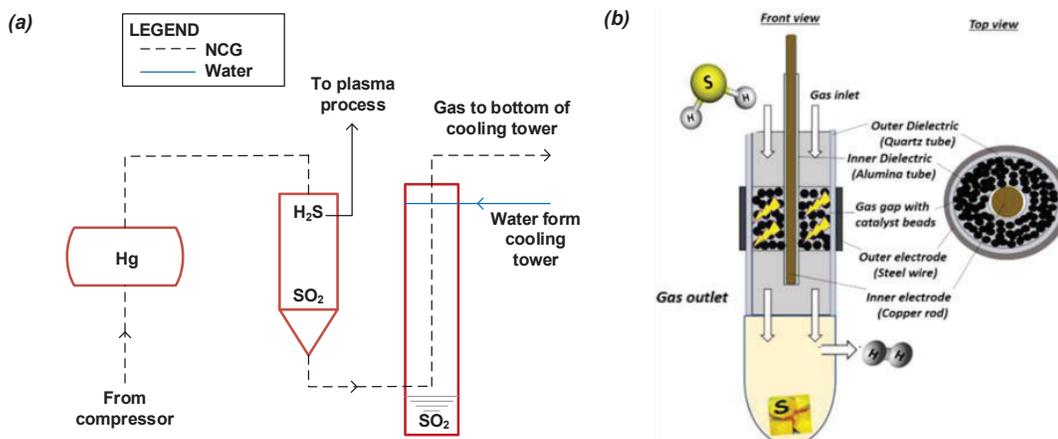


Figure 4. Schematic illustration of the: a) modified AMIS system (modified from [7]), b) PCR [8].

The electrified PCR is an innovative technology for H₂ production for waste streams or H₂S: compared to other technologies, it allows to achieve a good conversion at low temperatures (100-200°C). In addition, the purity of hydrogen is very high (99%) [6].

The plasma-assisted catalytic H₂S decomposition is performed at atmospheric pressure in a non-thermal dielectric barrier discharge (DBD) plasma reactor consisting of one or two coaxial dielectric tubes (quartz, alumina). The DBD plasma is created between two electrodes surrounded by the dielectric material (direct electric heating of the catalyst located between the two electrodes). The main electrode is connected to the high voltage supplied by an AC generator [8]. From stoichiometry (H₂S → H₂+S), the amount of H₂ obtainable from hydrogen sulphide is 11.78 kg/h with a specific electricity consumption of 1.2 kWh/Nm³ of H₂ [6]. The estimated production of H₂ is 103.2 t/year, so the energy demand would be 1378 MWh/year.

5.2. Alkaline water electrolysis section

Alkaline water electrolysis (AEL) is a low-temperature process to produce hydrogen in a commercially mature technology, namely the alkaline electrolyser. This type of electrolyser is here considered in place of the PEM technology, as large-scale units are needed. Water electrolysis is carried out in a liquid alkaline electrolyte solution of a base (KOH or NaOH), where hydroxide ions OH⁻ cross a diaphragm separating the electrodes. Typically, AELs operate between 60 and 90°C, while the operating pressure spans from ambient pressure up to 3.5 MPa [9]. In the present case, we assumed to perform the AEL at 3 MPa and 85°C, with a power consumption of 3.6 MW for a hydrogen flow rate of 72 kg/h, leading to a specific energy consumption of approximately 50 kWh/kgH₂ (4.5 kWh/Nm³H₂), which is consistent with values reported in the literature [10].

Inside the reactor, water electrolysis is accomplished with the following reaction (R1):



which is given by the combination of the cathode reaction (Eq. R2) and anode reaction (Eq. R3, R4):



In this case, three electrolyzers are used along the CO₂ pipeline path, requiring on the whole an electricity consumption of 31536 MWh/year. It is assumed that electrolyzers are powered by renewable energy, thereby enabling the possibility of producing at the end of the process green synfuel: this corresponds to the category of Power-to-X technologies. The electrolyzers are assumed to be operational an average of 8 hours per day, thereby using with profit the photovoltaic energy available in Italy (2920 h/year equivalent operational time per year). In this way, it is estimated that it would be possible to produce 215 kg/h of hydrogen (630 t/year).

