Multiscale analysis for the utilization of CO_2 towards the production of chemicals at the country level: Case study of Spain

Guillermo Galán[a], Mariano Martín[a1], and Ignacio E. Grossmann[b]

[a] Department of Chemical Engineering, University of Salamanca, Plz Caídos 1-5, 37008, Salamanca, SPAIN
[b] Department of Chemical Engineering, Carnegie Mellon University, 5000 Forbes Ave, Pittsburgh, PA, U.S.A.

Abstract

This work evaluates a systematic comparison between the production of methanol and methane using CO_2 and renewable hydrogen. CO_2 is captured from point and dilute sources using aqueous MEA solutions and a conventional DAC process. Hydrogen is obtained through water electrolysis, powered by PV panels and wind turbines. First, a techno-economic evaluation is developed to detail the characteristics of the production facilities and the renewable energy systems. Finally, a Facility Location Problem (FLP) is developed to determine the centralized and decentralized CO_2 use in Spain. This supply network is formulated as a mixed-integer linear programming (MILP) problem, selecting the optimal amount of CO_2 to capture, the number and location of the facilities, the distribution of the PV panels for a fixed available area in the territory, and the number of wind turbines across the 47 Spanish peninsular provinces. Methanol is the selected product, with prices between 1,000-2,600 €/$t_{Methanol}$. MEA solutions are preferred over DAC. Methane production is also considered through decentralized CO_2 capture due to abundant CO_2 availability and high transportation costs. A sensitivity analysis was performed, obtaining prices from 18.97-20.36 €/MMBTU to 8.90-9.09 €/MMBTU in the years 2022 and 2050, covering 5 times the methane production for that period. The implementation of carbon taxes could lower methane prices to around 2-3 €/MMBTU by 2050, aligning closely with natural gas prices.

Keywords: Facility location, Supply chain, Methanol production, Methane production, CO_2 Capture

[1] Corresponding author: mariano.m3@usal.es

Nomenclature

a	First parameter related to wind turbine power equation (8.322 m/s)
AEM	Anion Exchange Membrane
BPM	Bipolar Membrane
BPMED	Bipolar Membrane Electrodialysis
BTU	British Thermal Unit
CAPEX	Capital Expenditures (€/kW-€/t)
CCUS	Carbon capture, utilisation, and storage
CO_{2eq}	Equivalent CO_2
DAC	Direct Air Capture
DEA	Diethanolamine
EU	European Union
FLP	Facility Location Problem
GAMS	General Algebraic Modelling System
GHG	Greenhouse gas
IEA	International Energy Agency
IGN	Instituto Geográfico Nacional
INE	Instituto Nacional de Estadística
kWp	kW peak
kWh_e	kWh of electrical energy
L	Litre
m	Second parameter related to wind turbine power equation (0.806 m/s)
MEA	Monoethanolamine
MILP	Mixed integer linear programming
NEA	Nuclear Energy Agency
OPEX	Operational Expenditures (€/kW-€/t)
P_{Sun}	Power generated by PV panels (kW)
P_{Wind}	Power generated by the GE.15sle wind turbines (kW)
PSA	Pressure swing adsorption
PV	Photovoltaic
SI	International System of units
SP	Supplementary Material
TEA	Triethanolamine
TSA	Temperature swing adsorption
v	Air velocity (m/s)
VSA	Vacuum swing adsorption

Subindexes

e	Electrical
WindNominal	Nominal value refers to wind turbines
PVPanel	PV panel
Sun	From sun
Wind	From wind

Symbols

η	Efficiency of PV panel

1. Introduction

Human activities, particularly industrial development, have significantly impacted the environment by increasing greenhouse gas (GHG) emissions, notably CO_2. GHG concentrations have risen from 280 ppm in the late 19th century to 421 ppm in 2022 (NOAA, 2023). This has caused a 1°C rise in global temperatures, resulting in extreme weather events like droughts, heavy rainfall, melting ice, increased snowfall, and frequent fires (Easterling et al., 2012). To combat climate change, 195 countries agreed in the 2015 Paris Climate Agreement to reduce emissions and limit global warming to 1.5°C (Masson-Delmotte et al., 2019; UNEP, 2021). This entails a 55% emission reduction by 2030 (European Commission, 2020) and achieving net-zero emissions by 2050. However, annual CO_2 emissions in 2022 surpassed 36.8 $GtCO_2$ (IEA, 2023). Drastic emission reductions and CO_2 capture solutions are essential to address this critical issue. On the one hand, the development of vegetation and forest mass is the traditional way to capture CO_2 from the atmosphere. They use the CO_2 through the photosynthesis process to build new structures. Thus, lignocellulosic waste biomass can be employed for multiple applications, for instance, obtaining value-added products, such as DME (Peral and Martin, 2015), green methanol, and diesel (Mbatha et al., 2021; Martín and Grossmann, 2014, 2017a). However, the growth of biomass from cultures has some major issues, such as the high use of land, water, and fertilizer and the costs of collection, transportation, and pretreatment. On the other hand, industrially, carbon capture, utilisation, and storage (CCUS) is considered another alternative. It refers to the capture of CO_2 from various sources, and storing it, for instance, in geological deposits (Beuttler et al., 2019), and enhanced oil recovery (EOR) in depleted wells, among others (IEA, 2022). Related to that, the European Union stands as a proactive leader in the pursuit of ambitious CO_2 emissions reduction targets. It actively drives various initiatives and projects dedicated to carbon capture and reduction. In the year 2023, collaborative efforts from eleven countries resulted in the development of 36 CO_2 storage projects. Spain, distinguished by its substantial storage capacity, played a pivotal role in this endeavour. Noteworthy companies such as Repsol, Naturgy, Endesa, LafargeHolcim Spain, Carbon Clean, and Sistemas de Calor have been at the forefront of CCUS projects. An example is the ECCO2 project, located in Almería, which focuses on the capture of CO_2 emissions from the flue gas of a cement factory (CO_2 VALUE EUROPE, 2023). The utilization of CO_2 for other purposes is the next step of the use to revalorize it The synthesis of components such as methanol from CO_2 captured industrially from different technologies is highly dependent on its concentration. Various methods are employed for capturing CO_2 emissions, depending on the source. Traditional approaches like chemisorption processes with amine solutions, such as MEA, are widely used for point sources like steel and thermal power plants (Hasan, 2017). However, these methods prove less efficient when dealing with dilute CO_2 sources like air. Alternatives like microalgae-based photobioreactors have been explored, but their low yield remains a challenge (Yan et al., 2016; Zhu et al., 2016). Another promising approach is DAC, which utilizes fans to circulate air through an alkaline solution, primarily KOH, where CO_2 dissolves due to its equilibrium with water. In the conventional DAC process, a $Ca(OH)_2$ solution regenerates KOH and converts CO_2 into $CaCO_3$, which is then dried and calcined to release CO_2 and obtain CaO (Keith et al., 2018). An alternative DAC method, bipolar membrane electrodialysis (BPMED) (Sabatino et al., 2020), separates CO_2 into HCO_3^- and CO_3^{2-} ions using ionic membranes. A systematic comparison conducted by Galán et al. (2023) favoured the conventional DAC process in terms of energy and economics. Physisorption-based processes capture CO_2 using sorbent beds like pressure swing adsorption (PSA), temperature swing adsorption (TSA), or vacuum swing adsorption (VSA) (Gupta and Li, 2022). However, stability issues, humidity, and energy-intensive regeneration necessitate multiple parallel beds for continuous operation (Leonzio et al., 2022a, 2022b; Ketabchi et al., 2023). Captured CO_2 can be utilized for chemical synthesis or reduced with hydrogen generated through water splitting using electrolytic cells powered by PV panels and wind turbines (Martín, 2016a, 2017). Methanol and methane are increasingly significant in the Fischer-Tropsch process for synthesizing hydrocarbons. Methanol, a major industrial product, plays a crucial role in energy production (IEA, 2018). Methane's importance stems from its potential as a natural gas alternative. Europe's recent natural gas shortages, exacerbated by the Ukrainian conflict disrupting supplies from Russia's Nord Stream pipelines, highlight the relevance of these chemicals. Despite new gas discoveries, Europe's high consumption and decarbonization goals complicate natural gas utilization. These could alternatively be generated depending on the location, market situation, the evolution of the energy and chemical production costs, and the political decisions that are the factors to decide which chemical to produce. Inside the European countries, Spain has an adequate network to regasify and distribute natural gas. Inside the Spanish framework, Taifouris and Martin (Taifuris and Martin) have developed a network to produce biogas from wastes in Spanish counties. In addition, the production of methanol from CO_2 and electrolytic hydrogen (Martin, 2016a), the production of fuels using renewable energy (Martín and Grossmann, 2018), and the production of methanol from CO_2 captured from atmospheric air using renewable energy (Galán et al., 2023) aims to join the technologies in a systematic comparison of the source of CO_2 and the technologies to remove it, either from a point source as well as dilute has been performed based on a mathematical optimization framework that also allows selecting the best product with the CCUS initiative. In this work, an extended facility location problem (FLP) that includes CO_2 capture from point and diluted sources, hydrogen production from renewable energy sources such as PV panels and wind turbines, and methanol and/or methane production is proposed for the systematic selection of CO_2 use and the location of the facilities. The rest of the work is organized as follows: **Section 2** presents the methodology including the overall description of the processes to capture CO_2, renewable hydrogen production, and methanol and methane synthesis. The formulation of the FLP is described, presenting the modelling steps for the problem. **Section 3** includes the case study focused on Spain, the limitations, and the characteristics of the dataset. **Section 4** includes two case studies and summarizes the results obtained, the evaluation of the location of the different CO_2 capture, chemical production, and power generation technologies over a time horizon, considering the decentralized and centralized CO_2 use cases for methanol production. A sensitivity analysis is also carried out over a time horizon for methane production considering the different prices associated with the technologies. In **Section 5**, the conclusions of this work are discussed and summarized.

