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Renewable methane. Integrated configurations of power-to-gas and carbon capture by means of renewable energy surplus

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**RENEWABLE METHANE.
INTEGRATED CONFIGURATIONS OF
POWER-TO-GAS AND CARBON
CAPTURE BY MEANS OF
RENEWABLE ENERGY SURPLUS**

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Ingeniería y Arquitectura
Universidad Zaragoza



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Memoria presentada por Manuel Bailera a la Universidad de Zaragoza para la obtención del título de Doctor con Mención de Doctorado Internacional

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- iii Bailera M, Lisbona P, Romeo LM, Espatolero S. Power to Gas projects review: Lab, pilot and demo plants for storing renewable energy and CO₂. *Renewable & Sustainable Energy Reviews* (2017), 69, 292-312.
- iv Bailera M, Lisbona P, Romeo LM. Power to gas-oxyfuel boiler hybrid systems. *International Journal of Hydrogen Energy* (2015), Vol. 40, 32, 10168-10175.
- v Bailera M, Lisbona P, Romeo LM, Espatolero S. Power to Gas-biomass oxycombustion hybrid system: Energy integration and potential applications. *Applied Energy* (2016) 167, 221-229.
- vi Bailera M, Kezibri N, Romeo LM, Espatolero S, Lisbona P, Bouallou C. Future applications of hydrogen production and CO₂ utilization for energy storage: Hybrid Power to Gas-Oxycombustion power plants. *International Journal of Hydrogen Energy* (2017) Vol. 42, 19, 13625-13632.
- vii Bailera M, Espatolero S, Lisbona P, Romeo LM. Power to Gas-Electrochemical industry hybrid systems: A case study. *Applied Energy* (2017), 202, 435-446.

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PROLOGUE

After my graduation in BSc. Physics in 2013, I enrolled the official Master's program on Renewable Energy and Energy Efficiency of the University of Zaragoza. I first knew about Power to Gas at that time, thanks to Professor Luis M. Romeo, who proposed me to study this novel technology in my Master's thesis. The work analyzed Power to Gas acting as manager of the surplus coming from nuclear power, comprising the simulation of the plant and its economic evaluation. This study would be later awarded in 2015 as the best Spanish Master's Thesis in Carbon Capture, Transport, Storage and Utilization by the Spanish CO₂ Technology Platform.

The research line on Power to Gas technology was born in the former Zero Emissions Area of Fundación CIRCE, where Pilar Lisbona led an ongoing project. I had the opportunity to join this team and work in three publicly funded Power to Gas projects during the period 2014 – 2017. In fact, this thesis summarizes the work developed in the framework of these projects, in which my advisors as well as Sergio Espotolero strongly cooperated.

Nowadays, the research line is continued beyond this thesis by Universidad de Zaragoza through the MERCURIA project (ENE2016-76850-R). This three-year project, which started in January 2017, focuses on the design, construction and testing of a methanator at laboratory scale (15 kW output). Thus, all the gained experience since 2014 will be now put in practice.

PRÓLOGO

Tras licenciarme en Física en 2013, ingresé en el Máster Oficial en Energías Renovables y Eficiencia Energética de la Universidad de Zaragoza. La primera vez que oí hablar del Power to Gas fue por aquel entonces, gracias al profesor Luis M. Romeo, quien me propuso estudiar esta novedosa tecnología en mi Trabajo Fin de Máster. Este trabajo analizaba la función del Power to Gas como gestor del exceso eléctrico procedente de la generación nuclear, incluyendo una simulación de la planta y su análisis económico. El trabajo sería posteriormente premiado, en 2015, como el mejor Trabajo Fin de Máster en tecnologías de captura, transporte, almacenamiento y usos del CO₂, por la Plataforma Tecnológica Española del CO₂.

La línea de investigación en Power to Gas surgió en el antiguo Área de Reducción de Emisiones de Fundación CIRCE, donde Pilar Lisbona lideraba un proyecto en marcha. Tuve la oportunidad de formar parte de este equipo y trabajar en tres proyectos de financiación pública sobre Power to Gas, durante el periodo 2014 – 2017. De hecho, la tesis resume el trabajo realizado en estos tres proyectos, en los que tanto mis directores como Sergio Espatolero colaboraron activamente.

Actualmente, la línea de investigación es continuada en la Universidad de Zaragoza, a través del proyecto MERCURIA (ENE2016-76850-R). En este proyecto de tres años, que empezó en Enero de 2017, se pretende diseñar, construir y operar un metanizador a escala laboratorio (15 kW de salida). De este modo, se pondrá en práctica toda la experiencia adquirida desde 2014.

ABSTRACT

Carbon dioxide is the largest single contributor to global warming [1] and current atmospheric concentrations are increasing at the fastest ever observed rate (2.0 ppm/yr) [2]. To reverse this situation, the International Energy Agency (IEA) stated as top priority the decarbonization of electricity and heat generation sectors, because they produce more than two-fifths of global CO₂ emissions [3].

In Europe, the decarbonization of the energy system is based on largely deploying renewable energy sources (RES) [4]. This deployment has already allow to reduce CO₂ emissions a 12% with respect to 2009 levels [5]. However, moving forward in this direction implies high shares of intermittent sources in energy production that might cause temporary electricity surpluses, and make the system operation more complex [6][7]. Hence, the objective of the first part of the thesis is to quantify the potential energy surplus that might exist in the future Spanish energy mix due to the renewable penetration. This study was submitted to Energy, and presented in the 13th International Conference on Greenhouse Gas Control Technologies with an associated paper in Energy Procedia:

- i Energy storage in Spain: forecasting electricity excess and assessment of Power-to-Gas potential up to 2050, Energy 2017, Submitted (under 2nd revision)
- ii Power to Gas technology under Spanish future energy scenario, Energy Procedia 2017, 114, 6880-6885

Facing this situation, the European Commission proposed the development of large scale energy storage as a solution [8]. Energy storage can balance renewable electricity surplus from low to high demand periods, as well as displace fossil fuels in applications that traditionally were hardly covered by renewable energies (e.g., transport). Nevertheless, current energy storage technologies are hindered at large scale either by practical (e.g., special locations required, potential hazards) or technical constrains (e.g., low rate power, short storage durations) [9][10][11]. The most promising technique to overcome these limitations is the hydrogen energy storage. It uses electricity to feed electrolyzers that dissociate water and produce hydrogen (energy carrier), which can be later used to re-generate electricity [12]. Still, two main barriers must be overcome to make hydrogen storage feasible: the high cost (investments

above 1000 €/kW, and lack of distribution infrastructure) and the low round-trip efficiency (36.5% - 66.5%, LHV) [13].

To that end, a new concept known as Power to Gas (PtG) has stood out in the last years [14]. Power to Gas combines the H₂ from electrolysis with CO₂ to produce CH₄ (main component of natural gas), thus transferring the electricity surplus from the electric network to the gas infrastructure [15]. This synthetic natural gas widens the final uses of the stored energy, potentially enabling greater reconversion efficiencies and economic profits. Besides, safety measures and transport costs associated to hydrogen are avoided. So, the second part of this thesis reviews worldwide existing PtG projects. The objective is to gather practical experiences regarding the construction and operation of Power to Gas plants, in order to evaluate the remaining challenges facing industrial development. The review was published in *Renewable & Sustainable Energy Reviews*:

- iii Power to Gas projects review: Lab, pilot and demo plants for storing renewable energy and CO₂, *Renew Sust Energ Rev* 2017, 69, 292-312

To date, 46 experimental PtG projects have been developed worldwide, but the high cost of the equipment and the low efficiency still restrict the profitability of the concept, and so do the number of field experiences at industrial scale. The motivation of the thesis is to overcome these barriers. Otherwise, PtG deployment will be restricted until future favorable energy scenarios become a reality (those in which renewable sources predominate and economic penalizations on CO₂ emissions strongly apply). The hybridizing potential of Power to Gas [15] (heat from methanation and oxygen from electrolysis) is the key that allows to broaden the suitable scenarios for industrial development.

Thus, the core objective is to propose novel PtG hybrid concepts to rise efficiency, make a better use of the available resources, remove part of the initially required equipment, and widen the potential uses of this technology. The thesis analyses and characterizes the proposed systems to show that significant improvements in PtG systems can be achieved by means of proper hybridizations.

Some remarkable hybridizations to enhance PtG are those that avoid carbon capture energy penalties, since these are significant when CO₂ has to be captured from diluted sources. The efficiency drops between 9 and 12 points [16][17], what hides the positive aspect of CO₂ recycling in PtG, and its environmental advantages with respect to the other energy

storage technologies (CO₂ recycling puts carbon dioxide emissions in a closed loop to continuously regenerate the fuel that is consumed).

A suitable option to avoid the carbon capture penalty is the hybridization with an oxy-fuel combustion facility. In oxy-fuel combustion, pure oxygen is used as comburent instead of air [18]. The large N₂ content present in conventional air-fired combustion is substituted by the combustion products (CO₂ and H₂O), so flue gas achieves high concentrations of carbon dioxide. Energy penalty associated to this capture process mainly comes from the air separation unit (ASU) that produces the required oxygen (typically 190 kWh/to₂) [19]. Hence, Power to Gas-oxyfuel combustion systems use the oxygen from electrolysis to suppress the electrical consumption demanded by the ASU. Besides, since CO₂ is recycled to fuel, the energy consumption of compression stage required to store carbon dioxide is avoided as well.

When this concept is implemented into an application that includes a single boiler, the exothermal heat from methanation can be directly integrated as a useful output of the system. In the case that the concept is used in a power plant, the heat can be integrated in the thermal power cycle to increase the overall electrical efficiency.

The PtG-Oxycombustion hybridization is the first proposal studied in this thesis. The ratio between the sizes of electrolysis and oxy-fuel combustion processes is used as a key parameter to define the operation strategy of the hybridization. Besides, different simulations are run to determine the influence of the type of fuel fed to oxy-fuel combustion. Then, the study of the proposal is completed with an application case that comprises the energy integration and efficiency evaluation of a hybrid PtG-oxy-fuel combined cycle power plant. The results were published in three papers:

- iv Power to gas-oxyfuel boiler hybrid systems, *Int. J. Hydrogen Energy* 2015, 24, 168-175
- v Power to Gas-biomass oxycombustion hybrid system: Energy integration and potential applications, *Appl Energy* 2016, 167, 221-229
- vi Future applications of hydrogen production and CO₂ utilization for energy storage: Hybrid Power to Gas-Oxycombustion power plants, *Int. J. Hydrogen Energy* 2017, Vol.42, 19, 13625-13632

Another option to avoid the drawback of attaining pure CO₂ is the integration of Power to Gas with amine scrubbing post-combustion capture. In this capture technique, flue gas from an air-fired boiler enters to an absorption column where inert gases bubble out, and CO₂ is absorbed by amine. The CO₂ rich solvent is then regenerated in a stripping column with counter flowing steam at 100 - 200 °C, thus obtaining a highly concentrated CO₂ flow [20]. The main efficiency penalty comes from the thermal energy required to regenerate the solvent, but it can be diminished by using the exothermal energy generated during methanation.

Amine capture is the most established and commercially deployed capture technology, hence there already exists studies regarding the application of PtG to power plants with amine capture systems coupled [21][22]. Therefore, the last part of the thesis proposes the novel application of PtG-Amine systems to the chemical industry. The study of this proposal comprises the evaluation of the technical and economic viability of this application for the first time, in which hydrogen is a byproduct coming from electrolytic lines of production of a chemical plant. The study was published in Applied Energy:

- vii Power to Gas-Electrochemical industry hybrid systems: A case study, Applied Energy 2017, 202, 435-446

RESUMEN

El dióxido de carbono es el principal causante del calentamiento global [1] y su presencia en la atmósfera se está incrementando al mayor ratio jamás observado (2.0 ppm/año) [2]. Para revertir la situación, la Agencia Internacional de la Energía (IEA) considera como principal prioridad la descarbonización de los sectores de generación eléctrica y térmica, dado que son responsables de dos quintas partes de las emisiones mundiales de CO₂ [3].

En Europa, la descarbonización del sistema energético se basa en la implementación masiva de las energías renovables (ER) [4], lo que ha permitido reducir las emisiones de CO₂ un 12% desde 2009 [5]. No obstante, moverse en esta dirección implica tener un mix energético con altos porcentajes de energía intermitente, que pueden causar excedentes eléctricos y hacer que la operación del sistema sea más compleja [6][7]. Por ello, el objetivo de la primera parte de la tesis es cuantificar el exceso eléctrico que podría existir en el futuro mix energético español a causa de la penetración de las renovables. Este análisis se envió a Energy, además de ser presentado en el 13th International Conference on Greenhouse Gas Control Technologies con un artículo asociado en Energy Procedia:

- i Energy storage in Spain: forecasting electricity excess and assessment of Power-to-Gas potential up to 2050, Energy 2017, Submitted (en 2ª revisión)
- ii Power to Gas technology under Spanish future energy scenario, Energy Procedia 2017, 114, 6880-6885

Frente a esta situación, la Comisión Europea propuso el desarrollo del almacenamiento de energía a gran escala como una posible solución [8]. Este permite balancear el exceso de electricidad renovable desde los periodos de baja demanda hacia los de alta demanda, además de desplazar a los combustibles fósiles en aplicaciones que tradicionalmente eran de difícil acceso para las renovables (e.g., transporte). Sin embargo, las tecnologías de almacenamiento actuales presentan limitaciones en su aplicación a gran escala ya sea por restricciones prácticas (e.g., requerimiento de localizaciones concretas, utilización de compuestos contaminantes) o técnicas (e.g., baja potencia, tiempos de almacenaje cortos) [9][10][11]. La técnica más prometedora para superar estas limitaciones es el almacenamiento de energía en forma de hidrógeno. Este proceso usa la electricidad para alimentar

electrolizadores que disocian el agua, produciendo así hidrógeno (vector energético) que puede ser utilizado más tarde para volver a generar electricidad [12]. No obstante, para hacer viable el almacenamiento de hidrógeno todavía se tienen que superar dos barreras: los altos costes (inversión de >1000 €/kW y falta de infraestructura de distribución) y la baja eficiencia global (36.5% - 66.5%) [13].

Con dicho objetivo en mente, un nuevo concepto conocido como Power to Gas (PtG) ha aparecido en los últimos años [14]. El Power to Gas combina el H₂ de la electrólisis junto con CO₂ para producir CH₄ (componente principal del gas natural), lo que permite transferir el exceso eléctrico desde la red eléctrica a la red de gas natural [15]. Este gas natural sintético amplía los usos finales de la energía almacenada, posibilitando mejores eficiencias durante la reconversión a electricidad y mayores beneficios. Además, así se evitan las medidas de seguridad y los costes de transporte asociados al vector hidrógeno. Por ello, la segunda parte de esta tesis revisa los proyectos existentes en el mundo que están desarrollando la tecnología. El objetivo es recopilar todas aquellas experiencias prácticas que comprenden la construcción y operación de plantas Power to Gas, para observar así los retos pendientes de cara a su industrialización. La revisión fue publicada en *Renewable & Sustainable Energy Reviews*:

- iii Power to Gas projects review: Lab, pilot and demo plants for storing renewable energy and CO₂, *Renew Sust Energ Rev* 2017, 69, 292-312

Hasta la fecha, 46 proyectos experimentales de PtG han sido desarrollados en el mundo, mostrando que el alto coste de los equipos y la baja eficiencia todavía restringen la rentabilidad del concepto, limitando por ello el número de experiencias que son llevadas a escala industrial. Estos problemas son la motivación principal de la tesis, la cual busca favorecer la industrialización de la tecnología Power to Gas. De otro modo, el PtG tendría que esperar a futuros escenarios favorables para poder desarrollarse, en los que las renovables fuesen mayoritarias y las penalizaciones económicas sobre las emisiones de CO₂ fuesen notorias. El potencial de hibridación del Power to Gas (energía exotérmica de la metanización y oxígeno de la electrólisis) [15] amplía los posibles escenarios para un desarrollo industrial propicio.

Así, el objetivo central de la tesis es proponer novedosos conceptos híbridos de Power to Gas, para incrementar la eficiencia, hacer un mejor uso de los recursos disponibles, reducir el equipo necesario y

favorecer nuevos usos de la tecnología. La tesis analiza y caracteriza los sistemas propuestos para mostrar que se pueden alcanzar mejoras sustanciales en la tecnología Power to Gas por medio de las hibridaciones adecuadas.

Algunas de las hibridaciones más relevantes para mejorar el Power to Gas son aquellas que evitan las penalizaciones energéticas asociadas a la captura de CO₂, dado que resultan considerables cuando tiene que ser capturado de mezclas de gases en los que se encuentra diluido. La eficiencia cae entre 9 y 12 puntos porcentuales [16][17], lo que enmascara las ventajas medioambientales del PtG y su rol como reciclaje de CO₂ frente a otras tecnologías de almacenamiento de energía.

Una buena opción para evitar dichos inconvenientes es la hibridación del PtG con el método de captura en oxidación. En una oxidación, el comburente es oxígeno puro en vez de aire [18]. El alto contenido de N₂ que está presente típicamente en la combustión con aire, es aquí sustituido por los propios productos de la oxidación (CO₂ y H₂O), por lo que los gases de chimenea alcanzan una alta concentración de dióxido de carbono. La penalización energética asociada a este proceso de captura procede principalmente de la unidad de separación de aire (ASU), la cual produce el oxígeno requerido (190 kWh/tO₂) [19]. Por tanto, la hibridación PtG-Oxidación puede usar el oxígeno procedente de la electrólisis para reemplazar a la ASU y eliminar su consumo eléctrico. Además, dado que el CO₂ es reciclado a combustible otra vez, se evita el consumo eléctrico de la compresión que sería necesario para almacenarlo.

Si el concepto se implementa en una caldera, la energía exotérmica de la metanización puede ser integrada directamente como una salida útil del sistema, mientras que si el concepto se aplica a una central eléctrica, la energía térmica se puede integrar en el ciclo de potencia para incrementar la eficiencia eléctrica global.

La hibridación PtG-Oxidación es la primera propuesta estudiada en esta tesis. Para ello, se usa el ratio entre los tamaños de la electrólisis y la oxidación como un parámetro clave a la hora de definir la estrategia de operación. Después, se realizaron diversas simulaciones para ver los cambios en el sistema en función del combustible que es alimentado a la oxidación (carbón, biomasa o gas natural). Por último, se completó el estudio con un caso aplicado que analiza la integración PtG-Oxi en un ciclo combinado para la producción de electricidad. Los resultados se publicaron en 3 artículos:

- iv Power to gas-oxyfuel boiler hybrid systems, Int. J. Hydrogen Energy 2015, 24, 168-175
- v Power to Gas-biomass oxycombustion hybrid system: Energy integration and potential applications, Appl Energy 2016, 167, 221-229
- vi Future applications of hydrogen production and CO₂ utilization for energy storage: Hybrid Power to Gas-Oxycombustion power plants, Int. J. Hydrogen Energy 2017, Vol.42, 19, 13625-13632

Otra opción para evitar la penalización de obtener CO₂ puro es la integración de la tecnología Power to Gas con la captura en post-combustión con aminas. En esta técnica, los gases de combustión entran a una columna de absorción donde los gases inertes escapan limpios por la parte superior, y el CO₂ queda absorbido por la amina. El solvente rico en CO₂ es posteriormente regenerado en una segunda columna, utilizando vapor a contracorriente entre 100 y 200 °C, y obteniendo así un flujo con alta concentración de CO₂ [20]. La mayor pérdida de eficiencia viene de la energía térmica requerida para regenerar el solvente (producción del vapor), pero puede ser disminuida integrando la energía exotérmica procedente de la metanización.

Dado que la captura con aminas es la tecnología de captura más madura, ya existen en literatura estudios que analizan su integración con el proceso PtG en centrales eléctricas [21][22]. Por ello, en la última parte de la tesis se propone y estudia por primera vez la aplicación del sistema PtG-Aminas en la industria química. El estudio de esta propuesta evalúa la viabilidad técnica y económica de la hibridación, en la que el hidrógeno es un subproducto proveniente de una línea de producción basada en la electrólisis. Los resultados fueron publicados en Applied Energy:

- vii Power to Gas-Electrochemical industry hybrid systems: A case study, Applied Energy 2017, 202, 435-446

CONCLUSIONS

The intermittent behavior of renewable sources is known to be a significant issue in future electricity systems. Nevertheless, this can be palliated with proper energy storage solutions, like Power to Gas. This technology has stood out as one of the most promising options in mid-term for massive energy management, as well as for natural gas decarbonization. In this thesis, novel PtG configurations able to recycle CO₂ in closed loops have been proposed and analyzed to avoid decentralized emissions typical of the conventional concept, and improve the technology in terms of efficiency, utilization of resources and profitability.

First, a model of the future Spanish electricity system was developed, in order to assess the potential electricity surplus up to 2050. A moderate increment on demand (1.36%/year, Scenario 1) agrees with prospective reports of Spanish institutions, while higher annual growth (1.73%/year, Scenario 2) requires exceeding the expected deployment of power capacity. In 2050, renewable sources would provide more than the 63% of electricity production while fossil fuels would fall below 11%. Nuclear power cannot be replaced in mid-term by increasing renewable installed capacity since the required backup power would be extremely underused. Thus, the electricity surplus in 2050 may be about 1.4 – 5.2 TWh for Scenario 1, and 6.1 – 13.5 TWh for Scenario 2, what clearly shows how imperative the energy storage will be in the coming decades. Potential storage situations are mainly found from March to June, with guaranteed surplus in April and May. The required PtG capacities for processing the 90% of total excess in 2050, regardless of wind patterns, would be 13 GW for Scenario 1 and 19.5 GW for Scenario 2.

A large number of researchers have revisited PtG technology in the last decade to better integrate renewable sources in the system. Although the first pilot plant was erected in Japan, the current leadership holds in Europe, mainly thanks to the support of the governments of Germany, Denmark and Switzerland. These experiences comprise pilot and demonstration plants with electrolysis power capacities that vary from several kW_e up to 6 MW_e. However, very few projects have experienced with innovative CO₂ sources such as industrial processes.

The first novel proposal of the thesis was the Power to Gas-Oxyfuel combustion hybridization. This system stores renewable electricity as H₂ and O₂ through electrolysis, to be later used in the oxycombustion

facility. Oxygen allows to reduce the energy penalty of the ASU, while hydrogen is used to react with flue gas and generate synthetic natural gas through methanation. Depending on the ratio between the size of electrolysis and the oxyfuel combustion, the byproduct oxygen might be enough to remove the air separation unit, and hydrogen might completely feed the methanation of the whole flue gas stream. District heating and industrial processes are found to be the most suitable applications, whose recommended sizes of electrolysis are about 4 MW and 38 MW, respectively. Small oxy-fuel combined cycles with 30 MW of net electric power are considered to be the upper limit case for PtG-Oxy applications, since they require 98 MW of electrolysis. The simulation of this PtG-OxyCC hybrid system showed that 88% of the methanation heat could be recovered with an optimized heat exchanger network. The absence of ASU unit and the use of this methanation heat allowed increasing the overall efficiency of the oxycombustion power plant from 55.9% to 67.5%.

The second novel system presented in this thesis was the Power to Gas-Electrochemical hybridization. It incorporates methanation as a new line of production in those chemical plants that have hydrogen available as byproduct. Carbon dioxide is captured by amine scrubbing from the flue gas of their gas-fired boilers, and then recycled into synthetic natural gas through methanation. This system was simulated using real operating data of an electrochemical company. Results show that the hybrid plant can operate about 6000 hours per year, consuming the 85% of available hydrogen and recycling almost the 60% of the CO₂ emitted by the chemical industry. A production of 518.5 Nm³/h of SNG is achieved, and 238 kg/h of steam are generated using the methanation heat. The economic analysis yields very remarkable figures, because it is not necessary commissioning new electrolyzers or consuming additional electricity. Thus, capital investment can be recovered in 8 years, generating a 4.8 M€ NPV at the end of the project lifetime, with an IRR of 9%.

Although some results are derived from particular case studies, conclusions can be generalized to speed up the deployment of Power to Gas at industrial scale. The proposed PtG concepts may help overcoming the economic barriers of erecting a commercial plant, either due efficiency increments (PtG-Oxycombustion) or economically profitable solutions (PtG-Electrochemical).

CONCLUSIONES

El comportamiento intermitente de las energías renovables es un importante problema que afectará en el futuro a las redes eléctricas. No obstante, este puede ser paliado con soluciones de almacenamiento energético adecuadas, como el Power to Gas. Esta tecnología se ha erigido como una de las opciones más prometedoras a medio plazo para la gestión masiva de energía, así como para la descarbonización del gas natural. En esta tesis se ha propuesto y analizado nuevas configuraciones de Power to Gas capaces de reciclar CO₂ en ciclo cerrado, con el objetivo de evitar las emisiones descentralizadas típicas del concepto clásico, así como para mejorar la tecnología en términos de eficiencia, utilización de recursos y rentabilidad.

Primero, se desarrolló un modelo del posible futuro sistema eléctrico español para cuantificar el exceso eléctrico hasta el año 2050. Un incremento moderado en la demanda eléctrica (1,36%/año, Escenario 1) concuerda con las prospectivas reportadas por diferentes instituciones españolas, mientras que un crecimiento mayor en la demanda (1,73%/año, Escenario 2) requiere sobrepasar el despliegue previsto de potencia instalada en el parque de generación. En 2050, las renovables proveerían en torno al 63% de la producción eléctrica y los combustibles fósiles caerían por debajo del 11%. La producción nuclear no puede ser sustituida mediante un incremento de la potencia renovable instalada, dado que la potencia de respaldo quedaría excesivamente infrautilizada. Así, el exceso eléctrico en 2050 estaría entre 1,4 TWh y 5,2 TWh para el Escenario 1, y entre 6,1 TWh y 13,5 TWh para el Escenario 2, lo que claramente muestra que el almacenamiento de energía resultará imperativo para las próximas décadas. Los periodos que más probablemente requerirán almacenamiento se encuentran comprendidos entre Marzo y Junio, estando garantizado el exceso eléctrico en los meses de Abril y Mayo. La potencia que se requeriría de Power to Gas para procesar el 90% del exceso generado en 2050, independientemente del patrón de generación eólica, sería 13 GW para el Escenario 1 y 19,5 GW para el Escenario 2.

En la última década, diversos grupos de investigación han vuelto a interesarse por la tecnología Power to Gas, buscando mejorar la integración de las energías renovables en el sistema energético. Aunque la primera planta piloto se construyó en Japón, el actual liderazgo recae sobre Europa, debido mayormente al respaldo de los gobiernos alemán,

danés y suizo. Las experiencias de estos países comprenden plantas piloto y de demostración, con potencias de electrólisis que varían desde unos pocos kilovatios hasta los 6 MW. No obstante, muy pocos proyectos han optado por utilizar fuentes de CO₂ innovadoras, como las existentes en procesos industriales.

La primera propuesta novedosa de esta tesis son los sistemas Power to Gas-Oxicombustión. Estos sistemas almacenan la electricidad renovable en forma de H₂ y O₂, producidos mediante electrólisis, para posteriormente utilizar estos compuestos en una oxicombustión. El oxígeno generado permite reducir la penalización energética de la ASU, mientras que el hidrógeno es usado para transformar los gases de combustión en gas natural sintético, por medio de un proceso de metanización. Dependiendo del ratio entre el tamaño de la electrólisis y de la oxicombustión, el oxígeno subproducto puede llegar a evitar por completo la necesidad de una unidad de separación de aire, y el hidrógeno puede ser suficiente para procesar la totalidad del CO₂ emitido. Las aplicaciones más adecuadas para este tipo de hibridación han resultado ser la calefacción de distrito y la industria, ya que requieren tamaños de electrólisis entorno a los 4 MW y los 38 MW, respectivamente. Los ciclos combinados de pequeño tamaño (30 MW de potencia eléctrica neta) pueden ser considerados como el caso límite de aplicación de los sistemas PtG-Oxicombustión, dado que necesitan 98 MW de electrólisis. La simulación de este sistema híbrido PtG-OxiCC muestra que el 88% del calor de metanización puede ser recuperado como energía térmica útil gracias a una red de intercambio optimizada. La ausencia de ASU y la integración del calor de metanización permiten incrementar la eficiencia global del oxi-ciclo combinado desde el 55,9% hasta el 67,5%.