5.3. Hydrogen from the soda-chlorine process

Some of the hydrogen needed can be harvested from the soda-chlorine process at the Rosignano Solvay plant. Hydrogen is here a co-product of the electrolysis of brine (approximately 28 kg of H₂ per ton of chlorine). This high-quality hydrogen (purity > 99.9%) is currently used on-site (mainly as a fuel in co-firing steam boilers) or is sold to a distributor.

The alkaline electrolyser works following a membrane cell technology [11]. The basic principle in the electrolysis of a sodium chloride solution is the following:

- at the anode, chloride ions are oxidised and chlorine (Cl₂) is formed;
- at the cathode, water decomposes to form hydrogen (H₂) and hydroxide ions (OH⁻).

The anode reaction is:



The cathode reaction is:



The overall reaction is:

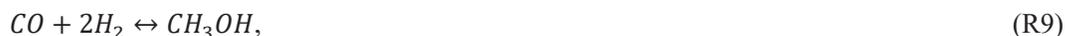


The products of the electrolysis are 1070–1128 kg of NaOH (100 wt-%) and approximately 28 kg of H₂ per ton of Cl₂ produced. The plant operates in a continuous cycle for 24 hours/day, for a nominal 350 days/year. The theoretical capacity of the plant is about 14.5 tons/hour of Cl₂, which correspond to about 125 kton/year of chlorine gas [12]. Considering the molar mass of chlorine gas equal to 70.906 kg/kmol, stoichiometry shows

that the amount of hydrogen resulting is 3.463 kton/year or 412.2 kg/h. The calculated consumption of electrical energy is equal to about 2600 kWh/t Cl₂ [11], or 6,23 kWh/Nm³ of H₂.

6. Methanol synthesis section

The MSS allows the production of liquid fuel, which is used to store energy. The main blocks are the adiabatic reactor, where the catalytic CO₂ hydrogenation process is carried out, and the distillation column, where the purification process is carried out. Methanol is produced through the three main reactions of the CO₂ hydrogenation process: CO is given by the water gas shift reaction (R8) and converted into methanol by the CO hydrogenation reaction (R9), while methanol is also produced through the CO₂ hydrogenation reaction (R10).



At equilibrium conditions only two of these three reactions are sufficient to describe the composition [13]. Only Eqs. (R8) and (R10) were thus considered in the developed model.

The production of methanol was set considering the hydrogen production and recovery. It is supposed to locate two methanol production systems along the pipeline path, one near the GPP to exploit the hydrogen produced by electrolyzers and that recovered from hydrogen sulphide (MSS1), the other plant is instead near Solvay Chimica S.p.A. (MSS2). Assuming the stoichiometric molar ratio of reactants (reaction (R10)), Table 2 was been obtained.

Table 2. Stoichiometric reactants and products flow rates for MSS reactors [kg/h].

Flow rate Species	MSS1	MSS2
H ₂	83.68	412.2
CO ₂	609.04	3000
CH ₃ OH	443.43	2184

The methanol production system is supposed to operate 8760 hours per year and the production was based on the study of [14]; the simulation was performed in the UNISIM DESIGN (Honeywell) modelling environment.

The methanol synthesis reactor operates at 6.5 MPa requiring the hydrogen and CO₂ to be compressed. CO₂ is compressed only when it is taken from the vapour pipeline at 4 MPa from the vapour pipe. Since MSS1 always takes carbon dioxide in the vapour phase, in this study we consider that CO₂ is taken from the vapour pipe for both MSS. A future investigation should concern the case of CO₂ withdrawal from the liquid pipe; when it is taken from the liquid tube at 10 MPa it must be laminated and then heated to have only steam entering the reactor. The number of compressor stages for the H₂ stream depends on the source. The hydrogen obtained from the reduction of hydrogen sulphide is compressed to the operating electrolysis pressure, and then joins the flow of hydrogen produced by the alkaline electrolyser.

