Title Page

Title: Comprehensive Analysis of Renewable Energy Integration in Decarbonised Mobility: Leveraging Power-to-X Storage with Biogenic CO_2 Sources

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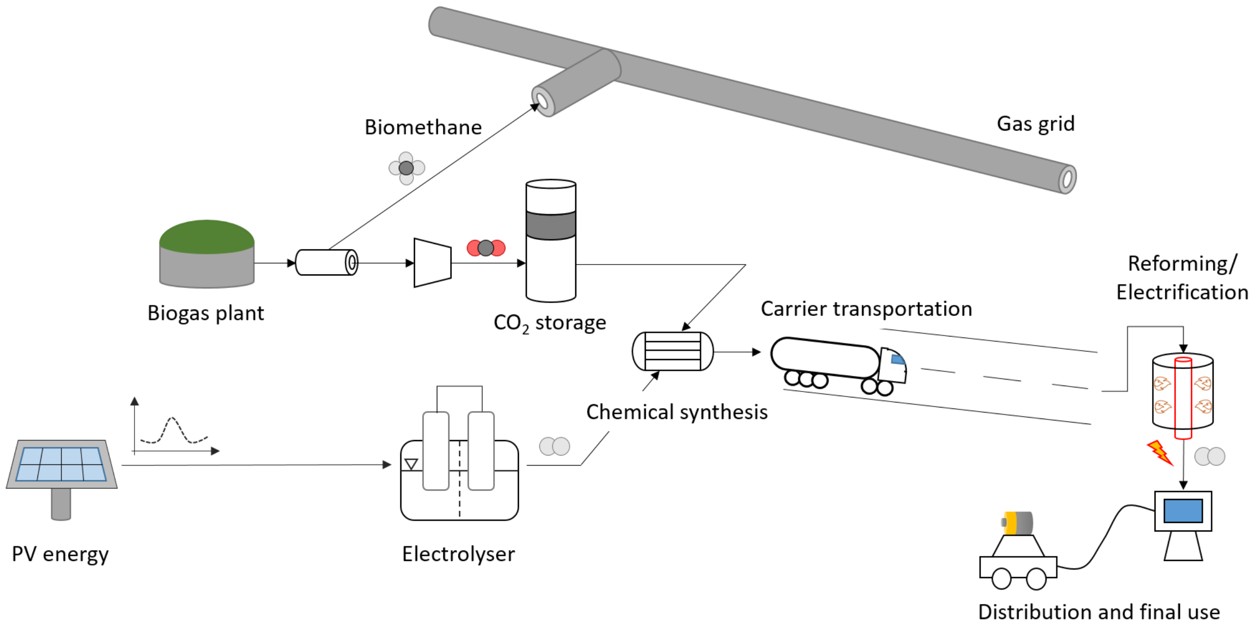


This study analyses the potential of biogenic CO_2 as platform for the energy storage towards the realisation of a carbon-free mobility system.

Abstract

In this study, we conducted the conceptual design of a system aimed at delivering constant energy supply for a decarbonised urban mobility setting. To this scope, we designed two systems based on battery electrical vehicles (BEV) and fuel cell electric vehicles (FCEV). The supply is primarily provided by renewable electricity, eventually converted to H_2 in an electrolyser to feed FCEV. Excess electricity is stored in methane or methanol, synthesised using CO_2 coming from biogas upgrading. We calculated technical performance indicators based on input values obtained for the city of Zurich. We observed that the electrical mobility is the most efficient option from various perspectives, including the efficiency of the engine and the lower amount of electricity required for conversion to H_2. The study shows that for electrical mobility the system would work in storage mode for ca. 70 % of the time (i.e., converting the excess electricity in methane or methanol), requiring the re-conversion of electricity for the remaining time. Methane appears as the best storage molecule for electricity, due to the higher efficiency of the conversion processes, however limiting the electricity-to-electricity efficiency to 29 %. Methanol proves to be the best molecule for H_2 storage, with 43 % H_2-to-H_2 efficiency. The total cost of the system is evaluated considering the case study of a biogas plant close to Zurich. It was found that the cost of the generated electricity and H_2 would range between 0.18-0.21 €/kWh. Combined with the low cost of renewable electricity that is offered to customers for 70 % of the time, this makes the proposed solution a cost-competitive option for the decarbonisation of mobility. Additionally, we observed how the designed system would allow a simple option to integrate carbon capture, operating the transfer of CO_2 from decentralised emitters to a centralised reforming plant. Thanks to this, we calculated that the carbon capture penalty would only range to 0.01-0.02 €/kWh.

Keywords: Power-to-Methanol, Methanol synthesis, Biogas, Techno-economic-environmental analysis, renewable energy, small-scale energy storage

1. Introduction

The reduction of CO_2 emissions in the society cannot prescind from a drastic reduction of the emissions caused by transportation. Currently, in the European Union (EU), the transportation activities (passenger cars and goods transportation) cause more than 20 % of the total greenhouse gas (GHG) emissions [1]. This makes the reduction of the carbon intensity of transportation a key factor to reach the "net-zero" GHG emissions. The electrification of transportation is envisaged as the most promising option for the reduction of such emissions and several countries declared the intention to phase-out combustion engine vehicles [2]. This will mainly be achieved by using battery electric vehicles (BEV). Additionally, fuel cell electrical vehicles (FCEV) can be considered an alternative, as they do not cause any direct carbon emission during the oxidation cycle that produces electricity. This latter technology is of particular interest for heavy duty vehicles [3]. Several studies discussed in literature the environmental impact of BEV; most of them concluded that these vehicles originate lower GHG emissions over their entire lifecycle than equivalent internal combustion engine vehicles [4–9]. However, this assumption is only valid if the source of electricity or H_2 is accompanied by a low carbon footprint [10].

As the main sources of renewable energy are affected by intrinsic stochastic availability, the sustainability of electrified mobility hangs substantially on the energy supply. A constant renewable energy supply is dependent on an appropriate application of energy storage technologies, avoiding the appearance of the so called 'winter hole' [11]. This term refers to the shortage of electricity that can appear in countries where the energy supply is solely based on seasonal-subject resources. The historically available energy storage methods, such as batteries, pumped storage hydroelectricity and flywheels have limited capacity on the time scale and would require excessive space and investment to be extensively used on the seasonal scale [12]. For this reason, the seasonal storage of electricity in chemical bonds has raised as a promising option over the last few years [13]. In this context, production of H_2 by water electrolysis is regarded as the most mature technology to produce an energy vector from electricity [14]. However, direct H_2 storage presents various challenges, due to the low volumetric energy density of gaseous H_2 and to the low boiling point. Hence, for practical applications, H_2 should better be converted to chemical molecules that carry H_2 in solid (e.g. metal hydrides [15]) or in liquid form (e.g. liquid organic carriers [16]).

An important improvement in the energy density of the energy carrier can be obtained by reacting H_2 with CO_2 in the production of synthetic fuels. For example, H_2 can be converted to methane in CO_2 methanation (also referred to as Sabatier reaction):

$$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O \tag{1}$$

$$\Delta H_R^0(298\,K) = -165\,\frac{kJ}{mol}$$

Alternatively, H_2 can be used to produce methanol following the reaction:

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O \tag{2}$$

$$\Delta H_R^0(298\,K) = -49.5\,\frac{kJ}{mol}$$

To model the reactors for methane and methanol synthesis, the water-gas-shift reaction must be considered at the same time:

$$CO + H_2O \leftrightarrow CO_2 + H_2 \tag{3}$$

$$\Delta H_R^0(298\,K) = -41\,\frac{kJ}{mol}$$

Methane and methanol can be stored in the existing energy infrastructure (gas grid, compressed or atmospheric vessels), simplifying the energy storage problem. When needed, these molecules can then be reconverted into H_2 in the reforming reaction (reverse of equations 1 and 2). Additionally, these molecules can be used in the production of electricity, for example in turbines, engines or fuel cells [17–19]. Thanks to this energy storage strategy, one can provide electricity or H_2 to mobility at the times when renewable electricity is scarce [20].

The production of methane from CO_2 was subject of intense research work over the last few years. Several different reaction technologies were applied, both using catalytic or biological reactors [21–25]. The process efficiency observed in the cited references is relatively high, approaching the thermodynamic limit of ca. 60 % for the conversion from electricity to synthetic natural gas (SNG). The production of methanol from CO_2 was demonstrated in some industrial applications, showing that the electricity-to-methanol efficiency is affected by the need of compression of the feed gas to overcome the thermodynamic limitations [19,26–28]. Based on these relevant examples, this work developed detailed models of the CO_2-to-SNG and CO_2-to-methanol reactions. These models were used to perform a techno-economic assessment of the energy carrier production from renewable energy in a decentralised way. As the CO_2 source, biogas was considered, taking advantage of the low-cost CO_2 that can be recovered through power-to-X coupling with biogas upgrading (biomethane production) [29]. The produced methane and methanol are transferred in a centralised storage unit, where the fuels are kept in compressed (CNG) and liquid form, respectively. From this centralised location, the energy carriers collected from several biogas plants with power-to-X are either used as fuels for electrification or delivered to a steam reforming unit to produce H_2 [17,30–32]. These units can be operated either with or without CO_2 capture units, leading to different impacts on carbon emissions and operational costs [33,34].

The final goal of this study is to determine the average yearly final cost of the car fuel (electricity or H_2). This involves considering both the direct production of the fuel when renewable electricity is available and the recovery of electricity or H_2 from the stored intermediate molecules when renewable electricity is not sufficient to cover the demand. To contextualise the relevance of the study, the findings are then applied to a case study relative to the city of Zurich, where several biogas plants are available and could be used as a platform for fuel production via power-to-X. The fuels can be transported to a centralised fuelling station, where they are used to produce electricity or H_2 at the times when renewable energy is not available in sufficient amount. The centralised electrification or reforming reduces the cost of carbon capture. The case study allows performing a thoroughly economic calculation referring to real costs recorded at the location, validating the assumptions of this work versus existing geographical and operation data.