El segundo sistema novedoso presentado en esta tesis ha sido la hibridación Power to Gas-Electroquímica. Esta incorpora la metanización como una línea de producción adicional en plantas químicas que tengan hidrógeno subproducto disponible. El dióxido de carbono es capturado, mediante lavado de aminas, de los gases de combustión de las calderas de gas natural que tengan instaladas y, posteriormente, reciclado en gas natural sintético gracias a la metanización. Este sistema fue simulado utilizando datos de operación real de una compañía química. Los resultados muestran que la planta híbrida puede operar 6000 horas al año, consumiendo el 85% del hidrógeno disponible y reciclando entorno al 60% del CO₂ emitido por esta industria química. Se alcanza una producción de 518,5 Nm³/h de gas natural sintético y, adicionalmente, 238 kg/h de vapor por medio del calor exotérmico de metanización. El análisis económico deja resultados muy positivos, debido a que no es

necesario instalar nuevos electrolizadores ni consumir electricidad adicional. Así, la inversión de capital puede recuperarse en 8 años, generando 4,8 M€ de beneficio neto al final de la vida del proyecto, con una tasa interna de retorno del 9%.

Aunque algunos resultados proceden de casos de estudio particulares, las conclusiones pueden ser generalizadas para acelerar el despliegue del Power to Gas a escala industrial. Los conceptos PtG propuestos pueden ayudar a superar las barreras económicas de erigir plantas comerciales, ya sea por los incrementos en eficiencia (PtG-Oxicombustión) o por la mejora en los resultados económicos (PtG-Electroquímica).

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1 General introduction

1 General introduction

1.1 INTRODUCTION AND JUSTIFICATION

Global warming is nowadays unequivocal and extensively endorsed by scientific community. In 2016, the global land-ocean surface temperature had increased 1.26 °C with respect to the pre-industrial period (1880 – 1920), and the mean sea level had risen 0.23 meters [23]. Heat waves occur more often and last longer, while extreme precipitations have become more intense and frequent [1]. According to the IPCC, this has affected many species that have shifted their geographic ranges, seasonal activities or migration patterns in response to ongoing climate changes. Moreover, hydrological systems are continuously altered, what harms fresh water resources and food production [1].

Carbon dioxide is the largest single contributor to these perturbations on Earth's energy balance (greenhouse effect), and human beings are undoubtedly the main source [1]. Current atmospheric CO₂ concentration is increasing at the fastest ever observed rate (2.0 ppm/yr), what made 2016 the first year in history in which CO₂ concentration did not fall below 400 ppm at any time (Figure 1) [2]. At the United Nations Climate Change Conference held in Paris at the end of 2015, about 190 countries agreed to reduce emissions of greenhouse gases (GHG) –US recently rejected to join–. The aim is to limit global temperature increase below 2 °C by the year 2100, related to pre-industrial levels [24]. However, those scenarios that limit warming to 2 °C would require CO₂ atmospheric concentrations below 450 ppm, which is hardly accomplishable [1].

As the International Energy Agency stated [3], key measures to achieve such mitigation lie in decarbonizing electricity and heat generation sector, since it produces more than two-fifths of global CO₂ emissions

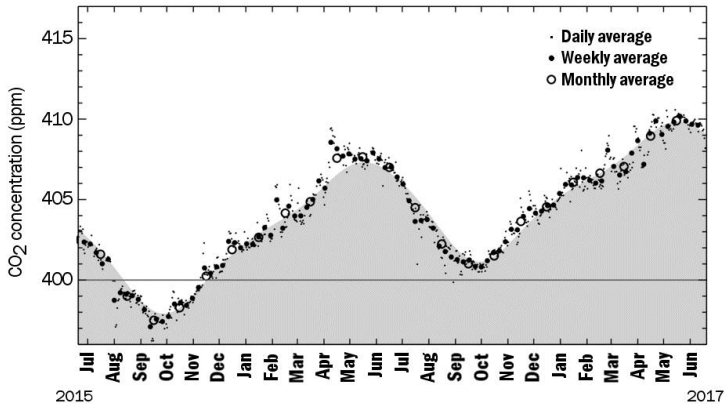
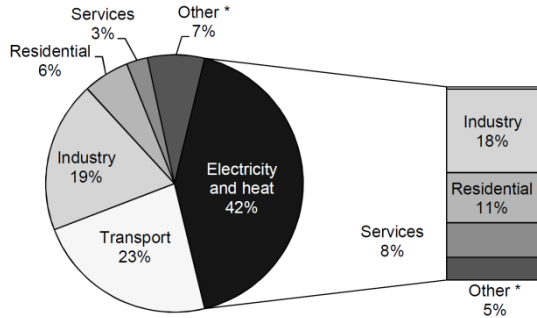


Figure 1. Atmospheric CO₂ concentration (ppm) [2]

(Figure 2). This is particularly notable in China, where total electricity output almost quadrupled since 2000 mainly based on carbon intensive coal-fired plants. In North America, the shift from coal towards natural gas, together with improvements in generation efficiency, allowed them to slightly reduce their CO₂ emissions related to the electricity sector. Meanwhile, Europe established in 2009 a common policy (Directive 2009/28/EC) [4] to achieve renewable shares of 34% and 21% in the electricity and heat sectors by 2020. This clearly boosted the decarbonization of the European energy system, what have reduced the associated emissions more than a 12% since then [5].

Hence, the European Commission proved the relevance of largely deploying renewable energy sources (RES) to help palliating climate change. Most of European Member States are expected to meet their 2020 renewable energy targets [25], and by 2050 Europe aims to produce the 53% of its electricity with renewable sources [26]. However, moving in this direction implies large amounts of intermittent energy production in the electricity market [8].

The most recent data from Eurostat (2014) [27][28] indicates that the 27.5% of the European electricity came from renewable sources (877 TWh). This was mostly composed by hydropower (368 TWh), wind power (245 TWh) and solar photovoltaic (79 TWh). Hydropower does not represent an issue, since hydro-electric plants handle short-term variability thanks to dams and reservoirs. However, wind and solar power exhibit a highly intermittent dispatch that cannot be suitably managed. Photovoltaic production has a peak around noon as well as significant variations over



*Other includes agriculture, forestry, fishing and other emissions not specified

Figure 2. World CO₂ emissions by sector (2013) [3]

minutes or hours due to cloud coverage. Besides, wind generation fluctuates significantly over periods of days to weeks, and needs to be balanced [8]. Generators and system operators can typically change and control just the 5-10% of the output coming from these types of plants (the degree of control in Spain is about 5%, in Sweden 6% and in Germany 7%) [29]. Thus, this variable nature leads to mismatches between supply and electrical demand that diminish the operational predictability and stability of the energy system.

Traditionally, irregularities are balanced through a fossil-based regulation to keep frequency and voltage within a stable range. Nowadays, due to the growing renewable share, fossil fuel power plants are compelled to additionally increase their flexibility and availability beyond the classic behavior of a backup facility. This kind of operation deteriorates the equipment of the power plants, and causes drops in efficiency that lead to additional CO₂ emission. For instance, 50% partial loads imply efficiency falls from 55% to 35% in combined cycles (427 g_{CO2}/kWh increases to 670 g_{CO2}/kWh), and losses of 10 percentage points in coal-fired plants (987 g_{CO2}/kWh increases to 1316 g_{CO2}/kWh) [29][30].

In conclusion, increasing renewable share under current scenario actually leads to instability and safety drawbacks in the energy networks, together with an increment in specific CO₂ emissions from the fossil-based backup power. Therefore, the key for a successful energy transition is an efficient management of these intermittent RES.

Facing such situation, the European Commission has proposed energy storage to overcome these problems [8]. Energy storage can balance centralized and distributed electricity generation, as well as

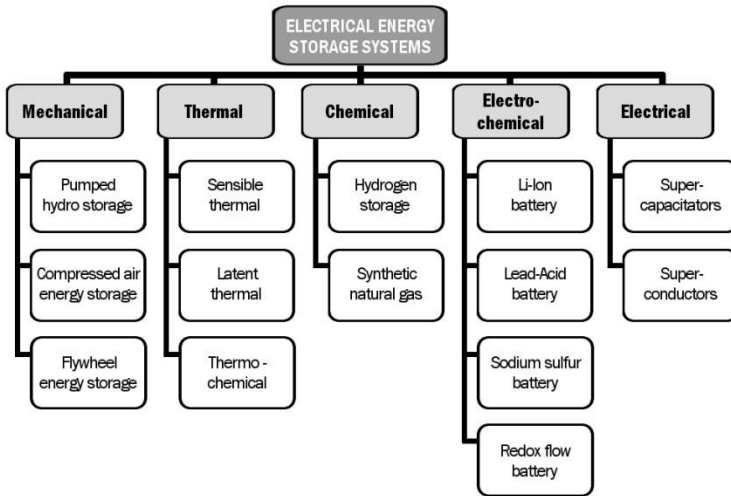


Figure 3. Electrical energy storage systems. Adapted from [8]

contribute to the decarbonization of other sectors such as transport, buildings or industry, by applying on them the stored renewable energy. Hence, the European Commission aims to progressively remove market, regulatory and administrative barriers affecting storage facilities, so that storage operators can provide services to electricity system operators in the same way that current flexibility solutions [8].

Nevertheless, and despite of the suitability of energy storage to this purpose, the use at large-scale of current technologies (Figure 3) is hindered by either practical constraints or low rate powers (Table 1). Flywheels, lithium-ion battery, redox flow battery, and super-capacitors are only developed at small- or mid-scale [9]. Regarding technologies with high rate powers, the deployment of pumped hydro storage and compressed air energy storage is limited by the requirement of special locations [9]. The efficiency of sensible and latent heat storage decreases with time due to heat losses, leading to short storage durations. Although the thermo-chemical route does not present this issue, the discharge time of the stored energy may be slow; besides, the technology is still under development [10]. Lead-acid battery and sodium sulfur battery are potentially hazardous [11]. Finally, the short storage duration of super-conductors (<hour) is a high constraint for network management [31]. Hence, energy storage as H₂ is the only technology that has no restrictions on rate power, location, environmental aspects, or storage duration.

Table 1. Energy storage technologies [9][10][11][32]

Technology	Power rating Discharge time Storage duration Efficiency round-trip Capital cost Stored energy cost	Description Advantages Disadvantages
Mechanical		
Pumped hydro storage	100 - 5000 MW 1 hour - days months 65 - 85% 600 - 2000 \$/kW 5 - 100 \$/kWh	Energy stored as gravimetric potential energy + Large scale energy storage + Long life time - Requires special locations - Low energy density
Compressed air energy storage	5 - 300 MW hours days - month 50 - 70% 400 - 800 \$/kW 2 - 140 \$/kWh	Air is compressed and stored in reservoirs + Large scale energy storage + Long life time - Requires special geological sites - Environmental concerns
Flywheel energy storage	0 - 250 kW ms - 15 min < hour 85 - 95% 250 - 350 \$/kW 1000 - 5000 \$/kWh	Energy stored in the angular momentum of a spinning mass + Environmentally friendly + High efficiency - Short term storage due to friction - Low scalability
Thermal		
Thermal energy storage based on (a) Sensible heat (b) Latent heat (c) Chemical reactions	0-300 MW hours Hours - weeks 30 - 60% 150 - 220 \$/kW 2 - 40 \$/kWh	(a) materials with high heat capacity, (b) phase-change materials, or (c) exo/endo-thermic reactions + Low cost + Waste heat can be used - Heat loss over time (a, b) - Technically complex (c)
Chemical		
Hydrogen storage	0 - 50 MW s - days months 20 - 40% 10000 \$/kW 2 - 15 \$/kWh	Hydrogen production and later utilization in fuel cells + High energy density + Clean energy carrier - Low round trip efficiency - High capital cost
Electro-chemical		
Li ion battery	0 - 100 kW min - hour hour - days 85 - 90% 1200 - 4000 kW 600 - 2500 \$/kWh	Rechargeable batteries based on lithium salt electrolyte + Low self-discharge rate + High energy density - Fragile with temperature - Low scalability due to cost

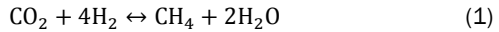
Table 1 (Continued). Energy storage technologies [9][10][11][32]

Technology	Power rating Discharge time Storage duration Efficiency round-trip Capital cost Stored energy cost	Description Advantages Disadvantages
Electro-chemical		
Lead-acid battery	0 - 10 MW minutes day - month 75% 200 - 450 \$/kW 100 - 830 \$/kWh	Rechargeable batteries based on lead / lead-dioxide electrodes + Low cost + Fast response - Toxicity of Pb - Relatively low efficiency
Sodium sulfur battery	0.05 - 8 MW s - hours 6 hours 80-90% 1000 - 3000 \$/kW 300 - 500 \$/kWh	Rechargeable batteries based on molten sulfur and sodium + Prompt and precise response + High efficiency - High capital cost - Operational hazard
Redox flow battery	0.03 - 3 MW s - 10 h months 85 - 90% 600 - 1500 \$/kW 150 - 1000 \$/kWh	Rechargeable batteries based on vanadium reduction and oxidation + Low maintenance cost + Tolerance to overcharging - Low energy density - High cost
Electrical		
Super-capacitors	0 - 300 kW ms - 1 hour < 1 hour 90 - 95% 100 - 300 \$/kW 300 - 2000 \$/kWh	High-capacity electrochemical capacitors + High efficiency + Fast discharge times - Limited scale-up - Short-term storage
Superconductor magnetic energy storage	0.1 - 10 MW ms - s min - hour 95 - 98% 200 - 300 \$/kW 1000-10000 \$/kWh	Uses magnetic fields to store energy in superconductors + Rapid response operation + Long life time - Cryogenic temperatures - High cost

The hydrogen energy storage technology uses electricity to feed an electrolyzer that dissociates water and produces the storable hydrogen. Then, hydrogen is used as fuel to generate electricity through gas turbines or fuel cells. The main barriers to make this process feasible are the high investment and the low round-trip efficiency. In practice, despite alkaline and PEM electrolyzers are already commercial, their cost (>1000 €/kW)

and efficiency (36.5% - 66.5%, LHV) are far from feasibility [13]. In addition, transport and compression of hydrogen may lead to 10% efficiency loss, while reconversion to electricity leads to another strong penalty (efficiency of gas turbines is about 40%, fuel cell applications 50%, and combined cycles 60%) [9][33].

To widen the application of hydrogen as energy carrier, and soften these drawbacks, a new concept known as Power to Gas (PtG) has stood out in the last years. Power to Gas uses the stored H₂ to produce methane (the main component of natural gas) via the methanation of CO₂ (Equation 1). Thus, the electric and gas network can be interconnected to increase the flexibility of the energy supply [15].



This connection makes easier the distribution of the stored energy through an already established infrastructure (gas network), thus avoiding the transport efficiency penalty, and any additional safety measure. Besides, it allows RES to participate in other sectors such as industries, household heating, or transport, what would enable new final uses with greater reconversion efficiencies.

Methane from Power to Gas can be considered carbon-neutral whenever H₂ is renewably produced, since methanation consumes the same amount of CO₂ that is later emitted during combustion. However, its decentralized use is only recommended when original CO₂ comes from sources as biomass (i.e., when it is initially neutral), because CO₂ will be re-emitted from a large number of distributed sources (e.g., cars and households), making unlikely the possibility to re-capture it [34] (Figure 4). If carbon dioxide is originated from fossil combustion, the way to avoid its later emission would be a continuous CO₂ recycle in power plants (Figure 5) or industry (Figure 6), what will finally displace fossil fuels. In both cases, it could reduce the amount of fossil fuels going into the economy, thus leading to significant reduction on CO₂ emissions.

Despite of the advantages of Power to Gas, the high capital cost and the low efficiency are strong barriers that make the concept not feasible yet. These unsolved problems are the key motivation of the present thesis, in which potential hybridizing synergies between PtG and other industries are proposed and analyzed to reduce costs, enhance the resource use, and increase the round-trip efficiency. Thus, the large-scale energy storage called Power to Gas will be promoted, favoring its participation as a climate change measure during the coming decades, with the aim of increasing the penetration of renewable energy production in the electricity system.

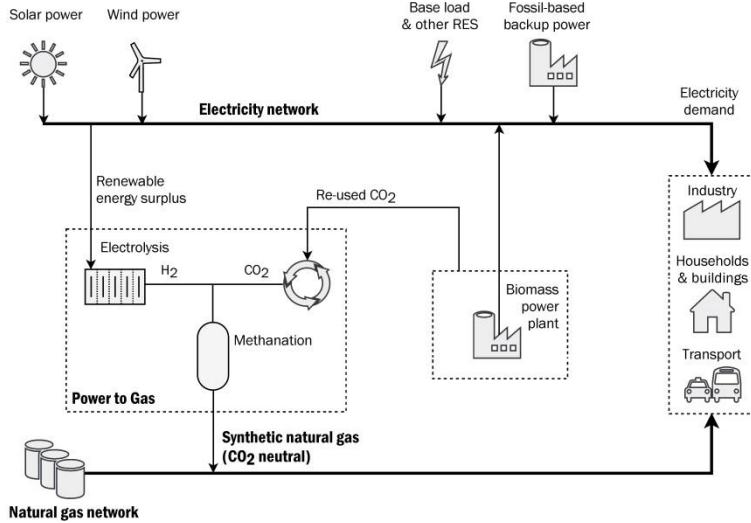


Figure 4. CO₂ neutral configuration of PtG for decentralized use of SNG

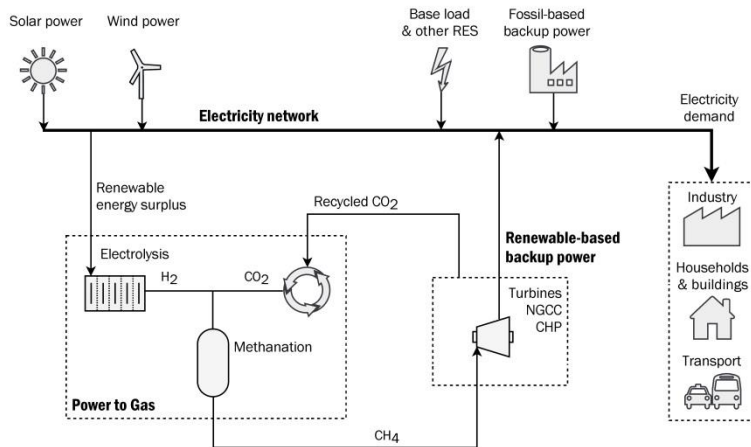


Figure 5. CO₂ recycling configuration of PtG for renewable-based backup power generation

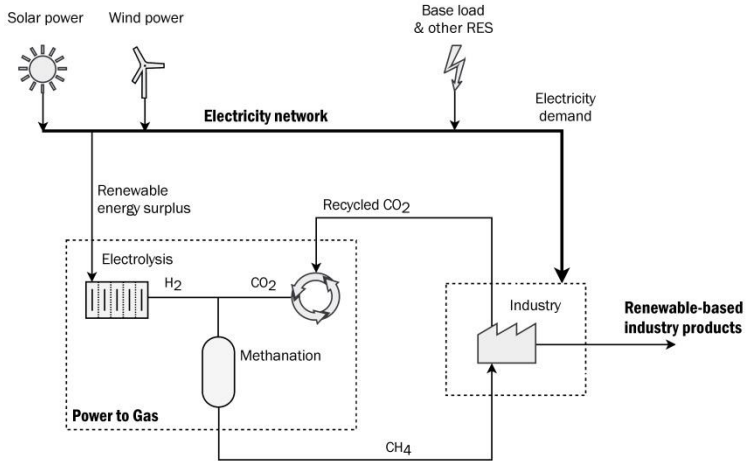


Figure 6. CO₂ recycling configuration of PtG for renewable-based industry

1.2 OBJECTIVES

The core objective of this thesis is to propose new configurations of Power to Gas that recycle CO₂ in closed loops, and which can improve the technology in terms of efficiency, utilization of resources and profitability. These hybridizations will help to overcome the current technical and economic barriers of erecting commercial PtG plants, in order to gain operational experience at industrial scale. Otherwise, the deployment of this energy storage technology relies on scenarios with greater shares of renewable sources and higher carbon credit prices.

To achieve this general aim, the thesis is divided in four specific tasks that comprise the justification, the state of the art, and the study of two novel hybridizations.

Task I: Assessment of expected electricity surplus under potential future Spanish energy scenarios

Power to Gas has been proposed as a potential technology able to solve some energy-related issues that will intensify during the next decades. Intermittent power generation is starting to affect network

regulation, and it is not clear how significant this effect could be in the future. So far, only some research groups from central and northern Europe have assessed the amount of energy surplus that might be produced in the next years, as well as the consequent energy storage power capacity and backup power that will be required to suitably manage the electricity dispatch [6][35][36].

So, the first task of this thesis is to highlight the importance of this issue in the Spanish context, by studying the potential electricity surplus that might occur in Spain up to the year 2050. Thus, new data will be given to support justifications to research on large scale energy storage, also showing that this is a generalized problem that not only affect to northern European members.

To reach this goal, three sub-tasks should be fulfilled: (I.a) To hypothesize plausible future energy scenarios of electricity demand and production, based on historical trends and prospective studies from relevant institutions; (I.b) To develop a model that temporarily distribute the expected electricity demand and production; and (I.c) To quantify the potential electricity surplus that might exist in the coming decades.

Task II: Review of the state of the art of Power to Gas plants

The next step of the thesis is to evaluate the state of the art of Power to Gas. Since the application of this technique to the energy store concept is still in an early research stage, the available information in literature is limited. There only exist two relevant reviews concerning Power to Gas [37][13], which were released early in 2016 by the Karlsruhe Institute of Technology. However, they just approach technical aspects of methanation (e.g. operating conditions, reactor configurations or catalysts performance), and do not review specific experiences in Power to Gas facilities.

Therefore, the second task of this thesis is to thoroughly review the construction and operation of Power to Gas pilot-, demo- and lab plants all around the world, to fill the knowledge gap. To accomplish this, three sub-tasks are required: (II.a) To classify and frame all the technologies relating to Power to Gas concepts, understood as the simultaneous storage of renewable energy and carbon dioxide in the form of methane; (II.b) To gather and filter information about all the existing PtG projects in the world; and (II.c) To build a timeline to clearly represent the evolution and concatenation of the projects with years, and compare technical data of all the installations.

Task III: Analysis of the Power to Gas-Oxyfuel combustion hybrid concept

Up to date, 46 experimental PtG projects have been developed worldwide, but they rely on high renewable penetrations and strong fines on CO₂ to make Power to Gas profitable. At present, the development of the technology is mostly restricted by the high cost of the equipment, and the low round-trip efficiency. This situation limits the number of useful field experiences on Power to Gas from which to learn scaling the technology and managing energy surplus.

Thus, the third task of this thesis focuses on studying the Power to Gas-Oxyfuel combustion hybrid concept to rise the overall efficiency and better use the available resources. The sub-tasks are: (III.a) To simulate the PtG-Oxyfuel combustion hybridization using different fuels; (III.b) To characterize the system and evaluate the most suitable applications; and (III.c) To quantify the efficiency of the system when it is applied to a specific case study: an oxy-combined cycle power plant.

Task IV: Analysis of the Power to Gas-Electrochemical industry hybrid concept

Under the same framework of previous aim, the fourth task of the thesis comprises the study of the Power to Gas-Electrochemical industry hybridization. This novel concept avoids some required equipment to improve the economics of the whole plant. Three sub-tasks are considered: (IV.a) To model and simulate the PtG-Electrochemical industry hybrid concept; (IV.b) To size and analyze the system under a specific application case; (IV.c) To evaluate the profitability of the concept.

1.3 STRUCTURE OF THE THESIS AND RELATED DISSEMINATION

So far, the main global issues related to the growing increment of renewable share in energy production have been presented, together with the four tasks that this thesis aims to fulfill. These goals were accomplished through the development of three activities, in which the dissertation is divided. The related dissemination (published JRC papers and international conferences) and those research projects in whose framework this thesis has been partially developed, are shown in Table 2.

Section 2.1 presents a prospective study assessing the future Spanish electricity surplus in order to approach Task I. The model and results were submitted to Energy, and presented in the 13th International Conference on Greenhouse Gas Control Technologies (with an associated

paper in Energy Procedia). Besides, the obtained results shaped the core of the research project “Energy storage through methane. Preliminary analysis of scenarios with high share of renewable energy in the Spanish electricity market”, funded by Fundación Iberdrola (2014 – 2015).

Section 2.2 expounds on Task II. First, the structure classification of Power to Gas is proposed, and then the technology is reviewed. The revision includes a summary of the main technical aspects of methanation from literature, and the thorough review of the existing projects covering applied research. This work was published in Renewable & Sustainable Energy Reviews.

Section 2.3 is the most relevant part of the thesis, in which solutions are proposed and analyzed (Tasks III and IV). The two hybrid concepts are individually studied, since they are characterized by different synergies. Regarding PtG-Oxycombustion hybridization, three papers have been published: two in the International Journal of Hydrogen Energy, and one in Applied Energy. Each paper delves into the behavior of the system under different fuels for oxycombustion –coal, biomass and natural gas–. The approach to the coal-based PtG-Oxy system was assessed as part of the research project titled “Innovative processes: Implementation of Power-to-Gas Technology in the Aragonese Pyrenees”, funded by Dirección General de Industria y de la Pequeña y Mediana Empresa (2014 – 2015).

The obtained results about the PtG-Electrochemical industry hybridization were published in Applied Energy. The research project “Energy storage (Power-to-Gas) and carbon capture integration in chemical industry with hydrogen production” funded by Departamento de Industria e Innovación Gobierno de Aragón (2015 – 2016) was the framework to assess the case study of an actual industrial facility.

The results gathered in Section 2.3 have been widely disseminated in seven international conferences. The full list of the conferences is presented in Table 2.

Special mention is given to future work, in section 3, since it is related to the research project “Metano a partir de Energías Renovables y Captura y Utilización de CO₂ en el sector Residencial, Industrial y Automovilístico (MERCURIA)” funded by the Spanish Ministry of Economy, Industry and Competitiveness. This project started in January of 2017 and aims to design, build and operate a lab-scale system of Power to Gas in Departamento de Ingeniería Mecánica of Universidad de Zaragoza.