Figure 5 shows a simplified functional scheme of the methanol synthesis and purification section. The compressed H₂ (2) and CO₂ (5) are mixed with the re-circulated gases (23) and preheated (HX1) to 210 °C prior to entering the synthesis reactor (R1). Within the adiabatic reactor, the exothermal CO₂ hydrogenation reaction increases the temperature up to about 280 °C and 231 °C for MSS1 and MSS2 respectively. The reactor outlet is mainly composed of hydrogen (about 85% by vol in MSS1 and 97% by vol in MSS2), whereas the methanol content is 4.1% by volume in MSS1 and 1.5% by volume in MSS2. To boost the production of methanol, two flash processes are performed (F1 and F2) and the un-reacted incondensable gases (18 and 21) are re-circulated back to the reactor. The first flash occurs at 6.5 MPa, after reducing the temperature to 50 °C in two heat exchangers (HX1 and HX2), that supply heat to other points in the process, and a cooler (C1). Here the gases are separated to liquid raw methanol and non-reacted gases. The non-reacted gases (18) are recycled to the reactor after purging 1% in order to prevent the accumulation of by-products and inert gases in the system. The second flash process takes place reducing the pressure and temperature of the liquid stream to about 0.12 MPa and 22 °C. Here raw methanol is expanded to further remove the non-reacted gases, especially CO₂, and by-products in order to ease the distillation process. The resulting liquid product (12), namely crude methanol, is mainly composed of methanol and water (both about 50% by vol in both systems) with a small content of CO₂. To boost the methanol purity, the separation of water and methanol takes place in a distillation column (D1). From the bottom of the distillation column, water (15) is recuperated in the liquid phase and can be recycled back to the electrolyzers. The distillate at the top of the column (14) is

pure methanol; the CO₂ in the residue (16) is recycled to the inlet and mixed along with fresh CO₂ (3). Methanol is then sent to the storage tank. The resulting methanol has a purity greater than 99.85% in both systems and is therefore compliant with the IMPCA specification [15]. Table 3 reports the main MSS operating parameters.

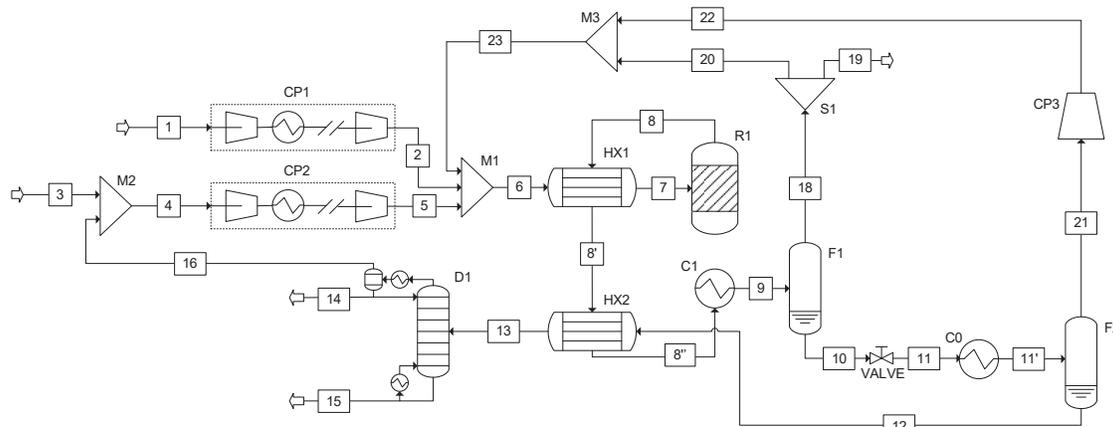


Figure 5. Simplified functional scheme of the MSS, modified from [14] (C=Cooler; CP=Compressor; D=Distillation column; F=Flash; HX=Heat exchanger; M=Mixer; R=Reactor; S=Splitter).

Table 3. MSS main operating parameters.