2. Computational methods

2.1. Simulated processes

The scope of this study is to assess the feasibility and cost of the autarchic supply of electricity or H_2 to mobility customers, using as main output parameters the average cost of the fuel per kWh and for km driven for these two energy sources using methanol or methane as energy storage molecules. To achieve this target, two different main energy supply chains were considered: the electricity and the H_2 product streams. These are depicted in figure 1 and in figure 2. The demand is considered constant over time and equals to a certain amount of km/day, as specified in the results section. For both cases, the initial source is an (intermittent) renewable electricity production plant. To adhere with the case study discussed in the second part of the study, the resource displayed is PV electricity. However, the source could be any other renewable technology (e.g., wind or hydropower).

The scheme reported in figure 1 shows how electricity is primarily used to supply the mobility requirements. The system can be equipped with batteries to operate a peak shaving, allowing for a certain intra-day flexibility. In this study, batteries are accounted to ensure a maximum capacity equivalent to 12 hours of supply. This allows a continuous supply over the day for about 50 % of the solar year. When electricity supply overcomes the demand and the batteries are full, the excess electricity is fed to the chemical synthesis unit, which is interconnected with a biogas plant. The chemical synthesis unit includes an electrolyser, a H_2 buffer tank and the synthesis section, where H_2 and CO_2 obtained from biogas upgrading are mixed and converted to methane or methanol. These products are stored either as compressed natural gas (CNG) or as liquid methanol. The products are transferred to a centralised re-electrification facility, which has a larger capacity than the synthesis location. This allows increasing the efficiency and decreasing the cost of the electrification process by economy of scale. For this reason, it is considered that the reforming/combustion of the energy storage molecules utilises only 1/5 of the capacity of the centralised unit, generating CAPEX saving thanks to the economy of scale. The specific CAPEX considered hence refers to a plant that is 5 times larger than the biofuel output of the designed plant. The electricity production is performed in a combined cycle for methane and in a fuel cell for methanol. The fuel-to-electricity efficiency is similar for the two cases, and it is approximately 50 %. In the future efficiency of methanol turbines could increase significantly, with efficiencies up to 60 % [35]. These units can be equipped with a post-combustion carbon capture, to reduce the carbon footprint of the electricity produced.

Figure 2 shows the equivalent supply chain for H_2-based mobility. The working principle is similar to the previous case, but the entire electricity input is converted into H_2. This generates additional complexity to the system, as excess H_2 must be transported from the production site to the chemical synthesis plant, requiring H_2 transport infrastructure if the two locations do not coincide. In the electricity case, the separation of fuelling station and storage molecule production is made possible by the existing infrastructure or the use of virtual flows. For instance, the surplus of electricity at the fuelling station can be sold to the neighbouring users, while an equivalent amount of electricity is purchased at the fuel synthesis plant. To correctly evaluate this case, a sensitivity analysis considering the effect of a grid utilisation fee is included. The use of two different electrolysers at the two different location is an option, but it is economically less viable. This is because it reduces the overall utilisation factor of the electrolysis unit: the fuelling station electrolyser would work throughout the year, while the electrolyser at the biogas plant would work only when excess electricity is available. The excess H_2 delivered to the biogas plant is used in the synthesis unit, which operates identically to the electricity case. The produced methanol or methane are transported to the final location and stored in liquid or compressed form, respectively. When H_2 is needed, due to lack of renewable electricity, methane and methanol are reformed with steam to produce H_2. This is performed in a dedicated unit, including steam reforming and water-gas-shift reaction and which can be operated with pre-combustion CO_2 capture.

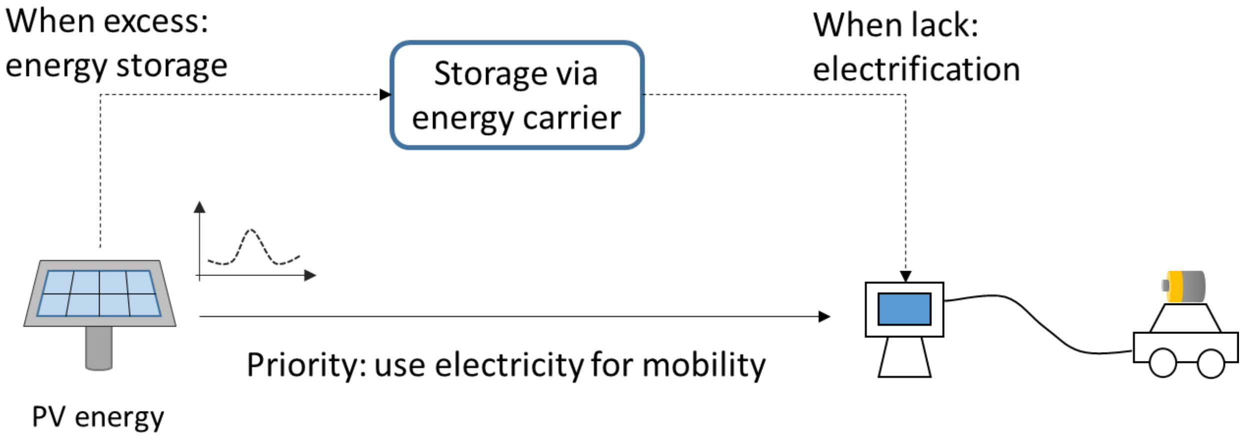


Figure 1 The process scheme to provide electricity for mobility: electricity is primarily utilised for mobility. When electricity is available in excess, the energy storage molecule is produced (methane or methanol). When the electricity is not available in sufficient amount, the storage molecules are utilised to produce the required power.

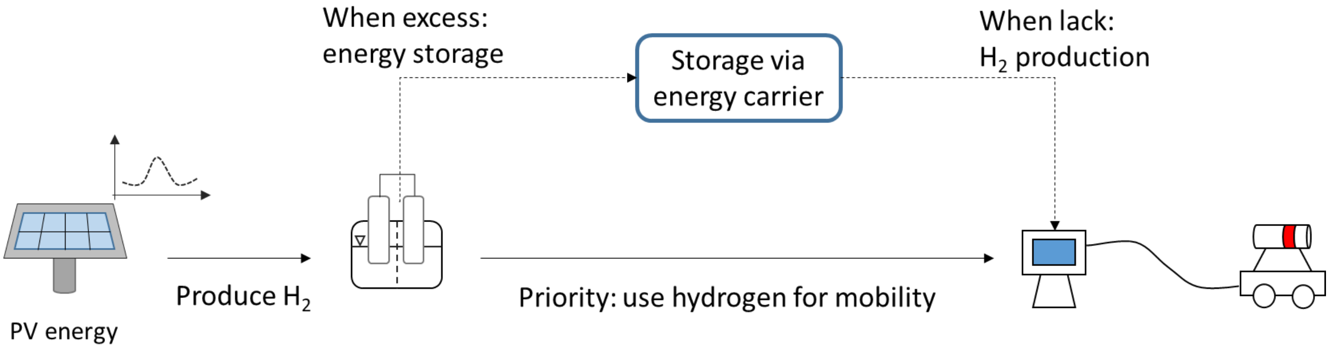


Figure 2 The process scheme to provide hydrogen for mobility: hydrogen is produced and primarily consumed in mobility. When hydrogen is available in excess, the energy storage molecule is produced (methane or methanol). When the hydrogen is not available in sufficient amount, the storage molecules are reformed to produce the required hydrogen.

Figure 3 shows the process analysed in the case study. The case study targets a process to enable negative emissions by entirely utilising the biogenic CO_2 originated by a biogas plant. The plant analysed is in Zurich Werdholzli, where the organic waste and wastewater of the city of Zurich are treated, with a total biogas production of 1400 Nm^3/h. The biogas plant already produces biomethane by upgrading and currently vents the CO_2 waste stream [21]. In the designed process, this CO_2 stream is directed to a storage tank, which operates as a seasonal storage, allowing the utilisation of CO_2 at the times when renewable H_2 is available. A photovoltaic system is designed to provide over the year sufficient H_2 to convert the entire CO_2 stream (560 Nm^3/h in average). The H_2 production section includes a battery and a H_2 tank with peak shaving purposes (capacity defined to ensure the electrolyser continuous operation in summer). In the case study, both methanol and methane are assessed as energy carrier molecules. These molecules are transported to the centralised storage site and kept in liquid form or as compressed gas, respectively. The final products, electricity or H_2, are then produced at the centralised location, as already discussed in the previous paragraphs. The case study allows understanding the required CAPEX and OPEX, as well as the dimensioning of the various units in relevant conditions. Additionally, the reference to a real scale plant helps in the determination of the cost of generating negative emissions by coupling waste management system and mobility.