2. Methodology

A multiscale approach is proposed to characterize the operation of the transformation facilities to capture and use CO_2, and at the strategy level select the product and locations of these features. At the process level, the results from the facilities are employed to characterize the yield and economy of the different stages:

CO_2 capture, hydrogen production, and methanol and/or methane synthesis. This extended FLP is formulated considering decentralized or centralized CO_2 use through the power provided by PV panels and wind turbines.

The following sections evaluate, first, the process level analysis for the capture and utilization of CO_2. Next, surrogate models are developed, and finally, an FLP is formulated considering the decentralized and centralized use of CO_2 on a country scale, see Figure 1.

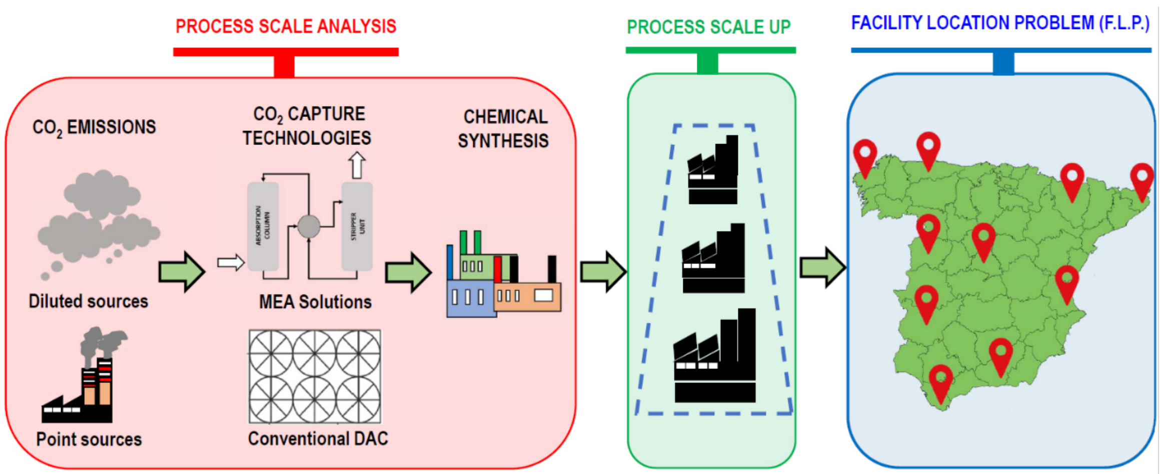

Fig 1. Schematic representation for CO_2 capture, chemical synthesis, and distribution of the facilities.

2.1. Process level analysis

This section describes the different sections involved in the capture and further utilization of CO_2 to produce chemicals following a power-to-x approach. CO_2 capture, energy collection, hydrogen production and synthesis

2.1.1 CO_2 capture modelling

Point sources: CO_2 capture from point sources like steel and thermal industries uses absorbent solutions, mainly aqueous amine solutions (MEA, DEA, TEA). The absorption process takes place at low temperatures (25ºC to 30ºC) and CO_2 partial pressures above 0.05 bar. It achieves removal efficiencies of 90% to 95% at 0.1 bar (Sánchez and Martín, 2021). A scrubber places in contact the amine solution with the CO_2-containing gas phase. The amine flow rate depends on the pickup ratio and concentration of the solution, 20% for MEA, 35% for DEA, and 45% for TEA (GPSA 2004, GPSA 2012). Regeneration of the amine solution requires heating at around 90°C, resulting in solution losses that require replenishment. Refrigeration is used to maintain isothermal operation and to prevent a decrease in capture process efficiency. Concentrations of CO_2 in exhaust gases range from 1% to 33% (Wang and Song, 2020). Despite the efficiency and the cost depending highly on the CO_2 concentration in the emissions, since the granularity of the analysis is clustered in the point sources by province, and therefore an average yield for the MEA is assumed. These emissions have a concentration of CO_2 between 17 and 550 times higher than diluted air. For more details, see the Supplementary Material.

Diluted sources: The CO_2 capture from diluted sources, such as atmospheric air, is carried out using DAC technology (Holmes and Keith, 2012; Keith et al., 2018; Galán et al., 2023). The conventional DAC process involves fans and alkaline solutions like NaOH, Na_2CO_3, and KOH (Keith et al., 2018). Among the solutions, KOH is highly efficient in capturing CO_2, converting it into HCO_3^- and CO_3^{2-} ions through equilibrium reactions with pH playing a significant role. Recycling KOH captures atmospheric CO_2. The solution is regenerated using $Ca(OH)_2$, producing $CaCO_3$ that is separated and dried using the heat released during the hydration of fresh CaO. The steam generated can be used for heating or power generation. The process requires temperatures around 900ºC and can use methane or biogas as fuels to enhance efficiency. For more details, see Supplementary Material.

2.1.2. Hydrogen production

Renewable hydrogen, produced via water electrolysis, eq. (SP-5), using solar or wind power, is mixed with captured CO_2. The hydrogen stream contains water vapour and small amounts of oxygen, which are removed through condensation and a deoxygenation reactor, where oxygen reacts with hydrogen to form water. Zeolite is used to dehydrate the hydrogen. As a byproduct, an oxygen stream is obtained, which also contains water vapour and hydrogen. These impurities are eliminated through condensation and zeolites. Oxygen is mainly used to be sold. For more details, see Supplementary Material.

2.1.3. Energy collection

Wind energy: A GE.15sle turbine model (SAM) is considered, with a nominal power of 1,500 kW. Wind power P_{Wind} is calculated using the turbine power from eq. (SP-6). The estimated cost for installing and operating the turbines in 2022 is approximately 1,600 €/kW (Stehly et al., 2018), and the cost per kilowatt-hour is 0.026 €/kWh (Tovar-Facio et al., 2021). The wind turbine curve is based on literature (Davis and Martín, 2014a).

Solar energy: The PV panels are used to generate power from the sun (P_{Sun}, see eq. (SP-7) in the Supplementary Material). Each PV panel with an effective area of 4 m^2 produces 1 kWp, P_{panel}, with an efficiency, η, of 25%. The area is increased to 7 m^2 to account for necessary spacing. The associated costs for installing and operating PV panels in 2022 are 1,050 €/kWp (Fu et al., 2018) and 0.042 €/kWh (Tovar-Facio et al., 2021), respectively.

2.1.4. Synthesis

Methanol production: Methanol synthesis is achieved by combining renewable hydrogen generated through water splitting using power from PV panels and/or wind turbines with the CO_2 captured through MEA solutions or the conventional DAC process. The gas mixture is conditioned to optimal pressure and temperature values

(50 bar and 200ºC, respectively) using compressors and heat exchangers. Methanol production is controlled by equilibria with the $Cu/ZnO/Al_2O_3$ catalyst. Since the reaction is not fully complete, the unreacted reactants are recycled back to the reaction section. Methanol purification is carried out through distillation, and the final product is stored for sale or transportation to other processes. For more detailed information on the process and its modelling, please refer to the provided references (Martín and Grossmann, 2017a, 2017b).

Methane production*:* Methane synthesis involves mixing renewable hydrogen with captured CO_2 to produce methane, similar to methanol synthesis. The gas mixture's pressure and temperature can range from 1 bar to 30 bar and from 140ºC to 350ºC (Gassner and Marechal, 2009). Methane production relies on the equilibria of methanation and water gas shift reactions, requiring precise temperature control due to the exothermic nature of the $H_2/CO/CO_2$ mixture. The resulting methane composition should be over 95% after removing water. If higher composition values are desired, additional purification steps can be applied. Further details can be found in the references (Davis and Martín, 2014a, 2014b).

2.2. Process technologies surrogate modelling

To include the technologies at the country scale, yields, energy requirements, CO_2 availability from sources in every location, as well as linearized CAPEX and OPEX, and installation costs represent the surrogate models for each one (see Tables 1, 2, 3, and Tables SP-1, SP-4, and SP-12 in the Supplementary Material).

Table 1.- CAPEX and OPEX for the different CO_2 capture processes.

Process	year	CAPEX (€/t_{CO2})	OPEX (€/t_{CO2})
MEA	2022	10.72 (Wang and Ji, 2019)	43.78 (Wang and Ji, 2019)
	2030	10.72[b] (Wang and Ji, 2019)	43.78[b] (Wang and Ji, 2019)
	2050	10.72[b] (Wang and Ji, 2019)	43.78[b] (Wang and Ji, 2019)
DAC	2022	516.06 (Keith et al., 2018)	19.49 (Keith et al., 2018)
	2030	378 (Fasihi et al., 2019)	13.99 (Fasihi et al., 2019)
	2050	222 (Fasihi et al., 2019)	8.21 (Fasihi et al., 2019)

a: This value is taken from the literature for the long term.

b: For the capture of CO_2 with MEA, the same values of CAPEX and OPEX are considered due to the lack of studies of estimates for 2030 and 2050.

Table 2.- CAPEX and OPEX for the different production processes.