Table 2. Structure of the thesis

Section/Task	Papers	Conferences	Research projects
2.1 Spanish outlook on electricity surplus	<ul style="list-style-type: none"> • "Power to Gas in Spain: a case study of the development potential up to 2050", 2017 Energy, Submitted 	<ul style="list-style-type: none"> • "Power to Gas technology in Spanish future energy market", 13th GHGT 2016 	<ul style="list-style-type: none"> • "Energy storage through methane. Preliminary analysis of scenarios with high share of renewable energy in the Spanish electricity market", Fundación Iberdrola 2014 - 2015
Task I	<ul style="list-style-type: none"> • "Power to Gas technology under Spanish future energy scenario" 2017 Energy Procedia, 114,6880-85 		
2.2 Power to Gas as hybrid storage	<ul style="list-style-type: none"> • "Power to Gas projects review: Lab, pilot and demo plants for storing renewable energy and CO2", 2017 Renew Sust Energ Rev 69, 292-312 	n/a	n/a
Task II			
2.3 Hybrid Power to Gas concepts	<ul style="list-style-type: none"> • "Power to gas-oxyfuel boiler hybrid systems", 2015 Int. J. Hydrogen Energy 24, 168-175 	<ul style="list-style-type: none"> • "Analysis of power-to-gas technology with oxyfuel combustion integration" 2nd REGATEC 2015 	<ul style="list-style-type: none"> • "Innovative processes: Implementation of Power-to-Gas Technology in the Aragonese Pyrenees", Dirección General de Industria y de la Pequeña y Mediana Empresa 2014 - 2015
Task III, IV	<ul style="list-style-type: none"> • "Power to Gas-biomass oxycombustion hybrid system: Energy integration and potential applications" 2016 Appl Energy 167, 221-229 	<ul style="list-style-type: none"> • "Reducing energy penalty of oxycombustion through Power-to-Gas hybridization", 1st BCC 2016 Pyrenees", 21st WHEC 2016 	<ul style="list-style-type: none"> • "Energy storage (Power-to-Gas) and carbon capture integration in chemical industry with hydrogen production", Departamento de Industria e Innovación Gobierno de Aragón 2015 - 2016
	<ul style="list-style-type: none"> • "Future applications of hydrogen production and CO₂ utilization for energy storage: Hybrid Power to Gas-Oxycombustion power plants" 2017 Int. J. Hydrogen Energy 19,625-632 	<ul style="list-style-type: none"> • "Future applications of hydrogen production and CO₂ capture for energy storage", 21st WHEC 2016 	
	<ul style="list-style-type: none"> • "Power to Gas-Electrochemical industry hybrid systems: A case study" 2017 Appl Energy 202, 435-446 	<ul style="list-style-type: none"> • "Power to Gas and CO₂ capture. Smart storage of renewable energy", 2nd Aportando Valor CO₂ 2017 • "CO₂ recycling based on Power to Gas-carbon capture hybrid systems", 9th TCCS 2017 	<ul style="list-style-type: none"> • "Metano a partir de Energías Renovables y Captura y Utilización de CO₂ en el Sector Residencial, Industrial y Automovilístico", MINECO 2017 - 2019

2 Thesis

2 Thesis

2.1 SPANISH OUTLOOK ON ELECTRICITY SURPLUS

First official data of the Spanish electricity system date from 1901, which registered an installed power capacity of 78.2 MW including hydropower (39%) and thermal power (61%) [38][39][40]. Since then, the energy supply has continuously been transformed because of social evolution and historical milestones such as intense droughts, European regulations or the Great Recession. Today, Spain is considered as a European representative example of the influence of renewable energy sources on the entire energy infrastructure.

Between 2002 and 2009, Spain experienced a sustained growth of installed renewable capacity, which led to a later overcapacity in the system when the energy demand decreased between 2008 and 2010. This effect is particularly detrimental for backup plants (coal power plants and combined cycles), which have to diminish their market share despite they are essential for the network management. As example, between fall 2009 and spring 2010 a very rainy year combined with the windy season led several coal units to be kept idle for more than six months [29].

This kind of situations makes the wholesale price become more volatile and the system operation more complex, so countries from central and northern Europe are assessing the amount of energy surplus that might occur in the next years. Especially, some researchers who investigate Power to Gas have specified the estimated surplus in terms of required PtG power capacity. In Germany, Jentsch et al. [6] found that the economic optimum for PtG implementation is between 6 GW and 12 GW for a 85% renewable scenario. Schneider L. and Kötter E. [7] thoroughly studied the geographical limitations for installing PtG facilities in the German state of Rhineland-Palatinate, and extrapolated the result to the entire country. Thus, they determined that the maximum PtG capacity that can be implemented in Germany is 15.4 GW. In Great Britain, Qadrdan M.

et al. [41] modelled the impact of integrating the gas and electricity networks through Power to Gas, given the large capacity of wind power expected to be installed in the northern parts of England and Wales. Thus, they found that wind curtailment could be reduced between 27% and 62% depending on demand, and the daily operation cost of the network would be reduced a 11%. In this case, the PtG capacity estimated to be installed would be in the range 5 – 12 GW. In Austria, Reiter G. and Lindorfer J. [36] showed that available CO₂ sources are enough to store all the national fluctuating power coming from photovoltaics and wind power.

In this section, a prospective of the Spanish case is presented to highlight the relevance of large-scale energy storage research, and justify the development of this thesis in worldwide and local context. This study was submitted to the international journal ‘Energy’ (Power to Gas in Spain: a case study of the development potential up to 2050), and presented in the 13th International Conference on Greenhouse Gas Control Technologies. Besides, results from this analysis built the basis of the project titled “Energy storage through methane, Preliminary analysis of scenarios with high share of renewable energy in the Spanish electricity market” funded by Fundación Iberdrola (2014 – 2015).

2.1.1 Future energy scenario model

The main objective of this model is to estimate the annual electricity surplus that the Spanish energy system might have in the next decades. This is calculated from the difference between the daily production and demand under different renewable generation patterns.

The estimation of the electricity demand is based on *The Global Calculator* [42], a tool that models the world’s energy, land and food systems to explore future energy scenarios. Meanwhile, the electricity production is calculated as the product of the installed power capacity and the operating hours, which are heuristically inferred from the analysis of historical data. Since demand and production are established separately, additional restrictions are imposed to validate the feasibility of these scenarios. Whenever the imposed constraints are not met, the installed power capacity is accordingly modified and a new estimation is set (Figure 7). The prospective data from Spanish institutions allow to propose realistic scenarios while restrictions guarantee the technical consistency.

Energy demand scenarios

As stated, the electricity demand is based on *The Global Calculator* tool [42], funded by the UK Government’s International Climate

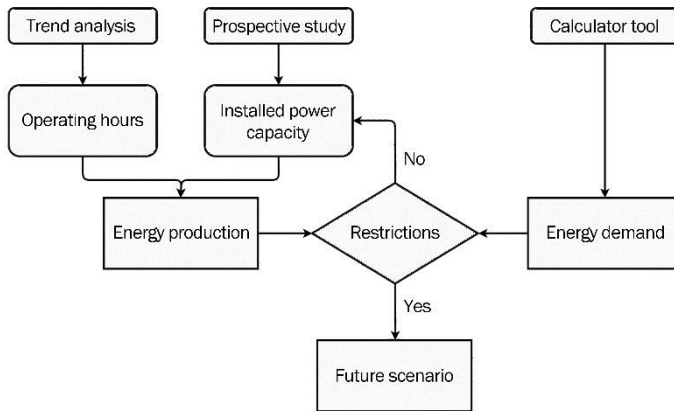


Figure 7. Energy scenario model flow chart

Fund and the EU's Climate-KIC. Different scenarios can be outlined considering multiple variables like social habits, industrial investments, or policies [43] (Annex A). It must be noted that *The Global Calculator* models the world energy system, but in this study results are used for a country.

Two scenarios are proposed to limit the increment of the global mean temperature up to 2 °C by year 2100. Some of the social assumptions that make this possible are to increase the average occupancy in cars and trains by a 15%, maintain the temperature of buildings at 18 °C and 26 °C during winter and summer respectively, and significantly promote the recycling.

Both scenarios present different growth rates for the electricity demand (Figure 8). In Scenario 1, the demand moderately increases a 1.36% per year, whilst in Scenario 2 the annual growth rate is 1.73%. To control the demand growth, investments must be focused on improving the efficiencies of fossil power plants, paper industries and cement industries, instead of on electrifying the transport. Besides, to enhance the appliance's efficiency and the treatment of wastes result crucial.

Energy production scenarios

The energy production is calculated through the operating hours and the installed power capacity, which are both initially estimated and then modified through restrictions to arrange a coherent scenario. These modifications should keep the new capacity as close as possible to the first estimation. The restrictions are:

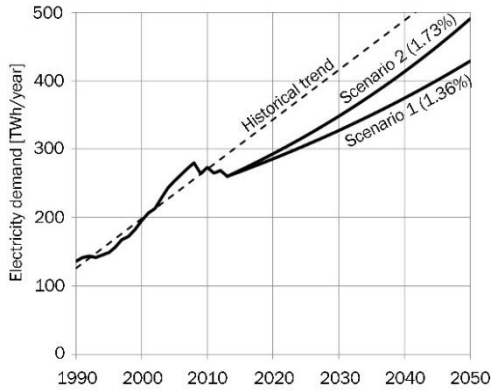


Figure 8. Electricity demand scenarios for Spain. Historical data from [44]

- 1) When backup power is required, biomass is preferred.
- 2) Coal's share is maintained at 7.0% – 8.0% for the year 2020 [45], and then progressively diminished.
- 3) The participation of combined cycles varies depending on the availability of renewable sources.
- 4) Backup power (biomass, coal and natural gas) must be able to satisfy demand when only the 45% of renewable power and 95% of base power (nuclear and CHP) are available.

The operating hours of renewable and nuclear energy sources are proposed following the trend inferred from historical data, current policies, technology maturity and future prospective. Contrarily, the operating hours of fossil energy sources are derived after accounting the constraints of the model, since the renewable participation determines the backup necessities. When historical operating hours are analyzed [46], four general trends can be distinguished (Figure 9): (a) Wind power, hydropower, small hydro, and nuclear power have become mature technologies that operate steadily on average; (b) Photovoltaics and solar thermal energy rose rapidly in 2 – 3 years coming to a stagnant between 1800 – 2000 hours; (c) CHP and biomass power plants have increased slowly their operation since 2002; (d) Coal power plants and combined cycle plants have decreased in favor of renewable sources from 2007.

Although hydropower and small hydro have periodic fluctuations according to natural, wet and dry cycles, the average is not expected to change. In nuclear plants, fuel replacement also produces periodic

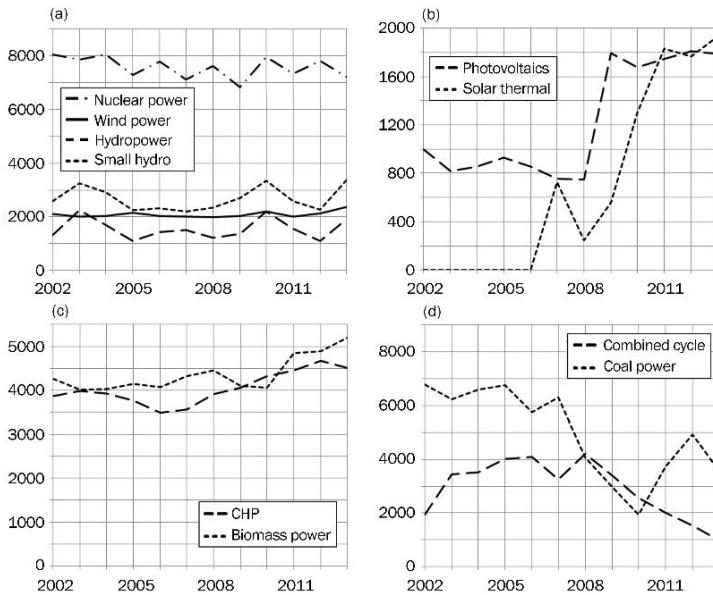


Figure 9. Operating hours [h] in the Spanish electricity system [46]

variations in annual operation, but in this case the hourly average slightly diminishes with time. Since all nuclear plants date from before 1988, unplanned shutdowns get more frequent [47]. Wind power has stood just above 2000 annual operating hours, mostly due to weather conditions but also because of government's policies that limited support to renewable generation. In the period 2010 - 2014, wind power received additional retribution only for the first 2350 hours [48]. Photovoltaics case is illustrative since operation swiftly grew up to the bonus limit [49]. Nowadays, these subsidies to renewable sources are progressively lessened, so operation of wind and PV power will increase looking for profitability [50][51]. In the case of solar thermal power, restrictions started from 2350 hours so they did not affect operation [48], whilst CHP and biomass power were not even limited. Therefore, their operating hours increase according to the technology development. Lastly, the resulting participation of coal power and combined cycles, that match demand, falls below 2200 hours (Table 3).

Regarding installed capacity, a plausible initial scenario is established based on reports from institutions like IDAE, Fundación para Estudios sobre la Energía, or Foro de la Industria Nuclear Española. The

whole prospective on installed power capacity may be found in the related published paper. Despite of constraints, Scenario 1 properly fits the installed capacity initially estimated. Thus, for example, for the year 2050 the electricity production from CHP is doubled, small hydro participation increases up to 4.0% – 4.5%, and biomass installed capacity reaches 5 GW. In Scenario 2, the higher demand requires exceeding the initially estimated power capacity (Table 4). For both scenarios, the nuclear power generation must be maintained in operation instead of being replaced by additional renewable power. Otherwise, the required backup power would be excessively underused.

Table 3. Operating hours [h] in the future Spanish electricity system

Scenario	Scenario 1 Demand growth rate: 1.36%				Scenario 2 Demand growth rate: 1.73%			
	2020	2030	2040	2050	2020	2030	2040	2050
Hydropower	1600	1620	1640	1660	1600	1620	1640	1660
Small hydro	2700	2720	2740	2760	2700	2720	2740	2760
Wind power	2450	2600	2650	2700	2450	2600	2650	2700
Photovoltaics	1850	2000	2300	2650	1850	2000	2300	2650
Solar thermal	2200	2600	3050	3500	2200	2600	3050	3500
Biomass	5500	6000	6350	6750	5500	6000	6350	6750
CHP	4700	5000	5300	5600	4700	5000	5300	5600
Nuclear power	7200	7000	6850	7300	7200	7000	6850	6000
Coal	2204	2080	2084	2005	1980	1500	817	715
Combined cycle	1243 - 1338	1045 - 1212	995 - 1171	1277 - 1466	1865 - 1917	1716 - 1911	1489 - 1775	745 - 1110

Table 4. Installed capacity [GW] in the future Spanish electricity system

	Scenario 1 Demand growth rate: 1.36%				Scenario 2 Demand growth rate: 1.73%			
	2020	2030	2040	2050	2020	2030	2040	2050
Hydropower	17.9	18.1	18.6	19.2	17.9	19.6	21.7	23.9
Small hydro	2.4	3.8	6.1	6.4	2.4	3.7	4.2	4.7
Wind power	26.0	28.7	32.1	35.8	24.5	32.6	39.8	44.4
Photovoltaics	5.4	7.3	8.2	9.1	5.4	7.3	9.8	15.7
Solar thermal	10.6	13.2	16.4	20.3	9.7	13.0	17.5	23.6
Biomass	1.2	2.8	3.8	5.3	1.2	2.0	3.5	6.2
CHP	8.1	9.9	10.8	11.6	8.1	10.8	13.2	16.1
Nuclear power	7.9	7.9	7.9	6.1	7.9	7.9	8.4	8.1
Coal	10.4	9.4	9.0	8.6	10.4	9.3	7.6	6.9
Combined cycle	24.2	22.5	21.4	20.4	24.2	22.5	21.4	20.4
Total	114.1	123.6	134.3	142.8	111.7	128.7	147.1	170.0

Time pattern of the energy demand and energy production

The scenarios previously defined only quantify annual amounts of energy demand and energy production. To identify surplus situations, these quantities must be distributed throughout the year in daily intervals.

For most technologies, generation pattern is independent of energy demand (Table 5). Hydropower, wind and solar power are weather-dependent and present seasonal productions. CHP, linked to industrial processes, produces stable monthly power that only diminishes in august due to summer break. Nuclear also provides base-load power, occasionally modified by fuel replacements and unplanned shutdowns. Similarly, biomass plants work steadily, since they are still emerging in Spain.

According to reviewed data, differences in daily energy production throughout a month are not remarkable except for wind power. Therefore, the model homogeneously distributes the monthly amounts of solar power and hydropower among days. Besides, nuclear power and CHP are simplified disregarding monthly differences and equally dividing the generation throughout the 365 days. Then, since daily wind production cannot be suitably modeled [52], calculations are performed by analyzing the wind patterns of years 2009 – 2013, which lead to a range of possible daily productions. The utilization of an average pattern for wind production would eliminate the intrinsic irregularities. Lastly, biomass, coal and natural gas lack a specific pattern since they act as backup power when the rest of technologies do not fulfill demand.

In the case of energy demand, the time patterns mainly depend on aspects concerning way of living, festivities and seasons, which barely vary in long-term. In Table 6, the entire year is classified in day-types together with their historical average demand between 2010 and 2013 [52]. Thus, future daily demand is calculated considering the day-type and the total annual demand.

Table 5. Average monthly production [%] throughout years 2008 – 2013 [46]

	Jan.	Feb.	Mar.	Apr.	May.	June	July	Aug.	Sep.	Oct.	Nov.	Dec.
Hydropower	11.2	9.8	11.2	10.7	9.6	8.1	6.7	5.6	4.5	5.3	7.6	9.7
Wind power	9.6	9.8	9.7	8.3	7.6	6.6	6.4	6.4	6.3	7.7	10.6	11.0
PV	4.9	6.5	7.9	8.9	10.7	10.8	11.8	10.9	9.2	8.0	5.5	4.9
Solar th.	2.4	4.2	4.6	6.2	9.9	12.5	15.9	14.8	12.2	8.7	4.3	4.3
Biomass	8.3	7.7	8.0	8.1	8.1	8.1	8.7	8.5	8.2	8.7	8.6	9.0
CHP	8.7	8.1	8.7	8.3	8.4	8.1	8.5	7.1	8.3	8.6	8.6	8.6
Nuclear	8.9	8.4	8.7	8.1	7.4	7.6	8.7	9.4	8.7	8.3	7.7	8.1

Table 6. Average daily demand (annual percentage) [%] throughout years 2010 – 2013 [52]

Day	Jan.	Feb.	Mar.	Apr.	May	June	July	Aug.	Sep.	Oct.	Nov.	Dec.
Working day (1 st half-month)	0.3036	0.3145	0.2924	0.2695	0.2765	n/a	0.2992	0.2772	0.2800	0.2765	0.2788	n/a
Working day (2 nd half-month)	0.3220	0.3060	0.2838	0.2695	0.2844	n/a	0.2992	0.2940	0.2800	0.2607	0.2952	n/a
1 st Saturday	0.2484	0.3060	0.2666	0.2541	0.2291	0.2400	0.2728	0.2436	0.2400	0.2449	0.2460	0.2816
2 nd Saturday	0.2852	0.2890	0.2580	0.2541	0.2370	0.2400	0.2640	0.2436	0.2400	0.2291	0.2460	0.2640
3 rd Saturday	0.2852	0.2720	0.2408	0.2310	0.2449	0.2400	0.2552	0.2604	0.2400	0.2291	0.2460	0.2904
4 th and 5 th Saturday	0.2852	0.2805	0.2580	0.2310	0.2449	0.2400	0.2552	0.2604	0.2400	0.2449	0.2624	0.2728
1 st Sunday	0.2392	0.2805	0.2494	0.2156	0.2054	0.2320	0.2552	0.2184	0.2240	0.2212	0.2378	0.2552
2 nd Sunday	0.2576	0.2720	0.2408	0.2233	0.2370	0.2320	0.2376	0.2184	0.2240	0.2212	0.2542	0.2552
3 rd Sunday	0.2760	0.2550	0.2408	0.2310	0.2291	0.2320	0.2376	0.2268	0.2240	0.2054	0.2378	0.2640
4 th and 5 th Sunday	0.2668	0.2720	0.2236	0.2079	0.2212	0.2320	0.2376	0.2352	0.2240	0.2291	0.2460	0.2376
New Year (1 st Jan.)	0.2300	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
Epiphany (6 th Jan.)	0.2576	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
Maudy Thursday	n/a	n/a	n/a	0.2310	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
Good Friday plus weekend	n/a	n/a	n/a	0.2233	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
Workers' Day (1 st May)	n/a	n/a	n/a	n/a	0.2133	n/a	n/a	n/a	n/a	n/a	n/a	n/a
Assumption of Mary (15 th Aug.)	n/a	n/a	n/a	n/a	n/a	n/a	n/a	0.2352	n/a	n/a	n/a	n/a
National Day (12 th Oct.)	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	0.2291	n/a	n/a
All Saints' Day (1 st Nov.)	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	0.2214	n/a
Constitution's Day (6 th Dec.)	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	0.2816
Immaculate Conception (8 th Dec.)	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	0.2464
Christmas Eve (24 th Dec.)	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	0.2728
Christmas (25 th Dec.)	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	0.2376
New Year's Eve (31 st Dec.)	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	0.2288
Working day (last week of June)	n/a	n/a	n/a	n/a	n/a	0.2960	n/a	n/a	n/a	n/a	n/a	n/a
Working day (week of 6 th Dec.)	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	0.2992
Working day (after 25 th Dec.)	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	0.2376
Working day (rest)	n/a	n/a	n/a	n/a	n/a	0.2720	n/a	n/a	n/a	n/a	n/a	0.3080

2.1.2 Electricity surplus in Spain by 2020 - 2050

The proposed scenarios essentially differ in the demand growth rate, which leads to different evolutions of the Spanish energy mix. As mentioned, surplus situations are calculated through the daily differences between production and demand –an hourly discretization would have been excessively accurate, given the large errors present in the assumed scenarios–. The electricity surplus spans within a range that is determined by the used wind production patterns. Greater energy storage potential means worse agreement between electricity demand and wind production, what varies the required natural gas share in the energy market (Table 7).

In 2050, renewable sources would provide more than the 63% of the power production, whilst fossil fuels fall below 11%. The annual renewable surplus amounts to 1.4 – 5.2 TWh for Scenario 1, and 6.1 – 13.5 TWh for Scenario 2. Potential storage situations are mainly found within the period from March to June. In fact, surplus power is guaranteed in April and May regardless of the time horizon and scenario. Meanwhile, December presents strong variability depending on the agreement between renewable production and the decay in demand during the last week of the year. In contrast, January and February might present a lack of energy excess in 2050 even existing high shares of renewable power in the energy mix (Figure 10).

Table 7. Power production [TWh] in the future Spanish electricity system

	Scenario 1				Scenario 2			
	Demand growth rate: 1.36%				Demand growth rate: 1.73%			
	2020	2030	2040	2050	2020	2030	2040	2050
Hydropower	28.7	29.3	30.6	31.9	28.7	31.8	35.5	39.7
Small hydro	6.4	10.4	16.6	17.7	6.4	10.0	11.5	12.9
Wind power	63.2 - 60.9	74.3 - 70.5	84.0 - 80.2	95.2 - 91.4	59.9 - 58.6	84.3 - 79.9	103.0 - 96.9	113.8 - 106.4
Photovoltaics	10.1	14.6	18.9	24.1	10.1	14.6	22.6	41.6
Solar thermal	23.3	34.2	49.9	71.2	21.3	33.9	53.5	82.4
Biomass	6.7	16.7	23.9	35.9	6.7	12.0	22.1	41.5
CHP	38.3	49.6	57.0	65.2	38.3	54.2	70.0	90.2
Nuclear	56.6	55.1	53.9	44.7	56.6	55.1	57.3	48.7
Coal power	22.9	19.6	18.7	17.2	20.5	13.9	6.2	4.9
Combined cycle	30.0 - 32.3	23.5 - 27.3	21.3 - 25.1	26.0 - 29.8	45.0 - 46.3	38.6 - 43.0	31.9 - 38.0	15.2 - 22.6
Total	286.2	327.3	374.8	429.1	293.5	348.4	413.6	490.9
Surplus power	0.49 - 2.80	0.45 - 4.20	1.02 - 4.79	1.41 - 5.24	0.17 - 1.44	0.51 - 4.90	2.46 - 8.60	6.10 - 13.54

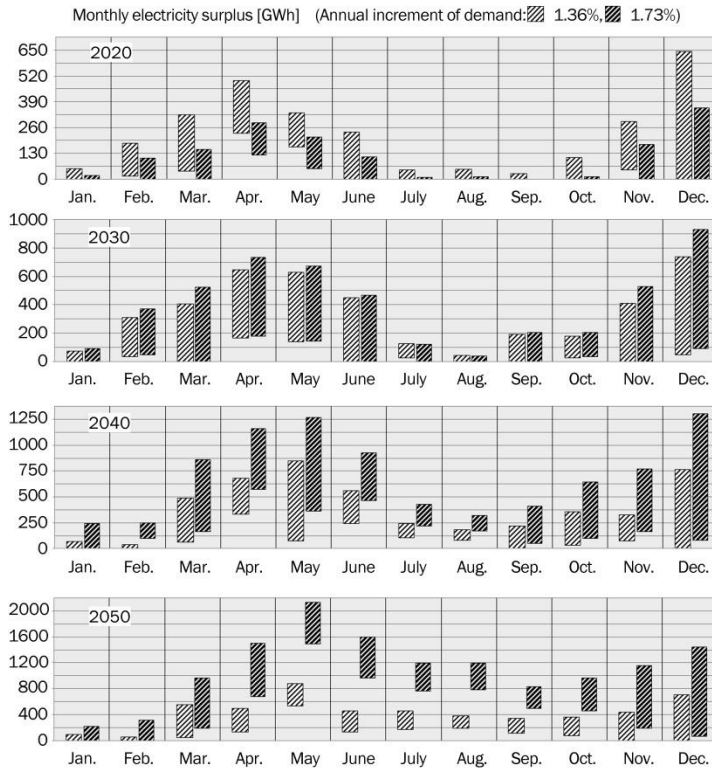


Figure 10. Ranges of possible monthly electricity surplus [GWh] in the future Spanish electricity system

If a short-term prospective is considered (i.e. 2020), both scenarios present almost the same installed power capacity. So, energy surplus is greater in Scenario 1 due to the lower demand. Contrarily, in long-term prospective (i.e. 2040, 2050), the installed capacity of Scenario 2 had to grow faster to satisfy the greater demand, and therefore the electricity surplus is higher in absolute value. Actually, electricity surplus is below 3% of the total electricity production in both cases, since the mixes of installed capacity have similar renewable shares.

In order to size the required power capacity to completely handle the energy surplus, it must be taken into account the maximum hourly excess of electricity production. In systems characterized by base loads

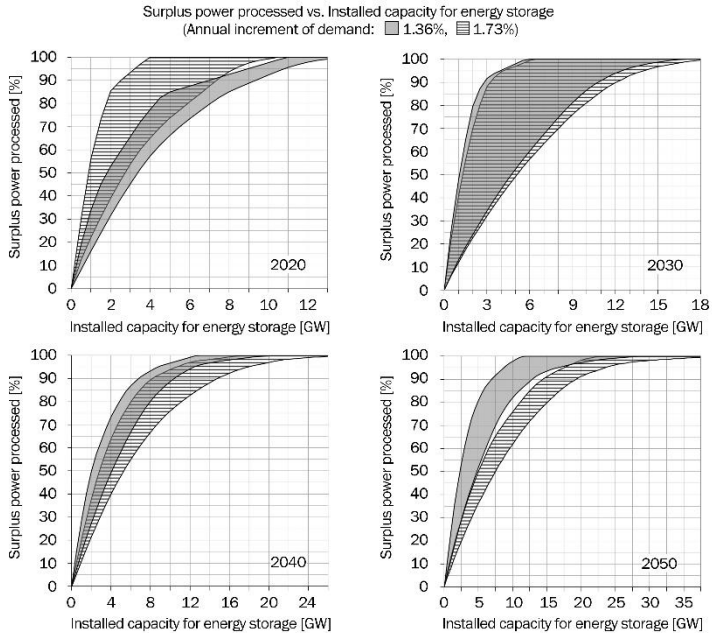


Figure 11. Surplus electricity processed [%] as a function of installed capacity for energy storage [GW]

around 20 GW and high shares of wind power (like the Spanish case), surplus behaves smoothly with hourly peaks that rise up to the 8% of the daily excess at most [53]. Therefore, the upper limit for capacity to be installed should be able to process, in an hour, the 8% of the energy excess produced during the day of the highest daily surplus power. However, these days of highest surplus are exceptional, and there is no point in sizing the storing capacity for those situations (the facility would be underused). Up to the 90% of annual excess could be treated with less than the half of that installed capacity (Figure 11).