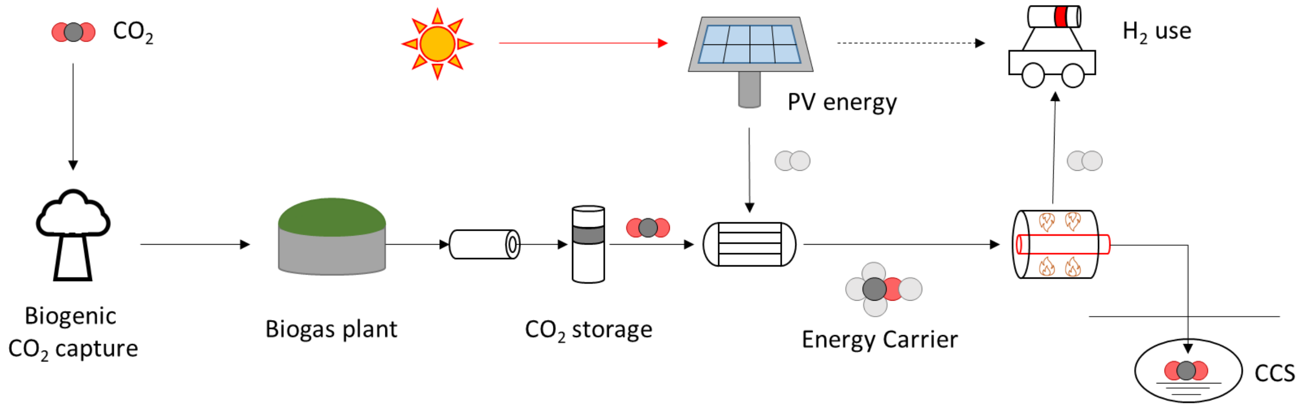


Figure 3 the case study discussed in this study. The biogas plant processes only biogenic waste, which carries carbon that was fixated from the atmosphere. The CO_2 obtained after upgrading is used for fuel synthesis. The fuel is then moved to a centralised unit for reforming. In this way, carbon is moved with the fuel logistics to the final (centralised) consumer side. Here the pre-combustion CO_2 capture is performed, simplifying the CO_2 logistics towards permanent storage.

2.2. Process models

Biogas production

The anaerobic digestion process is not modelled in detail, as this lies out of the scope of this study. According to the expected product composition from biogas plants similar to the case study, the average biogas composition was set to 40 % CO_2 and 60 % CH_4 [36]. Biogas is cleaned to remove impurities such as H_2S, volatile organic compounds and light tars. These steps are operated at low temperature and accounted for in the economic calculations. The estimated cost of biogas is set at 0.06 €/kWh. This cost is not the actual production cost, but rather a minimum cost to make the power-to-X process more convenient than combined heat and power production for the plant operator [37,38]. Biogas is then upgraded in a membrane plant, to produce an injection-ready biomethane. The cost of the upgrading is estimated in 3000 €/Nm_{biogas}^3/h installed and the operative expenditures are accounted as 0.15 €/Nm_{CH4}^3/h. The methane losses in the upgrading are projected as 1 % of the feed [39]. The produced biomethane is sold at 0.12 €/kWh [40]. The produced CO_2 is delivered to the PtX section or, when in excess, compressed to the liquefaction point and stored in a cryogenic tank, whose capacity is determined to contain the maximum reject CO_2 during the year.

Synthesis section

The chemical synthesis section is modelled in detail, to obtain a reliable dimensioning of the units. H_2 is produced in an alkaline electrolyser, whose cost is 1200 €/kW_{el}. The CO_2 methanation reactor is a fixed-bed reactor dimensioned to reach grid-compliant SNG after upgrading (excess CO_2 and H_2 removal). For the upgrading the same membrane as for biogas upgrading is used [41]. The grid regulations are set to a maximum of 2% H_2 and 4 % CO_2 [42]. The reactor is operated with boiling water at 230 ˚C as coolant and at 8 bar [24]. The reactor is modelled with the following 1D pseudo-homogeneous model:

$$\frac{d(uc_i)}{dz} = \nu_i \eta \rho_b r \tag{4}$$

$$(u\rho_b c_{tot})\frac{dT}{dz} = \nu_i \eta \rho_b r(-\Delta H_R) + \frac{4}{d_{tube}} U_T (T - T_w) \tag{5}$$

The kinetic model used are from Xu and Froment [43] (water-gas-shift) and from Koschany et al. [44] for CO_2 methanation. The catalyst efficiency factor is calculated via the Thiele modulus:

$$\phi = \frac{V_p}{S_p}\sqrt{\frac{n+1}{2}\cdot\left(\frac{k c_{i,s}^{n-1}}{D}\right)} \tag{6}$$

$$\eta = \frac{3}{\phi^2}(\phi \coth(\phi) - 1) \tag{7}$$

The heat transfer coefficient is calculated considering the transport phenomena on tube and shell side, as well as the conductivity of the tube:

$$\frac{1}{U_A} = \frac{1}{k_i} + \frac{k_c}{\ln\left(\frac{r_i}{r_e}\right)} + \frac{1}{k_e} \tag{8}$$

k is calculated considering a stagnant and a dynamic contribution:

$$k = k_0 + 0.024 \cdot \frac{l \cdot Re}{d_p} \tag{9}$$

According to the calculated reactor volume, the reactor cost is estimated using a bare module cost, as explained in [45]:

$$C_{BM} = f(C_p, F_M, F_P) \tag{10}$$

C_{BM} is the bare module cost, C_p is the capital cost (depending on reactor geometry), F_M is the material factor (in this case stainless steel) and F_p is the pressure factor. The total installation costs (C_{inst}) include further cost factors, as shown in table 2. The total equipment cost is calculated as:

$$C_{inst} = C_{BM} \cdot (1 + F_c) \tag{11}$$

Table 1 Cost factors for the various components (from [45]*)*

Element	Cost factors (on C_{BM})
Connections	0.4
Instrumentation	0.1
Electrical connections	0.2
Construction	0.13
Planning & permissions	0.3
Total (F_c)	**1.13**

The calculated costs are actualized to the current prices through the Chemical Engineering Plant Cost Index (CEPCI). The CEPCI is calculated as (current = October 2023):

$$CEPCI = \frac{CEPCI\ (current)}{CEPCI\ (2004)} = 1.779 \tag{12}$$

The resulting total cost of the reactor is:

$$C_{tot,today}(€) = C_{BM} \cdot (1 + F_C) \cdot CEPCI \tag{13}$$

The cost of the methanation catalyst is set to 100 €/kg and it is exchanged every 2 years.

The methanol reactor is operated at 70 bar and with boiling water cooling at 240 ˚C. Biogas is compressed in a multi-stage centrifugal compressor, whose cost is calculated as:

$$C_{comp,today} = C_p \cdot F_m \cdot F_p \cdot CEPCI \tag{14}$$

Where the C_p factor is a function of the installed power in kW ($C_p = f(P[kW])$ [45]. The process is operated with three reactive stages with intermediate condensation of the products, to achieve high conversion. The methanol reactors are modelled with a 1D pseudo homogeneous model as described by equations (4)-(9). The kinetic model is derived from Vanden Bussche and Froment [46]. The cost of the methanol synthesis catalyst is set to 20 €/kg and it is exchanged every 2 years. The intermediate heat exchanger cost is determined with the formula (14), where the C_p factor is dependent on the surface area required ($C_p = f(A[m^2])$. The raw methanol is not purified, as the final scope is to reform it back to H_2 and water would be needed in this latter step. For this reason, the electricity production from raw methanol is performed in a fuel cell.

The technical performance of a reformer is calculated by modelling the reaction with a 1D pseudo-homogeneous model (equations (4)-(9)), using a Ni-based steam reforming catalyst, as described by Xu and Froment [43]. As the reforming is performed in large scale, the cost of the unit is estimated according to real plant data, with a total cost of 8’000 €/Nm^3_{CH4} [47]. The CO_2 capture unit is operated with methyl diethanolamine (MDEA) with a CO_2 capture rate of 98% [48]. The CCS cost equals to approximately 80 €/t_{CO2}, with an energy requirement of 200 kWh/t_{CO2} [49,50].

The requirement of electricity and photovoltaics are defined as follows. The data for solar irradiation for Zurich are recovered from [51]. The surface required is set to provide globally sufficient electricity or H_2 to cover the demand from cars to drive 10^9 km/year (process design section). This distance is also considered equivalent to $280 \cdot 10^6$ km/year of a H_2 fuelled bus fleet. In the case study the surface is selected to completely convert the CO_2 originated from the biogas upgrading process of the selected biogas plant to transportable products. CO_2 is stored in tanks of 200 m^3 volume, which cost 150’000 € each. The installation cost of PV panels is set to 900 €/kW peak [52]. The main parameters for the techno-economic analysis are summarised in table 2.

Table 2 Parameters for the techno-economic assessment of the main process units integrated in this study.

Item	Cost [units]
Solar panels	900 [€/kW]
Electrolysis	1200 [€/kW]
Carbon capture	80 [€/t_{CO2}]
Methanation catalyst	100 [€/kg]
Methanol catalyst	20 [€/kg]
Biogas upgrading	0.15 [€/Nm_{CH4}^3/h]
Biogas production cost	0.06 [€//kWh]
Biomethane value	0.12 [€//kWh]
Electricity grid fee	0.05 [€//kWh]

2.3. Technical performance indicators

The main performance indicators are defined as follows.

CO_2 conversion:

$$X_{CO_2} = \frac{CO_2in - CO_2out}{CO_2in} \tag{15}$$

H_2 conversion:

$$X_{H_2} = \frac{H_2in - H_2out}{H_2in} \tag{16}$$

Methanol yield:

$$Y_{MeOH,CO_2} = \frac{MeOH_{out}}{CO_2in} \tag{17}$$

CH_4 yield:

$$Y_{CH_4} = \frac{CH_{4out}}{CO_2in} \tag{18}$$

The process efficiency is defined as:

$$\eta_e = \frac{HHV_{prod}}{HHV_{H_2} + e-} \tag{19}$$

Where HHV is the higher heating value and e- is the electricity employed in the process.