Process	year	CAPEX (€/kW)	OPEX (€/kW)
Water Electrolysis	2022	710.30 (Lazard, 2021)	10.65 (Lazard, 2021)
	2030	619.50 (IEA, 2019)	9.29 (IEA, 2019)
	2050	398.23[a] (IEA, 2019)	5.97[a] (IEA, 2019)
Methanation	2022	747.79 (IEA, 2019)	29.91 (IEA, 2019)
	2030	650.44 (IEA, 2019)	26.04 (IEA, 2019)
	2050	500[a] (IEA, 2019)	20[a] (IEA, 2019)
Methanol Synthesis	2022	699.12 (IEA, 2019)	10.49 (IEA, 2019)
	2030	526.55 (IEA, 2019)	7.90 (IEA, 2019)
	2050	336.28[a] (IEA, 2019)	5.04[a] (IEA, 2019)

a: This value is taken from the literature for the long term.

Table 3.- Cost of installation and operational costs of renewable energy.

Renewable Energy	year	Cost of Installation (€/kW)	Operational Costs (€/kWh)
PV Panels	2022	1,050 (Fu et al., 2018)	0.042 (NEA, 2015)
	2030	402.910 (IEA, 2021b)	0.009 (IEA, 2021b)
	2050	297.800 (IEA, 2021b)	0.009 (IEA, 2021b)
Wind Turbines	2022	1,600 (Stehly et al., 2018)	0.026 (NEA, 2015)
	2030	1,243.760 (IEA, 2021b)	0.013 (IEA, 2021b)
	2050	1,138.650 (IEA, 2021b)	0.013 (IEA, 2021b)

2.3. CO_2 utilization at the country scale

2.3.1. Description of resources

The facility location problem (FLP) is extended to include the features of the different CO_2 capture technologies and utilization. The problem relies on the data, CO_2, and energy availability across the provinces.

CO_2 Availability: The CO_2 emissions are posted in kt_{CO2} per year and come from point and diluted sources (see Table SP-11 in the supplementary Material). The aqueous MEA solutions are employed to capture CO_2 from point sources. The data available corresponds mainly to the emissions of steel, and thermal industries installed, among others (see Table SP-11 in the Supplementary Material). In addition, the conventional DAC process is employed to capture CO_2 from diluted sources, atmospheric air. Here, emissions from transportation, agriculture, livestock, and other human activities are considered.

Sun and wind availability: The availability of sunlight is determined by the annual average value of direct solar irradiance in kW per m^2 (Global Solar Atlas). The values in the database represent the entire 24-hour period rather than an average value based on 8 hours of sunlight. Therefore, a full year is used to calculate the total power generated by PV panels. Wind availability is measured using the annual average value of wind velocity in m per s (Global Wind Atlas).

Province distribution: The available surface is calculated as a percentage of the total surface area in km^2 (see Table SP-11 in the Supplementary Material). This approach is suitable considering the limitations of space for installing facilities and renewable power generation technologies, as well as the diverse terrain and its characteristics. The modelling was developed to determine the spatial distribution of the implied facilities, PV panels, and wind farms.

2.3.2. Formulation of the FLP problem

Case a: FLP with decentralized CO_2 use

Each province is determined by a representative point, using the latitude and longitude of the most representative city, typically the capital. Moreover, the availability of CO_2 captured from point and diluted sources is considered. The annual sun and wind availability, and the province area to locate the space for the PV panels.

The aim is to capture as much CO_2 as possible within the area and energy availability constraints minimizing the cost. The source of CO_2 and its final use are major decisions as well as the location of the different facilities. Each section includes CO_2 captured from the point sources, from the diluted sources, hydrogen production, PV panels, and wind turbines, and the final synthesis product is modelled. Surrogate models are developed for each one of the transformation stages considering the yield, resource consumption, and production and investment costs. They are based on experimental data and first principles, assuming they are validated since the modes fit the experimental data, including the detailed process scale cost estimation used to formulate the FLP model. This complete modelling can be found in the Supplementary Material. An issue with CO_2 data availability in certain provinces has arisen during this work. Ideally, emissions data should include other chemicals like NO_2, SO_2, and organic volatiles, contributing to the greenhouse effect. Currently, only CO_2 captured is considered, but the framework presented in this paper can be applied to other chemicals with information updates as needed. Sensitivity analysis relies on estimated data from official sources.

Case b. *FLP with centralized CO_2 use*

The CO_2 captured may be transported among the provinces depending on the CO_2 availability, reservoirs of water to carry out the water electrolysis, the feasibility of producing methanol or methane production, available space to place the facilities, etc. The model is based on section 2.2, including several modifications to adjust the problem features. The distance between the provinces is calculated as the module of the vector that joins them, which is employed to determine the transportation costs (eq. (SP-56)-eq. (SP-62)).

3. Case study

3.1. Setting scenario and limitations

The FLP is applied to the 47 Spanish provinces. Excluded from the analysis are the Spanish sovereign territories of Ceuta and Melilla, the Balearic, Canary, Chafarinas, Alborán, and Alhucemas islands, Vélez de la Gomera rock, and others (see Figure SP-17 in the Supplementary Material). Two cases are considered, decentralized, and centralized CO_2 use. The problems are formulated as a MILP, presenting the first case with 3,237 equations, 2,787 continuous variables, and 400 binary variables. The second case is composed of 8,538 equations, 10,285 continuous variables, and 450 binary variables. The models are formulated in GAMS® using the CPLEX solver, and it is flexible enough to be used for any other region across the globe by just modifying the regional availability of CO_2.

Concerning the limitations, mainly directed to the information available. An ideal scenario would be to have data on the total availability of CO_2 from the facilities and the transportation sector. MEA solution's efficiency depends on the concentration of CO_2 in the flue gas, but it is not possible to extend the absorption kinetic in the network because will be different for each MEA solution. In this line, the composition of the flue is not provided. Another limitation is the lack of variation in some parameters of the technologies in the time horizon. Some approximations related to the CO_2 emissions from the PV panels and the wind turbines, and the water consumption were employed.

3.2. Parameters, variables, and dataset source description

The time horizon of this work covers the years 2022, 2030 and 2050. On the one hand, the parameters related to the amount of CO_2 from point and diluted sources were obtained from the latest available data. The CO_2 from point sources was calculated considering the number of industrial plants in each province. The CO_2 emissions from diluted sources at the provincial level were obtained from the CO_2 emissions in the Spanish autonomous communities, taking the total and the province population as a weighting element. The total population of the provinces, and their total surface, have been obtained from the National Institute of Statistics of Spain (INE). The data relating to the latitude and longitude of the different locations were obtained from the National Geographic Institute of Spain (IGN). The values of the direct solar irradiance, and wind velocity for each location were obtained from Global Solar Atlas, and Wind Global Atlas respectively.

On the other hand, CAPEX and OPEX for MEA solutions, conventional DAC process, water electrolysis, methanation, methanol synthesis, and the energy costs for the PV panels and wind turbines were mainly obtained from the International Energy Agency (IEA), and Nuclear Energy Agency (NEA), see tables in section 2. The rest of the data related to the energy requirements for the processes, the methane consumption in Spain, the methanol prices, the required ratios of CO_2, H_2, O_2, and water for methane and methanol production, and the carbon taxes employed to make the processes more profitable were collected from different individual authors.

The units employed along the work for the parameters and variables belong to the International System of Units (SI), except when the characteristics of the equations and the problem make use of different units or multiples to allow better adaptation to the conditions of the processes. The values of the parameters employed are available in the Tables provided in the main text and the Supplementary Material. In addition, the full dataset and the sources where the data were consulted and collected are available in an accessible format such as an Excel file.

4. Results and discussion

This section is structured into two different subsections, considering the decentralized and centralized use of the captured CO_2 in the supply chain network for methanol and methane production. Each subsection contains a sensitivity analysis focused on the reduction of technology costs, considering the current state in the year 2022 and the time horizon of the years 2030, and 2050. For each year, the cost reduction is a consequence of the reduction in costs associated with the improvement of the technology and its efficiency (Tables 1, 2, and 3).

4.1. Decentralized CO_2 use

4.1.1. Case 1: Optimal products

Among the chemicals considered, methanol is selected as the most economically attractive. Its production is analysed over the years 2022, 2030, and 2050 (see Figure 2, and Figures SP-1, and SP-2 in the Supplementary Material). The total amount of CO_2 emitted in the year 2022 reached 223.8 $MtCO_2$ (see Table SP-11 in the Supplementary Material). As a first approximation, the same available amount of CO_2 is considered for the years of study due to the large uncertainty concerning the amount of CO_2 that will be emitted from the facilities, as well as by the transportation sector, among others in a 30-year time horizon. Thus, that value was taken as a reference for future scenarios and sensitivity analysis. The captured CO_2 amounts achieved 51.76%, 74.72%, and 96.57% as the maximum feasible percentage of total capture considering the total surface available for PV panels installation of 1%, 1.5%, and 2%. This represents 115.8 MtCO_2, 167.2 MtCO_2, and 216.1 MtCO_2 respectively.

4.1.1.1. Current state. The year 2022

The analysis of the results is divided into the CO_2 capture technologies and locations, the selection of the renewable energy sources suggested to power both the capture and the chemicals production and the production of hydrogen and the optimal product or set of products.