Thus, in Scenario 1, the required power capacity to handle the 90% of total excess would be about 7.5 – 9.5 GW for the year 2020, and 7.0 – 13.0 GW for the year 2050. In Scenario 2, 2.5 – 7.5 GW by 2020 and 14.5 – 19.5 GW by 2050. In both cases, the results are in the range of a few GW, accordingly to the conclusions of the studies for similar countries (e.g., Germany and Great Britain).

In short, the developed model has shown the significant role that renewables will play in the future Spanish energy mix, and the necessity of implementing large scale storage systems (in the GW scale) linked to the electricity generation.

2.2 POWER TO GAS AS HYBRID STORAGE

The Power to Gas concept, understood as an option to store renewable energy and carbon dioxide in the form of methane, was first proposed by Koji Hashimoto in 1994 [54]. The difficulties associated to long-distance electricity transport in Japan inspired the research on energy carriers. The combination of electrolysis –driven by solar energy– and Sabatier reaction (Equation 1) allowed the synthesis of methane and, thus, the distribution of renewable electricity without requiring new infrastructures. Moreover, as CO₂ is recycled, the global warming would be mitigated in some extent [55]. Later, in 2009, Michael Sterner refreshed the Power to Gas concept to focus on the management and long-term storage of renewable power surplus, rather than on electricity transportation or CO₂ recycling. He also proposed alternative carbon dioxide sources for the methanation stage, such as biogas or syngas [15].

Nowadays, a large number of techniques involve a simultaneous storage of carbon dioxide and renewable energy in the form of a valuable product. Up to now, none has presented a clear classification of these processes in literature. To clarify the existing information about hybrid storage of renewable energy and CO₂, Power to Gas is compared with others techniques based on the same concept, in Figure 12. It will provide to the reader a more structured understanding. The proposed generalization was published in the related paper 'Power to Gas projects review: Lab, pilot and demo plants for storing renewable energy and CO₂', *Renew. Sust. Energ. Rev.* 2017; 69, 292-312.

The first proposed route is called Solar-to-Fuel, a 1-step path that directly converts sunlight and CO₂ into valuable products, without an intermediate transformation into electricity. Three techniques can be distinguished: photosynthesis-based metabolic routes, photocatalysis, and thermochemical cycles.

Photosynthesis is a biological capture of CO₂, in which carbon and sunlight are fixed as chemical energy contained in newly grown organisms. Since the efficiency of photosynthesis increases when the generated organic structures present very small sizes, single-cell microalgae and cyanobacteria are the common options for this kind of

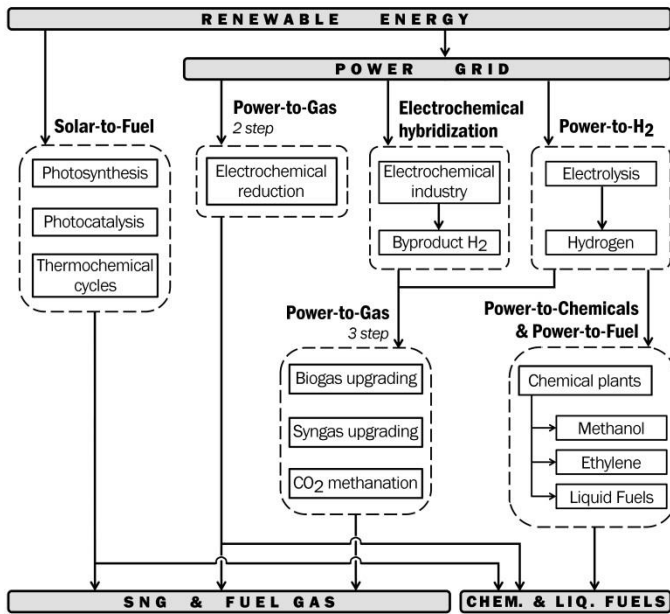


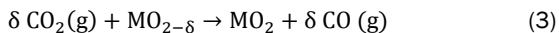
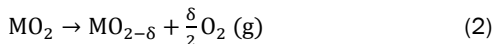
Figure 12. Techniques for hybrid storage of renewable energy and CO₂

process. Photons are absorbed by antenna proteins thus transferring their energy to the production of storage components, e.g., glucose, carbohydrates, lipids and proteins [56][57]. The development of biofuels from algal biomass has already completed the lab-stage development, and it is currently focused on addressing environmental, technological and economic drawbacks [58]. Biofuels from cyanobacteria are still far from its commercial development since greater efficiencies and improved reactor designs are needed [59][60].

In photocatalysis, CO₂ is reduced using semiconductor materials thanks to the electric current generated by the absorption of photons [56]. This technique is not feasible yet due to the absence of scalable reactors capable to produce significant amounts of fuel [61].

Thermochemical cycles comprises two stages, the reduction of metal oxides (Equation 2) inside of cavity receivers in concentrating solar plants at high temperatures (1200 – 1600 °C), and the later regeneration of the metal oxide by oxidation with carbon dioxide. From this process, a syngas mainly composed of CO is obtained, which can be burnt or

methanized (Equation 3) [62][63]. The technique has been successfully demonstrated at bench- and pilot-scale, but some crucial technical challenges remain unsolved for its commercial exploitation [64].



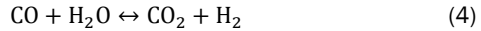
The second route is the electrochemical reduction, a 2 step Power to Gas concept. Electricity is supplied to establish a potential between two electrodes to reduce CO₂ [65]. Hence, renewable energy must be previously converted to electricity and later to the valuable chemical. Some high added value products that can be obtained through this method are formic acid, methanol or methane, which are produced by two-, six- and eight-electron reduction pathways, respectively [66]. However significant improvements in energy efficiency are needed before this technique becomes cost effective, in comparison with the commercial ways to produce the same products [67].

The third route is Power-to-Hydrogen, i.e., the dissociation of water by means of electrolysis to directly generate H₂ from an electric input. Great efforts have been done worldwide to develop a hydrogen-based economy, but its deployment is limited due to the requirement of a larger infrastructure and a well-established market [68].

The fourth route widens the application of hydrogen by means of the methanation reaction, to produce synthetic natural gas and take advantage from the existing natural gas infrastructure. This is the 3 step Power to Gas concept, which can be subdivided in three techniques depending on the carbon source: CO₂ methanation, biogas upgrading, and syngas upgrading. The CO₂ methanation transforms carbon dioxide taken from carbon capture technologies, like post-combustion or oxyfuel combustion. Biogas upgrading uses the gas produced by anaerobic digestion of biomass or wastes, which is mainly composed by CO₂ and CH₄. Syngas from gasification can also be used for methanation since it is composed by CO, CO₂, CH₄ and H₂. Although H₂ already exists in syngas, it is hardly ever enough to transform the whole amount of CO and CO₂ [69], so an additional input –considered as the stored energy– is required.

It should be noted that, traditionally, biogas had always been upgraded by separating its two main components, i.e., rejecting CO₂ and obtaining a purified stream of methane [70]. This option cannot be considered as a Power to Gas technique since it neither stores electricity nor makes use of the carbon dioxide obtained in the fermentation process. Similarly, conventional syngas upgrading plants are not PtG concepts

since they do not use additional H₂. The CO₂:H₂ ratio of syngas is commonly adjusted in a prior stage by means of water-gas shift reaction (Equation 4), and the remaining unreacted CO₂ is later removed [71][72].



The fifth route comprises two possibilities: Power-to-Chemicals and Power-to-Fuel. Chemical products that require H₂ and CO₂ for their production could be considered as hybrid storage of energy and CO₂, whenever H₂ is renewably produced. Some important chemicals in this field are methanol, ethylene, propylene, formic acid and liquid fuels [73].

Besides these five routes that can be found in literature, a novel sixth route is first proposed and studied in this thesis. This is the Power to Gas-Electrochemical concept, which uses byproduct hydrogen and emitted CO₂ coming from electrochemical industries, to continuously produce the SNG used in the chemical plants (CO₂ recycling). Instead of replacing the methanation process as in the Power to Chemical concept, this PtG-Electrochemical hybridization avoids the electrolysis stage by using byproduct H₂ that has been produced with renewable energy.

The core of this thesis focus on the CO₂ methanation processes, which belongs to the 3 step Power to Gas concept. As stated in the introduction (section 1.1), this route is the most promising energy storage technology to reduce the issues related to renewable energy production. The presented scheme (Figure 12) may be used to classify new emerging concepts, or to discern among similar technologies under development.

2.2.1 Power to Gas (3 step): State of development

In literature, there exist two relevant reviews of the 3 step Power to Gas route (abbreviated as Power to Gas, from this point on) [37][13]. Both are focused on technical aspects of the methanation, such as operating conditions, reactor configurations or catalysts performance. However, there is no detailed information in literature referred to worldwide PtG projects. Therefore, the objective of this section is to thoroughly review the construction and operation of Power to Gas pilot-, demo- and lab plants, to complete the available information. First, a brief summary of the methanation process is presented, in order to introduce the technology.

The methanation is an exothermic reaction (1,8 kWh/Nm³CH₄) that combines hydrogen and carbon dioxide to produce methane and water (Equation 5) [13]. This synthetic methane can be obtained through catalytic or biological via (Table 8).



Biological methanation uses unicellular microorganisms (methanogenic archaea) that grow by obtaining energy from CO₂-reducing / H₂-consuming metabolic routes. The process takes place in aqueous solution, at 20 – 70 °C and 1 – 3 bar. As the reaction occurs in liquid phase, the system presents high thermal inertia. This allows controlling changes in temperature caused by load variations that modify the released exothermal energy. Besides, archaea tolerate impurities that are commonly present in biogas or syngas (e.g., H₂S, NO_x, and NH₃). Its main drawbacks are the low reaction rate (GHSV < 10 h⁻¹) and therefore the requirement of big reactor volumes, what limits the industrial scalability [13][14].

Catalytic methanation uses active materials like nickel, ruthenium, or cobalt to promote the Sabatier reaction. It is widely accepted that the catalytic process comprises two intermediate reactions. First, CO₂ is reduced through a reverse water-gas shift reaction (Equation 6), and then a subsequent CO methanation completes the process (Equation 7) [13].



The catalytic process is favored by high pressures and low temperatures, although it can operate between 250 °C and 750 °C, and at pressures between 1 and 100 bar [13]. This operating conditions are suitable for heat integration with industries, while the higher reaction rate (GHSV = 2000 – 5000 h⁻¹) makes easier its scalability. Drawbacks are the low tolerance against the presence of impurities in the CO₂ source, and the limited flexibility to manage temperature fluctuations caused by load variations [13][14].

Table 8. Characteristics of biological and catalytic methanation [13][74]

	Biological methanation	Catalytic methanation
Status	Laboratory / Pilot	Pilot / Commercial
Typical size [MW]	< 1	< 6
Temperature [°C]	20 – 70	250 – 700
Pressure [bar]	1 – 3	1 – 100
GHSV [h ⁻¹]	< 10	2000 – 5000
Impurity tolerance	High	Low
Heat integration	Low	Regular / High
Minimum load [%]	10	40
Load variation flexibility	High	Low / Regular

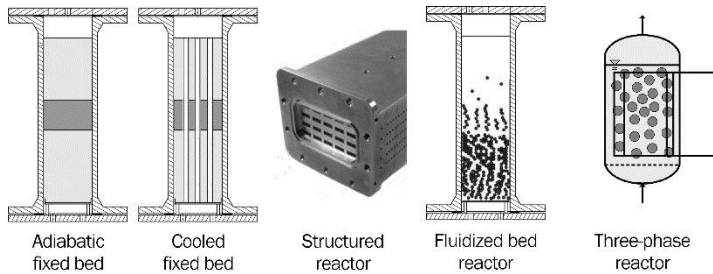


Figure 13. Types of reactors for catalytic methanation [75][76][77][78]

Continuous stirred-tank reactors (CSTR) are most commonly used to perform biological methanation. Since methanation takes place in the aqueous solution, and hydrogen has a poor solubility in water, improving the gas liquid mass transfer is the main challenge on reactor design. Greater stirring rates increase the transfer of hydrogen to the liquid, but the power consumption for the agitation becomes a strong energy penalty. Other kind of reactors, such as trickle-bed and fixed-bed reactors are also used in biological methanation research [13].

Regarding catalytic methanation, five types of reactors have been proposed in literature to carry out this process: adiabatic fixed-bed, cooled fixed-bed, structured reactor, fluidized bed reactor, and three-phase reactor (Figure 13). In adiabatic fixed-bed reactors, inlet gases react passing through fixed catalyst layers located inside the reactor. Since high temperature inhibits the process, from 2 to 5 reactors in series (with intermediate cooling or recycling loops), are needed to reach CH_4 concentrations above 90% vol. The large amount of energy released inside the reactor also produces hot-spots that can damage the catalyst, and limits the operability under load fluctuations. Its main advantages are the low residence times and the high potential for heat integration (Table 9) [37][13].

Cooled fixed-bed reactors use internal cooling based on air, water or oil (without direct contact with gases), to favor the reaction and avoid sharp gradients of temperature [14]. Hence, the operation is less complex, although the possibilities of heat integration are reduced and the cost increases [37][13].

Structured reactors can mitigate drawbacks of fixed-bed reactors (i.e., hot-spots, and pressure drops due to catalyst layers). In these reactors the gas passes through an internal multichannel structure impregnated with catalyst. Thus, heat transfer can be two orders of

magnitude greater than in fixed-bed reactors. However, if catalyst is deactivated, the whole structure has to be re-impregnated [37][13].

Fluidized bed reactors present high mix ratios between catalyst particles and gas, leading to isothermal operation. This allows working at lower temperatures and, therefore, reduces the number of required reactors. But, the lifetime of the system is notably reduced, due to the mechanical stress over both the catalyst and the walls of the reactor [37][13].

Lastly, three-phase reactors use liquid with high heat capacity to precisely control the temperature inside the reactor and guarantee an isothermal process. The particles of catalyst are suspended in the liquid, and the gas bubbles through it. As it occurs in biological methanation, the mass transfer from the gas to the medium controls the reaction rate. Besides, some residual liquid in vapor form can appear in the final synthetic natural gas [37][13].

Review of worldwide projects

The following Power to Gas review gathers all those facilities at lab-, pilot-, or demo-scale that comprise methanation processes consuming renewable hydrogen (a description of every project can be found in the related published paper [14]).

Tohoku University is the pioneer in Power to Gas field, since they initiated this research line in 1996. However, although they erected the first worldwide pilot plant, nowadays the leadership holds in Europe. The current spearhead nation in developing Power to Gas systems is Germany, with 16 projects mainly focused on CO₂ catalytic methanation, followed by

Table 9. Characteristics of catalytic reactors [14][37][13]

	Adiabatic fixed-bed	Cooled fixed-bed	Structured reactor	Fluidized bed	Three-phase reactor
Status	Commercial	Pilot	Laboratory	Pilot	Laboratory
Operating mode	Adiabatic	Polytropic	Polytropic	Isothermal	Isothermal
Stages	2 - 7	1 - 2	1 - 2	1 - 2	1 - 2
Recycling	Usually	Sometimes	No	Sometimes	No
Temperature [°C]	250 - 700	250 - 500	250 - 300	300 - 400	300 - 350
Pressure [bar]	5 - 100	5 - 100	1 - 20	1 - 12	20
GHSV	High	High	High	Regular	Low
Catalyst arrangement	Fixed	Fixed	Impregnated	Fluidized	Suspended
Catalyst size	mm - cm	mm - cm	< 200 µm	< 500 µm	< 100 µm
Mechanical stress	Low	Low	Low	High	Regular
Thermal stress	High	Regular	Low	Low	Low
Complexity	High	Low	Low	Low	Regular
Cost	Regular	High	Very high	Low	Regular

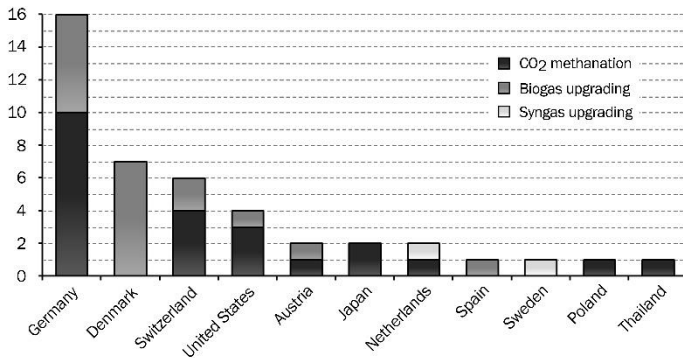


Figure 14. Existing PtG projects distributed by country and technology

Denmark with 7 projects on biogas upgrading (Figure 14). USA has also contributed to the deployment of the technology with four projects since 2009. To date, 46 experimental projects have been developed, which gather more than 180 institutions. All these experiences comprise pilot and demonstration plants whose electrolyzer sizes vary from few kW_e (lab-scale plants) up to 6 MW_e (largest existing plant). A timeline is built to clearly represent the evolution and concatenation of worldwide PtG projects with years (Figure 15). Most of the projects were launched from 2009 onwards, when the international community massively discovered the great potential of PtG as electricity surplus storage.

Regarding catalytic methanation, the Audi e-gas plant, built in Werlte, Germany, is currently the largest worldwide facility. It was commissioned by ETOGAS in 2013, and comprises three alkaline electrolyzers of 2 MW each, and an isothermal fixed-bed reactor, with an overall efficiency of 54% [79][80]. The CO₂ is captured by amine scrubbing from a nearby biogas plant, and it can produce up to 325 Nm³/h of synthetic natural gas [81][82]. Besides, the plant has been qualified for participating in the electricity balancing market, after successfully draw 6 MW of power from the grid within five minutes as well as run prescribed load profiles [83]. The main challenge was to smartly control the reactor's temperature, and to manage the exothermal heat redirected to the biogas plant [84][85]. Their next goal is to reach commercialized PtG systems around 20 MW, with efficiencies above 80% after heat integration [86].

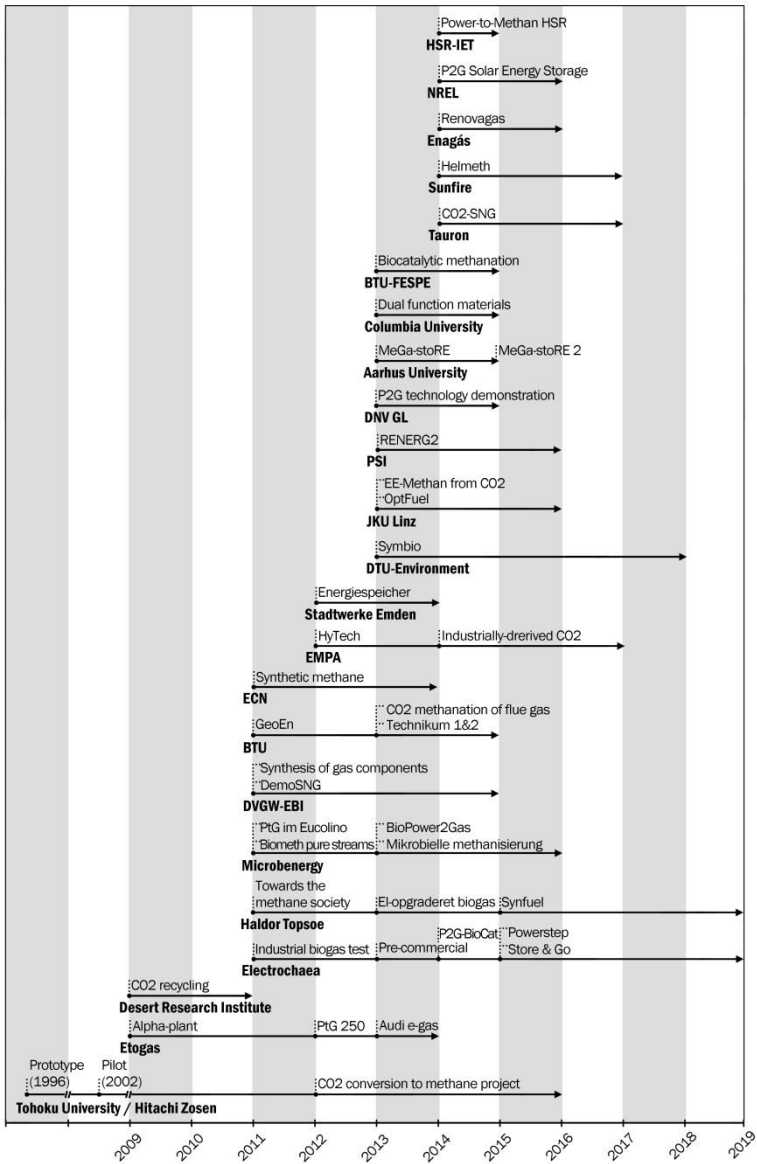


Figure 15. Timeline of worldwide existing Power to Gas projects

Hitachi Zosen Corporation has already simulated and designed a larger PtG facility to be commissioned in Thailand, able to produce 1000 Nm³/h of synthetic natural gas (SNG) [87][88]. It will be used to convert CO₂ generated during the extraction of natural gas from natural reservoirs [87][89], where the hydrogen will be produced by alkaline electrolyzers [90] fed with desalinated seawater [88][91]. The following most important project, in terms of size, was developed by Stadtwerke Emden GmbH to study the suitability of a wastewater treatment plant as CO₂ supplier [92]. The experimental research at lab-scale allowed dimensioning a pilot plant, which was announced to be built in Emden [93], comprising a 312 kW electrolyzer and an isothermal reactor at 335 °C with a SNG production of 59 m³/h [94]. Other relevant research comes from the HELMETH project, led by Sunfire. It aims to demonstrate efficiencies above 85% in Power to Gas systems by integrating high temperature electrolysis and CO₂ methanation [95]. Electrolysis is conducted in a 15 kW SOEC [96] working at 800 °C and 15 bar, whilst methanation comprise two reactors in series at 300 °C and 30 bar, with intermediate water removal [97]. The plant is designed to manage partial loads down to 20 % [97], and produce up to 5.4 m³/h of SNG [98]. At the same scale of 15 kW, Enagas S.A. leads the RENOVAGAS project, whose final goal is to produce SNG with enough quality for its injection into the Spanish gas grid [99]. The plant is expected to produce up to 2 Nm³/h of SNG, using a modular multichannel reactor at 25 bar and 275 – 330 °C (oil-based cooling) [99].

Below 10 kW, there exist other three relevant projects. First, the DNV GL Group commissioned a Power to Gas plant that provides natural gas to 30 nearby apartments in Rozenburg, Netherlands [100]. The facility comprises a 7 kW commercial PEM electrolyser and four methanation reactors. The plant works at 377 °C and less than 8 bar, and it can be started up in approximately 40 minutes [101][102]. The hydrogen production is partially supplied by four solar panels, and carbon dioxide comes from a wholesale distributor [101]. Meanwhile, DVGW-EBI led the SEE project focused on comparing fixed-bed and slurry methanators at lab-scale [103], besides studying dynamic operation of a 6kW PEM electrolyzer [104]. The methanator was 73 cm high and 10 cm in diameter, with a 10 cm catalyst layer in the middle, and fed by pure gas bottles [105]. Lastly, the Desert Research Institute (DRI) built a lab-scale reactor, in Reno (United States), to demonstrate the feasibility of catalytic methanation [106]. A 5 kW PEM electrolyzer, supplied by solar panels and wind turbines [107], produced high purity hydrogen at 13.8 bar. The carbon dioxide source was a gas mixture of 2% CO₂ in N₂, thus avoiding excessive temperature rises [106].

Many others institutions have developed relevant applied research in catalytic methanation, such as the Karlsruhe Institute of Technology (KIT), the Energy Research Centre of the Netherlands (ECN), the National Renewable Energy Laboratory (NREL), the Johannes Kepler University Linz (JKU Linz), or the Paul Scherrer Institute (PSI). Those catalytic projects, from which technical information is available, are gathered and presented in Table 10 to facilitate the comparison between operating parameters.

Table 10. Technical parameters of selected catalytic PtG projects

Project and main institution	Reactor	Temp. [°C]	Pressure [bar]	Electrolyser [kW]	SNG [Nm ³ /h]	Ref.
CO ₂ conversion to methane project (Hitachi Zosen)	Fixed-bed	200	n/a	n/a Alkaline	1000.0	[87] [108]
Audi e-gas (ETOGAS)	Isothermal fixed-bed	n/a	n/a	6000 Alkaline	325.0	[80] [82]
Energiespeicher (Stadtwerke Emden)	Isothermal	335	n/a	312 n/a	59.0	[92] [94]
CO ₂ -methanation of flue gas (BTU)	Fixed-bed	350	10	n/a Bottled H ₂	8.3	[109] [110]
HELMETH (Sunfire)	n/a	300	30	15 SOEC	5.4	[95] [111]
EE-methan from CO ₂ (JKU Linz)	Honeycomb	> 350	1 - 20	n/a	3.0	[112] [113]
RENOVAGAS (Enagás)	Multichannel	275 - 330	25	15 Alkaline	2.0	[99] [114]
P2G project (DNV GL)	Fixed-bed	150 - 700	8 - 15	7 PEM	n/a	[100] [101]
Synthesis of gas components (DVGW-EBI)	Fixed-bed / Slurry	n/a	n/a	6 PEM	n/a	[103] [105]
CO ₂ recycling (Desert Research Institute)	Fixed-bed	300 - 350	n/a	5 PEM	n/a	[115] [107]
Industrially derived CO ₂ (EMPA)	Fixed-bed	n/a	1.2	n/a	0.1	[116] [117]
DemoSNG (DVGW-EBI)	Honeycomb	< 300	n/a	n/a PEM	n/a	[118] [119]
MeGa-stoRE (Aarhus University)	Air cooled	270	8	Bottled H ₂	n/a	[120]
Synthetic methane (ECN)	n/a	230 - 240	6	Bottled H ₂	n/a	[121] [122]
Dual function materials (Columbia University)	Fixed-bed	n/a	1	Bottled H ₂	n/a	[123] [124]

Regarding biological methanation (Table 11), Electrochaea has commissioned in Denmark the first worldwide plant that reaches the MW scale (P2G-BioCat project) [125]. As carbon source they may use raw biogas from an anaerobic digester, or pure CO₂ from a conventional biogas upgrading system [126], while the hydrogen is produced through a 1 MW alkaline electrolyzer [127]. The by-product oxygen and the exothermal heat are recycled into the wastewater digester [128]. The methanation is performed in a liquid phase reactor by methanogenic archaea, which work at low temperatures (60 – 65 °C) and present tolerance to hydrogen sulfide, nitrogen oxides, ammonia, particles, oxygen and ethanol [128]. The plant is fed with local excess wind power, and the final synthetic natural gas is destined to be injected into the 4 bar distribution grid [128].