2.4. Economic indicators

To assess the economic performance of the processes, the discounted cash flow was calculated considering a discount rate of 6% and a plant lifetime of 20 years. We calculated the economic indicators net present value (NPV), internal rate of return (IRR) and payback time (PB) as follows:

$$NPV\ (€) = \frac{\sum_1^t R_t}{(1+i)^t} \tag{20}$$

$$\frac{\sum_1^t R_t}{(1+IRR\ )^t} = 0 \tag{21}$$

$$\frac{\sum_1^t R_{PB}}{(1+i)^{PB}} = 0 \tag{22}$$

Where R_t is the cash flow in the year t and i is the discount rate

The minimum cost of the fuel is set as the value that makes the NPV equal to 0:

$$C_{min,fuel} \rightarrow NPV = \frac{\sum_1^t R_t}{(1+i)^t} = 0 \tag{23}$$

3. Results and discussion

3.1. Analysis of the supply requirements

As the scope of this study is the determination of the cost of car fuel per kWh or per km driven, figure 1 recalls the values used in this study as energy requirement to drive 10^9 km. This value was chosen as a reference to simplify the scalability of the results and to represent the energy requirements of a middle-sized town. In fact, the value corresponds to approximately 30’000 cars driving 100 km/day. As a comparison, these values correspond to about 35 buses driving 500 km/day each. The uncertainty bars include the variability effects caused by various properties, such as the different type of vehicle, the technology of the engine and the variance in efficiency over the seasons. The amount of energy required is different according to the fuel used (and hence to the technology of the engine). The battery electric vehicles (BEV) are significantly more efficient than the other cars, with an energy requirement of approximately 150 GWh. For this reason, an electric car can generally be operated with a more expensive fuel per kWh. The fuel cell electric vehicles (FCEV) show a consumption of 269 GWh to drive 10^9 km. This is almost double the demand than the BEV, confirming that electricity should be the favoured fuel for light cars due to the higher efficiency.

The FCEV instead demonstrate advantages for higher duty vehicles, where the weight of the battery can become impractical [3]. To remain as general as possible, this study considers the operation on both fuels, with the target of understanding the effects of various parameters on both supply chains. As a comparison, figure 1 shows also the energy requirements for mobility based on methane and methanol consumed in an internal combustion engine, which are approximately 620 and 540 GWh for 10^9 km. These requirements are significantly higher than the consumption of BEV and FCEV. Additionally, if these molecules are synthesised as e-fuels (i.e., from renewable electricity), the synthesis efficiency would be lower than H_2 production, due to the additional synthesis step. For these reasons, the direct use of these fuels will not be considered further in this study. We assume that e-fuels could play a role in the decarbonisation in the near future, thanks to the possible extension in the use of standard internal combustion engines, but in the long term the advantages of BEV and FCEV should become decisive to favour a complete technological switch towards these latter technologies [9]. However, methane and methanol can still play an important role as H_2 storage molecules, thanks to their higher volumetric energy density. Hence, the study will focus on utilising these fuels to foster the electrification of mobility, ensuring the stability of supply via energy storage in methane or methanol.

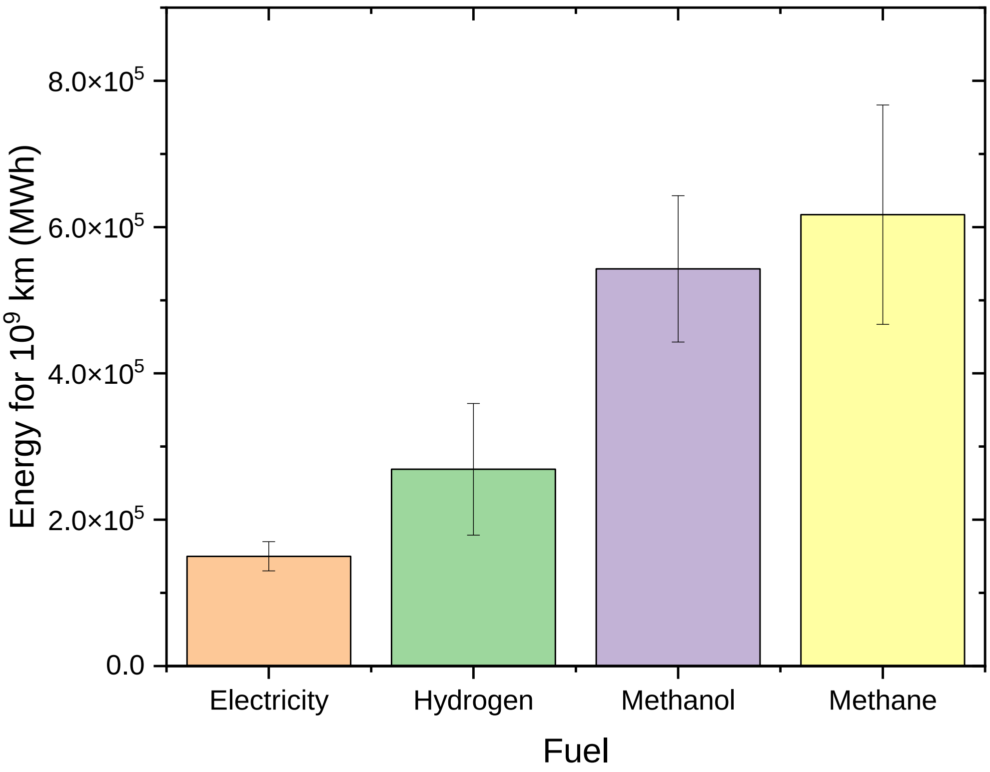
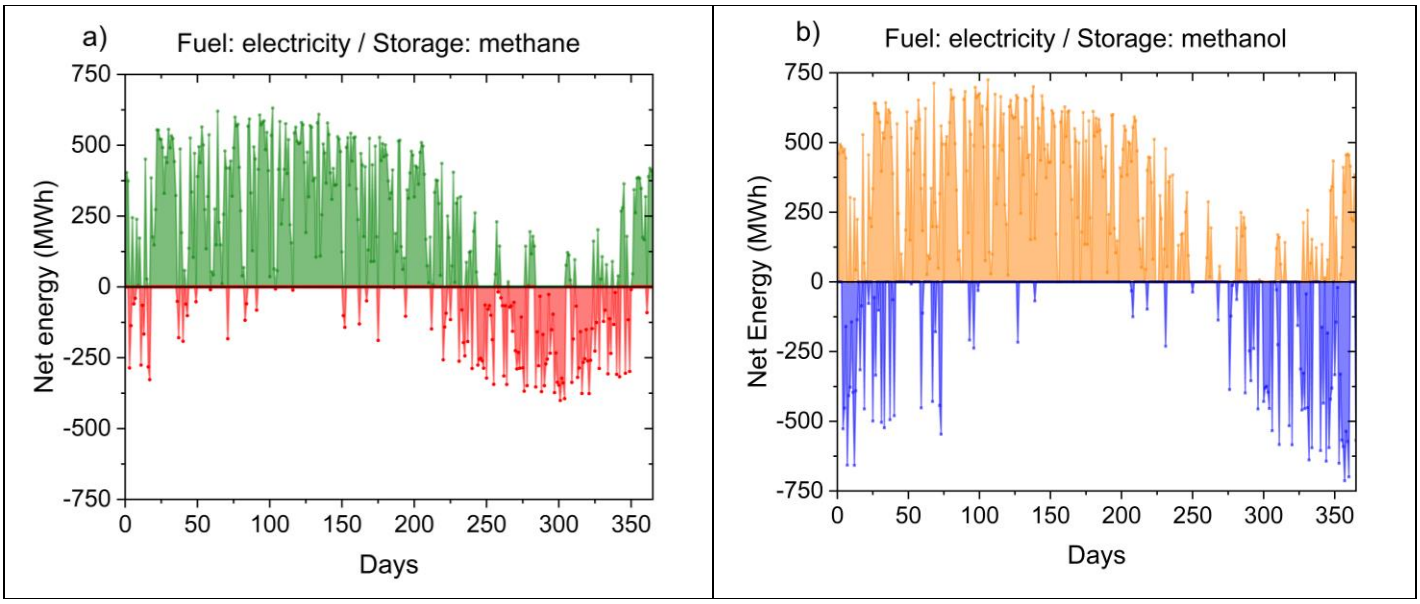


Figure 4 The energy requirements to drive a total of 10^9 km with the various fuels considered (10^9 km corresponds to ca. 30'000 cars driving 100 km/day)



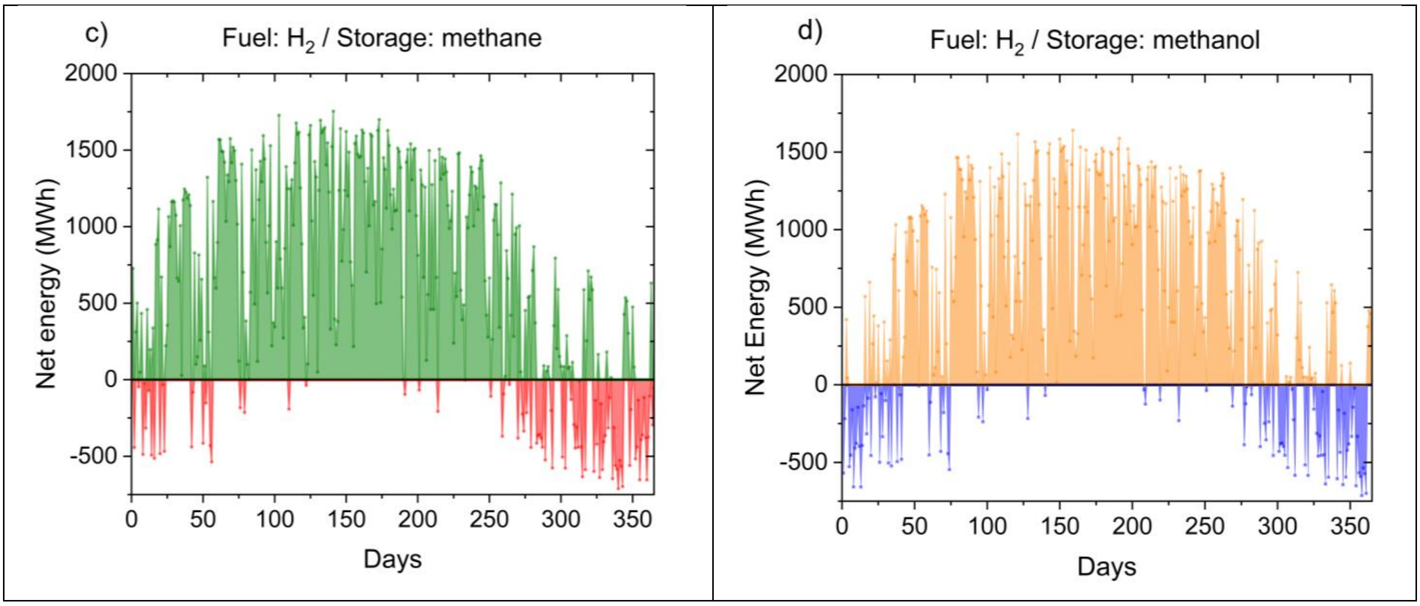


Figure 5 The energy profiles considering the photovoltaic production profiles in Zurich (Switzerland) and a constant demand from mobility of 2'750'000 km/day (10^9 km/year). The profiles are averaged over each day. The resulting net demand (corresponding to the 0 level in the figures) is 410 MWh/d for BEV and 737 MWh/d for FCEV. The profiles refer to: a) mobility on electricity, energy storage via methane; b) mobility on electricity, energy storage via methanol; c) mobility on hydrogen, energy storage via methane; d) mobility on hydrogen, energy storage via methanol.