CO_2 Capture: The CO_2 capture by MEA solutions and the conventional DAC process, and the investment needed to install these technologies are considered (see Figures 2 a, b, c and Figures SP-1 a, b, c, and SP-2 a, b, c in the supplementary Material). MEA solutions are selected first due to the lower costs than the conventional DAC process. It has a heterogeneous distribution, focused on the industrial areas of the coastline, such as Asturias, Barcelona, Tarragona, and Castellón, and the capital and its surroundings, such as Madrid and Toledo, with less presence in the centre of the peninsula. Huelva, Cádiz, and Murcia are selected as the southern provinces. These locations suggest that petrochemical industries, steel factories, and refineries in their territories, among others, concentrate values of emissions for the use of the 1% of the available surface above 10,000 ktCO_2/year in cases of Barcelona, Madrid, Cádiz, and Castellón, representing more than 12,500 ktCO_2/year in Asturias. The total investment costs correspond only with the use of MEA solutions (see Figure 2 and Figures SP-1, and SP-2). The provinces with the highest presence of MEA solutions technology have investments above 120 M€ with more than 130 M€ in Asturias. Thus, the total amount captured with this technology is 115,820 ktCO_2/year with an investment cost of 1,242 M€$_{2022}$ (Table 4).

The main difference between the CO_2 capture employing 1% of the available surface (See Figure 2 b, c in the Supplementary Material) and 1.5% (see Figures SP-3 b, c in the Supplementary Material) lies in the use of the conventional DAC process as an additional technology to CO_2 capture, which could be installed anywhere because of the availability of air. However, the emissions from the transportation sector, livestock, and others, are concentrated in high-population areas. Moreover, this technology determines the investment cost, which is higher in provinces with this type of capture. Madrid, Barcelona, La Coruña, and Sevilla are mainly selected, showing values above 6,000 ktCO_2/year captured and 4,000 M€ each of investment cost, reaching more than 8,500 ktCO_2/year and 4,500 M€ in the case of Madrid (see Figure SP-3 in the Supplementary Material). Therefore, changes in the distribution are present (See Figures SP-4). The total amount of CO_2 captured is 133,290 ktCO_2/year employing MEA solutions and 33,913 ktCO_2/year with conventional DAC process. The investment costs for CO_2 capture reach 18,923 M€$_{2022}$. The only varying total surface available is from 1,5% to 2%, allowing capturing more CO_2 by an increase of the share of the conventional DAC process (see Figures SP-6 a, b, c and Figures SP-7 a, b, c, and SP-8 a, b, c in the supplementary Material). As pointed out previously, 133,290 ktCO_2/year are captured with MEA solutions and 82,806 ktCO_2/year with conventional DAC process, 144.17% more than the use of 1.5% of the available surface only considering the CO_2 captured employing the conventional DAC process. The investment costs of CO_2 capture are 44,162 M€$_{2022.}$

Renewable energy sources: A description of the surface occupied by the PV panels, the number of wind turbines, and the investment required to install them is performed (see Figure 2 d, e, f, and Figures SP-3 d, e, f, and SP-6 d, e, f in the supplementary Material). The PV panels are distributed across all the territories, especially from the midwest to the northeast, since they have the highest values of solar direct irradiance, achieving values above 80 km^2 of surface used to install PV panels. This area increases when the size of the provinces becomes higher. Thus, some provinces, such as Ciudad Real, Cuenca, and Zaragoza, reach more than 180 km^2, summarizing more than 200 km^2 for Badajoz, Cáceres, and Toledo. The wind turbines have different performances because they are mostly located in the coastline provinces since they provide the highest values of wind velocities. When the amount of CO_2 to capture is low, wind turbines are preferred to generate energy, due to their smaller operation cost with respect to the PV panels (Table 3). However, with a gradual increase in CO_2 capture, it is necessary to increase energy production. Thus, the PV panels are chosen because their cost of installation is lower than the wind turbines (Table 3), increasing the used surface in the same way. When CO_2

capture reaches its limit value for a certain surface, the installation of more PV panels guarantees the most economical operation and power generation possible, but the lack of surface area makes it impossible.

Thus, this energy will be provided by wind turbines, which are located and installed in different provinces depending on the wind velocity. This increases the operating expenses since there is a large installed production capacity but little of it is used. This phenomenon becomes more noticeable when the limit value of the amount of CO_2 is approached, this is the reason why almost all the provinces have wind farms with 400 wind turbines as a maximum. Concerning the investment costs, these are mainly represented as the cost of PV panels. As indicated above, the highest values for investment costs are found following the line from the midwest to the northeast, with Badajoz, Cáceres, Ciudad Real, Cuenca, and Zaragoza involving values of investment costs above 30,000 M€. For 1% of the available surface, a total of 4,935 km^2 of PV panels and 15,635 wind turbines are needed, generating 143.20 GW with investment costs of 777,800 M€$_{2022}$, (Table 4), When the available surface increases up to 1.5% the surface dedicated to PV panels increases in proportion, having more than 320 km^2 for Badajoz, Cáceres, and Toledo. In addition, the number of wind turbines has also increased, in provinces such as Ávila, and Valladolid, with provinces of Cuenca and Jaén involving values of around 100 turbines. Investment cost follows the same distribution of surface for PV panels, increasing the investment cost from the midwest to the northeast above 45,000 M€$_{2022}$. A total of 7,403 km^2 of PV panels and 17,221 wind turbines are required, generating 212.84 GW, and showing investment costs of 1,151,800 M€$_{2022}$ (Table 4). This power represents around 20% and 78% more of the power production in Spain, 119.2 GW at the end of the year 2022 (Red Eléctrica, 2022).

For an available surface of 2%, more than 420 km^2 are involved in Badajoz, Cáceres, and Toledo, while decreasing the number of wind turbines installed in Ávila, Granada, León, Salamanca, Soria, Valladolid, and Zamora, showing values around 400 turbines (see Figures SP-6 in the Supplementary Material). The large surface area devoted to PV panels allows producing almost all of the energy required, making it feasible to use fewer wind turbines, and reducing the costs. Thus, a total of 9,870 km^2 of PV panels and 14,883 wind turbines are required. Although the number of wind turbines has been reduced by 13.6%, the area devoted to the PV panels has increased by 2,467 km^2, representing 33.3% more. Power generation reaches 282,10 GW, with investment costs of 1,516,300 $M€_{2022}$.

Chemicals production: For the electrolytic hydrogen and methanol production, their total investment and those related to the CO_2 capture facilities are discussed next (see Figure 2 g, h, i and Figures SP-1 g, h, i, and SP-2 g, h, i in the supplementary Material). For the decentralized case, the locations selected for the CO_2 capture facilities are the same as for the electrolytic hydrogen and methanol production facilities. Thus, for the 1% of the available surface, Barcelona, Madrid, Cádiz, and Castellón are the main production sites, with values above 1,500 ktH_2/year, 8,500 $kt_{Methanol}$/year, and 5,500 M€, being more than 1,700 ktH_2/year, 9,000 $kt_{Methanol}$/year, and 6,500 M€ in Asturias. The total amount of chemicals produced is 15,512 ktH_2/year, 82,723 $kt_{Methanol}$/year, having an investment cost of 62,253 $M€_{2022}$. The use of 1.5% of the available surface (see Figure SP-3 g, h, i in the Supplementary Material) the same distribution of the facilities is obtained, with the amount of total chemical produced as 22,393 ktH_2/year, 119,430 $kt_{Methanol}$/year, showing investment costs of 107,010 $M€_{2022}$. The increase of the available surface to 2% allows obtaining up to 28,941 ktH_2/year, and 154,350 $kt_{Methanol}$/year, with an investment cost of 157,990 $M€_{2022}$. Regarding the methanol market in Spain and Europe, the consumption for the year 2022 was 932.37 $kt_{Methanol}$/year (ChemAnalyst, 2023) and 10,770 $kt_{Methanol}$/year (EMR, 2023). Thus, considering the maximum methanol produced it could be obtained a level of substitution in Spain and Europe of 164 times and 13 times more respectively. The methanol that can be produced in this way, would be possible to satisfy the demand beyond Europe.

The calculated cost of methanol production is in the range of 2,673 €/$t_{Methanol}$ to 2,838 €/$t_{Methanol}$ (Table 4), which represents between 5.68-6.10 times more than the market price for the year 2022, 400 €/$t_{Methanol}$ (Table SP-2). These processes will be decreased when the carbon taxes are considered in the analysis. Due to stricter environmental policy in the European Union, the companies are responsible for the CO_2 emissions, paying taxes for them. The value of the carbon tax depends on the country and the policy that is carried out. (see Table SP-10 in the Supplementary Material) It can be considered that the process avoids the emission of CO_2 directly into the atmosphere, making the process more profitable and reducing the production cost of the chemicals produced. Thus, for the year 2022, the carbon tax in Spain is 80.87€/t_{CO2}, being the cost of methanol production in the range of 2,560 €/$t_{Methanol}$ to 2,674 €/$t_{Methanol}$ (see Table 4), representing between 5.4 and 5.69 more than the market price for the year 2022.