Parameter	Value
Reactor type	Adiabatic
Reactor pressure [bar]	65
Reactor inlet temperature [°C]	210
F1 pressure [bar]	65
F1 temperature [°C]	50
F2 pressure [bar]	1.2
F2 temperature [°C]	22
Methanol storage pressure [bar]	1
Methanol storage temperature [°C]	25

Since the reactor products are characterized by a high temperature, they can be employed to provide heat to some processes within the system, reducing the thermal energy that otherwise would be provided by an external source. Thermal energy is required by the following processes:

- the preheating of the reactants (6) from 80 to 210 °C;
- the heating of crude methanol (12) up to the inlet temperature of the distillation column (80°C).

Firstly, the reactor products are cooled (HX1) from 280 °C (8) to 144 °C (8') in MSS1 (from 231 °C to 84 °C in MSS2). Finally, the reactor products (8') are cooled (HX2) to about 132 °C in MSS1 and 80°C in MSS2, with the preheating of the crude methanol (12). To reach the first flash condition (50 °C), heat should be further removed from the reactor products in cooler C1. If a cooler heat recovery in the distillation column were also considered, the thermal self-sustainability of the section could be achieved.

7. Results and discussion

Drawing on the methodology presented in the previous section, the thermal energy demand and the district heating and cooling performance are discussed in detail as a first step. Then, the results of the two methanol production plants are shown. Finally, the energy requirements of the system and the emissions avoided are assessed.

7.1. Energy demand

Heating Degree Days (HDD) and Cooling Degree Days (CDD) patterns are presented in Fig 6 (a). The maximum daily values for HDD and CDD are 13.82 °C and 2.73 °C respectively. Moreover, the annual accumulated HDD is 1602°C and for CDD is 48°C.

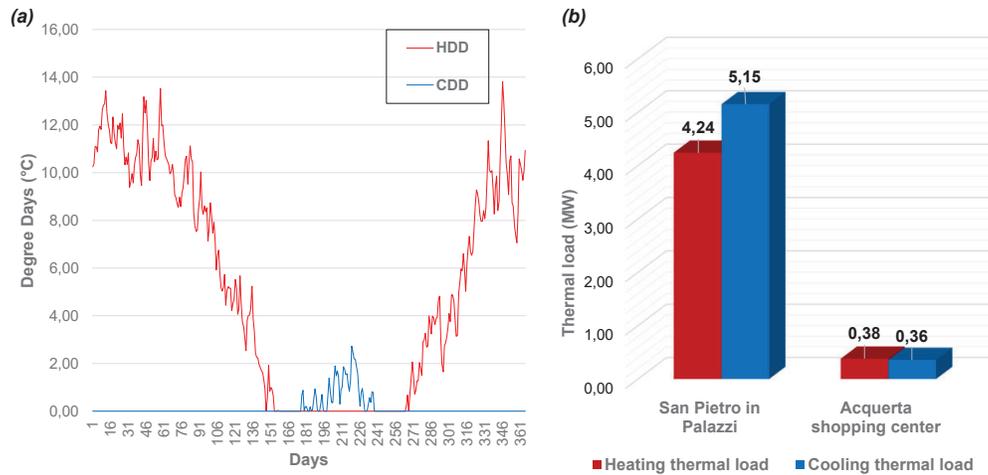


Figure 6. a) Annual evolution of heating and cooling degree days in the selected location, b) Energy demand for the area studied.

Figure 6 (b) illustrates the thermal needs of the Acquerta shopping centre - the main user to be satisfied - as well as those of the San Pietro in Palazzi community. The total thermal energy required annually by the shopping centre is 0.74 MW. 51.5% of which is for heating and 48.5% for cooling.

7.2. Heating and Cooling district

The CO₂ leaving the AMIS is brought to the desired conditions for the entrance to the steam pipe through three inter-refrigerated compressors up to 4 MPa and subsequent cooling up to 40 °C. A portion of the flow rate is sent to the methanol production system: the remaining CO₂ flow rate to be transported is 2.86 kg/s. The flow rate that must instead be introduced on the liquid side undergoes a further compression up to 10 MPa and subsequently, an absorption cooling (it is proposed the use of geothermal water for CO₂ cooling) is used to bring its delivery temperature to 20 °C.