3.2. Energy and storage demand

Based on the target annual mobility demand (10^9 km/year), the requirements in terms of PV area were determined. The surface for electricity harvesting was considered by matching the day-by-day demand (considered as constant) with the total supply, including the efficiency losses due to the production of the energy storage molecules and to their reforming to H_2 or combustion to produce electricity. Hence, the quantity of energy required is different according to the vehicle technology and to the molecules used for storage. The amount of energy produced or required per day is shown in Figure 5. In the figure, the positive values refer to excess of production, which is consumed in the storage unit and the negative values refer to the days when the demand overcomes the direct electricity availability, hence requiring the utilisation of the storage molecules. The figure represents the values over one year and are showing the profiles from January 1st to December 31st. To simplify the data representation, the results shown are averaged over the days. The figure is divided into 4 panels, each representing the coupling of one mobility type with a storage molecule.

The differing efficiency between FCEV and BEV is reflected in the results as the amount of energy for the H_2 cases is significantly higher. Additionally, as in the H_2 cases all the electricity must be converted into H_2 as a first step, the productivity is influenced by the efficiency of the electrolyser (which is ca. 70 % HHV-based). The results show a clear seasonal trend, with an excess of production in summer and the requirement of energy from storage in winter. In the March-September period, the demand needs to be covered by reforming/electrification only sporadically, hinting that these holes could be covered by some intermediate between-days storage, not considered here [53]. On the other hand, during the cold season, there are clusters of days when the synthesis reactor would be active (mainly periods of persistent atmospheric high pressure), showing that the storage unit cannot be deactivated during long time, due to the risk of curtailing a significant amount of electricity [54].

Figure 6 details the required PV area and the relative fraction of time in which the system operates in storage mode (i.e., when the chemical synthesis reactor is in operation). The error bars report the variability due to data incertitude (e.g., effective utilisation of the solar panels) and to the different possible vehicle technology used (car type). As already hinted by figure 5, the energy harvesting area to feed BEVs is much lower than for FCEVs, due to the higher efficiency of the global process (harvest-to-wheel). The surface required to feed the BEVs is in the order of $800 \cdot 10^3$ m^2, while the same for FCEVs is around $1800 \cdot 10^3$ m^2. The surface required shows a small variation between the storage molecules, with a slight advantage for methane in electricity storage and for methanol in H_2 storage. This depends mainly on the different efficiency in the reforming and electrification processes [55]. When looking at the fraction of time in which the system operates in storage mode (figure 6b), one can observe that the differences are less pronounced. The storage system is in operation for approximately 67% of the time to feed BEVs and ca. 75% for FCEVs. Once again, the storage molecule does not make a strong difference, with a slight favour for electricity storage in form of methane and for H_2 storage in form of methanol. Combining the information from figure 5 and 6b, it is evident that the differences in the switch between operation modes are limited between electricity and H_2, mainly due to the electricity availability profile. On the contrary, the amount of energy to store is significantly different, so for H_2 storage, the system needs to be significantly larger.

To elaborate further on this aspect, figure 7 shows the volume and weight of the storage molecule globally produced over one year for the four cases. The amount of fuel to produce is two to three times larger for FCEVs than for BEVs in all the cases studied. Methanol shows a significant advantage in terms of volume required for storage (at 200 bar), even though the mass produced is much larger. This is due to the different physical properties of the two fuels and to the lower combustion enthalpy of methanol. It is important to highlight that this large difference can become decisive in the selection of the storage molecule, especially when the storage volume available is limited, or when the products need to be transported over long distances [19]. The difference between electricity and H_2 efficiency of use has an important influence also on the chemical synthesis plant size, which is in the order of 25-30 MW for the storage of electricity and 60-70 MW for the storage of H_2.

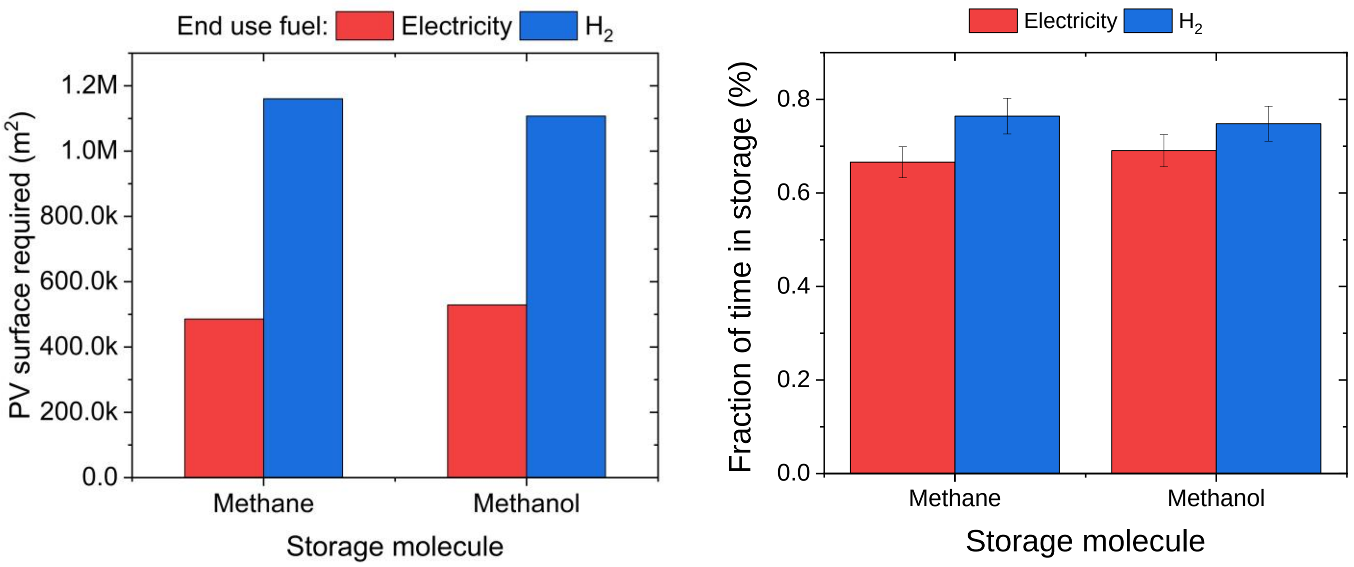


Figure 6 a) The calculated amount of PV surface to supply sufficient energy to mobility and b) the fraction of time over the year in which the storage reactor is active.

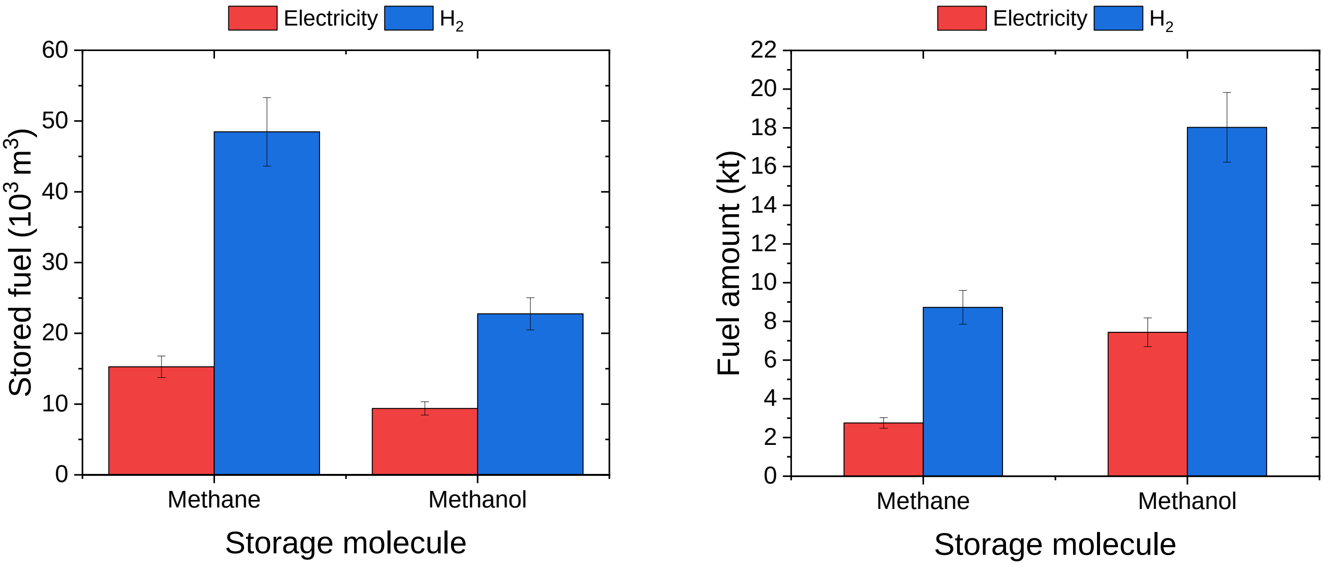


Figure 7 a) the volumetric and b) the massive amount of storage molecule production required to ensure a constant supply of electricity or H_2 over one representative year.