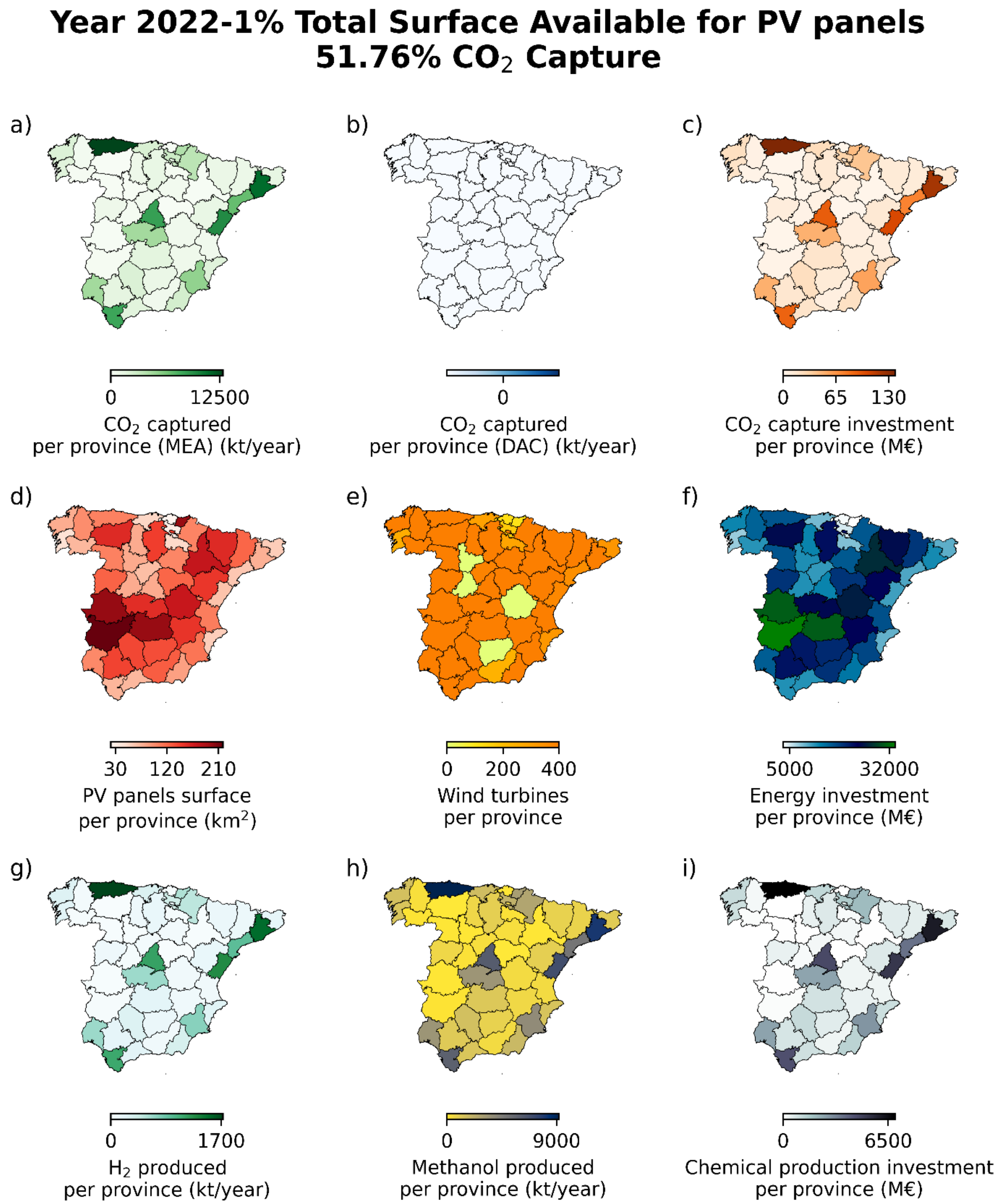

Fig 2. Distribution of CO_2 capture, renewable energy generation, methanol production technology, and their total investments by the province in 2022 using 1% of the available area in Spain.

Table 4.- Parameters of the installation's methanol production for the years 2022, 2030, and 2050.

	year								
Parameter	2022			2030			2050		
Available surface (%)	1	1.5	2	1	1.5	2	1	1.5	2
Total CO_2 captured with MEA ($ktCO_2$/year)	115,820	133,290	133,290	115,820	133,290	133,290	115,820	133,290	133,290
Total CO_2 captured with DAC ($ktCO_2$/year)	0	33,913	82,806	0	33,913	82,806	0	33,913	82,806
Total CO_2 capture Investment cost (M€)	1,242	18,923	44,162	1,242	14,248	32,730	1,242	8,958	19,812
Total PV panels surface (km^2)	4,935	7,403	9,870	4,935	7,403	9,870	4,935	7,403	9,870
Total wind turbines	15,635	17,221	14,883	15,635	17,221	14,883	15,635	17,221	14,883
Total power generation Investment cost (M€)	777,800	1,151,800	1,516,300	313,230	458,220	595,890	236,670	344,350	445,330
Total H_2 produced (ktH_2/year)	15,512	22,393	28,941	15,512	22,393	28,941	15,512	22,393	28,941
Total Methanol produced ($kt_{Methanol}$/year)	82,723	119,430	154,350	82,723	119,430	154,350	82,723	119,430	154,350
Total chemical production Investment cost (M€)	62,253	107,010	157,990	54,303	90,846	131,730	35,347	58,191	83,443
Total generated power (GW)	143.20	212.84	282.10	143.20	212.84	282.10	143.20	212.84	282.10
Production cost (€/$t_{Methanol}$)	2,673	2,764	2,838	1,634	1,680	1,715	1,037	1,053	1,062
Production cost with a carbon tax (€/$t_{Methanol}$)	2,560	2,674	2,768	1,424	1,513	1,585	827	852	907

4.1.1.2. Future state. Time horizon 2030 and 2050

The presentation of the results for the next years and decades follows the same structure as before, but it includes the expected variation in the prices of the energy collection devices as well as the emissions related to them over time.

CO_2 Capture: For the years 2030, and 2050 there is a reduction in the investment costs promoted by the decreases in technology costs (Tables 1, 2, and 3). MEA solutions do not change their costs in the time horizon, involving the same investment costs, 1,242 M€. However, the expected reduction of the conventional DAC process costs (see Table 1) allows for improved operation. With 1.5% of the available surface, the investment costs to CO_2 capture are 14,248 $M€_{2030}$, and 8,958 $M€_{2050}$, which represent a reduction of 24.7% and 52.66% concerning 2022. A similar trend is followed when the surface available is 2%, where the investment costs of CO_2 capture are 32,730 $M€_{2030}$, and 19,812 $M€_{2050}$, reducing 25.89% and 55.14% with respect to 2022.

Renewable energy sources: Here an analysis for the years 2030 and 2050 is performed considering that annual values of direct solar irradiance and wind velocity do not vary, taking the values corresponding to the year 2022, and assuming the same behaviour, showing the same surface dedicated for the PV panels and the number of wind turbines, varying only the installation costs (Table 3) and investment. For 1% of the available surface, the investment costs reach up to 313,230 $M€_{2030}$, and 236,670 $M€_{2050}$ (Table 4), representing a reduction of 59.73%, and 69.57% with respect to 2022 due to the reduction of the cost in the time horizon (see Table 3). This trend is observed when the available surface reaches 1.5%, where the investment costs are 458,220 $M€_{2030}$, and 344,350 $M€_{2050}$ (Table 4), with a reduction of 60.22%, and 69.57% with respect to 2022. These investment costs require 595,890 $M€_{2030}$, and 445,330 $M€_{2050}$ (Table 4), meaning reductions of 60.70% and 70.63%, with respect to 2022.

Chemicals production: For the time horizon considered, the use of 1% of the available surface does not present a variation of the spatial distribution due to the total amount of CO_2 captured being carried out employing MEA solutions. Thus, the investment cost achieved is 54,303 $M€_{2030}$, and 35,347 $M€_{2050}$, yielding 12.77%, and 43.22%

of the reduction referred to in 2022 (Table 4). However, to satisfy the renewable hydrogen and methanol production for the use of 1.5% of the available surface (see Figures SP-3 g, h, SP-4 g, h, and SP-5 g, h in the Supplementary Material) is installed in provinces where MEA solutions are installed, capturing 3.93 times more CO_2 than the conventional DAC process for this scenario. The costs decrease over time (see Table 2), allowing to allocation of more facilities around Madrid and Barcelona, and following the coastline. Asturias, Barcelona, Cádiz, Castellón, Madrid, and Tarragona are the preferred provinces to locate chemical production. Its evolution passes from a maximum of 2,200 ktH_2/year, 12,000 $kt_{Methanol}$/year, and 32,000 $M€_{2022}$ (see Figure SP-3 in the Supplementary Material), to 1,700 ktH_2/year, 9,000 $kt_{Methanol}$/year, and 6,200 $M€_{2030}$, in the year 2030, and 1,700 ktH_2/year, 9,000 $kt_{Methanol}$/year, and 4,500 $M€_{2050}$ in the year 2050. As a result, the total amount of the chemical produced is 22,393 ktH_2/year, 119,430 $kt_{Methanol}$/year, with investment costs of 107,010 $M€_{2022}$, 90,846 $M€_{2030}$, and 58,191 $M€_{2050}$, following a reduction of 15.11%, and 45.62% with respect to 2022 (Table 4), due to the reduction of the cost in the years 2030 and 2050 (see Table 2). For the use of 2% of the available surface (Figures SP-6 g-h, SP-7 g-h, and SP-8 g-h) reach maximum values of 2,400 ktH_2/year, 13,000 $kt_{Methanol}$/year, and 14,000 $M€_{2022}$ (Figure SP-3), 11,500 $M€_{2030}$, and 7,000 $M€_{2050}$ favoured for a reduction in the production and investment costs (Table 2). Thus, the total amount of chemicals produced is 28,941 ktH_2/year, 154,350 $kt_{Methanol}$/year, with investment costs of 157,990 $M€_{2022}$, 131,730 $M€_{2030}$, and 83,443 $M€_{2050}$, with a reduction trend of 16.62% and 47.18% compared to 2022 (Table 4).