MicrobEnergy, within the BioPower2Gas project, has built the first commercial plant based in biological methanation. The facility plant is composed by two PEM electrolyzers of 150 kW, and a 5 m³ biological reactor [130]. The biogas used in methanation comes from two nearby biogas plants [131]. Their next goal is to scale up to 1.2 MW, aiming to reduce the specific cost of the entire facility from 10000 €/kW to 1200 €/kW [136]. Other relevant project is the P2G Solar Energy Storage, carried out by NREL, aiming to promote higher penetrations of solar power through its storage into the gas network. Besides, it is the first demonstrative project of the USA that includes methanation [132]. The hydrogen is produced in a 150 kW electrolyzer under simulated profiles of photovoltaic electric generation, and the CO₂ is transformed by single-cell methanogens in a liquid media reactor. Then, the product gas is used to produce electricity in a fuel cell [133]. Other relevant institutions involved in various biological projects are Audi, Hydrogenics, NEAS Energy, Swiss Federal Laboratories for Materials Science and Technology (EMPA), Deutscher Verein des Gas- und Wasserfaches e.V. (DVGW), University of Southern Denmark (SDU), and German Biomass Research Center (DBFZ).

Table 11. Technical parameters of selected biological PtG projects

Project and main institution	Reactor	Temp. [°C]	Pressure [bar]	Electrolyser [kW]	CH ₄ [%vol.]	Ref.
P2G-BioCat (Electrochaea)	Liquid phase	60 - 65	n/a	1000 Alkaline	n/a	[129] [128]
BioPower2Gas (MicrobEnergy)	n/a	n/a	n/a	300 PEM	n/a	[130] [131]
P2G Solar ES (NREL)	Liquid phase	n/a	n/a	150 n/a	n/a	[132] [133]
Biocatalytic methanation (BTU-FESPE)	Anaerobic trickle-bed	37	1	n/a	98	[134] [135]

In summary, a larger number of projects cover catalytic processes due to its scale up potential, although biological projects recently rose up to the MW range. Most recent pilot plants chose biogas as source of CO₂ since the energy penalty associated to carbon capture vanishes. Few others have experienced with more innovative CO₂ sources, such as natural gas extraction processes or wastewater treatment plants. In general, the average budgets for demo-plants projects are around one million euro per planned year.

There is large room for further investigation to address the real potential of this technology as a system for decarbonizing natural gas. To tackle the current high costs of this kind of systems, research must focus on the study of new sources of CO₂ that present low energy penalty, and on the optimization of the heat integration. Besides, promoting the utilization of CO₂ with a renewable origin (biomass, wastes, etc.) will allow closing the CO₂ cycle. In the following section, two hybrid concepts to improve the overall efficiency of the catalytic Power to Gas process are presented and analyzed. Thus, future applied research could take advantage from these synergies to economically facilitate the development of the technology.

2.3 HYBRID POWER TO GAS CONCEPTS

The main purpose of Power to Gas concept is to establish a connection between the electric and gas networks, through which renewable energy surplus can be stored and later used to satisfy backup or end-use demand (Figure 16). Whenever RES oversupply the electricity network, the excess may feed electrolyzers to dissociate water in hydrogen and oxygen. Then, captured CO₂ is recycled via methanation thanks to the renewably-produced hydrogen. The resulting methane can be reconverted to electricity by gas-fired turbines, natural gas combined cycles, CHP or fuel cells, to substitute the fossil-based backup power. Besides, it can be directly consumed in end-use necessities (industry, households, buildings and transport) using the existing gas network, to displace fossil fuels in applications that are hardly penetrable by renewable energies.

The exothermal behavior of methanation and the by-production of oxygen during electrolysis allow energy and mass flows integrations with various CO₂ sources and capture methods [15]. Likewise, Power to Gas hybridization with industries or backup power plants makes possible to improve the round-trip efficiency and the economic performance of the classic PtG concept.

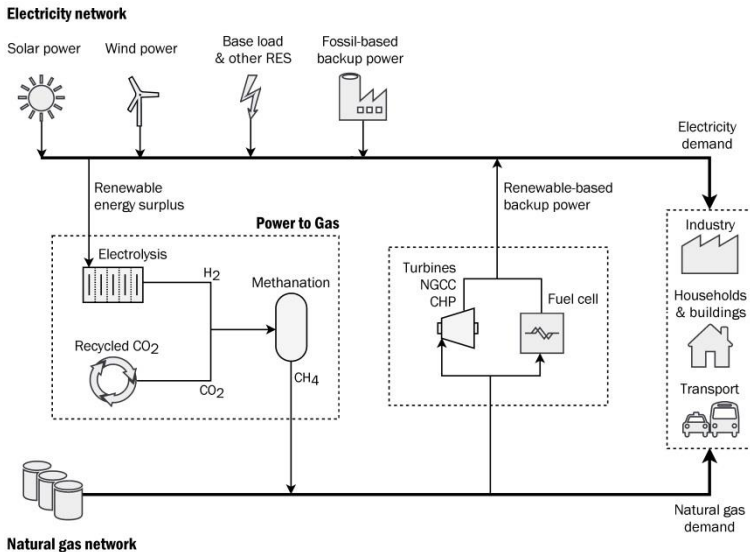


Figure 16. Power to Gas concept

The simplest option to perform methanation would be a high-purity CO₂ stream. However, most intensive carbon dioxide sources come from fuel combustion in electric and thermal energy production, and the resulting flue gas typically presents CO₂ concentrations below 15% [137]. Hence, carbon capture methods are necessary to attain concentrated CO₂ streams, although they lead to efficiency penalties between 9 and 12 points depending on the CO₂ concentration and capture technology [16][17][138]. In this framework, Power to Gas integration with CO₂ capture may help to diminish the associated energy consumption of carbon capture in the corresponding power plant or industrial process.

Amine scrubbing post-combustion capture is the most established carbon capture technology [20]. In this technique, flue gas enters an absorption column, where inert components bubble out and CO₂ is absorbed by the amine. The CO₂ rich solvent is then regenerated in a stripping column with counter flowing steam at 100 – 200 °C. The produced mixture of amine, steam, and CO₂ is cooled down to 40 – 65 °C, thus condensing steam and obtaining a highly concentrated CO₂ flow. The stripped solvent is finally recycled back to the absorber [20]. In these systems, the main energy consumption is the thermal energy required to regenerate the solvent, which can be integrated from the methanation

process. However, under this configuration, the by-produced oxygen from electrolysis would remain unused (Figure 17).

A suitable option to take advantage of this oxygen would be the integration with oxy-fuel combustion capture. During oxy-fuel combustion, pure oxygen is used as comburent instead of air [18]. Thus, the large N₂ content in air is substituted by the combustion products (mainly CO₂ and H₂O), and flue gas can achieve a high carbon dioxide concentration once steam is condensed. Energy penalty associated to this capture process mainly comes from the air separation unit that produces the required oxygen (typically 190 kWh/t_{o2}) [19]. Therefore, by using the oxygen from electrolysis, the electrical consumption of the ASU would be suppressed. Furthermore, CO₂ is recycled to fuel, so the energy consumption related to its compression and storage is also avoided (Figure 17).

Besides high concentrated CO₂ streams, other gases can be used in methanation. For instance, biogas allows avoiding carbon capture stage since it already consists of a mixture of CH₄ (50% - 85%) and CO₂ (50% - 15%) [139]. These systems (Figure 17) can also make use of the methanation heat in the digestion processes. Moreover, if the biogas producer is a sewage plant, it could employ the byproduct O₂ coming from electrolysis for sludge activation. Nevertheless, current sewage plants prefer to burn the biogas in engines for electricity self-consumption, because they already achieve heat and electricity autonomies above 90% and 68% respectively [140].

Similarly, syngas from gasification neither requires carbon capture, since it is composed by CO, CO₂, CH₄ and H₂ (fractions depends on feedstock and gasification conditions [69]). It also has the advantages that oxygen may be used as gasification agent and heat can be integrated [15]. However, hydrogen content in syngas is commonly high (14% - 56%, dry basis [141][142]), and the lacking amount is usually supplied through the water-gas shift reaction using the CO present in the syngas (Equation 4). So, the energy storage potential of this type of integration is limited.

From these five configurations, the two most interesting ones to carry out energy and mass integrations are those related with carbon capture, since their significant energy penalty may be palliated. In this thesis, both are studied under hybrid applications that promote the use of byproducts and continuously recycle CO₂ in closed loops (Figure 5 and 6). The first one applies Oxy-PtG integration in boilers or power cycles, to convert exothermal heat from methanation in one of the main products of the facility. The other application comprises the hybridization of Amine-PtG with chemical industries, where hydrogen is actually a byproduct coming from the electrolysis of sodium chloride and potassium chloride.

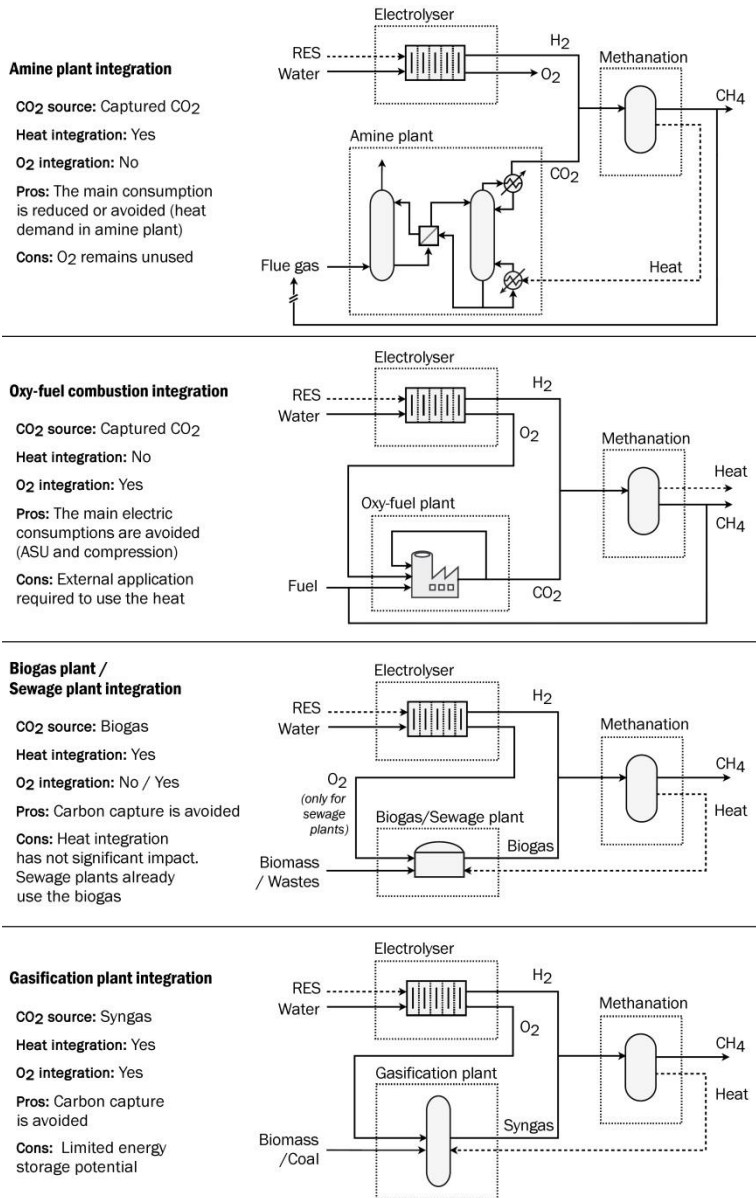


Figure 17. Power to Gas integrated configurations

2.3.1 Power to gas-oxyfuel combustion

As stated, Power to Gas-oxyfuel combustion systems store renewable electricity as methane, taking also advantage from the O₂ by-produced during the electrolysis stage. This oxygen acts as comburent in the oxycombustion plant, overcoming the energy penalty of the ASU. Besides, if the system includes a boiler, the exothermal heat from methanation can be directly integrated as a useful output. Meanwhile, if the concept is applied to a power plant, the heat can be integrated in the thermal power cycle to increase the generated electricity.

With the aim to characterize this concept, a generic PtG-oxyfuel combustion system has been modelled under chemical equilibrium and steady state operation in Aspen Plus®. The model combines an oxy-fuel boiler –provided with an air separation unit and a CO₂ storing-compression train–, electrolyzers, and a methanation plant (Figure 18). The ASU and the CO₂ compression train are included to correctly describe those situations in which by-produced oxygen is not enough, or flue gas is not completely consumed in methanation, respectively.

Fuel, \dot{m}_f , and comburent, \dot{m}_c , enter the boiler, where they reach chemical equilibrium. After combustion, flue gas reduces its temperature down to 270 °C in heat exchangers, while producing steam. This transferred energy is the useful output of the boiler, \dot{Q}_b . Besides, flue gas is used to preheat the comburent up to around 150 °C (HEX). Then, once ashes, \dot{m}_{ash} , and sulfur compounds, \dot{m}_s , are removed, exhaust gas is divided in a recycled stream (80%), $\dot{m}_{r,o}$, and a usable flow in methanation (20%). Before adding the oxidizer to the recycled gas, a condensation stage is included to avoid large contents of water in the combustion chamber. Thus, comburent is composed by O₂ from ASU, $\dot{m}_{O_2,ASU}$, O₂ from electrolyzer, $\dot{m}_{O_2,ele}$, and partially-dried flue gas.

The ASU is modelled to provide pure oxygen at 15 °C and 1 bar, with an electrical consumption of 190 kWh/t_{o2} [19]. A programming constraint modifies ASU's production according to the electrolysis installed capacity, to always maintain 15% O₂ excess in the oxyfuel boiler. Meanwhile, electrolyzer unit splits water in pure oxygen and a mixture of hydrogen with unreacted water. Water conversion is fixed at 99.9% and the electrical consumption at 4.4 kWh/Nm³H₂, with an outlet temperature of 80 °C [143][144]. These operation conditions lead to an efficiency of 61.8% (LHV basis). The input power determines the produced hydrogen, \dot{m}_{H_2} , and the required flue gas for methanation, $\dot{m}_{FG,m}$ (stoichiometric process).

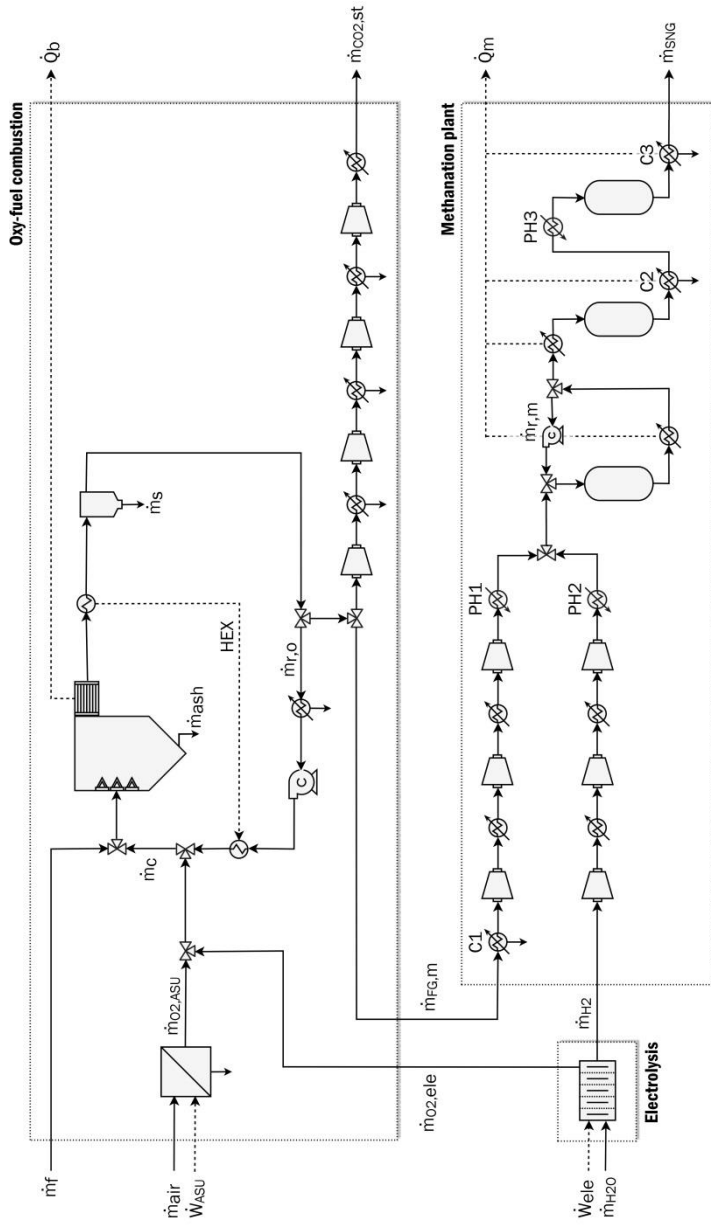


Figure 18. Power to Gas-Oxyfuel combustion integration

The flue gas not used in the methanation stage is directed to the compression train to be stored, $\dot{m}_{\text{CO}_2,\text{st}}$. It comprises three compressors with pressure ratios of 3.5 and a fourth one with pressure ratio of 3.0, thus reaching storage pressures in the range of 100 bar. Three intermediate condensers at 40 °C remove water, leading to final CO₂ purities about 95%.

Methanation plant is designed to produce a gas with methane molar fractions above 95% (requirement of the Spanish legislation for grid injection [145]). The modelled scheme, based on TREMP™ process from Haldor Topsøe [146], consists of three adiabatic reactors, one intermediate condensation stage, and a recycle loop [146]. Reactors operate at 30 bar and 250 °C – 550 °C, and the outlet gas composition is calculated at equilibrium state by minimizing Gibbs free energy in adiabatic conditions.

The percentage of flue gas directed to methanation, Φ_{FGM} , is calculated considering two constraints. Firstly, a stoichiometric H₂:CO₂ ratio is set at the inlet of the first reactor (Equation 5), so the required flue gas will depend on the CO₂ concentration of the stream, $y_{\text{CO}_2,\text{FG}}$, and on the produced hydrogen, \dot{n}_{H_2} . Secondly, part of this hydrogen must be used to consume the oxygen present in flue gas (Equation 8) since it would poison the catalyst [72]. Hence, the oxygen content, $y_{\text{O}_2,\text{FG}}$, reduces the amount of H₂ available for CO₂ methanation, and therefore the amount of flue gas that can be treated. The consideration of both conditions allows deriving Equation 9, where $\dot{n}_{\text{CO}_2,\text{Loss}}$ stands for the CO₂ that may be lost with water during the condensation stage C1.



$$\Phi_{\text{FGM}} = 100 \left[\left(y_{\text{CO}_2,\text{FG}} + \frac{1}{2} y_{\text{O}_2,\text{FG}} \right)^{-1} \frac{(\dot{n}_{\text{H}_2}/4 + \dot{n}_{\text{CO}_2,\text{Loss}})}{\dot{n}_{\text{FG}}} \right] \quad (9)$$

Two compression trains pressurize the inlet flows of the methanation scheme up to 30 bar. The temperature of the inlet gas to reactor 1 must be 300 °C, so preheating might be required (PH1 and PH2) [147]. After first methanator, the gas is cooled to 300 °C and most of the stream (70% – 80%) is recirculated, $\dot{m}_{\text{r,m}}$, to maintain the temperature below 600 °C inside the reactor. The loss of active surface area in the catalyst becomes critical above this temperature [148]. Besides, high temperatures inhibit the reaction.

The temperature of the stream directed to reactor 2 is reduced to 250 °C. Lower inlet temperatures in second and following methanators are

typical in methanation schemes to promote the process [149]. At the exit of this second stage, steam content is partially condensed (C2) to avoid the inhibition of methanation reaction inside the third reactor. However, some water must remain since an excessively low steam atmosphere might lead to solid carbon depositions [150]. Hence, the inlet stream to reactor 3 has to be preheated again to 250 °C (PH3), because of the mentioned condensation. Finally, the outlet gas is cooled to 40 °C to condense steam (C3) and reaches a purity of methane above 95%.

The energy efficiencies of the different subsystems involved in the PtG-Oxycombustion concept can be defined through Equations 10 to 14. Equation 10 corresponds to the boiler efficiency, where \dot{Q}_b is the power output, \dot{m}_f the mass of fuel consumed per unit of time, LHV_f the lower heating value of the fuel, and $\dot{W}_{aux,oxy}$ the power consumed in the recycling loop. Equation 11 defines the efficiency of the oxy-fuel combustion plant, where \dot{W}_{ASU} is the power consumption of the ASU, and \dot{W}_{comp} the consumption of the CO₂ compression train. Equation 12 presents the efficiency of the electrolyzer, in which \dot{m}_{H_2} is the amount of hydrogen produced per unit of time, LHV_{H_2} its lower heating value, and \dot{W}_{ele} the consumed power. Methanation plant efficiency is calculated through Equation 13, where SNG stands for synthetic natural gas (the outlet gas of the methanation facility), and $\dot{W}_{aux,meth}$ includes the compression of the inlet gases, and blowers. Lastly, Equation 14 expresses the efficiency of the Power to Gas subsystem. All of these efficiencies are the ratios between useful energy output and energy input for the different control volumes established in Figure 18.

$$\eta_b = \frac{\dot{Q}_b}{LHV_f \dot{m}_f + \dot{W}_{aux,oxy}} \quad (10)$$

$$\eta_{oxy} = \frac{\dot{Q}_b}{LHV_f \dot{m}_f + \dot{W}_{aux,oxy} + \dot{W}_{comp} + \dot{W}_{ASU}} \quad (11)$$

$$\eta_{ele} = \frac{LHV_{H_2} \dot{m}_{H_2}}{\dot{W}_{ele}} \quad (12)$$

$$\eta_{meth} = \frac{LHV_{SNG} \dot{m}_{SNG}}{LHV_{H_2} \dot{m}_{H_2} + \dot{W}_{aux,meth}} \quad (13)$$

$$\eta_{PtG} = \frac{LHV_{SNG} \dot{m}_{SNG}}{\dot{W}_{ele} + \dot{W}_{aux,meth}} \quad (14)$$

The overall efficiency of the hybrid plant, without integrating methanation heat, \dot{Q}_m , is given by Equation 15. Depending on the operation strategy of the system, some of the addends may be neglected.

$$\eta_{PtG+oxy} = \frac{\dot{Q}_b + LHV_{SNG} \dot{m}_{SNG}}{LHV_f \dot{m}_f + \dot{W}_{aux,oxy} + \dot{W}_{comp} + \dot{W}_{ASU} + \dot{W}_{ele} + \dot{W}_{aux,meth}} \quad (15)$$

Operation ranges of the hybrid system and fuel influence

The proposed variable to define the operation strategy of the PtG-Oxycombustion hybridization is the ratio between the sizes of electrolysis and oxy-fuel combustion. This parameter has been defined as the quotient, ξ_{oxy} (Equation 16), that relates the chemical energy contained in the hydrogen coming from electrolysis, and the net energy output of the oxy-fuel application (ξ_{oxy} for boilers, and ξ'_{oxy} for power plants). In the case of electrical outputs, it accounts for the consumed electricity by the ASU and the auxiliary equipment in the form of Equation 17.

$$\xi_{oxy} = \frac{LHV_{H_2} \cdot \dot{m}_{H_2}}{\dot{Q}_{oxy}} \left[\frac{kW_{H_2}}{kW_t} \right] \quad \text{or} \quad \xi'_{oxy} = \frac{LHV_{H_2} \cdot \dot{m}_{H_2}}{W_{net,oxy}} \left[\frac{kW_{H_2}}{kW_e} \right] \quad (16)$$

$$W_{net,oxy} = \dot{W}_{gross,oxy} - \dot{W}_{aux,oxy} - \dot{W}_{ASU} \quad [kW_e] \quad (17)$$

The selection of these factors aims to facilitate the sizing of PtG-Oxy hybridization for specific applications. The numerator makes ξ_{oxy} independent of the electrolysis technology (alkaline, PEM or SOEC), while the denominator corresponds to the thermal or electrical demand that shall be satisfied in a given situation (\dot{Q}_{oxy} or $W_{net,oxy}$). Hence, the selected operation point (ξ_{oxy}) allows to directly determine the required amount of hydrogen for a given application, from which the corresponding power consumption can be calculated under the technical characteristics of any electrolyzer.

These Power to Gas-Oxycombustion systems are characterized by two relevant operation points. The operation point will be denoted as ξ_{ASU} when electrolysis is large enough to cover the oxyfuel process by only using the byproduct oxygen. Hence, for this and greater values of ξ_{oxy} , the air separation unit is not required. The other characteristic operation point is reached when the installed electrolyzer capacity produces sufficient hydrogen to process the whole flow of flue gas, denoted as ξ_{CO_2} .

The type of fuel used in oxycombustion modifies the values of ξ_{ASU} and ξ_{CO_2} (Figure 19). For instance, the use of biomass leads to lower values of ξ_{ASU} (1.14) in comparison with coal (1.33), due to its greater oxygen content. Besides, the typically smaller C:H ratio of biomass also gives minor values of ξ_{CO_2} (2.17) than coal (2.29) due to the less amount of CO₂ produced per generated kWh [151]. The latter effect is more pronounced for natural gas oxycombustion, thus decreasing ξ_{CO_2} down to meet with ξ_{ASU} (1.29). Furthermore, despite of the differences between the compositions of natural gas and coal, the combustion of both of them require comparable amounts of oxygen per MJ of fuel (2.80 molO₂/MJ_{fuel})

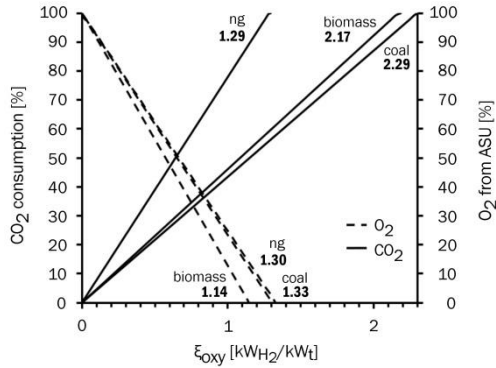


Figure 19. Behaviour of ξ_{oxy} for coal, biomass and natural gas

for natural gas, and 2.86 mol_{O₂}/MJ_{fuel} for coal, for the selected fuel compositions, Table 12), what implies similar values of ξ_{ASU} (1.30 and 1.33, respectively).

It should be noted that, for the natural gas case, $\xi_{\text{CO}_2} \lesssim \xi_{\text{ASU}}$ instead of $\xi_{\text{CO}_2} = \xi_{\text{ASU}}$. In principle, the assumption of complete combustion of CH₄ and stoichiometric methanation reaction, would lead to equal values of ξ_{CO_2} and ξ_{ASU} . However, second order effects modify the values of ξ_{oxy} , namely:

- Requirement of O₂ excess during combustion
- Presence of O₂ in the flue gas directed to methanation
- Presence of H₂ in the input fuel

The effect (a) increases the required O₂ in oxy-fuel combustion ($\xi_{\text{ASU}} \uparrow$), while (b) implies to produce more hydrogen to methanize the flue gas ($\xi_{\text{CO}_2} \uparrow$). Nevertheless, both make ξ_{ASU} and ξ_{CO_2} to grow in the same manner, so they are not the cause of the discrepancies between both values. This behavior can be checked through Equation 8, since the production of more O₂ consequently involves the co-production of the H₂

Table 12. Ultimate analysis of selected coal and biomass fuels (%w.b.), and natural gas composition (vol.%)

	C	H	O	N	S	M	Ash
Coal	66.1	3.6	7.1	1.6	0.6	8.6	12.4
Biomass	43.9	5.5	41.6	0.3	0.0	5.5	3.2

	CH ₄	H ₂	CO ₂	H ₂ O
Natural gas	95.3	3.5	0.8	0.4

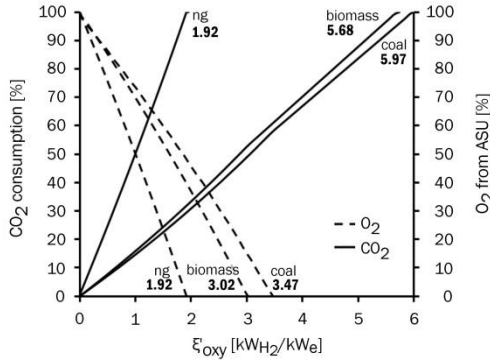


Figure 20. Behaviour of ξ'_{oxy} for coal, biomass and natural gas

that will have later to react with it (the O₂ added as excess is the same that is latter present in flue gas). Actually, the difference comes from effect (c), since it implies a larger amount of required O₂ in combustion per mol of CO₂ generated (i.e., per mol of CO₂ to be methanized), thus making ξ_{ASU} slightly greater than ξ_{CO_2} .