3.3. Comparison of the solutions

The comparison of the designed solutions is summarised in terms of efficiency in table 3. The efficiency of electricity-to-H_2 in the storage units is 36.75% for methane and 43.47% for methanol. For both cases, this corresponds to the product of the efficiencies of electrolysis, chemical synthesis and reforming. The higher efficiency of methanol process is originated from the lower exothermicity of the methanol synthesis from CO_2 (compared to the Sabatier reaction) and the lower heat requirement of the reforming reaction. This is at the origin of the better indicators for methanol as an H_2 carrier than methane. The situation is reversed when considering the electricity-to-electricity efficiency, where methane shows a higher value (28,87%) compared to methanol (21.73%). In any case, the re-electrification of the chemical bonds suffers from significant penalisation in efficiency due to the low effectiveness of the electricity production step.

When looking at the global efficiency of the system (i.e., total electricity to customers/total electricity from PV), the efficiency value strongly favours the utilisation of methane as an electricity storage molecule. The efficiency values are calculated with a weighted average between the direct utilisation of renewable energy to feed mobility when available (ca 60-70 % of the year) and the used of stored molecule when renewable energy is insufficient. The resulting efficiency value for methane is 69.74%, while the value for methanol is 53.67%. This difference is originated by both the higher efficiency of electricity production from methane and by the larger amount of storage needed for the case of methanol. Note that the higher efficiency for the methane use in electricity production is mainly originated by the larger combustion enthalpy, which causes an increase in the Carnot efficiency of the thermodynamic transformation. In the best case, the energy penalty caused by using fuel storage to provide a constant autarchic renewable energy supply is thus ca. 30%. This value depends on the input profile used and would be decreased when the input is less subject to seasonality or vice versa. When looking at the global efficiency in H_2 delivery to the customers (i.e., total H_2 to customers/total electricity from PV), one can note that the differences are less pronounced, as methanol is a more efficient H_2 storage molecule than methane, decreasing the negative effect caused by the larger amount of storage molecules needed. Nevertheless, methane remains the most efficient storage fuel, with 62.67% efficiency vs. 56.28% of methanol. Note that the maximum efficiency is mainly limited by the electrolyser, whose efficiency value is ca. 70%.

Table 3 The calculated efficiency values according to the set boundary limits

Case	Methane (%)	Methanol (%)
Electricity – to – H_2	36.75	43.47
Electricity – to – electricity	28.87	21.73
Global efficiency to electrical mobility (including direct el. use)	69.74	62.67
Global efficiency to H_2 mobility (including direct el. use in H_2 production)	53.67	56.28

To summarise the main findings of this study, table 4 shows a rating of the four options studied with respect to the main performance indicators of the system. The solutions involving H_2 as final product are more favourable concerning the storage efficiency, fuel handling at the gas station (as H_2 is easier to store temporarily than electricity) and possibility of carbon capture (as this can be employed as pre-combustion carbon capture). Electricity is instead the preferred final product for the PV surface required (as the global efficiency for mobility is higher), for the quantity of storage molecule to produce, for CO_2 feed required and for the efficiency in the final use (more km driven with the same amount of fuel). As highlighted previously, when the storage molecule plays a role in defining a property (i.e., for storage efficiency, PV surface, storage and CO_2 amount) methanol is generally a better vector than methane to store H_2, while the opposite holds for electricity.

Table 4 summary of the rating of the process option analysed with respect of several key performance indicators (+: positive performance; -: negative performance)

	Storage efficiency	**PV surface required**	**Fuel handling (at gas station)**	**Storage required**	**Biogenic CO_2 required**	**Possibility of CCS**	**Car efficiency**
Electricity via CH_4	-	++	-	++	++	-	++
Electricity via MeOH	--	+	-	+	+	-	++
H_2 via CH_4	+	-	++	-	-	++	--
H_2 via MeOH	++	--	++	--	--	++	--

3.4. Economic analysis with a case study

The analysis performed until this point only includes the technical performance of the system. To incorporate the economic evaluation of the system and to determine the final cost of H_2 and electricity to the final users, the investigation is continued considering a specific case study. As the electricity input profile selected corresponds to the PV electricity availability around Zurich, the CO_2 input source investigated is the biogas plant of Werdhölzli, where biogas is produced from organic waste and wastewater treatment. The plant is equipped with a biogas upgrading unit, which produces CO_2 as a waste stream with a total average flow of 700 Nm^3/h. In the case study, it is envisioned that the entire CO_2 stream is utilised as a platform for energy storage, enabling possible negative CO_2 emissions by transporting CO_2 in the form of fuel and by capturing it at the final utilisation point. To ensure the utilisation of the entire CO_2 stream, a CO_2 storage unit in liquefied form is envisaged. The economic analysis includes the installation cost of the PV plant to convert the entire CO_2 production, the electrolysis unit to produce H_2, the synthesis unit (methane or methanol production), the CO_2 storage and the fraction of the cost for the reforming or electrification of the product in a centralised unit. Additionally, the cost for carbon capture at the utilisation point of the product is included. The results of the calculations are reported in figure 9. For clarity, the results are also reported in tabular form in the appendix. The total cost of the plant depends strongly on the storage molecule selected, as more electricity (and hence H_2) is required to convert CO_2 in methane than methanol. This is visible in figure 9, as methanol plants have a size between 12 and 13 MW, while the methanation plants need to handle between 15 and 16 MW of H_2. The investment costs for the delivery of electricity to the customers is higher than the corresponding cost for H_2 production, due to the lower electricity-to-electricity efficiency, as already explained in the previous sections.

Figure 9 allows the determination of the contribution of the single cost elements to the total investment cost. The main fraction of the cost involves energy harvesting and H_2 production (electrolysis). These elements correspond to slightly more than 50 % of the cost in every investigated case. The CO_2 conversion unit (methanation or methanol synthesis unit, including reactor vessel and ancillaries) is responsible for approximately 20 – 25 % of the costs. The cost of the methanation reactor is lower than the methanol reactor because it is simpler, working at lower pressure and achieving higher conversion in a single pass. This confirms what calculated in several similar works available in literature [38,56–59]. CO_2 handling (liquefaction and storage) is almost constant independently from the storage molecule (as the CO_2 amount is the same) and corresponds to ca. 5 % of the total investment cost. The final conversion unit (methane or methanol to H_2 or electricity) shows a different cost according to the final product, being electricity production more expensive than reforming. In particular, the reforming of methanol covers only 3 % of the total cost, as the reforming unit is simple (operation at low temperature) and the amount of methanol to reform is the minimum among the cases considered. In the most expensive case, methanol reforming to electricity, the electrification unit covers 13% of the total costs. The nature of the final product influences also the cost of the carbon capture unit, where the pre-combustion unit connected to the reformer is relatively cheap, accounting for 2-3% of the total costs for both methane and methanol. The post-combustion capture after electrification is instead more expensive, requiring 7-8% of the total CAPEX for this unit. This is in line with the estimations normally accepted in literature [19,33,34,48].

All the units designed can process the same CO_2 input, from the 700 Nm^3/h produced by the biogas plant on average. However, due to the different process efficiencies and range of the engines, the distance that can be driven with the same $CO2_2$ input is significantly different for the four processes. The various distances that can be driven with the products of the four process configurations is shown in figure 9. The range for FCEV is similar for methanol and methane storage, with approximately 400 km per hour of CO_2 production. The driven range with BEV is much higher, with ca. 800 km for the methanol storage and 1180 km for methane storage. Hence, the larger cost for the equipment required to store electricity than H_2 is largely compensated by the higher final output in terms of final output. This reconfirms what elucidated in the previous sections and what described in literature [5,9].