The initial three compressors are about 300 kW each, the fourth – operational for the final liquid flow delivery rate - needs about 173 kW; the flow rate of water required (sets a maximum outlet temperature of 95 °C) for the two inter-refrigerations is a total of about 2 kg/s, that for cooling the steam up to 40 °C is 1.2 kg/s, while the thermal power that must be dissipated with the absorption cycle is 851 kW.

During winter operation, given the potential of the available CO₂ flow rate, it is possible to satisfy a 430kW thermal user. In this condition, therefore, the system is able to meet the heating needs of the Acquerta shopping centre, with the possibility of distributing about 50kW of heat to San Pietro in Palazzi buildings.

Figure 7 shows the representation of the system just described on the T-s diagram. The subcritical vapour at 4 MPa is compressed to 10.3 MPa (1-2 process) and then is cooled in the trans-critical heat pump to 45°C by rejecting heat to an external fluid (2-3 process, useful heating effect). Carbon dioxide at high pressure is further cooled to 25°C in the air heat exchanger (3-4 process).

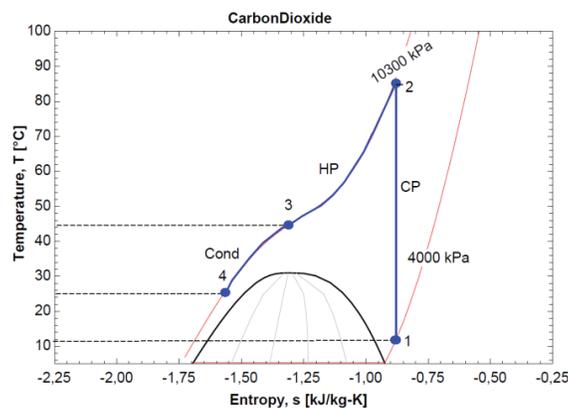


Figure 7. Representation of winter operation on the T-s diagram (CP=Compressor, HP=trans-critical Heat Pump, Cond=Condenser).

The conditions of the CO₂ entering the heat pump, which represents the user, depend on the losses that occurred upstream. In particular, the pressure remains at 4 MPa, but the temperature drops along the pipeline to an estimated value of 10.5 °C, despite the insulation of the pipeline. The power required by the compressor to compress CO₂ to 10.3MPa is 147.3 kW. The calculated COP of the heat pump is about 3. The thermal power required to cool down the CO₂ stream in the air exchanger to bring it back to the liquid state is 229.8kW. Figure 8 (a) illustrates the heat transfer profiles of the first heat exchanger, showing a good coupling between the resource and the user (a result of the selection of a trans-critical Heat Pump). Figure 8 (b) shows the heat transfer profile of the air exchanger that produces the liquid CO₂ recovery stream.

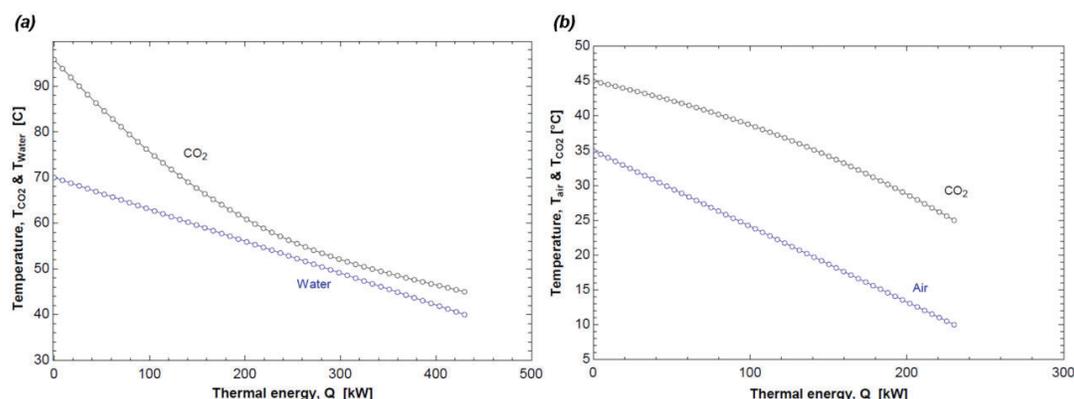


Figure 8. Heat exchange profiles of a) the transcritical heat pump, and b) the air exchanger.