In the case of electrical demands (i.e., ξ'_{oxy}), the values of ξ'_{ASU} and ξ'_{CO_2} are also influenced by the type of power plant. Figure 20 shows the behaviour of ξ'_{oxy} for a subcritical power plant with a LHV efficiency of 38.6% (coal and biomass), and for a combined cycle of 64% LHV efficiency (natural gas) [152]. The greater efficiency of the combined cycle allows reducing the amount of fuel used per kWh produced, and thus $\xi'_{CO_2,CC} \ll \xi'_{CO_2,SPP}$. For the same reason, the required oxygen for oxycombustion is lower in combined cycles (i.e., $\xi'_{ASU,CC} < \xi'_{ASU,SPP}$). Besides, $\xi'_{CO_2} = \xi'_{ASU}$ for natural gas case since pure CH₄ was used –effect (c) is not present–.

Potential applications

The final application of the PtG–oxycombustion system will determine the suitable operation range of ξ_{oxy} and ξ'_{oxy} . In Table 13, five potential uses are presented. At small and mid-scale, boilers are preferred, since they can be applied on households, district heating, or industrial processes. At large-scale, electricity is easily dispatched, so the chosen applications are combined cycles for natural gas, and subcritical power plants for coal and biomass.

Small scale installations (households and district heating) are usually not compelled to capture their emissions because they are not

large enough. Hence, the investment on installing electrolysis power capacity should be limited to ξ_{ASU} , just to avoid the ASU penalty. In medium scale facilities (industrial applications), avoiding greenhouse gas emissions might be economically interesting under some CO₂ credit prices, so they could operate in the range between ξ_{ASU} and ξ_{CO_2} . Lastly, power plants may be compelled to capture their carbon dioxide; therefore, a ratio next to ξ_{CO_2} would be the most suitable operation point.

The technical feasibility of these applications is strongly limited by the high specific cost and the maximum achievable size of electrolyzers. Nowadays, electrolyzers are commercially available from few kW_e up to 2 MW_e [153]. Therefore, coal and biomass power plants applications are unfeasible because they require more than 160 electrolysis units. Industry and district heating are the most suitable applications, since they would combine less than 30 units of 2 MW_e size electrolyzers. In the following section, the analysis and integration of a small combined cycle power plant ($\dot{W}_{net,oxy} \approx 30$ MW) are presented as an example of the upper limit case for PtG-Oxy applications.

Applied case: Combined cycle power plant

A combined cycle in oxycombustion hybridized with Power to Gas technology has been modelled with Aspen Plus® for steady state operation and chemical equilibrium. The greater efficiency of combined cycles reduces the required electrolysis power capacity to avoid the air separation unit, while the heat from methanation can be integrated as low pressure steam in the steam cycle to produce more power. This study was done in collaboration with the Centre Efficacité énergétique des Systèmes (CES) from MINES ParisTech, thanks to a research fellowship of the PhD candidate.

The electrolyzers of the hybrid plant store electricity from the

Table 13. Generic applications for PtG-oxycombustion systems at different scales and operation points ξ_{oxy} ($\eta_{ele} = 68.1\%$)

Application (thermal output)	\dot{Q}_{oxy} [MW]	Electrolyser [MWe]			ξ_{oxy}
		Coal	Biomass	Natural gas	
Households	0.01	0.02	0.02	0.02	$\approx \xi_{ASU}$
District heating	2	3.9	3.4	3.8	$\approx \xi_{ASU}$
Industry	20	39.1 – 67.3	33.5 – 63.7	39.1 – 37.9	$\xi_{ASU} - \xi_{CO_2}$

Application (electrical output)	$\dot{W}_{net,oxy}$ [MW]	Electrolyser [MWe]			ξ'_{oxy}
		Coal	Biomass	Natural gas	
Subcritical PP	50	438.3	417.0	n/a	$\approx \xi'_{CO_2}$
Combined cycle	50	n/a	n/a	141.0	$\approx \xi'_{CO_2}$

network –as H₂ and O₂– whenever renewable energy surplus exist (low electricity demand periods). Then, during the periods of high demand, the electrolyzers stop storing energy, and the oxy-combined cycle generates electricity. The stored oxygen is used to replace the ASU, while the hydrogen is employed in the methanation process to convert the CO₂ emissions of the power plant into synthetic natural gas.

The generated amount of SNG is nearly the same amount that is consumed. Hence, the final electricity production can be considered as renewable, since methane and carbon dioxide act as the charged and discharged forms of an energy carrier that is continuously recycled.

In order to quantify the advantages of the hybrid concept, the overall operation of a stand-alone Oxy-CC power plant (Figure 21) is first analyzed. Pure oxygen, SNG and recycled flue gas are fed to the combustion chamber where the temperature is raised up to 1330 °C, and the O₂ excess is 8.2%. The resulting exhaust gas is expanded in a gas turbine (GT) to atmospheric pressure, producing 35.7 MW_e of electric power. Then, heat from exhaust gas is recovered as steam, through an economizer (EC), a vaporizer (VA) and a superheater (SH). This allows generating 13.4 MW_e in a high pressure steam turbine (HP) that operates at 530 °C and 150 bar. The isentropic efficiency of all turbines is assumed to be 90%.

The total electric consumption of the Oxy-CC is the sum of the ASU consumption (3.0 MW), the multi-staged compressor of the recycle loop (13.8 MW), and the water pump in the Rankine cycle (0.2 MW). Thus, assuming a 98% efficient electric generator (G), the total 49.1 MW_e that the plant is able to generate translates into 31.1 MW_e of net power. This leads to an overall plant efficiency of 55.9% (Equation 18), comparable to other NGCC power plants from literature with CO₂ capture [154].

$$\eta_{\text{oxyCC}} = \frac{W_{\text{gross,oxy}} \cdot \eta_G - W_{\text{aux,oxy}} - W_{\text{ASU}}}{\text{LHV}_{\text{SNG}} \dot{m}_{\text{SNG}}} \quad (18)$$

Table 14. Main streams of the oxycombustion combined cycle

	SNG	O ₂	Recycled flue gas	Exhaust Gas	Flue Gas
T [°C]	40.0	27	382.0	1329.5	30.0
P [bar]	26.0	40.0	40.0	40.0	1.0
Flow [Nm ³ /h]	5775.9	11210.8	67679.4	84581.4	5859.1
CO ₂ [vol.%]	0.8	0.0	94.5	82.2	94.5
H ₂ [vol.%]	3.5	0.0	0.0	0.0	0.0
CH ₄ [vol.%]	95.3	0.0	0.0	0.0	0.0
H ₂ O [vol.%]	0.4	0.0	4.3	16.8	4.3
O ₂ [vol.%]	0.0	100.0	1.2	1.0	1.2

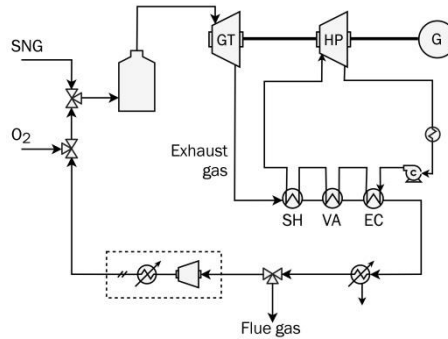


Figure 21. Scheme of the oxycombustion combined cycle

This Oxy-CC produces 5859.1 Nm³/h of flue gas (94.5vol.% CO₂) that can be directed to methanation. The modelled Power to Gas facility is the one previously described. In this case, the required amount of hydrogen is calculated as a function of the molar flow of flue gas, \dot{n}_{FG} , and its molar concentrations of CO₂ and O₂ (Equation 19).

$$\dot{n}_{H_2} = 4 \cdot \left(y_{CO_2,FG} + \frac{1}{2} y_{O_2,FG} \right) \cdot \dot{n}_{FG} \quad (19)$$

Hydrogen and flue gas are pressurized to 30 bar prior the methanation plant, and no preheating is required. The recirculation of the first reactor is fixed at 72.5%, and the condensation stage after the second methanator reduces water content to 12%. Besides, the pressure drops are assumed to be 3% along reactors and 2% in condensation stages. The main streams of the methanation plant are presented in Table 15. The produced SNG has a LHV of 34.68 MJ/Nm³, so the plant generates 55.45 MW of SNG. In addition, the required electrical power capacity of electrolysis is 98.2 MW ($\eta_{ele} = 68.1\%$).

Table 15. Main streams of the Power to Gas plant

	H ₂	Flue gas	R1 Inlet	R1 Outlet	R2 Inlet	R2 Outlet	R3 Inlet	R3 Outlet	SNG
T [°C]	80.0	30.0	307.7	592.1	250.0	421.9	250.0	366.3	40.0
P [bar]	1.0	1.0	30.0	29.1	29.1	28.2	27.7	26.8	26.3
Flow [Nm ³ /h]	22310	5859	78319	69143	18994	17578	7545	7091	5757
CO ₂ [%]	0.0	94.5	9.9	4.5	4.5	1.6	3.6	0.7	0.8
H ₂ [%]	99.9	0.0	41.3	20.0	20.0	6.3	14.7	2.9	3.5
CH ₄ [%]	0.0	0.0	15.3	24.0	24.0	29.9	69.7	77.3	95.2
H ₂ O [%]	0.1	4.3	32.9	50.8	50.8	62.2	12.0	19.1	0.4
CO [%]	0.0	0.0	0.5	0.7	0.7	0.0	0.0	0.0	0.0
O ₂ [%]	0.0	1.2	0.1	0.0	0.0	0.0	0.0	0.0	0.0

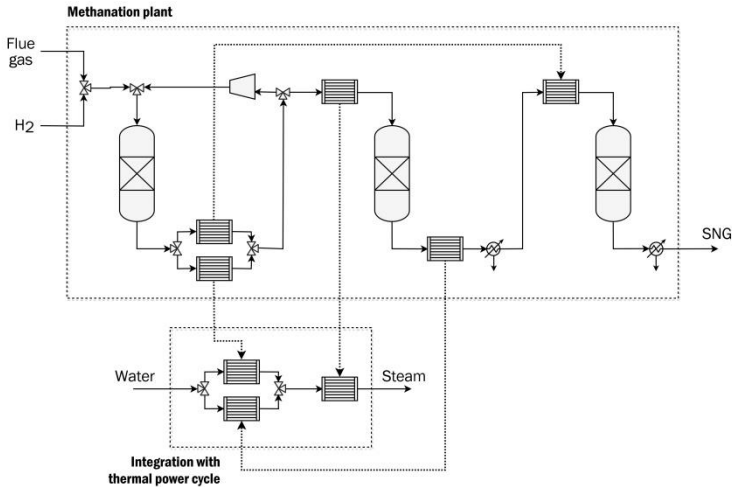


Figure 22. Scheme of the heat exchanger network of the methanation plant

The integration between both plants is established through the pinch analysis methodology ($\Delta T_{\text{Pinch}} = 10 \text{ K}$) [155]. The resulting optimal heat exchanger network (HEN) shows that part of the heat from the first reactor shall be used to pre-heat the inlet of the third reactor (Figure 22). The remaining heat can be used to generate 24 t/h of low pressure steam (124 °C, 2 bar) by using 3 heat exchangers. To take advantage of this recovered heat, the steam is mixed with the outlet flow of the HP turbine and introduced to a newly-added low pressure turbine (Figure 23). The flow exiting the LP turbine is then separated to retrieve the portion which will be pumped back to the heat exchanger network of the methanation plant. This configuration allows running the oxycombustion and Power to Gas processes separately if required.

The integrated OxyCC-PtG power plant is able to produce 53 MW_e of gross power (about 8% more) thanks to the methanation heat. Besides, the removal of the ASU avoids the consumption of 3.0 MW_e, although the compression of the O₂ coming from the electrolyzer penalizes the system with 2.1 MW_e. Thus, modifications finally lead to a net power generation of 35.8 MW_e, what means that the total efficiency of the combined cycle rises up to 64.3% (8.5 points increment, LHV based). Moreover, in this applied case, the final value of ξ_{CO_2} is 1.87, which is a bit lower than the previously determined for a CC with 64% efficiency ($\xi_{\text{CO}_2} = 1.92$, Figure 20). The main difference comes from the reduced O₂ excess in

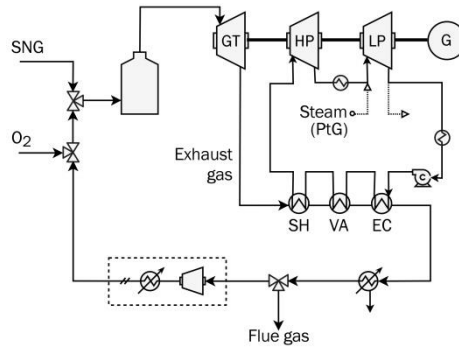
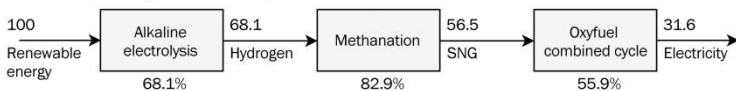


Figure 23. Scheme of the OxyCC plant after integration

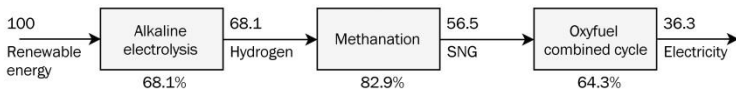
combustion for this case (8.2% instead of 15%), what leads to less O_2 and H_2 required.

Regarding the round-trip efficiency, it increases from 31.6% to 36.3% thanks to the hybridization (Figure 24). It should be noted that strongest energy penalties come from electrolysis and combined cycle. Since future developments on SOEC electrolyzers might lead to efficiencies about 82.0% for the electrolysis stage [156], the round-trip efficiency could reach the 43.7%.

Power to Gas and Oxyfuel combined cycle



Power to Gas hybridized with Oxyfuel combined cycle



Power to Gas based on SOEC and hybridized with Oxyfuel combined Cycle

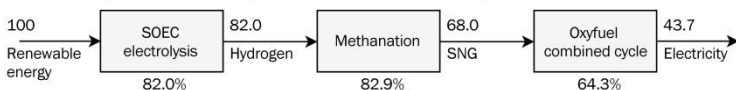


Figure 24. Round-trip efficiency of the PtG-OxyCC system

2.3.2 Power to gas-electrochemical industry

The proposed Power to Gas-Electrochemical hybridization looks for implementing methanation in electrochemical plants that by-produce H₂. This hybridization avoids the electrolysis stage of Power to Gas, since hydrogen is directly provided by the electrolytic lines of production of these factories. Thus, the large investment associated to water electrolyzers and the operational costs of the electricity consumption are removed from the conventional Power to Gas concept.

Moreover, typical chemical plants produce heat or steam with boilers for self-consumption, so CO₂ could be captured in situ to reduce their emissions. In addition, SNG could be reutilized in the boilers to keep CO₂ in a closed recycling loop. In this case, the most suitable option for carbon capture would be a post-combustion chemical absorption based on amines. The exothermal heat from methanation could reduce or even suppress the energy penalty of the regeneration step in the capture cycle.

This novel concept shall not be confused with the Power to Chemicals concept that can be found in literature (Figure 12) [157]. In Power to Chemicals, storage-compounds are those that require H₂ and CO₂ inputs in their lines of production (e.g., methanol). So, in these cases, methanation stage is substituted instead of electrolysis stage (Figure 25).

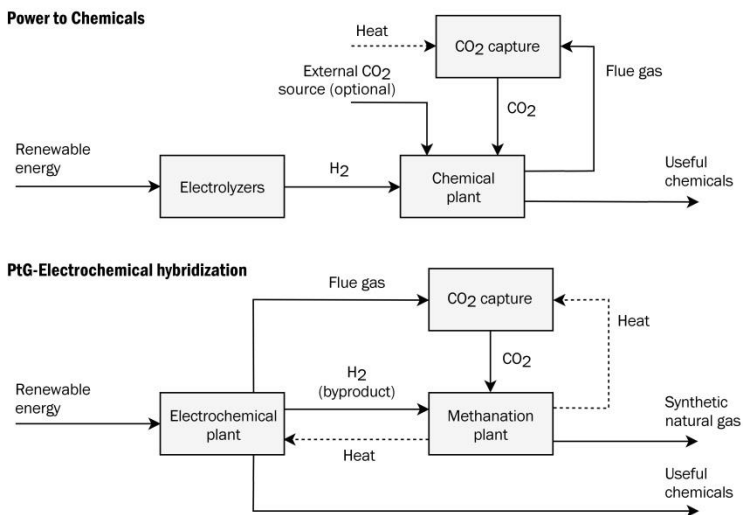


Figure 25. Power to Chemicals against PtG-Electrochemical hybridization

In order to study the PtG-Electrochemical hybridization, a plant combining amine capture with methanation is modeled and simulated in Aspen Plus® (Figure 26). Firstly, since flue gas is assumed to come at high temperature from combustion, it must be cool down to 70 °C prior entering the amine capture plant. Then, flue gas is introduced upwards in the absorber to react with the solvent in countercurrent. This solvent is an aqueous solution with 20wt% monoethanolamine (MEA), which absorbs CO₂ at low temperatures (60 °C – 70 °C). The clean gas vent at the top of the absorber, and the solution rich in CO₂ leaves the column at the bottom. The column is sized to capture more than 90% of the CO₂ introduced with the flue gas.

To separate the solvent and the CO₂ (amine regeneration), the rich solution is passed through a stripper column. A reboiler heats part of the outlet flow to recycle it and make it rise along the column, thus exchanging energy with the rich solution. The mixture of steam and CO₂ that exits the stripper at the top is finally condensed and separated in a flash unit, leading to CO₂ concentrations higher than 94 vol.%. In order to prevent high MEA degradation and corrosion problems, the temperature of the reboiler is limited to 120 °C, with regeneration requirements below 6 GJ/t_{CO₂}.

As the solvent exits the stripper at 103 °C, the stream is used to preheat the rich CO₂ solution from 64 °C to 80 °C. Besides, an additional cooler is used to reduce its temperature down to 37 °C. The cycle is closed when the solution with the regenerated amine at low temperature is sent back to the absorber.

The methanation scheme of the modelled plant is the same used in the study of the PtG-Oxycombustion hybridization. It is composed by three adiabatic reactors at 30 bar, a recycling loop in the first reactor, and an intermediate water condenser after the second stage. First, hydrogen and carbon dioxide are pressurized through two multi-stage compressors, increasing the temperature of the gas up to 300 °C. The outlet gas of Reactor 1 is cooled down to 300 °C and partially recirculated (72%). The temperature of the remaining flow is reduced to 250 °C prior entering into the next reactor. After this second stage, water content normally exceeds the 60 vol.%, what inhibits the reaction. Hence, water content is reduced to 13% by condensation. Then, the gas flow has to be preheated back to 250 °C for the last methanation stage. Lastly, water is removed again to achieve SNG quality. The plant is simulated considering pressure drops of 0.3 bar at methanation reactors and 0.6 bar at condensation tanks.

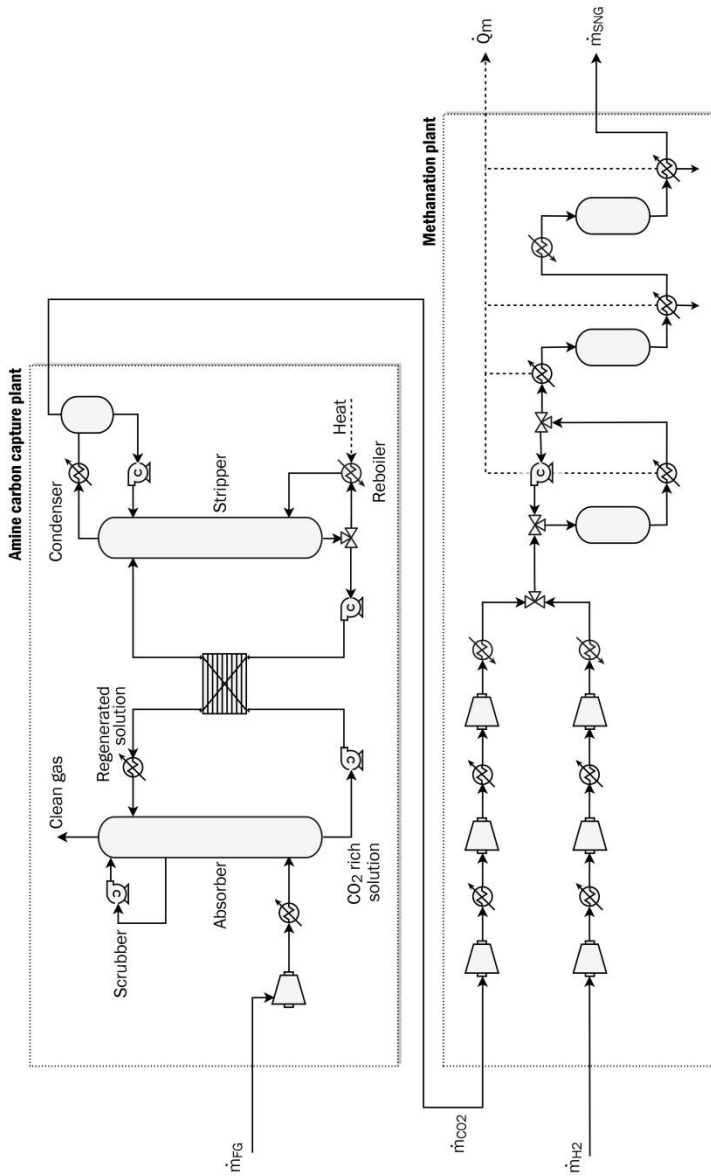


Figure 26. Amine carbon capture-Methanation plant

Influence of the industry's yearly-round operation

The key parameter while dimensioning Power to Gas integrated in an existing electrochemical industry is the temporal distribution of the operating hours for the different lines of production. This will determine the degree of CO₂ and H₂ usage, as well as the potential necessity of a buffer to manage these resources. The following analysis is based on the operation of a real facility for a whole year. Nevertheless, operating rules lay on economic aspects, so main conclusions and issues might be generalized for a typical chemical plant.

These kind of electrochemical plants present intensive energy consumptions, so their operation must strictly follow the electricity market to reduce the operational costs. In Spain, industries are typically subject to an electricity price that varies among 6 time periods established by legislation [158]. This divides the year in 650 hours of P1, 902 hours of P2, 438 hours of P3, 730 hours of P4, 1056 hours of P5, and 4984 hours of P6 (Figure 27). Thus, plants accordingly adapt holidays and maintenances to mostly operate during the cheapest period (Period 6), as well as diminish the production load during periods P1 to P5. This operation strategy, together with the unplanned shutdowns, will determine the hourly availability of H₂ along a year.

This variable operation leads to irregular agreements between H₂ and CO₂ availabilities, what limits the potential use of resources. For instance, Figure 28 shows the analyzed availabilities of H₂ and CO₂ in a real factory (right axis is adjusted to also indicate the methanizable CO₂

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
January, February, December (Working days)																							
P6									P2			P1			P2			P1			P2		
16 th - 30 th June, July (Working days)																							
P6									P2			P1			P2								
1 st - 15 th June, September (Working days)																							
P6									P4			P3			P4								
March, November (Working days)																							
P6									P4			P3			P4								
April, May, October (Working days)																							
P6									P5														
August, national holidays, and weekends																							
P6																							

Figure 27. Hourly distribution of the Spanish pricing period [158]

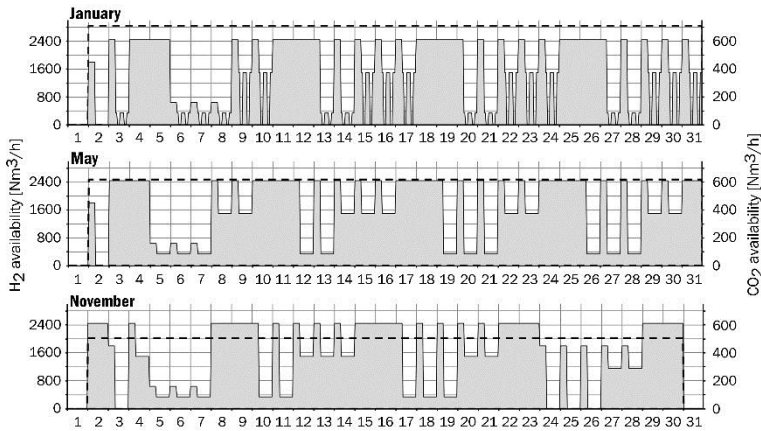


Figure 28. H₂ (grey area) and CO₂ (dashed line) availabilities for January, May and November

that corresponds to the H₂ amounts of the left axis). Most of the time, the boiler provides enough CO₂ to consume the produced hydrogen through methanation (e.g. January or May). However, the limited emissions during months like November make CO₂ insufficient at H₂ production peaks, forcing to discard some of the available H₂ (in this case study, it occurred during 1344 hours in a year). Moreover, there exist periods in which the hydrogen production is too low to reach the minimum operating load to keep the methanation plant working (set at 60% according to literature [13]), so it must be stopped. Hence, these two issues limit the maximum potential use of CO₂ and H₂ (Annex B).

Due to the high variability of the hydrogen source, a methanation plant able to process maximum H₂ production peaks would be excessively underused. Hence, the most suitable size for a methanation plant integrated in a chemical industry should balance the equivalent full-load operating hours with the percentage of used H₂. Besides, a hydrogen buffer to soften the intermittent supply may help to greatly increase the operating hours if it is correctly sized. In the studied case (Figure 29), the followed design criterions are a minimum of 6000 operating hours and 85% of H₂ utilization, which give the area hold by the dashed line. Moreover, it can be seen that, under this criteria, the H₂ buffer that has a more remarked influence is in the range of 750 – 1000 Nm³.

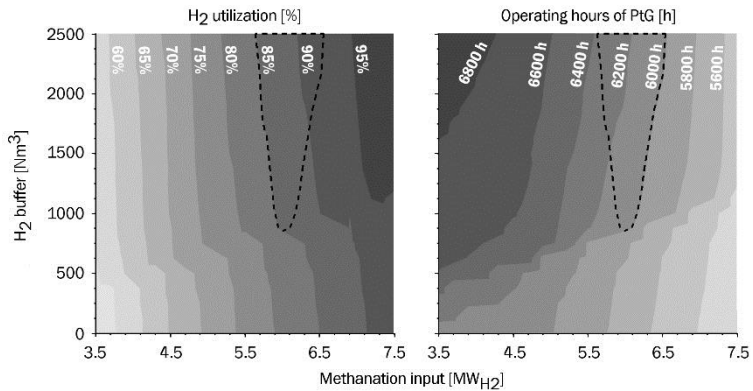
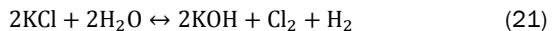
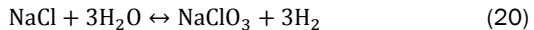


Figure 29. Operating hours and H₂ utilization as a function of the methanation plant size and the H₂ buffer

Application case: Chlorine industry

To assess the advantages of this novel hybridization, a plant that combines methanation and amine carbon capture (Figure 26) is modeled and simulated in Aspen Plus®. This model resembles a real facility of the chlorine industry, from which Figure 29 has been elaborated. This electrochemical plant by-produces hydrogen through one line of production that generates sodium chlorate, NaClO₃, (Equation 20), and another that produces chlorine, Cl₂, and potassium hydroxide, KOH (Equation 21). Besides, the plant has a purification system to further use the byproduct hydrogen.