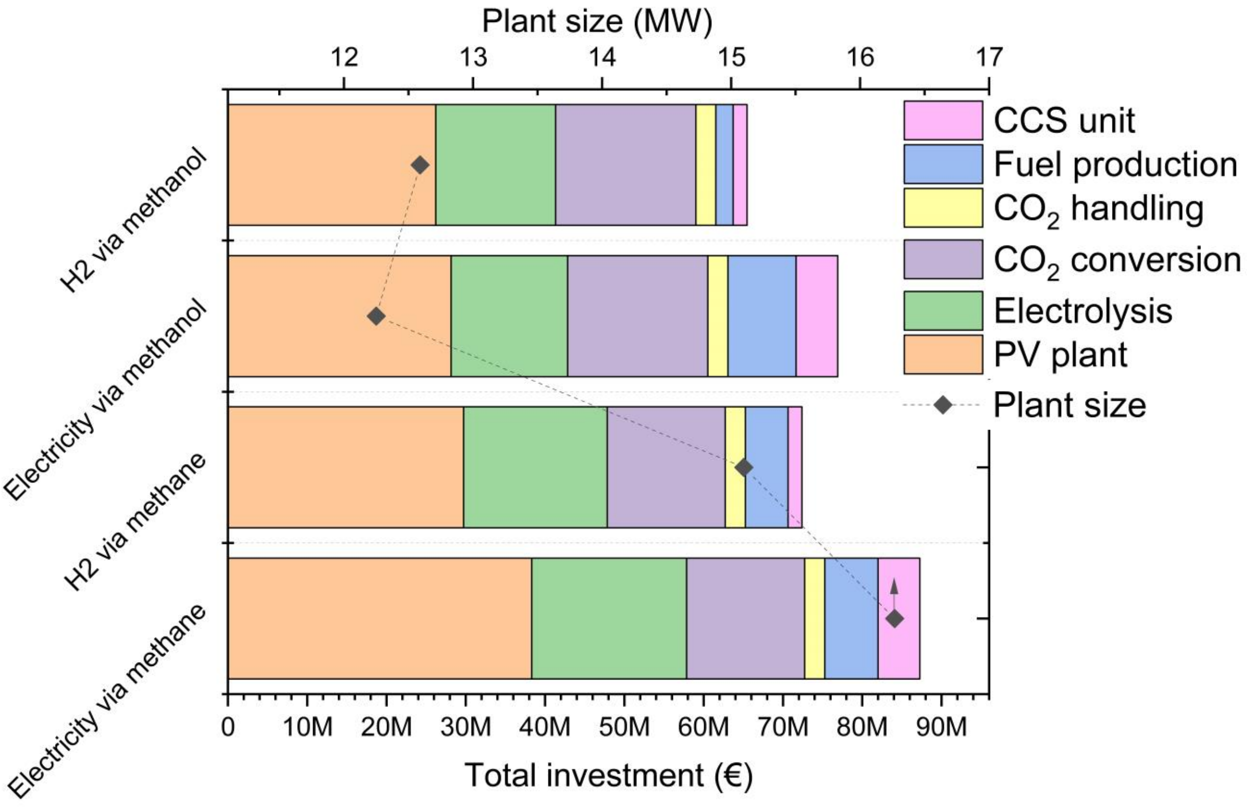


Figure 8 The investment cost for the various solutions analysed in the case study.

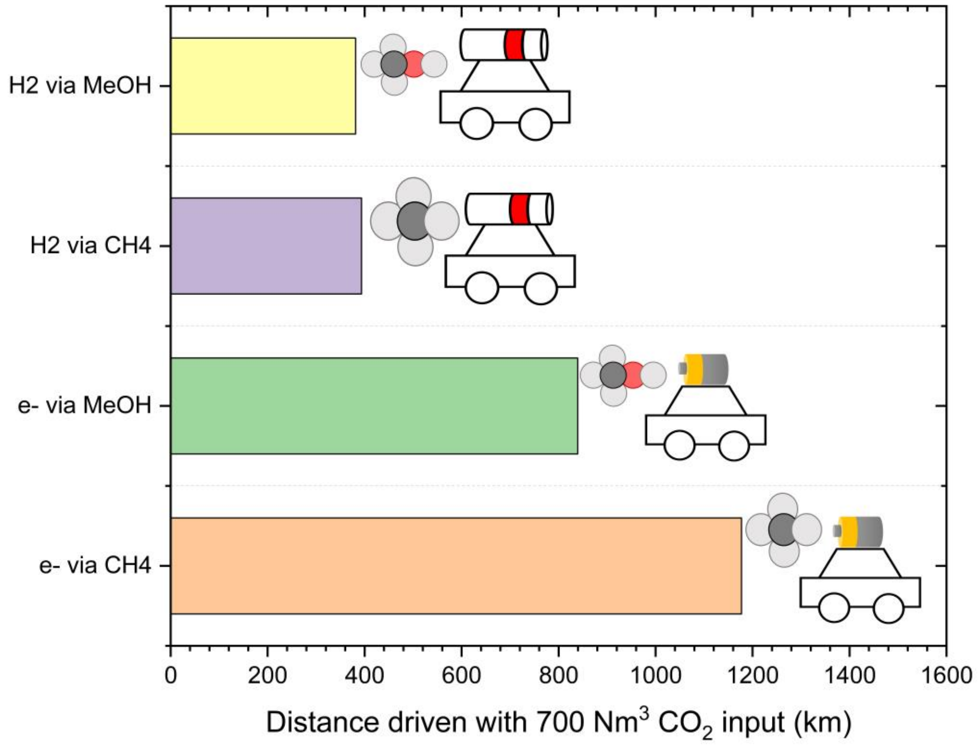


Figure 9 The total distance that can be driven with the fuel produced in the four process configurations, considering the same CO_2 input.

According to the previous calculations, it is possible to determine the total break-even price of the final product (H_2 or electricity). The costs incorporated in the product include the annualised investment cost explained in figure 8 and the operating and maintenance costs of the entire plant. The results of the calculations are reported in figure 10a. The cost of electricity produced for the final customers is higher for methanol storage than for methane storage, reaching ca. 0.22 and 0.19 €/kWh, respectively. The cost structure is reversed for H_2, with 0.18 €/kWh for storage in methanol and 0.22 €/kWh for methane storage. The costs of figure 10a reflect entirely the effects of the various process efficiencies, as reported in table 3. Note that the costs are not affected by any OPEX related to CO_2 supply, as CO_2 is derived from the waste stream of biogas upgrading. Figure 10a also reports the limited influence of carbon capture at the utilisation point on the total product cost for all the cases considered. The cumulated cost of CC is ca. 0.01 €/kWh of product for the H_2 cases and ca. 0.02 €/kWh of product for the electricity cases. These values are quite limited compared to the total fuel cost, showing how the transport of CO_2 from localised emitters in the form of fuels and its successive capture in a larger reforming unit can enable an efficient implementation of negative emission strategies [39,50]. Note that the costs of the CO_2 transport to sequestration plants (not considered here) strongly depend on the boundary conditions such as proximity to harbours and pipelines and are estimated to be more than 100 €/t_CO_2. Figure 10b shows the sensitivity analysis for a variation of the installation cost of the PV system. The highest values in the graph refer to a more conservative assumption in the PV cost, considered as 1500 €/kW. One can note that this variation affects approximately in the same way all the cases of this study. The cost of the products increases significantly, with electricity and H_2 prices lying in the range between 0.33-0.40 €/kWh.

The results of the calculation in terms of final production cost of the fuel recovered from reforming/combustion of stored molecules in various cases are summarised in table 5.

Here, also the influence of various process configurations is elucidated. The first two rows of the table report the same results of figure 10 and are not analysed further. The raw 'PtX with CO_2 from capture' refers to the case in which the CO_2 is not available as a waste stream but must be separated from a flow gas stream (post-combustion carbon capture). In this case, the cost of the products increases significantly. The cost increase is in the order of 200% for electricity production and 300% for H_2 production. This shows that the source of CO_2 is a critical point with the current state of the energy systems, highlighting that the coupling of PtX with energy storage purposes is essential to favour the market entry of these technologies.

Table 5 is also useful to analyse the actual influence that the storage cost has on the fuel supply for mobility. When supported by cheap renewable electricity, direct electricity and H_2 supply would cost approximately 0.033 and 0.064 €/kWh respectively [52,60]. For the case analysed here, this situation would occur for approximately 60% of the total supply time (see also figure 5). This means that the actual price to be charged to the customers would be the pondered average between the second and fourth or fifth row of table 5, respectively. This results in a global average price of ca. 0.096 €/kWh for electricity and 0.112 €/kWh for H_2. The additional cost due to supply security is hence quantifiable in ca. 0.064 €/kWh for electricity and 0.048 €/kWh for H_2. Note that despite the high cost of storage, the total cost of supply is relatively low if compared to current prices of gasoline, which are in the range of 0.20 €/kWh including taxes (i.e., about 0.10 €/kWh prior to taxes). This is due to the low price of renewable electricity that can already be accounted now, when installing new PV plants. This shows how a higher penetration of renewables could be simplified by an appropriate sector coupling, avoiding that the storage requirements become an excessive hurdle for a wider use of clean energy.

The results here presented are valid for a completely autarchic system. Unfortunately, due to the large surface required for electricity production from PV, it may occur that a complete self-production of H_2 is unfeasible. In this case, part of the electricity should be purchased from other suppliers of renewable energy. This electricity would be subject to a grid use fee, which is here set to 0.05 €/kWh (the average value in Switzerland). Figure 11 shows how the use of external electricity would change the cost of the final product. The cost of the final product increases linearly with the decrease of the degree of self-sufficiency, reaching high values for a system purchasing 100 % of the electricity. The slope of the lines is higher to produce H_2, as in this case more electricity needs to be purchased. These results show that the boundary conditions in terms of availability of renewable energy and the policies in terms of grid use have a substantial influence in the economic performance of the PtX system. It is therefore essential to check carefully the local boundary conditions of the location where the hypothetical PtX plant would be located prior to extrapolating the results of this research paper.