Concerning the methanol consumption in Spain and Europe, for the year 2030 is expected 1,379 $kt_{Methanol}$/year (ChemAnalyst, 2023) and 13,250 $kt_{Methanol}$/year (EMR, 2023). Employing the methodology used for the year 2020, the level of substitution in Spain and Europe reached 111 times and 10.65 times more respectively. The reduction in the cost of methanol production is notable, achieving values in the range of 1,634 €/$t_{Methanol}$ to 1,680 €/$t_{Methanol}$ in the year 2030 (Table 4), and 1,062 €/$t_{Methanol}$ to 1,037 €/$t_{Methanol}$ in the year 2050. These ranges represent almost 3 times and 5 times more than the methanol prices for the years 2030 and 2050, 390 €/$t_{Methanol}$ and 185.44 €/$t_{Methanol}$, respectively (Table SP-2). This reduction will be increased when the carbon taxes are considered. It is expected an increase in carbon taxes due to the tightening of legislation. The values of carbon taxes considered are 150 €/t_{CO2} and 180€/t_{CO2} (see Table SP-10 in the Supplementary Material). The cost of methanol production obtained is in the range of 1,424 €/$t_{Methanol}$ to 1,585 €/$t_{Methanol}$ for the year 2030 and 827 €/$t_{Methanol}$ to 907 €/$t_{Methanol}$ for the year 2050. These ranges are between 3 times and 4 times more than the methanol prices for the years 2030 and 2050.

Table 5.- Parameters of renewable energy sources for methanol production for the years 2022, 2030, and 2050.

	year								
Parameter	2022			2030			2050		
Available surface (%)	1	1.5	2	1	1.5	2	1	1.5	2
CO_2 capture from total (%)	51.76	74.72	96.57	51.76	74.72	96.57	51.76	74.72	96.57
Amount of CO_2 captured from the total ($MtCO_2$/year)	115.8	167	216.1	115.8	167	216.1	115.8	167	216.1
CO_2 emitted from PV panels ($MtCO_2$/year)	58.13	87.20	116.27	58.13	87.20	116.27	58.13	87.20	116.27
CO_2 emitted from wind turbines ($MtCO_2$/year)	0.52	0.57	0.59	0.52	0.57	0.59	0.52	0.57	0.59
Net CO_2 emitted from renewable energy sources ($MtCO_2$/year)	58.65	87.77	116.86	58.65	87.77	116.86	58.65	87.77	116.86
Relation of CO_2 emitted from PV panels to the total (%)	50.20	52.22	53.80	50.20	52.22	53.80	50.20	52.22	53.80
Relation of CO_2 emitted from wind turbines to the total (%)	0.45	0.34	0.27	0.45	0.34	0.27	0.45	0.34	0.27
Net relation of CO_2 emitted from renewable energy sources to the total (%)	50.65	52.56	54.07	50.65	52.56	54.07	50.65	52.56	54.07
Water consumed by PV panels (m^3/year)	$4.00\cdot10^8$	$6.00\cdot10^8$	$8.00\cdot10^8$	$4.00\cdot10^8$	$6.00\cdot10^8$	$8.00\cdot10^8$	$4.00\cdot10^8$	$6.00\cdot10^8$	$8.00\cdot10^8$
Water consumed by wind turbines (m^3/year)	$1.86\cdot10^6$	$2.05\cdot10^6$	$2.11\cdot10^6$	$1.86\cdot10^6$	$2.05\cdot10^6$	$2.11\cdot10^6$	$1.86\cdot10^6$	$2.05\cdot10^6$	$2.11\cdot10^6$

Water consumed by renewable energy sources (m^3/year)	$4.02 \cdot 10^8$	$6.02 \cdot 10^8$	$8.02 \cdot 10^8$	$4.02 \cdot 10^8$	$6.02 \cdot 10^8$	$8.02 \cdot 10^8$	$4.02 \cdot 10^8$	$6.02 \cdot 10^8$	$8.02 \cdot 10^8$

Renewable technology CO_2 emissions and water consumption: Renewable energy sources have associated their operation with a set of impacts on the environment. The data summarized in Table 5 focuses on the CO_2 emissions from the maintenance of the operation of PV panels and wind turbines, as well as the water required for cleaning and maintenance. The emissions parameters and water consumption ratios are kept constant with time due to the lack of future forecasts. Based on that, the corresponding emission ratio was calculated based on the 0.048 $kgCO_2/kWh_e$ and 0.012 $kgCO_2/kWh_e$ ratios and the corresponding electricity generated by PV panels and wind turbines, respectively (Martín and Grossmann, 2018). The emissions from the use of PV panels represent 50.20%, 52.22%, and 53.80% of the total CO_2 captured, being 0.45%, 0.34%, and 0.27% for wind turbines (Table 5). The large difference is firstly due to the different emission ratio, which is 4 times higher for PV panels than for wind turbines, and the actual use of these technologies. Moreover, PV panels are selected as the preferred renewable technology for power production for cost purposes. Almost all the generated power comes from their use, facilitating the large contribution of PV panels to the total emissions from renewable technologies. The rest of the CO_2 to capture, 49.35%, 47.44%, and 45.93% would be captured from industrial effluents and atmospheric air. However, from Table 4, the capture of CO_2 carried out with MEA solutions increased to a total of 133,290 $ktCO_2$/year while employing the conventional DAC capture was 33,913 $ktCO_2$/year, and 82,806 $ktCO_2$/year with respect to the use of 1.5%, and 2% of the available province. From Table 5, 87,200 $ktCO_2$/year and 116,270 $ktCO_2$/year are emitted using PV panels, which is 157.13%, and 40.41% more than the values captured from the atmosphere with the conventional DAC process (Table 4). Despite the global data presented in Table 5, the CO_2 emitted from PV panels and wind turbines exceeded the amount of atmospheric CO_2 that is captured. Moreover, the water consumed for cleaning and maintenance of PV panels and wind turbines is given for the ratios 0.33 L/kWh_e and 0.043 L/kWh_e (Jin et al., 2019). The total water consumed comes from the use of the PV panels, which is summarized in Table 5. Indeed, the water consumption increases from 402 hm^3/year to 602 hm^3/year, and 802 hm^3/year, which represents 0.72%, 1.07%, and 1.43% to 56.069 hm^3 of total water storage capacity available in Spain (Embalses.net, 2023). More precise data about CO_2 emissions from the PV panels and wind turbines maintenance, their evolution with the improvement in efficiency, and better use of water could provide more detailed results.

4.1.2. Case 2: Methane

The optimal selection consists of the production of methanol. However, methane is also an interesting product due to its wide use in the industry and the boilers of residential areas. Thus, a study considering the production of methane is carried out using its significative parameters (see Table SP-4 in the Supplementary Material), following the same distribution features as methanol production (see Figure 3, and Figure SP-9 -Figure SP-16), highlighting that methane production needs a more area available for PV panels, but it uses a smaller number of wind turbines due to the costs (see Table SP-5 in the Supplementary Material).

The methane production requires 3 $kgCO_2/kg_{methane}$ and 0.41 $kgH_2/kg_{methane}$, which represents twice as many reagents as the production of methanol. This constitutes a serious limitation since a large amount of raw material, CO_2, and H_2, have to be captured and produced. Although oxygen production is also 2 times high, the income earned from its sale does not allow for a balancing increase in the costs. Additionally, the slight difference in the current price of methane, 0.480 €/$kg_{Methane}$ (Eurostat, 2022), compared with the price of methanol, 0.400 €/$kg_{Methanol}$ (Methanol Institute, 2022), does not compensate for the cost of raw materials needed. Based on that, a sensitivity analysis of methane production was performed, employing as the parameters the provinces available surface to install PV panels, 1%, 1.5%, and 2%, the time horizon constituted by the years 2022, 2030, and 2050, and the parameter costs (Tables 2, and 3). The results obtained show the prices for methane production over the range of 18.97-20.36 €/$MMBTU_{2022}$ (see Table SP-7 in the Supplementary Material). The price increase is promoted for increases in the CO_2 captured, since the increase in the CO_2 capture increases the costs, such as the power requirements. The maximum amount of methane produced reaches 38,607.22

$kt_{Methane}$/year, 55,732.83 $kt_{Methane}$/year, and 72,030.50 $kt_{Methane}$/year representing 147.20%, 212.50%, and 274.64% (Table SP-7), over the amount of methane consumed in Spain in 2022, 26,227.20 $kt_{Methane}$/year (ENAGAS, 2023). This value is reached using 35.16% of the CO_2 captured from the total, an equivalent of 78,681.6 $ktCO_2$/year. The methane substitutions and the province surface available may vary depending on the methane consumption required each year. The estimations for the years 2030 and 2050 are summarized in Table 6.