This particular facility allocates 50% of the by-produced hydrogen to ammonia production, NH₃, 25% to hydrochloric acid, HCl, and 20% to hydrogen peroxide, H₂O₂; the remaining 5% are losses (Figure 30). Since ammonia is a low profitable product, the proposed hybrid plant was sized to replace it with synthetic natural gas production. To that purpose, the hourly distribution of the H₂ consumed by ammonia was analyzed (Figure 28). The largest by-production takes place when both lines of production simultaneously operate at Period 6 (the most economic period), what leads to a maximum flow of 2462.9 Nm³/h (Table 16). Contrarily, during Period 1 there is no hydrogen available for methanation. The high cost of

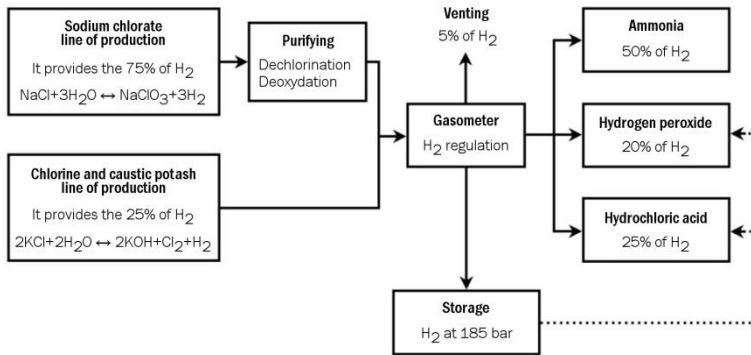


Figure 30. Hydrogen routes in the electrochemical plant

electricity in P1 strongly limits the availability of byproduct H₂, so it is preferred to entirely dedicate it to the production of hydrochloric acid or hydrogen peroxide.

The CO₂ source for the methanation process is a natural gas boiler located in the electrochemical plant. The boiler is assumed to be operative 24 h per day whenever the factory is open. Hence, monthly emissions are equally divided between the operating days, what results in hourly emissions in the range of 464 – 726 Nm³/h (Figure 28).

This analysis allowed sizing the hybrid plant (Figure 29). The selected configuration includes a methanation plant of 6 MW_{H₂} input (1998.7 Nm³/h), an amine capture plant with a nominal output of 496 Nm³/h of CO₂, and a small H₂ buffer of 1000 Nm³. Under these conditions, methanation would operate 6070 hours per year (equivalent full-load), and would use the 85.9% of the available hydrogen and the 58.2% of the produced CO₂.

The amine carbon capture plant produces a flow of 524.3 Nm³/h with a composition of 94.6 vol.% CO₂ and 5.4 vol.% H₂O (Table 17). The auxiliary consumption amounts to 14.2 kW, while the thermal energy demand is 5.5 GJ/t_{CO₂}. Meanwhile, the methanation plant produces 518.6 Nm³/h of SNG mainly composed by methane, 95.2 vol.%, and hydrogen,

Table 16. Rates of H₂ by-production and operating hours

	NaCl electrolysis			KCl electrolysis		
	P1	P2-P5	P6	P1	P2-P5	P6
H ₂ total [Nm ³ /h]	0.0	2333.0	3629.1	486.3	689.0	1296.9
H ₂ ammonia [Nm ³ /h]	0.0	1166.5	1814.5	0.0	344.5	648.4
h [year]	0	1581	4584	570	2846	4584

4.1 vol.%. The LHV of the generated gas is 49.8 MJ/kg, the density is 0.694 kg/Nm³, and the Wobbe index is 49.76 MJ/m³. The auxiliary consumption of the methanation plant (513.7 kW) mostly comes from the multi-stage compressors (402.9 kW for H₂, and 105.7 kW for CO₂), while blowers' consumption represents less than 1%. Besides, whenever the plant is simultaneously operating at full load and storing H₂, the consumption of the hydrogen compressor may rise up to 495.6 kW.

The overall cooling and heating needs of the hybrid plant are 3675.3 kW and 1533.7 kW, respectively. Most of the heat requirement takes place during the CO₂ desorption at the amine plant. Nevertheless, this external heating demand is suppressed by integrating the streams of both systems (Figure 31, empty-dot exchangers). Besides, after integration, cooling needs are diminished down to 2141.6 kW, while the cooling necessity of Reactor 1 allows to produce 238.8 kg/h of steam at 180 °C to be used in the electrochemical plant. The rest can be cooled with water since the temperatures to reach are not lower than 34 °C (Figure 31, solid-dot exchangers). The thermal integration was carried out

Table 17. Aspen Plus® simulation data of the PtG-Electrochemical plant

Output stream	Carbon capture	Methanation plant			
Temperature [°C]	34.0	40.0			
Pressure [bar]	1.0	29.1			
Volume flow [Nm ³ /h]	524.3	518.6			
Mass flow [kg/h]	997.5	359.9			
Mole fraction [%]					
CO ₂	94.6	0.3			
CH ₄	0.0	95.2			
H ₂	0.0	4.1			
H ₂ O	5.4	0.4			
Pinch analysis		Stream	T_i [°C]	T_r [°C]	ΔQ [kW]
Amine capture plant					
Solvent cooler	Hot	85.0	37.8	-937.6	
Flue gas cooler	Hot	175.0	70.0	-238.0	
Stripper condenser	Hot	88.9	88.7	-270.4	
Flash unit	Hot	89.0	34.0	-443.8	
Reboiler	Cold	120.0	120.5	1494.3	
Methanation plant					
R1 outlet	Hot	582.7	300.0	-920.9	
R2 inlet	Hot	300.0	250.0	-42.6	
R2 outlet	Hot	414.1	136.1	-645.5	
R3 inlet	Cold	141.1	250.0	39.4	
R3 outlet	Hot	358.1	40.0	-176.5	
Electrochemical plant					
Cold water	Cold	20.0	25.0	1939.2	
Steam	Cold	50.0	180.0	202.4	

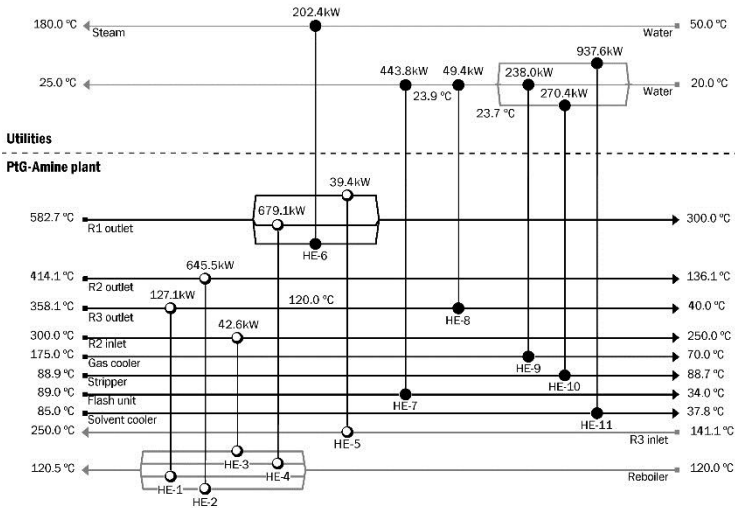


Figure 31. Optimized heat exchanger network
(Black lines – Hot streams, Grey lines – Cold streams)

with Aspen Energy Analyzer through the Pinch analysis technique [159]. The minimum temperature difference between hot and cold streams for the design of the exchanger network was 10 °C.

Once the plant is sized, simulated and properly integrated, the next step is to evaluate the economic viability of the hybrid concept. Table 18 and Table 19 gather the capital expenditures (CAPEX), the operating expense (OPEX), and the incomes of the hybrid plant. CAPEX includes the equipment costs, other direct costs (e.g. building and land) and the indirect costs; OPEX accounts for electricity, waste management, MEA and catalyst renovation, and maintenance; lastly, the economic incomes are the produced synthetic natural gas, and the useful steam coming from the heat exchanger network. The natural gas price was obtained according to the market (28.99 €/MWh), and the medium pressure steam price was obtained as the saving for its generation in conventional gas fired boilers (24.64 €/l_{steam}). Some costs associated to the amine plant were included in the exchanger network, in order to not duplicate equipment costs (solvent cooler, gas cooler, flash and condenser at the stripper).

Table 18. CAPEX of the PtG-Electrochemical hybrid plant

Reference	Equipment/ Process	Cost [€]	Parameter, A	Cost equation [€]
CAPEX – Direct costs (Equipment)				
Amine plant (Total cost, 523486 €)				
[160]	Amine plant	523486	CO ₂ captured [t/h]	$26.094 \cdot 10^6 \cdot (A/408)^{0.65}$
Methanation plant (Total cost, 2158644 €)				
	H ₂ compressor	286978		
	CO ₂ compressor	101916		
[155]	Recirculation blower	10390	Power [kW]	$26.7 \cdot 10^4 \cdot (A/445)^{0.67}$
	Blower	6150		
[161]	Reactors	1660500	SNG Power [kW]	$300 \cdot A$
[162]	H ₂ storage tank	50614	H ₂ [kg] at 30bar	$563 \cdot A$
[155]	Catalyst	42097	Catalyst [m ³]	$187500 \cdot A$
Heat exchanger network (Total cost, 179642 €)				
	HE-1	13908		
	HE-2	22992		
	HE-3	10135		
	HE-4	14894		
	HE-5	10546		
	HE-6	11276		
	HE-7	13459		
	HE-8	11822		
	HE-9	45716		
	HE-10	9912		
	HE-11	14981		
Simulation Model			Area [m ²]	Aspen Energy Analyzer $9016.3 + 721.3 \cdot A^{0.8}$
Total equipment cost: 2861772 €				
CAPEX – Direct costs (Others)				
	Installation	400648		$14\% \cdot A$
	Instrumentation & Control	286177		$10\% \cdot A$
[160]	Piping	457884	Total equipment costs [€]	$16\% \cdot A$
	Electrical	85853		$3\% \cdot A$
	Building	57235		$2\% \cdot A$
	Land	28618		$1\% \cdot A$
Total direct costs: 4178188 €				
CAPEX – Indirect costs				
	Engineering	292473	Total direct costs [€]	$7\% \cdot A$
	Legal expenses	51387		$1\% \cdot A$
[160]	Construction expenses	102774	Total CAPEX [€]	$2\% \cdot A$
	Contingency	513869		$10\% \cdot A$
Total indirect costs: 960503 €				
TOTAL CAPEX: 5138691 €				

Table 19. OPEX and incomes of the PtG-Electrochemical hybrid plant

Reference	Equipment/Process	Cost [€/y]	Parameter, A	Cost equation [€/y]
OPEX				
[155]	MEA renovation	27679	MEA [t/year]	1520 · A
-	Catalyst renovation	6315	Initial catalyst cost [€]	15% · A
-	Waste management	2000	-	-
[158]	Electricity	25512	[kWh]	Pricing period
[160]	O&M	154161	Total CAPEX [€]	3% · A
Total OPEX: 215666 €/year				
Incomes				
	Natural Gas	976990	SNG [MWh/year]	28.99 [€/MWh] · A
	MP steam	35716	MP steam [t/year]	24.64 [€/t] · A
Total Incomes: 1009706 €/year				
ANNUAL BENEFIT: 794040 €/year				

Total CAPEX of the facility is 5.13 M€, of which 56% correspond to the equipment. OPEX is about 0.216 M€/year and total incomes are 1 M€/year. The Net Present Value (NPV), the Internal Rate of Return (IRR) and the Pay-back (PB) of the investment are presented in Table 20, under different discount rates (a 20 years lifetime was assumed). The economic analysis shows positive values that can make attractive the PtG-Electrochemical plant operation. Depending on the discount rate, the capital investment could be recovered in 9 - 7 years, generating a NPV of 3.3 M€ to 6.7 M€ at the end of the project lifetime, with an IRR of 7 to 11%. Results related to the opportunity cost of the current ammonia production are confidential, but it should be said that future scenarios are preferred. Nevertheless, comparing economic results with worldwide research projects, current case study is really interesting compared with other previously studied solution [14]. Since electrolyzers are not needed, the highest cost of a Power to Gas facility is avoided, and it makes feasible to recover the capital investment in a reasonable period of time.

Furthermore, sensitivity analyses show how natural gas price and CO₂ credit price can positively influence the economic viability of the

Table 20. PB, IRR and NPV evaluation for different discount rates

Discount rate [%]	PB [years]	IRR [%]	NPV [M€]
3.0	7.3	11.07	6.68
4.0	7.6	10.00	5.65
5.0	8.0	8.96	4.76
6.0	8.4	7.93	3.97
7.0	8.9	6.92	3.27

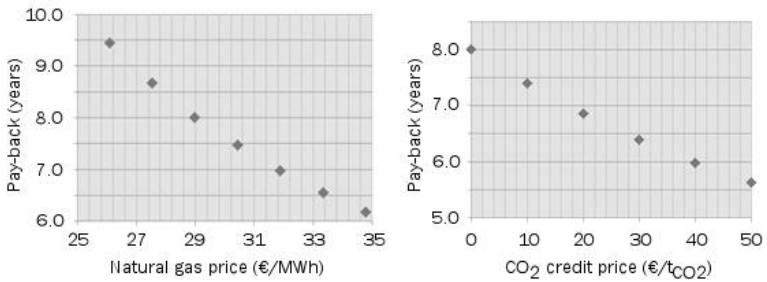


Figure 32. Pay-back as a function of natural gas price and CO₂ credit price

hybrid concept (Figure 32). Despite natural gas price is usually quite variable, a future rise may be expected. Besides, the final use of the SNG may also increase the sale price (e.g., transport, gas-fired facilities, and network injection). For instance, a 15% increase of natural gas price (from 29.0 to 33.3 €/MWh) would reduce pay-back to 6 years and a half, thus achieving very remarkable results for this kind of projects.

Regarding CO₂ credit price, no revenue has been considered in the initial analysis. This particular industry does not have to pay for its emissions, although economic savings may exist in a general case. In this kind of systems, CO₂ emissions are avoided (CO₂ utilization), even if SNG is fired in the own industry boilers (CO₂ recycling). The lack of a clear regulation or definitive taxes for these singular facilities make difficult to establish a future price for the CO₂ avoided. Nevertheless, 30 €/tCO₂ is a reasonable value for making competitive the most CO₂ capture technologies. With this CO₂ credit price, PB is reduced below 6 years and a half.

3 Published papers



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Power to Gas technology under Spanish future energy scenario

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Abstract

Power to Gas (PtG) has been pointed out in the last years as a promising energy storage technology to smartly manage the renewable intermittent power generation that limits the operational flexibility of the network. In this work, we present a prospective study for the Spanish case, in which the implementation potential of PtG technology is evaluated in terms of the estimated renewable surpluses. We found that the annual surplus for the year 2050 would vary between 1.4 TWh and 5.2 TWh, and the PtG capacity required would be in the range 7.0 – 13.0 GW, depending on the renewable production pattern considered. © 2017 The Authors. Published by Elsevier Ltd.

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Keywords: Power-to-Gas; methanation; SNG; Spain; prospective

1. Introduction

The increase of the renewable share in the energy production mix brings along fluctuating surplus power that limits the operational predictability and flexibility of the electricity market. To smartly manage this renewable intermittent power, energy storage technologies will play an important role in the future energy infrastructure. Power to Gas is one of most promising methods for energy storage, since it overcomes the limited storage potential of other

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technologies by presenting better discharge times and storage densities [1]. PtG stores electricity by converting H₂ and CO₂ into synthetic natural gas (SNG), which can be distributed in an easy way through the natural gas network.

Some European countries have evaluated the potential implementation of PtG in their electricity systems. In Germany, Jentsch et al. [2] found the economic optimum for PtG installation between 6 GW and 12 GW for a 85% renewable scenario. Moreover, Schneider L. and Köter E. [3] studied the geographical limitations of installing PtG and determined that the maximum capacity that can be implemented in Germany is 15.4 GW. In Great Britain, Qadrdan M. et al. [4] evaluated the possible benefits of Power to Gas given the large capacity of wind power expected to be installed in the northern parts of England and Wales. They found that wind curtailment could be decreased between 27% and 62% depending on demand, and the network operation cost would be reduced an 11%. In this case, the PtG capacity to be installed would be in the range 5 – 12 GW.

This study presents the implementation potential of Power to Gas technology in a future Spanish energy scenario. We estimate the evolution of the Spanish electricity system for 2050, in terms of power capacity, energy production, and demand. Then, we use this scenario for analyzing the amounts of renewable surplus that can be expected under different renewable generation patterns, and calculate the power capacity of Power to Gas that could be installed in Spain.

2. Framework and prospective of the Spanish electricity system

Currently, hydropower presents 20.3 GW of installed capacity and an estimated potential of 33 GW. Large projects are not expected to occur in mid-term since proper locations are unknown (last evaluation was in 1980) and public acceptance is quite limited. Future development may be based on already existing infrastructures by restoring plants, renovating equipment, or implementing turbines in irrigation dams [5].

Wind power has become the renewable source with the largest installed capacity in Spain. Total capacity is expected to rise up to 24 GW for 2020, whilst repowering could contribute by adding 5 GW in the mid-term. Besides, growth potential concerning off-shore wind power is estimated between 5 GW and 8.5 GW [6].

In 2010, the Spanish solar thermal power accounted for the 60% of worldwide capacity. Prospective establishes 4.8 GW – 10 GW to be installed for 2020, and 20 GW as a target capacity for 2050 [7].

In 2008, photovoltaics experienced the greatest annual growth of the Spanish energy mix, with an increment that amounted to the 60% of the current installed capacity. The generous bonuses destined to PV caused an accelerated implementation. Nowadays, due to reduction of bonuses, the expansion has been broken, and the expectative of 7.25 GW for 2020 will probably take more time [8].

The maximum potential for biomass power, with a controlled exploitation of resources, would lie between 3 GW and 5 GW. In 2030, the expected share of biomass is around 5 % of total production [9].

CHP is industry-dependent so its development has come to a halt because of Great Recession. To overcome this situation, the Spanish CHP association intends to invest 1500 M€ for increasing the efficiency of more than the behalf of the installed capacity [10].

Combined cycles appeared in Spain in 2002, and in 2007 they had already become the most spread technology with the largest installed capacity in the country. This uncontrolled expansion has led yearly operations below 1000 h, and up to 16 plants –of a total of 49– without covering costs. So, progressive shutdowns are expected to occur whenever the government allows it [11].

Coal capacity has barely changed from 2007 onwards, but its participation has diminished since then. Combined cycles, which are less polluting, are fulfilling the demand thus setting coal aside. For the incoming years, the prospective regarding NO_x policies lead to 10.3 GW of installed capacity in 2020 [11]. Carbon capture technologies could soften the progressive reduction of coal share, but they are not expected to be reliable until 2030.

Nuclear power has not planned projects for increasing installed capacity. Since the period 1983–1988, 7 plants (about 1 GW each) participate in the energy market with average operations above 7700 hours. According to their licenses, all of them should shut down between 2020 and 2024, although the Spanish electricity system cannot face the loss of such thermal gap. Therefore, their lifetime should be periodically extended beyond 60 years as in other countries [12].

This information related to the different energy sources which are part of the energy mix in Spain has been used to build the plausible future energy scenarios which will be considered to assess the potential penetration of PtG in the country for 2050.

3. Methodology

The developed model of the future Spanish electricity system consists of two independent blocks: the projected energy demand and production. We estimated both separately, and cross results to check whether the restrictions imposed to arrange a coherent scenario are met (Fig. 1). Whenever restrictions are not fulfilled, the expected installed power capacity (Section 2) is modified accordingly.

The energy demand is based on The Global Calculator tool [13], which models the world's energy, land and food systems to explore the future thermal requirements, electric demands, and greenhouse gas emissions. Different scenarios can be outlined based on multiple variables like social habits, industrial investments, or policies. Based on standards of living and evolution trends in the country, we lay out a scenario in which demand increases a 1.36% per year, and the increment of the global mean temperature by 2100 is restricted to 2°C. To obtain this moderate growth in electricity demand, investments must be focused on improving the efficiencies of fossil power plants, paper industries and cement industries, instead of on electrifying the transport. Besides, the treatment of wastes and residues has to be highly promoted.

The energy production is calculated as the product of installed power capacity by the equivalent hours. The installed power capacity should preserve the expected development presented in Section 2, whilst the hours of operation for renewable and nuclear sources are estimated by taking into account the historical trend, current policies and technology maturity (operation of fossil sources is set once the scenario is established since they act as backup power). Hydropower and small hydro remain stable with periodic fluctuations according to natural, wet and dry cycles. Average nuclear operation slightly diminishes since all plants date from before 1988 and unplanned shutdowns get more frequent. Wind power stood just above 2000 annual equivalent hours, mostly due to weather but also because government's policies limited reimbursed retribution only for the first 2350 hours. Similarly, photovoltaics swiftly grew up to its bonus limit. Nowadays, subsidies to renewable sources are individualized and progressively lessened, so operation is expected to rise. Solar thermal power and CHP were not affected by this limitation, so their equivalent hours increase according to the development of the technology.

Finally, the imposed restrictions that help to arrange a coherent scenario might produce changes in the initial prospective. The main restriction establishes a minimum backup power (biomass, coal and natural gas) able to complete the demand when only the 45% of renewable power and the 95% of base power (nuclear and CHP) are available, thus taking into account the variability associated to the renewable sources. Besides, the backup capacity must have enough operating hours to ensure its economic viability. Furthermore, biomass will have preference against fossil fuels, and the equivalent hours of natural gas and coal should be balanced.

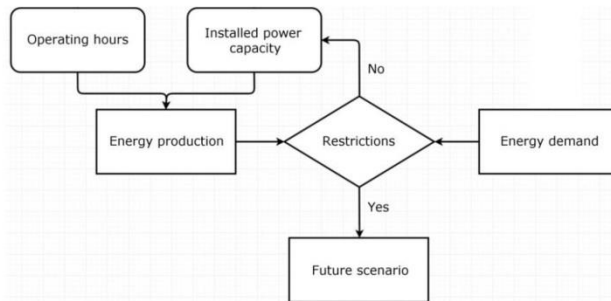


Fig. 1. Model flow chart.

3.1. Time discretization

Once the future scenario is defined, the potential energy storage is obtained as the difference throughout time between the demand and the expected energy production. We discretize the year in daily periods since an hourly interval would be unnecessarily precise (errors for long-term prospective might be important), and monthly periods would not allow detecting energy surplus situations.

Energy demand pattern mainly depends on aspects concerning everyday life, festivities and seasons, which barely vary in long-term. So, we classify the year in a list of day-types together with their typical demand (average from 2010 to 2013). Then, future daily demand is calculated as the product between the total annual demand and the corresponding daily consumption (in annual percentage).

The energy production patterns from renewable and base load power are not conditioned by the behavior of the energy consumption. CHP and nuclear permanently produces stable power, whilst renewable sources have seasonal productions. Among them, wind power is the only one presenting remarkable daily fluctuations. Therefore, we discretize energy production in monthly periods except for wind power, for which we use five historical wind patterns (2009 – 2013). Thus, we obtain an interval of possible productions reflecting the wind variability. Then, biomass, coal and natural gas patterns fulfill demand.

4. Results

The moderate annual increment (1.36%) fits properly the analysis of implementation trends. Thus, for the year 2050 the energy production from CHP is doubled, small hydro participation increases up to 4.0% – 4.5%, and biomass installed capacity reach 5GW (Table 1). Besides, renewable sources provide more than the 63% of the power production, and fossil fuels fall below to 11%.

The nuclear power must be maintained in operation. Such base load cannot be replaced by renewable energy from an economic point of view, since the required minimum backup power set for reaching a coherent scenario would be excessive and underused (biomass, coal and combined cycles). Even nuclear operations of 7300 hours lead to participations of coal power and combined cycled between 1270 and 2000 equivalent hours.

Data of wind power and natural gas are given as a range since surplus power varies according to historical wind patterns. Greater energy storage potential implies worse agreements between demand and wind production, what increase the requirement of natural gas power support. Surplus power may span between 1.4 TWh and 5.2 TWh depending on the wind pattern.

Table 1. Estimated equivalent hours, power capacity and power production for the year 2050 in Spain.

	Equivalent hours (h)	Power capacity (GW)	Power Production (TWh)
Hydropower	1660	19.2	31.9
Small hydro	2760	6.4	17.7
Wind power	2700	35.8	95.2 – 91.4
Photovoltaics	2650	9.1	24.1
Solar thermal	3500	20.3	71.2
Biomass	6750	5.3	35.9
CHP	5600	11.6	65.2
Nuclear power	7300	6.1	44.7
Coal power	2005	8.6	17.2
Combined cycle	1277 – 1466	20.4	26.0 – 29.8
Total	–	142.8	429.1
Surplus power	–	–	1.4 – 5.2

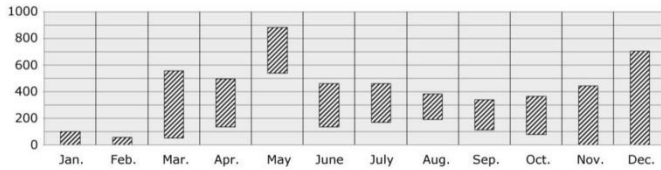


Fig. 2. Intervals of possible monthly surplus power [GWh] for the year 2050 in Spain.

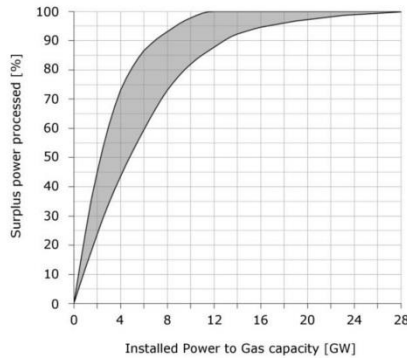


Fig. 3. Surplus power processed [%] as a function of installed PtG capacity [GW] for the year 2050 in Spain.

Through the difference between the demand (which has been assumed to annually rise a 1.36%) and the expected energy production, we calculate the energy excess. Potential storage situations are detected after distributing these production and demand through time, thus observing that they are gathered around May (Fig. 2). In addition, surplus power is guaranteed between March and October regardless of the wind pattern. Moreover, December presents strong variability because the different agreements that can take place between the renewable production and the scarce demand of the last week of the year. In contrast, January and February might lack of energy excess in 2050 even existing high shares of renewable power in the energy mix.

The sizing of the required Power to Gas capacity for processing the energy surplus must be adapted to the maximum hourly excess. In systems characterized by base loads around 20 GW and high presence of wind power, like the Spanish one, surplus behaves smoothly with hourly peaks that rise up to the 8% of the daily excess at most [14]. Therefore, maximum capacity to be installed should be able to process in an hour the 8% of the energy excess produced during the day of the highest daily surplus power. However, a capacity to process the 100% of energy surplus would be underused, because we could process even the 90% of annual excess with less than the half of that capacity (Fig. 3). Thus, a suitable option for the Spanish electricity system is to install 13 GW of PtG, what would guarantee to store more than the 90% of excess power regardless of the wind pattern. Besides, if the agreement between demand and wind production is favorably adjusted, the power capacity needed to process the 90% of excess could be reduced down to 7.0 GW.