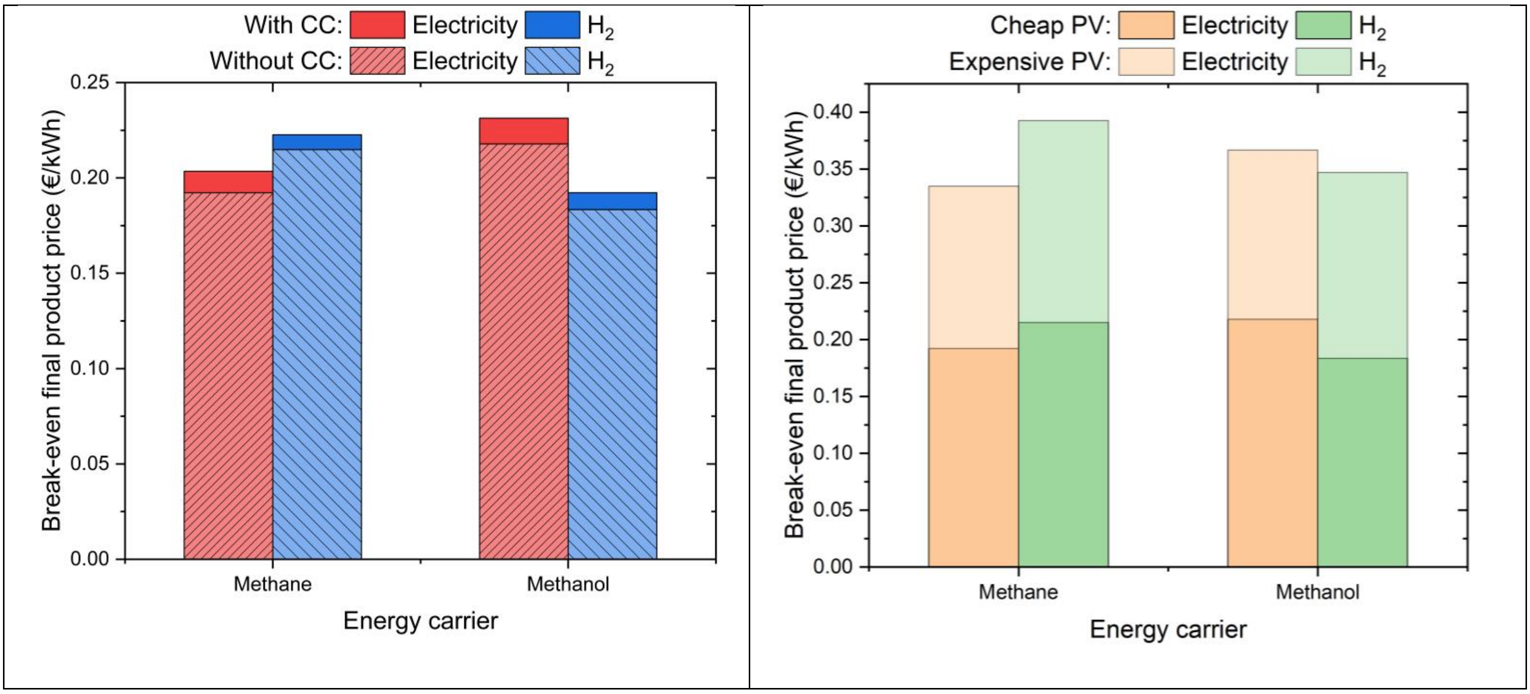


Figure 10 a) The calculated break-even cost of the produced fuel in the four process configurations analysed in the case study, with and without the carbon capture option. b) The influence of the installation cost of solar panels on the final cost of the products

Table 5 The calculated costs of the final products (electriciry and H_2) according to the storage molecule and the various process options.

Product cost (€/kWh)	**Methane for electricity**	**Methane For H2**	**Methanol for electricity**	**Methanol for H2**
With CC	0.203	0.223	0.231	0.192
Without CC	0.192	0.215	0.218	0.184
PtX with CO_2 from capture	0.433	0.647	0.582	0.623
Electricity from grid (incl. grid fee)	0.464	0.728	0.510	0.550
Electricity from high-cost PV	0.335	0.393	0.367	0.347
Electricity from PV	0.033	0.033	0.033	0.033
Green H_2 from PV	0.064	0.064	0.064	0.064

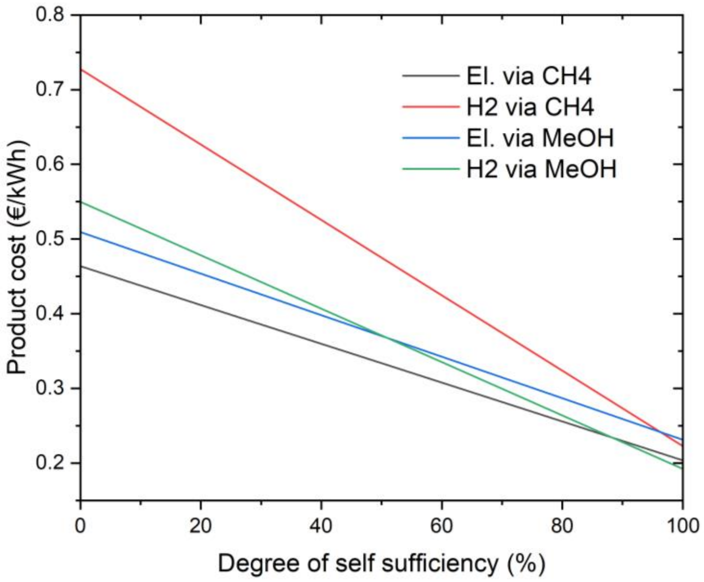


Figure 11 Sensitivity analysis of the cost of the final products according to the degree of self-sufficiency achievable. With degree of self-sufficiency is intended the fraction of electricity that is produced by own PV system, while the rest has to be purchased from the grid (including payment of grid fees).

4. Conclusions

This study shows that battery electrical vehicles (BEV) or fuel cell electrical vehicles (FCEV) can efficiently be supplied continuously with renewable electricity by coupling the direct supply of electricity or H_2 with the storage of electricity in synthetic fuels produced from biogenic CO_2. Methane and methanol were considered as the storage molecules. The system was designed according to the input/output profiles of the city of Zurich, using biogas as CO_2 supply and photovoltaics as renewable electricity input. It was underlined that the power-to-X system would need to operate for about 70% of the time, while for the remaining time, the supply of electricity or H_2 would rely on combustion/reforming of the stored molecules. Due to the different efficiencies of BEV and FCEV, direct electric mobility is advantageous from various perspectives, including the global efficiency of the system including storage. From a pure storage point of view, methane is the best option for electricity storage, while methanol is best for H_2 storage.

To assess the economic performance of the system, the complete system providing electricity/H_2 for mobility was evaluated considering a specific case study, including the biogas plant of Zurich Werdholzli. In this case, the option to completely convert the biogenic CO_2 produced from the biogas upgrading plant into synthetic fuels was assessed. This allows, in principle, the use of CO_2 as a carbon vector for energy storage, enabling subsequent centralised capture to generate negative emissions linked to the energy use in mobility. In this context, it was highlighted that the additional cost to achieve carbon neutrality and favour the capture of CO_2 would be limited to 0.01-0.02 €/kWh of fuel produced. The total cost of the electricity produced from stored methanol or methane would be between 0.192-0.218 €/kWh, while the cost of H_2 would range between 0.184 and 0.215 €/kWh. The lowest costs correspond to the use of methane for electricity storage and methanol for H_2 storage. Combining the information obtained from the operation time of the system and the calculated costs, one can estimate the average cost of the supply to mobility in approximately 0.096 €/kWh for electricity and 0.112 €/kWh for H_2.

This study shows how the adaptation of the strategies to provide renewable electricity to mobility via sector coupling can unlock significant optimization potential and increase the chances for penetration of renewable energies and decarbonisation in the mobility sector. The coupling of cheap CO_2 supply (e.g., from biogas upgrading in this study) and excess electricity that cannot be absorbed by the mobility sector unlocks favourable scenarios, minimizing the cost of energy storage and ensuring an optimal solution for the continuity of energy supply. Additionally, the coupling of decentralised fuel synthesis and centralised reforming allows a simplification of the CO_2 handling, as CO_2 is consumed in the localised (small-scale) emission points, while it is obtained back in a centralised location, where the processing of CO_2 towards permanent storage should result simpler. From a systemic point of view, this study shows that the combination of cheap renewable electricity supply and appropriate sector coupling in the energy storage can allow the realisation of a global system that can deliver decarbonised fuels to the final users without excessively increasing the cost of the carburants. In fact, with the adequate system design, the average production cost of the locally produced electricity or H_2 can be in the same range as the current carbon-intensive gasoline supply chain.

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CRediT authorship contribution statement

Hossein Madi: Formal analysis, Writing - original draft, Writing - review & editing, Funding acquisition. **Tilman Schildhauer:** Conceptualization, Methodology, Writing - original draft, Writing - review & editing, Funding acquisition. **Emanuele Moioli:** Conceptualization, Methodology, Formal analysis, Data curation, Writing - original draft, Writing - review & editing, Funding acquisition.

Declaration of Competing Interest

The authors do not have any conflict of interest to declare.

Nomenclature

AEL = Alkaline Electrolyser

BEV = Battery Electric Vehicles

CAPEX = Capital Expenditures

CEPCI = Chemical Engineering Plant Cost Index

FCEV = Fuel Cell Electric Vehicles

GHG = Greenhouse Gas

MeOH = Methanol

OPEX = Operative Expenditures

PtG = Power to Gas

PtX = Power to X

RWGS = Reverse Water Gas Shift Reaction

SNG = Synthetic Natural Gas

STY = Space Time Yield

C_{BM} = Bare Module Cost ($)

$C_{BM,today}$ = Current Bare Module Cost ($)

C_p = Equipment Purchase Cost ($)

F = Stoichiometric Factor (H_2: CO2)

F_C = Cost Factor

F_e = Exchange Rate

F_M = Material Factor

F_P = Pressure factor

X_i = Conversion of the component i

Y_i = Yield of the component i

a = Plant Lifetime (years)

i = Interest Rate (%)

ΔH^R = reaction enthalpy (kJ/mol)

Appendix

Table A1 reports the CAPEX estimation for the designed PtX plants.

	Electricity via methane	H_2 via methane	Electricity via methanol	H_2 via methanol
PV plant	38’319’900 €	29’714’800 €	28’144’800 €	26’220’700 €
Electrolysis	19’521’900 €	18’118’700 €	14’699’600 €	15’107’700 €
CO_2 conversion	14’895’500 €	14’895’500 €	17’683’400 €	17’683’400 €
CO_2 handling	2’528’453 €	2’528’453 €	2’528’453 €	2’528’453 €
Reactor(s)	1’393’917 €	1’393’917 €	4’181’750 €	4’181’750 €

Final conversion	6’719’007 €	5’393’214 €	8’592’754 €	2’176’520 €
CCS unit	5’260’557 €	1’753’519 €	5’260’557 €	1’753’519 €
Total	88’639’235 €	73’798’103 €	81’091’315 €	69’652’043 €

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