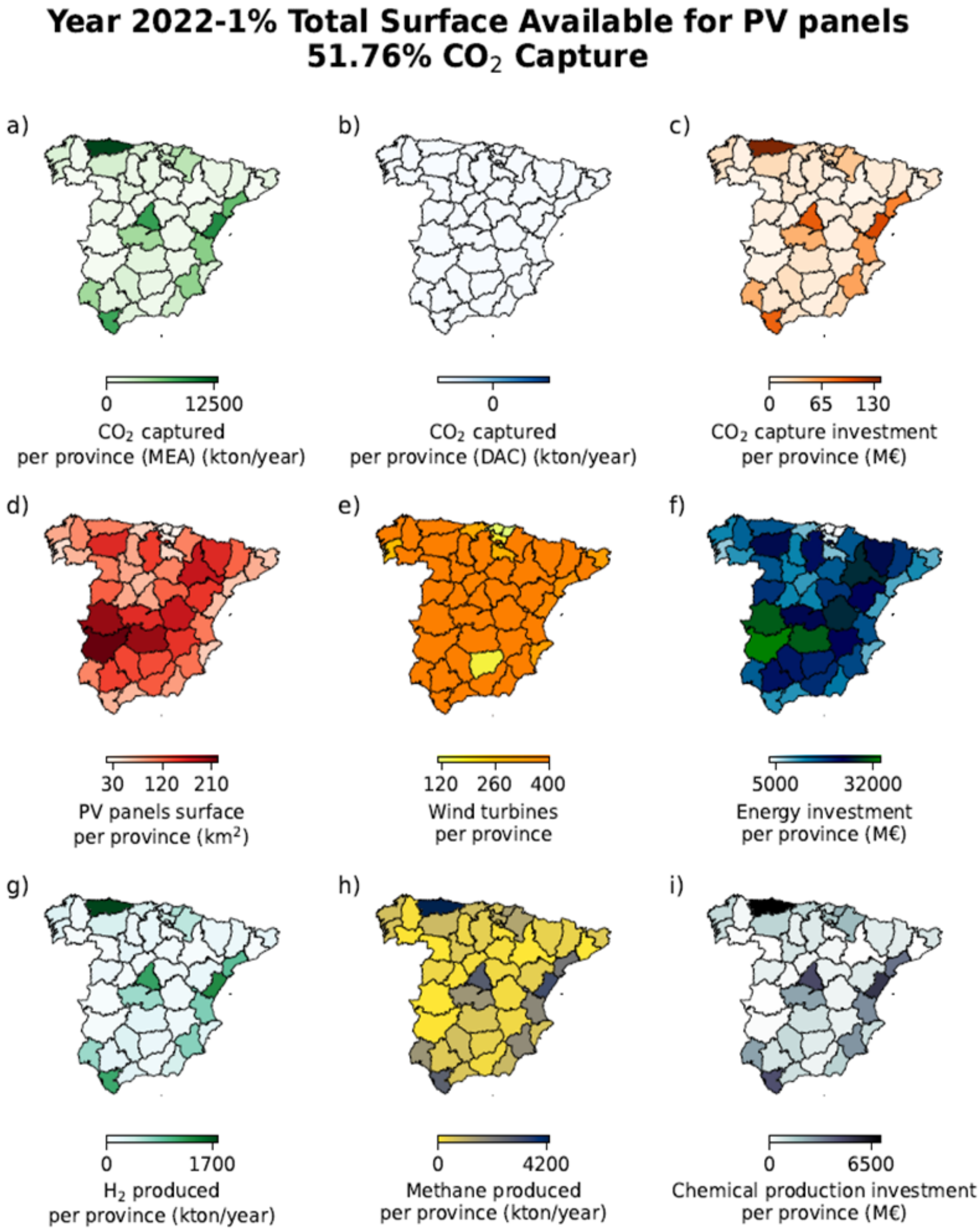

Fig 3. Distribution of CO_2 capture, renewable energy generation, methane production technology, and their total investments by the province in 2022 using 1% of the available area in Spain.

Table 6.- Methane consumption in Spain for the years 2022, 2030, and 2050.

Year	Methane consumption (TWh/year)	Methane consumption (kt/year)	Methane consumption reduction with respect to 2022 (%)
2022	364.30	26,227.20 (ENAGAS, 2023)	0
2030	263.77	18,989.71 (IEA, 2021a)	27.54
2050	191.90	13,815.18 (Monitor Deloitte, 2016)	47.32

The methane consumption for the years 2030 and 2050 reaches the value of 18,989.71 $kt_{Methane}$/year (IEA, 2021a) and 13,815.18 $kt_{Methane}$/year (Monitor Deloitte, 2016), presenting reductions of 27.54%, and 47.32% respect to 2022 (Table 6). The methane prices of 18.29-18.57 €/$MMBTU_{2030}$ or 0.867-0.880 €/$kg_{Methane2030}$ represent a reduction of 3.56%-8.82% with respect to the year 2022. The methane production is kept constant and equal to the year 2022 since the total amount of CO_2 captured does not change, since the total amount of 223.8 $MtCO_2$ captured in the year 2022 is used as a reference. However, the future consumption of methane will decrease (Table 6), presenting more methane produced than consumed. Thus, for the year 2030 (Table 6), the methane consumption substitution takes values of 203.31%, 293.49%, and 379.31% (Table SP-8), taking the 25.45% of the CO_2 captured from the total in 2022, resulting in 56,969.1 $ktCO_2$/year. Finally, for the year 2050 the methane prices of 8.90-9.09 €/$MMBTU_{2050}$, showing a reduction of 53.27%-55.34%. with the associated reduction in the prices with respect to the year 2022. The substitutions in the consumption are 279.46%, 403.42%, and 521.39% (Table SP-9) using 18.52% of the CO_2 captured from the total, 41,445.5 $ktCO_2$/year. This progressive reduction of the methane prices observed is shown in Figure 4.

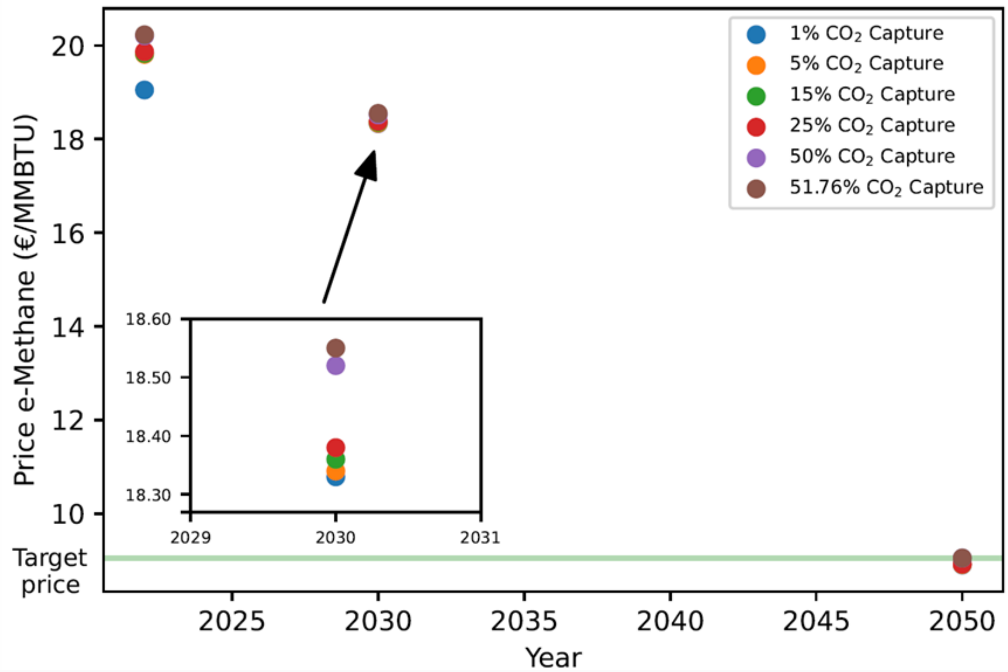

Fig 4. Variation of methane price for the years 2022, 2030, and 2050 using 1% of the available area in Spain.

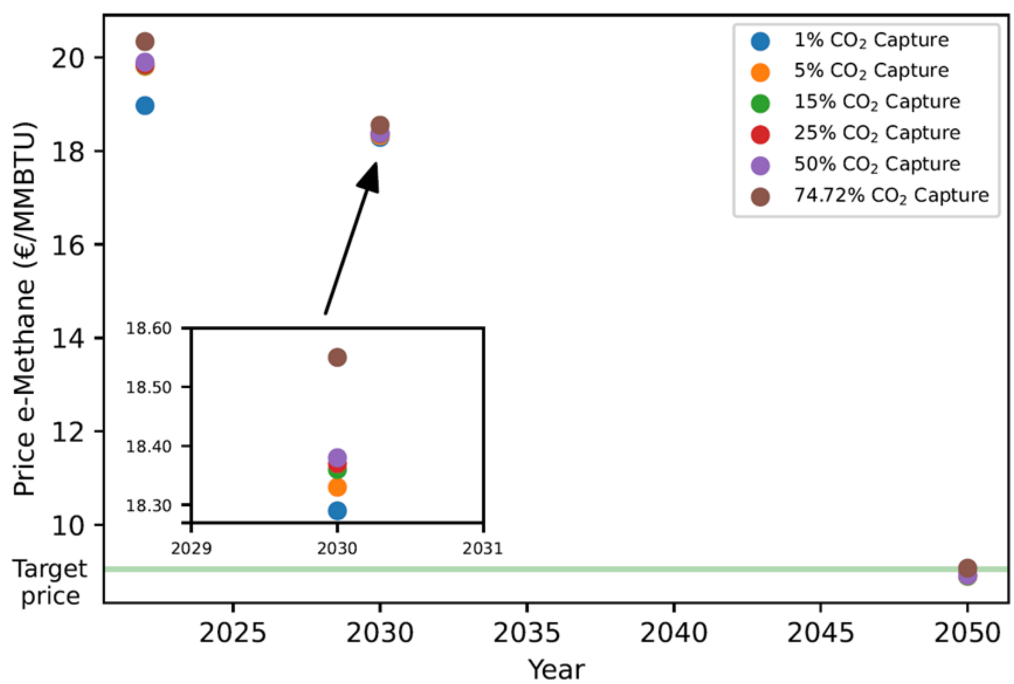

Fig 5. Variation of methane price for the years 2022, 2030, and 2050 using 1.5% of the available area in Spain.