During summer operation, given the potential of the available CO₂ flow rate, it is possible to satisfy a 480kW cooling load. In this condition, therefore, the system meets the cooling needs of the Acquerta shopping centre, with the possibility of distributing about 122kW of cold to the San Pietro in Palazzi households. The difference between summer and winter is dictated by the fact that in summer for cooling the load is greater for the individual user, especially considering the shopping centre.

7.3. Methanol Synthesis Systems

For the MSS1 system, hydrogen from H₂S is compressed to 3MPa in order to combine the hydrogen stream produced by the electrolyzers. Then the hydrogen flow is further compressed up to 6.5 MPa, the working pressure of the MSS. The power consumed is equal to 81.72 kW. Since the compression power required by the CO₂ is equal to 9.4 kW, the total power absorbed by all compressors in the MSS1 is about 93 kW.

Also for the MSS2 system, located at the Solvay Chimica S.p.A. premises, hydrogen must be compressed to 6.5 MPa. In this case, the power consumed is equal to 329.6 kW. As previously specified, it is supposed to take CO₂ from the vapour phase pipe (4 MPa); therefore, it must also be compressed. The total compressor power for the MSS2 is about 193.3 kW. For both MSS systems, the overall power requirement of the compressors is mainly due to hydrogen compression.

As described previously, several heating and cooling processes take place in different sections of the system, requiring an accurate analysis to identify a correct coupling between the different flows to enhance the system's performance. An internal heat recovery was performed to reduce the external requirements of thermal energy (Fig 5). In Table 4 the heating and cooling processes within the MSS are summarised.

Table 4. Main heat transfers in the MSS1 and MSS2.

Heat requirement	Process	Fluid	Thermal power [kW]	
			MSS1	MSS2
Heating	HX1	Reactor inlet	440	8100
	HX2	Methanol and water	46.65	211.5
Cooling	C1	Reactor product	559.6	2368
	C0	F1 liquid product	22.10	107.9

As shown in Table 4, since the MSS does not need external heat input (HX1 and HX2), the main thermal energy load can be identified in the cooling process of the synthesis reactor products (C1) that need to be cooled to about 50°C to separate methanol and water from incondensable gases.

436.55 kg/h of methanol are obtained for the MSS1 system and 2078.6 kg/h of methanol for the MSS2 system, which correspond to 98% and 95% of stoichiometric methanol, respectively. Considering an operation of 8760 h/y, the annual methanol production of the plants is equal to 22 kton. Bearing in mind that the annual carbon

dioxide emissions of the Valle Secolo plant are about 95 kton/year, the two MSS allow using of about 33% of these emissions.

7.4. Mass and energy balance

Table 5 collects the results from the mass balance of the system, showing that the yield is 0.7kg of methanol per kg of CO₂ supplied. The production of oxygen is 0.47kg per kg of CO₂ supplied. A further development of the MSS could be the combustion of the purge stream 19 (Fig 5) and thus the production of electrical energy. The results from the energy balance of the system are gathered in Table 6, which shows that water electrolysis corresponds to 87.6% of the net electricity consumed by the entire process.

Table 5. Mass balance (not including the remaining CO₂ transported to the final terminal).

Compound	In (t/h)	Out (t/h)
CO ₂	3.61	0.0121 ^a
CO	0	0.0036 ^a
H ₂	0	0.1278 ^a
H ₂ O	1.928	1.45
Methanol	0	2.52
O ₂	0	1.71 ^b

^a Contained in stream 19 (purge)

^b Oxygen generated by water electrolysis

Table 6. Energy balance.