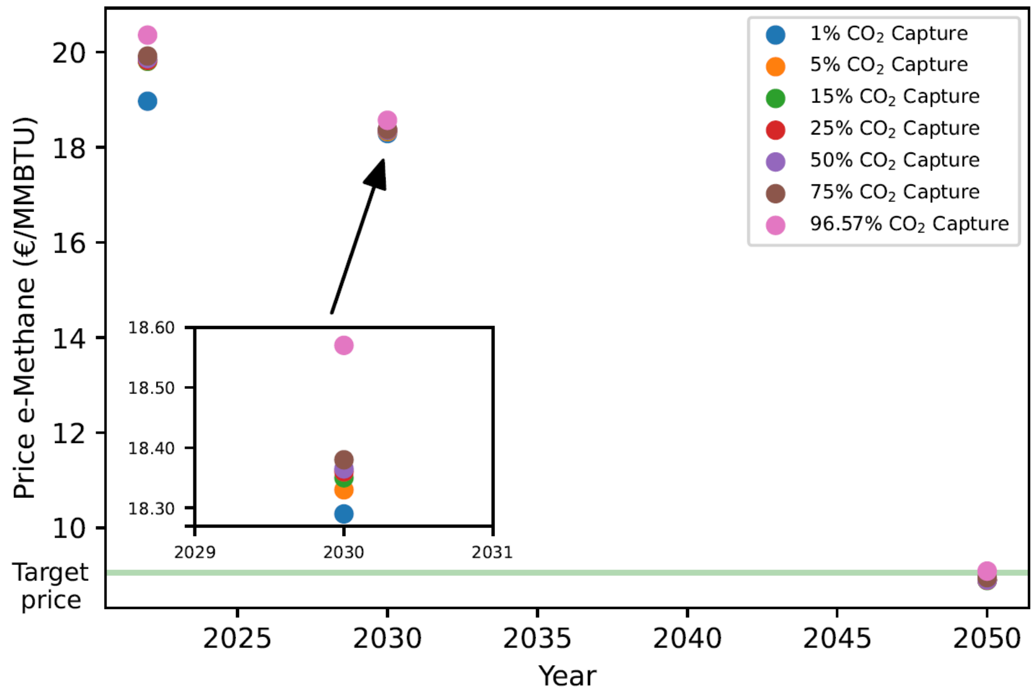

Fig 6. Variation of methane price for years 2022, 2030, and 2050 using 2% of the available area in Spain.

A considerable reduction in methane consumption is observed for the long-time horizon, represented by the year 2050 (Table 6). The green line shows the target price stipulated, which represents a reasonable value considering the volatility of the natural gas prices mainly due to the war in Ukraine and its lack of supply from Russia. Before the conflict, the international price of natural gas was over 4.24 €/MMBTU (Trading Economics, 2023), reaching 9.20 €/MMBTU (Trading Economics, 2023) as a maximum price after the conflict. The diplomatic rupture between the EU and Russia forced it to import liquefied natural gas by ships, mostly from the USA. This event increased the prices, reaching a maximum price of 62.07 €/MMBTU (Focus Economics, 2023), being reduced to around 10 €/MMBTU (Focus Economics, 2023). The reduction trend in the prices achieves 9 €/MMBTU, which can be considered as a target. This behaviour can be observed when the operation for methane production becomes more economically feasible in the year 2050 (Figure 4), presenting prices very similar to the target, which is considered the optimal price (see Figure 5, and Figure 6).

Furthermore, as in the case of methanol synthesis, the use of carbon taxes could help reduce the price of synthetic methane, since it would be possible to make the process more profitable. The results are summarised in Table 7.

Table 7.- Methane prices without and with carbon taxes in Spain for the years 2022, 2030 and 2050.

year	Available surface (%)	Methane price (€/t_{CH4})	Methane price with a carbon tax (€/t_{CH4})	Methane price with a carbon tax (€/MMBTU)	Methane price reduction (%)
2022	1	959	717	15.12	25.23
	1.5	964	771	16.26	20.02
	2	965	815	17.20	15.54
2030	1	879	429	9.05	51.19
	1.5	879	520	10.97	40.84
	2	880	602	12.70	31.59
2050	1	429	105	2.21	75.52
	1.5	430	117	2.46	72.79
	2	430	126	2.66	70.70

It can be observed that the prices with a carbon tax present an important reduction, from 15% to almost 70. Please note that the carbon tax increases over time, see supplementary material, Table SP10. The year 2022 is smaller due to the use of the lowest value of carbon tax. However, the use of higher values of the carbon tax allows for obtaining a reduction of the price above 30% and 70% for the years 2030 and 2050 respectively. Moreover, the profit obtained due to the carbon taxes will allow for the year 2050 obtaining prices of methane will be very close to the current price of natural gas, 2.88 €/MMBTU (Trading Economics, 2023).

4.2. Centralized CO_2 use

The FLP is complemented with another case, studying the supply chain problem formulation. This scenario contemplates the centralized use of the captured CO_2 between the facilities existing in the provinces to make the most of the economy of scale and could use the existing natural gas distribution network as a possible network to move the CO_2. The main issue lies in that the current distribution network only presents the transport between the provinces in certain cases, not considering all the scenarios shown in the problem. Moreover, the CO_2 transportation through pipelines implies to use of specific equipment, requiring standard prices of about 10 €/tCO_2, which could be located between about 4 €/tCO_2 to 45 €/tCO_2, depending on the features of the area (Smith et al., 2021). In addition, the presence of different sources of CO_2 in all the provinces allows the installation technologies for CO_2 capture to obtain the required amount of it without the use of transport, which would increase the cost of the operation. With these factors, the supply chain problem selects the optimal solution, the decentralized CO_2 use.

5. Conclusions

This work has presented a systematic comparison between methanol and methane production from the hydrogenation of CO_2 captured through MEA solutions and the conventional DAC process, using hydrogen from water electrolysis feed with power provided by PV panels and wind turbines. A FLP is formulated considering the decentralized and centralized CO_2 availability over 47 Spanish provinces as the case of study, using the net emissions in the year 2022, 223.8 MtCO_2, as a benchmark. The target is to capture as much CO_2 as possible given the constraints. The available surface to install PV panels is assumed to be 1%, 1.5%, and 2% of the different provinces, representing 4,935 km^2, 7,403 km^2, and 9,870 km^2.

The maximum CO_2 captured is based on the selection of the maximum area for PV panels, and later on wind turbines are selected to provide additional power. Up to 14,883 to 17,221 wind turbines are used across the territory, generating from 143,20 GW to 282,10 GW. It is possible to capture 51.76%, 74.72%, and 96.57%, being 115.8 MtCO_2, 167.2 MtCO_2, and 216.1 MtCO_2, for the different fractions of area. The utilization of CO_2 is towards the production of methanol since it constitutes the most economical of the two. The CO_2 is first captured from point sources by using aqueous MEA solutions because it represents the most accessible source. The regions primarily selected are in the centre of the peninsula and the coastline areas, capturing as maximum and for just 1% of the area available, only point sources are selected capturing 115.8 MtCO_2 producing 82,723 $kt_{Methanol}$/year with an investment of around 850 B€ for power production, CO_2 capture and methanol synthesis at 2022. Over the years it is expected that PV panels and wind turbines reduce their cost reaching 2050 around 275B€. The high energy consumption required for DAC and the additional costs result in the fact that only if an additional area is available the dilute sources are selected. In that case, 1.5% and 2% area are considered. For the last of the cases up to 216.1 MtCO_2 could be captured where 133,209 ktCO_2 comes from MEA captured and the rest, around 82,806 ktCO_2 from the conventional DAC process from the largest capitals across Spain Madrid, Barcelona, Sevilla as well as La Coruña producing 154,350 $kt_{Methanol}$/year and requiring an investment of 1,516 $B€_{2022}$. However, note that electricity production also has associated CO_2 emissions that correspond from 50.20% to 53.80% of the CO_2 captured.

Even if methanol is the suggested final product, methane synthetic production is also an interesting result since it can help with the current electricity system by substituting natural gas. It is possible to produce synthetic natural gas from CO_2 hydrogenation at prices in the range of 18.97-20.36 €/MMBTU for the year 2022, producing up to 72,030.50 $kt_{Methane}$/year. It would be possible to produce 2.5 times today's consumption of methane in Spain. For the years 2030 and 2050, it would be possible to reduce the prices as the technology evolves down to 8.90-9.09 €/$MMBTU_{2050}$. The use of carbon taxes would allow a reduction in the price of around 2-3 €/$MMBTU_{2050}$. As the consumption of natural gas is expected to decline over the years, with the CO_2 available as of 2022, it would be possible to reach 5 times the production. Note that it is possible that the CO_2 available may decline. The large availability of CO_2 and the transportation costs result in selecting a non-distributed CO_2 capture and utilization.

CRediT authorship contribution statement

Guillermo Galán: Writing - original draft, Software, Investigation, Methodology, Formal analysis. **Mariano Martín**: Conceptualization, Writing - reviewing & editing, Resources, Supervision, Funding Acquisition, Project administration. **Ignacio E. Grossmann**: Supervision, Conceptualization - reviewing & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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