Unit	Operation	Amount [MW _{el}]	Amount/tMeOh [kJ/ton MeOh]
Water electrolysis	Power to AEL	10.8	0.604
H ₂ S reduction	Power to PCR	0.157	0.003
CO ₂ preparation	CO ₂	1.09	0.02
	Compression		
Methanol synthesis and purification	Compressors	0.29	0.005
Total net electricity consumption		12.332	0.633

7.5. CO₂ emissions avoided

The assessment of avoided CO₂ emissions is done by investigating the difference between two scenarios: the conventional and the innovative. In the conventional scenario, emissions are due to conventional methanol production: most of the commercial methanol produced today comes from fossil fuels, typically using steam reforming from the natural gas feedstock. CO₂ emissions from conventional methanol generation are assumed equal to 0.555 kg CO₂/kg methanol [16]. In the innovative scenario, the emissions are only those of the scheme to produce methanol with the H₂+CO₂ reactor, i.e. 0.005 tons CO₂/t of methanol. It should be emphasized that the energy sources necessary for the processes described must be assumed consistently with the purpose of this investigation, therefore the use of electricity from renewables is necessary.

The total CO₂ emissions of both MSS are 105.7 tons/year, considering 8760 operating hours, and with a production of 22 kton/year of methanol; with the conventional system, on the other hand, 12kton/year of CO₂ would be emitted considering the same methanol production and the same operating hours.

The emissions avoided for utilities were calculated for heating from the values of the energy performance index already calculated in primary energy and assuming the use of natural gas with emissions of 199 g CO₂/kWh [17]. For the production of cold, the use of electricity for the supply of the refrigeration cycle with a COP 3 with emissions of 355 g CO₂/kWh for electricity was assumed [18]. Therefore, this results in a reduction in emissions related to the heating and cooling services provided of about to 237 tons of carbon dioxide per year.

8. Conclusion

This work tackles the problem of the greenhouse effect, which is a global problem, and something important on a regional scale. The Tuscany region has almost 1000MW of geothermal energy installed, the only region in Italy with a long tradition on this. Geothermal energy has raised problems, but it has also brought a lot of wealth: at present, geothermal is supplying the largest share (over 78%) of renewable energy in the Tuscany region [19]. The energy transition towards carbon waste-free urban districts relies on local renewable energy assets. As part of the ecological transition, some things will have to change, and this document investigates the possible circular uses of geothermal carbon dioxide, which represents a waste in electricity production, but also a fraction that would still have been released naturally from underground [20]. The scenario investigated in this study lies in some fundamental pillars:

- hydrogen recovery along the way: 103.2 tons/year of hydrogen from the reduction of hydrogen sulphide and 3463 tons/year from Solvay S.p.A.
- production of green hydrogen by electrolyzers powered with renewable energy: 630 tons/year of green hydrogen are produced;
- implementation of Power-to-X technology: 22033 tons/year of methanol are produced by converting about 32 kton/year of carbon dioxide (about 33% of the Valle Secolo total emissions);
- promote the co-generation and distribution of heat and cold for users: 869 MWh/year of thermal load for heating and 543 MWh/year of cooling demand are satisfied. In this way, 100% of the thermal and cooling requirements of Acquerta S.C. and 1.2% and 2% of that of San Pietro in Palazzi are fulfilled during winter and summer operations, respectively.

The circular use of CO₂ also makes it possible to reduce emissions due to heating and cooling operated in an unconventional way: about 240 t/year of CO₂ would be saved. There is also a saving of emissions in the methanol cycle because if the same amount of methanol had to be produced through fossil fuels, about 12 kton/year of CO₂ would be emitted. Hypotheses of sequestration of CO₂ not converted along the route could also be evaluated, as well as bottling, liquefaction and shipment from the port of Livorno. A further future study will concern the economic feasibility of the system.

In conclusion, this work focused on the Tuscany region represents a screening of interesting possibilities for sustainable development.

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Nomenclature

Abbreviations

AEL	Alkaline water Electrolysis
AMIS	Abatement of Mercury and Hydrogen Sulfide, in the Italian language
CDD	Cooling Degree Days
DBD	Dielectric Barrier Discharge
GPP	Geothermal Power Plants
HDD	Heating Degree Days
MSS	Methanol Synthesis Section
NCG	Non-Condensable Gases
PCR	Plasma Catalytic Reactor
PV	Photovoltaic

List of Symbols

D	Diameter, m
m_v	Volumetric flow rate, m ³ /s
p	Pressure, MPa
T	Temperature, °C
<i>Greek symbols</i>	
μ	Viscosity, Pa.s
ρ	Density, kg/m ³
<i>Subscripts</i>	
c	critical
i,opt	optimum inner
s	saturation

References

- [1] Somma R., Granieri D., Troise C., Terranova C., De Natale G., Pedone M. Modelling of hydrogen sulphide dispersion from the geothermal power plants of Tuscany (Italy). *Sci. Total Environ.* 2017;583:408-20.
- [2] Olah G. A. Beyond Oil and Gas: The Methanol Economy. *Angew. Chem., Int. Edit.* 2005;44:2636-2639.
- [3] ARPAT. Monitoraggio delle aree geotermiche toscane. Controllo alle emissioni delle centrali geotermoelettriche. 2014.
- [4] Zhang Z., Wang G., Massarotto P., Rudolph V. Optimization of pipeline transport for CO₂ sequestration. *Energ. Convers. Manage.* 2006;47:702-15.
- [5] Serpa J., Morbee J., Tzimas E. Technical and Economic Characteristics of a CO₂ Transmission Pipeline Infrastructure. JRC 2011.
- [6] Zaman J., Chakma A. Production of hydrogen and sulfur from hydrogen sulfide. *Fuel Process. Technol.* 1995;41(2):159-198.
- [7] Baldacci A., Mannari M., Sansone F. Greening of Geothermal Power: An Innovative Technology for Abatement of Hydrogen Sulphide and Mercury Emission. *Proceedings World Geothermal Congress, Turkey, 2005.*
- [8] Mikhail M., De Costa P., Amouroux J., Cavadias S., Tatoulina M., Gàlvez M.E., Ognier S. Tailoring physicochemical and electrical properties of Ni/CeZrOx doped catalysts for high efficiency of plasma catalytic CO₂. *Appl. Catal. B Environ.* 2021;294:120233.

- [9] Zeng K., Zhang D. Recent progress in alkaline water electrolysis for hydrogen production and applications. *Prog. Energy Combust. Sci.* 2010;36:307-26.
- [10] Gallandat N., Romanowicz K., Zuttel A. An analytical model for the electrolyser performance derived from materials parameters. *J. Power Energy Eng.* 2017;5:34-49.
- [11] Brinkmann T., Santoia G.G., Schorcht F. Best Available Techniques (BAT) - Reference Document for the Production of Chlor-alkali. JRC91156, 2014.
- [12] Solvay Chimica S.p.A. Sintesi non tecnica. 2007.
- [13] Graaf G.H., Winkelman J. Chemical Equilibria in Methanol Synthesis Including the Water-Gas Shift Reaction: A Critical Reassessment. *Ind. Eng. Chem. Res.* 2016;55:5854-64.
- [14] Lonis F., Tola V., Cau G. Assessment of integrated energy systems for the production and use of renewable methanol by water electrolysis and CO₂ hydrogenation. *Fuel* 2021;285:119160.
- [15] IMPCA. Methanol Reference Specification. Brüssel 2015.
- [16] Ravikumar D., Keoleian G., Miller S. The environmental opportunity cost of using renewable energy for carbon capture and utilization for methanol production. *Appl. Energy* 2020;279:115770.
- [17] Pylsy P., Lylykangas K., Kurnitski J. Buildings' energy efficiency measures effect on CO₂ emissions in combined heating, cooling and electricity production. *Renew. Sustain. Energy Rev.* 2020;139:110299.
- [18] ISPRA. Italian Emission Inventory 1990-2018. 2020.
- [19] TERNA group. L'elettricità nelle regioni. 2021. [Online]. Available: https://download.terna.it/terna/8%20-%20REGIONI_8dae445e263948d.pdf. [Accessed 2023].
- [20] Sbrana A., Lenzi A., Paci M., Gambini R., Sbrana M., Ciani V., Marianelli P. Analysis of Natural and Power Plant CO₂ Emissions in the Mount Amiata (Italy) Volcanic-Geothermal Area Reveals Sustainable Electricity Production at Zero Emissions," *Energies* 2021;14:4692.