5. Conclusions

The expected renewable surplus power and future PtG potential have been assessed in Spain for the year 2050, on the basis of historical data, current policies, technology maturity, and future prospective. A scenario of moderate increment in electricity demand was considered (1.36% annually), which has allowed respecting the prospective of Spanish institutions. However, the nuclear power should be maintained in operation beyond 2050. Such base load cannot be replaced by renewable energy since the minimum required backup power would be highly underused. Still, fossil sources present equivalent hours in the range 1270 – 2000, what makes clear that coal needs to improve its economic and environmental performance under flexible operations, as the H2020 program highly promotes [15].

In 2050, renewable sources would provide more than the 63% of the power production, whilst fossil fuels fall below to 11%. Thus, the annual amounts of renewable surplus would amount to 1.4 – 5.2 TWh depending on how the wind production pattern fits the energy demand. Potential storage situations gather mainly around May, with assured surplus power between March and October. The required PtG capacity for processing the 90% of total excess regardless of wind pattern is 13.0 GW, although it could be as low as 7 GW if the wind production favorably matches the energy demand. These values are similar to those previously presented from the studies of Germany and Great Britain.

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Power to Gas projects review: Lab, pilot and demo plants for storing renewable energy and CO₂



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ABSTRACT

Power to Gas (PtG) processes have appeared in the last years as a long-term solution for renewable electricity surplus storage through methane production. These promising techniques will play a significant role in the future energy storage scenario since it addresses two crucial issues: electrical grid stability in scenarios with high share of renewable sources and decarbonisation of high energy density fuels for transportation. There is a large number of pathways for the transformation of energy from renewable sources into gaseous or liquid fuels through the combination with residual carbon dioxide. The high energy density of these synthetic fuels allows a share of the original renewable energy to be stored in the long-term. The first objective of this review is to thoroughly gather and classify all these energy storage techniques to define in a clear manner the framework which includes the Power to Gas technologies. Once the boundaries of these PtG processes have been evidenced, the second objective of the work is to detail worldwide existing projects which deal with this technology. Basic information such as main objectives, location and launching date is presented together with a qualitative description of the plant, technical data, budget and project partners. A timeline has been built for every project to be able of tracking the evolution of research lines of different companies and institutions.

1. Introduction

One of the targets related to renewable energy penetration enclosed in the roadmap of the European Commission for 2020 is the achievement of a 20% of renewable energy in the overall energy mix of the European Union. In fact, renewables will continue to play a key role in helping the EU meet its energy needs beyond 2020 since EU countries have already agreed on a new renewable energy target of at least 27% of final energy consumption in the EU as a whole by 2030. Thus, renewable energy sources such as solar or wind will play a significant role in electric power generation. The last progress report towards the EU's 2020 renewable energy goals published in June 2015 presents an average share of the renewable electricity supply of 24% with strong differences among countries [1]. While countries as Malta have reached shares of renewable electricity production near 1%; shares above 60% have already been reached in several European countries such as Sweden and Austria becoming in some cases the largest primary source

of electricity [2].

Given the fluctuating and intermittent nature of these energy sources, mismatches between supply and electrical demand which affect to security and stability of the grid will appear. These mismatches must be balanced for grid stability purposes. This has become a critical challenge for future society which must be tackled by developing innovative energy storage solutions. Current storage systems present low energy density or limited storage potential. Therefore, new technologies must be developed to overcome these limitations and increase reserve production ratio.

A large number of pathways exists for the transformation of renewable energy into gaseous or liquid fuels through the combination with residual carbon dioxide. Up to now, a clear classification of these processes is not presented in literature. Thus, some confusion may appear when referring these new storage systems which convert solar energy or power from renewable into fuels. Among them, Power to Gas processes appear as promising systems which convert electricity into

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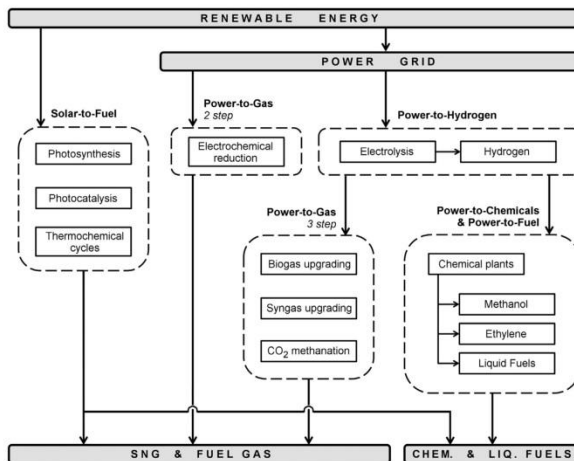


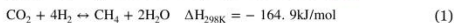
Fig. 1. Renewable energy and CO₂ hybrid storage techniques.

synthetic natural gas. The features of this technology allow the connection of electrical and gas networks in a single energy system introducing high flexibility in the balance of the grid [3].

The first objective of this work is to outline a generalization of the PtG concept, thus giving to the reader a more structured understanding of what is behind these ideas. Since there exists a lack of detailed information in literature referred to this promising long-term electricity storage technique, the second objective of the review is to compile worldwide PtG projects specifications in a structured manner. Thus, we present a thorough review which gathers the construction and operation of pilot-, demo- and lab plants destined to the storage of electricity into SNG.

2. Hybrid storage of renewable energy and CO₂

The Power to Gas concept, storage of renewable energy and carbon dioxide as natural gas, was first proposed by Koji Hashimoto in 1994 [4]. The difficulties associated to large-distance electricity transport in Japan inspired the research on energy carriers. The combination of electrolysis –run by solar energy– and the Sabatier reaction (Eq. (1)) allowed methane synthesis and the subsequent distribution of renewable electricity without the requirement of new infrastructures or alternative combustion systems. Moreover, as CO₂ is recycled, the global warming would be mitigated in some extent [5].



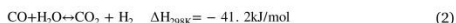
In 2009, Michael Sterner refreshed the Power to Gas concept to focus on the storage of the increasing renewable power surplus, rather than on electricity transportation necessities. Several configurations were outlined depending on the carbon dioxide source used in the methanation stage (biogas, syngas or pure CO₂) [3]. The simplest integration directly transforms CO₂ from carbon capture techniques, e.g. post-combustion and oxyfuel combustion. Other possibility involves the methanation of biogas produced by anaerobic digestion of biomass or wastes. In this case, methanation may be carried out by directly adding hydrogen, since biogas is mainly composed by CO₂ and CH₄.

Traditionally, biogas had always been upgraded through the separation of both components to reject CO₂ and obtain a purified

stream of methane [6]. This option cannot be considered as a Power to Gas technique since it neither stores electricity nor makes use of the carbon dioxide obtained in the fermentation process.

Similarly, Sterner proposed the upgrading of gasification syngas through the addition of renewable hydrogen –hydrogen obtained from renewable energy sources– as an alternative Power to Gas concept. Syngas is mainly composed by CO, CO₂, CH₄ and H₂, with specific volumetric fractions that significantly vary depending on the feedstock and the gasification process involved [7]. The hydrogen content is hardly ever enough to transform the whole amount of CO and CO₂ through a stoichiometric Sabatier process. Hence, the addition of hydrogen would be required to achieve complete methanation of these compounds.

Obtaining synthetic natural gas (SNG) from coal gasification syngas reached a commercial stage of development in the 80/90's [8], while from biomass syngas recently reached the demonstration scale with a 20 MW facility built in the framework of the GoBiGas project [9]. The CO-H₂ ratio of the syngas is commonly adjusted in a subsequent stage by means of water-gas shift reaction (Eq. (2)) without adding renewable H₂, and later removing the remaining CO₂ [10,11]. As stated for traditional biogas upgrading, this conventional syngas upgrading plants cannot be considered as Power to Gas concepts.



The very first PtG concept was associated with water dissociation by means of electrolyzers to directly generate hydrogen from an electric input. Hence, initial references to Power to Gas concept were only related to the production of H₂ from renewable energy sources (i.e. Power to Hydrogen) [12]. Great efforts have been done worldwide to develop a hydrogen-based economy and it has been proven that its definitive deployment is limited, among others, by the requirement of larger hydrogen infrastructure and a well-established hydrogen market [13]. Thus, several researchers left behind the initial Power to Hydrogen concept and proposed new configurations focused on the generation of other gaseous fuels such as methane to take advantage from the natural gas infrastructure.

The proposed generalization of Power to Gas concept, inspired by the initial ideas of Hashimoto in 1994, involves the simultaneous storage of carbon dioxide and renewable energy surplus in the form of a

Table 1
Summary of selected reviews of renewable energy and CO₂ hybrid storage techniques (2010 onwards).

Review	Path	Focus
Bennamoun, 2015[34]	Photosynthesis	Drying methods for algae
Bharathiraja, 2015[35]	Photosynthesis	Algae cultivation methods and processing technologies
Chen, 2015[36]	Photosynthesis	Microalgae productivity and influencing factors toward biofuel production
Sarsekeyeva, 2015[37]	Photosynthesis	Developments of biofuels produced from cyanobacteria
Song, 2015[38]	Photosynthesis	Feature and applications of brown algae
Sutherland, 2015[39]	Photosynthesis	Limitations and improvements of algae in light absorption and utilization
Trentacoste, 2015[40]	Photosynthesis	Policies for algae cultivation
Vijayakumar, 2015[41]	Photosynthesis	Potential pharmaceutical applications of cyanobacteria
Han, 2014[42]	Photosynthesis	Algae waste composting
Chow, 2013[43]	Photosynthesis	Thermal chemical transformation of algae to biofuels
Razzak, 2013[44]	Photosynthesis	Microalgae culturing for CO ₂ capture, waste-water treatment and biofuel production
Menetrez, 2012[45]	Photosynthesis	Environmental impact issues of algae
Rosgaard, 2012[46]	Photosynthesis	Genetic engineering for improving carbon fixation in cyanobacteria
Quadrelli, 2011[14]	Photosynthesis Power to Chemicals	Large-volume routes for chemical utilization of CO ₂ at preindustrial level
Brennan, 2010[47]	Photosynthesis	Algae production, harvesting and conversion to fuel
Kunjapur, 2010[48]	Photosynthesis	Large-scale reactors used to cultivate microalgae for biofuel production
Mata, 2010[49]	Photosynthesis	Production and processing of microalgae for biodiesel production
Ola, 2015[27]	Photocatalysis	Reduction by TiO ₂ photocatalyst. Material design and reactor configurations
Das, 2014[50]	Photocatalysis	Photocatalysts and reactor systems for CO ₂ transformation into fuels
Li, 2014[51]	Photocatalysis	Material design and reactor engineering
Liu, 2014[52]	Photocatalysis	Reduction with H ₂ O by TiO ₂ photocatalyst
Sun, 2014[53]	Photocatalysis	Reduction by nanostructured carbon catalyst
Habisreutinger, 2013[54]	Photocatalysis	Heterogeneous reduction by metal oxides, oxynitrides, sulphides and phosphides
Izumi, 2013[55]	Photocatalysis	Photocatalysis with water, hydrogen and recycling electron donors
Tahir, 2013[56]	Photocatalysis	Developments and applications of visible light sensitive TiO ₂ photocatalysts
Ganesh, 2011[57]	Photocatalysis	Reduction to Methanol
Agrafiotis, 2015[30]	Thermochemical cycles	Types of cycles, heat transfer issues and reactors employed
Scheffe, 2014[58]	Thermochemical cycles	Comparison of physical properties between metal oxide materials
Roeb, 2012[59]	Thermochemical cycles	Reactor technologies and

(continued on next page)

Table 1 (continued)

Review	Path	Focus
Loutzenhiser, 2010[60]	Thermochemical cycles	material properties regarding its technical implementation Kinetics, reactor technology and economics for Zn/ZnO cycles
Albo, 2015[31]	Electrochemical reduction	Reduction to methanol. Cathode materials, reaction media, cells and working conditions
Jones, 2014[61]	Electrochemical reduction	Comparison between methods
Lim, 2014[62]	Electrochemical reduction	SOFc, metal electrodes in aqueous solution and molecular catalysts
Qiao, 2014[32]	Electrochemical reduction	Catalysts for the reduction to low-carbon fuels
Costentin, 2013[63]	Electrochemical reduction	Comparison of performances between catalysts
Jhong, 2013[64]	Electrochemical reduction	Current status and remaining challenges
Kondratenko, 2013[65]	Electrochemical reduction	Design of metal electrodes and alternative approaches
Rittman, 2015[66]	Biogas upgrading	Scale-up issues for biological CH ₄ production
Götz, 2016[67]	Biogas upgrading Syngas upgrading CO ₂ methanation	Technological and economic issues of Power-to-Methane
Rüsch, 2016[68]	Biogas upgrading Syngas upgrading CO ₂ methanation	Methanation fundamentals (catalysts, mechanisms and modelling) and reactor concepts
Aziz, 2015[69]	Power-to-Chemicals	Reaction mechanism over heterogeneous catalysts
Gao, 2015[70]	Power-to-Chemicals	Methanation catalysts research and development
Wang, 2011[71]	Power-to-Chemicals	Catalytic reactivity and reaction mechanisms over heterogeneous catalysts
Ganesh, 2014[72]	Power-to-Fuel Solar-to-Fuel	Conversion of CO ₂ into methanol using any renewable energy source

valuable product. The classification of those techniques included under this definition is illustrated in Fig. 1.

Chemical products that require hydrogen and carbon dioxide in their production process could also be considered as hybrid energy storage when H₂ is renewably produced from surpluses. Some important chemicals in this field are methanol, ethylene, propylene, formic acid and liquid fuels [14]. They can directly use CO₂, or convert the CO from a prior reverse water-gas shift reaction (reverse Eq. (2)).

Besides the commercial processes for the production of chemicals that can be converted into hybrid storage concepts, various novel processes under research would extend the term as well. They are grouped into 1-step or 2-step processes, depending on the number of stages required to transform renewable energy into final products [15].

The 1-step paths directly convert sunlight into valuable products, without an intermediate transformation into electricity. It is worthy to distinguish three of these storing processes capable of consuming CO₂: (i) photosynthesis-based metabolic routes, (ii) photocatalysis and (iii) thermochemical cycles.

Biological capture of CO₂ fixes carbon and sunlight as chemical energy contained in newly grown organisms by means of photosynthesis. Since the efficiency of photosynthesis increases when generated organic structures present very small sizes, single-cell microalgae and cyanobacteria are the common options for this kind of process. Photons are absorbed by antenna proteins thus transferring their energy to the production of storage components, e.g., glucose, carbohydrates, lipids

and proteins [16,17]. The development of biofuels from algal biomass is currently focused on addressing related environmental, technological and economic drawbacks, since the lab-scale phase has been completed successfully [18]. However, algae are already commercially applied in other non-energetic uses as pharmaceuticals [19,20], cosmetics [21,22] and animal feed [23,24]. Contrarily, biofuels from cyanobacteria are still far from its commercial development since greater efficiencies and improved reactor designs are needed [25,26].

In photocatalysis, as in electrochemical processes, carbon dioxide is reduced by means of an electric current. The difference between both techniques is the nature of the electrons that produce the electricity, since photocatalysis is generated by the absorption of a photon in semiconductor materials, thus producing a current based in electron-hole pairs [16]. CO₂ photocatalysis is still not feasible due to the absence of scalable reactors able to produced significant quantities of fuel [27].

Thermochemical cycles reduce metal oxide materials (Eq. (3)) inside cavity receivers in concentrating solar plants at high temperatures (1200–1600 °C). Later, when the metal oxide is regenerated by oxidation with carbon dioxide, it is obtained a syngas mainly composed of CO that can be methanized (Eq. (4)) [28,29]. The technique has already been successfully demonstrated at bench- and pilot-scale, but some crucial technical challenges remain unsolved for its commercial exploitation [30].



The 2-step method involves the electrochemical reduction, where electrical energy is supplied to establish a potential between two electrodes in order to allow CO₂ to be transformed into reduced forms [31]. Hence, renewable energy must be previously converted to electricity and later to the valuable chemical. Some of the most interesting products that could be included in the scheme through this method are formic acid, methanol and methane, which are produced by two-, six- and eight-electron reduction pathways, respectively [32]. However significant improvements in energy efficiency are needed before this technique becomes cost effective, in comparison with the current ways to produce the same products [33].

A large number of reviews has been published so far in reference to the development of these conversion paths studying different aspects (Table 1). However, none of them is focused on 3step-Power to Gas plants and their future perspectives. Therefore, the main objective of the present review is to gather those research projects concerning the construction or management of pilot- and demonstration plants which carry out 3step-Power to Gas paths, thus summarizing the state of the art of the technology.

3. Review of Power to Gas (3 step) projects

In this section a thorough review of 3step-Power to Gas projects which investigate methanation through the application of renewable hydrogen (at least in the conception of the system) is presented.

As a preliminary overview of the information presented in the following, Fig. 2 shows the distribution of the number of projects among countries classified by type of methanation process. Germany is the spearhead nation in developing PtG systems, mainly focused on CO₂ catalytic methanation.

A timeline has been built to clearly represent the evolution and concatenation of worldwide PtG projects with years, Fig. 3. Tohoku University and Hitachi Zosen which initiated their research in PtG systems in 1996 appear as pioneers in this field. As shown in Fig. 3, most of the projects were launched from 2009 onwards when the international community massively discovered the great potential of PtG in excess electricity storage.

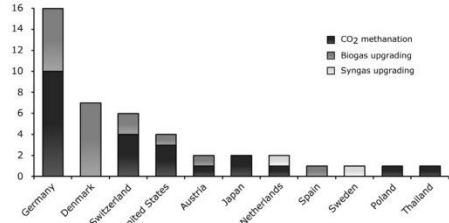


Fig. 2. Existing PtG projects distributed by country and technology.

General information of 3step-Power to Gas projects is summarized in Table 2, where related projects which imply an extension of a previous one are grouped in a same-colour block in order to historically follow the evolution of PtG technology.

There also exist other facilities and projects that apply methanation without making use of renewable hydrogen. However, they are beyond the scope of this review and are not included in the following subsections.

3.1. ETOGAS – Audi e-gas plant

The Audi e-gas plant, under operation since 2013 and located in Werlte (Germany), is the largest industrial Power to SNG facility built in the world (6 MW_e). It is based in the catalytic methanation of pure hydrogen and carbon dioxide in a single isothermal fixed-bed reactor [73,74].

The hydrogen comes from 3×2.0 MW_e alkaline electrolyzers powered by an offshore wind park in the North Sea, which comprises 4×3.6 MW_e turbines and it is co-financed by Audi AG and a regional power-supply company [75]. In addition, the required CO₂ is separated from the raw biogas of a neighbouring biomethane plant, belonging to EWE Biogas GmbH & Co. KG, by means of amine scrubbing [76].

The Power to Gas process of Audi has 54% efficiency (without accounting the utilization of the by-produced thermal energy), thus obtaining a SNG with 13.85 kW h/kg of energy content. The maximum output flow of the facility is 325 Nm³/h, but it is only expected a production of roughly 1000 t per year, because of the availability of the renewable energy consumed to produce the hydrogen (4000 h per annum) [77].

The Power to Gas plant, in contrast to the biogas plant, is not operated on a stationary basis but following the energy supply pattern. Furthermore, the plant has been recently qualified for participating in the electricity balancing market, after successfully draw 6 MW_e of power from the grid within five minutes as well as run prescribed load profiles [78]. The thermal management of the waste heat recovered from electrolysis and methanation, to supply the various heat consumers in the biogas and CO₂ removal plants (mainly amine regeneration), is highly complex [79]. Hence, the assessment and optimization of the plant operation is provided by the WOMBAT simulation [80].

The construction of the plant was born from a collaborative project between Audi AG, ETOGAS GmbH (formerly named Solar Fuel GmbH), the Centre for Solar Power and Hydrogen Research Baden-Württemberg (ZSW), the Fraunhofer Institute for Wind Energy and Energy System Technology (Fraunhofer IWES) and EWE Biogas GmbH & Co. KG [81].

The entire research plan dates back to 2009, in Stuttgart, with ETOGAS as manufacturer and ZSW as the chief developer. The several stages that have been required for achieving the current demonstration plant were performed in Germany in the following order [82]:

- Power to Gas α-plant with air purification (Stuttgart, 2009): A

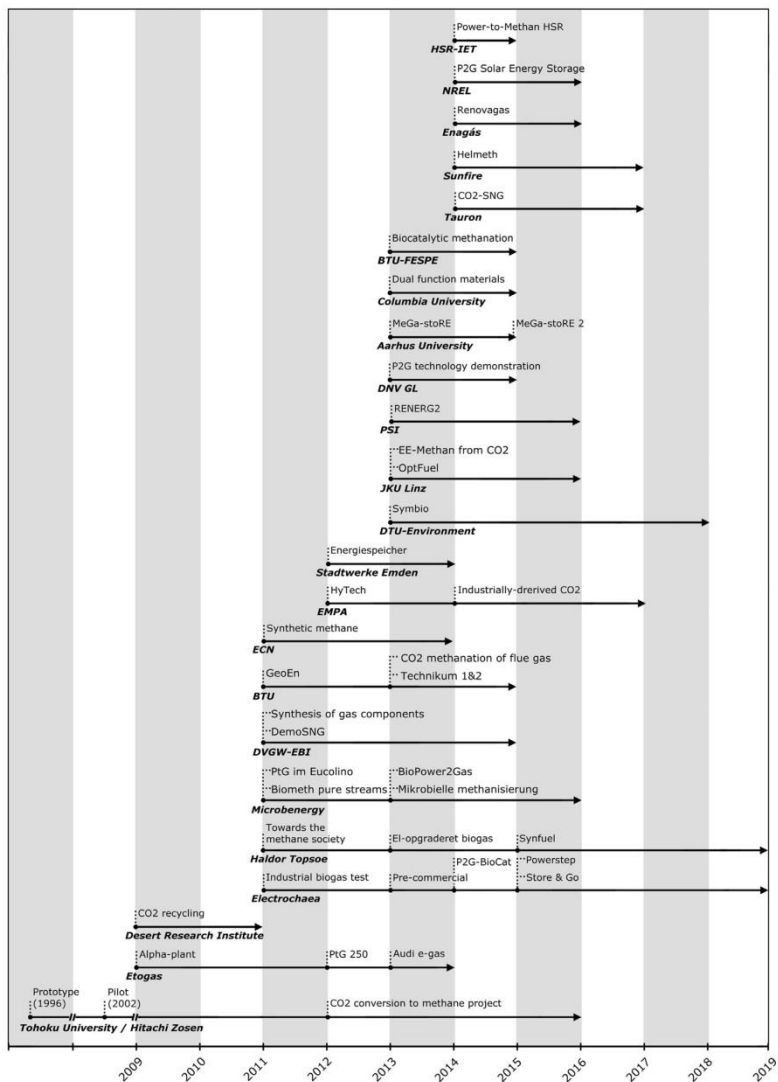


Fig. 3. Timeline of worldwide existing PtG projects.

25 kW_e electrolyser coupled to a CO₂ ambient air purification system was the initial installation used for demonstrating the basic feasibility of the Power to Gas process. The partner and co-developer of this early research stage was ZSW. The facility was built as a mobile container laboratory with a CH₄-filling station of 15 kg capacity at

200 bar. The total efficiency achieved without optimizations was 40% [83,84].

- Power to Gas α-plant with CO₂ from biogas purification (Werlte, 2010–2011): The second phase implied the implementation of the methanation with carbon dioxide captured by pressure swing

Table 2
3step-Power to Gas projects.

Process type	Project Name	Location	Period	Institutions	Ref.
CO ₂ methanation	Audi e-gas	Werlte, Germany	2013	ETOGAS, ZSW, Fraunhofer IWES, EWE Biogas, Audi	[74,77]
CO ₂ methanation	Power to Gas 250	Stuttgart, Germany	2012–2014	ETOGAS, ZSW, Fraunhofer IWES	[84]
Biogas upgrading	Alpha-plant	Bad Hersfeld, Germany	2012	ETOGAS, ZSW, Fraunhofer IWES, HBEZ	[87]
Biogas upgrading	Alpha-plant	Morbach, Germany	2011	ETOGAS, ZSW, Fraunhofer IWES, Juwi	[85,86]
CO ₂ methanation	Alpha-plant	Werlte, Germany	2010–2011	ETOGAS, ZSW, EWE Biogas	[85]
CO ₂ methanation	Alpha-plant	Stuttgart, Germany	2009	ETOGAS, ZSW	[83]
n/a	STORE & GO	Switzerland, Germany, Italy	2015–2019	Electrochaea, DVGW, E.ON, Regio Energie, EII Spa, HSR, PoliT0, JKU Linz-EI, RUG, Atmosstat, CEA, CImeworks, DBI-GUP, BFP, EDI, EMPA, EPFL-IPES, EPFL-MER, EPFL-CEN, Enery Valley	[98,106]
Biogas upgrading	POWERSTEP – Full scale demonstration of energy positive sewage treatment plant concepts towards market penetration	n/a	2015–2018	Electrochaea, KWB, TU Wien, Eawag, Fraunhofer IPM, Veolia, Veolia-WT, NEAS, Biofos, BWB, UBA, APS, Sustec, Atemis, Aertik	[97,104,105]
Biogas upgrading	P2G-BioCat project	Avedore, Denmark	2014–2016	Electrochaea, Hydrogenics, Audi, NEAS, HMN Gashandel, Biofos, Insero	[90,94,96]
Biogas upgrading	Pre-commercial	Foulum, Denmark	2013	Electrochaea, E.ON, Energie 360°, EWZ, NEAS, AU	[100,102]
Biogas upgrading	Industrial Biogas Test	Chicago, United States	2011	Electrochaea, UChicago, AB InBev	[99,100]
Biogas upgrading	BioPower2Gas	Allendorf, Germany	2013–2016	Microbenergy, Schmack, Carbotech, EnergieNetz, EAM EnergiePlus, CUBE, DBFZ, IDE	[107,108,109]
Biogas upgrading	Mikrobielle Methanisierung	Schwandorf, Germany	2013	Microbenergy, Schmack, FENES, ZVKSW	[114,115]
Biogas upgrading	Power-to-Gas im Eucolino	Schwandorf, Germany	2011	Microbenergy, Schmack	[73,112]
CO ₂ methanation	Biological methanation of pure streams	Schwandorf, Germany	2011	Microbenergy, Schmack	[73]
CO ₂ methanation	HELMETH	n/a	2014–2017	Sunfire, KIT, PoliT0, ERIC, TS-Torino, NTUA, DVGW	[116,123]
Syngas upgrading	SYNFUEL	n/a	2015–2019	Haldor Topsoe, DTU, AAU, Chalmers, DONG, Energinet.dk, INSA, TU Berlin, NU, CAS, MIT, AVL	[137]
Biogas upgrading	El-opgraderet biogas	Foulum, Denmark	2013–2016	Haldor Topsoe, Ea, AU, PlanEnergi, HMN Naturgas, NGF, EnergiMidt, DGC, Cemtec, Xergi	[124,125]
Biogas upgrading	På Vej Mod Metansamfundet /Towards the methane society	Midtjylland, Denmark	2011–2012	Haldor Topsoe, AU, AgroPark, HIRC, Planenergi, GreenHydrogen, HMN Naturgas, Lemvig Biogas, DTU, INBIOM	[130]
Biogas upgrading	MeGa-stoRE 2 – Optimising and Upscaling	n/a	2015–n/a	AU, NGF, DTU, Elplatek, GreenHydrogen	[141,142]
Biogas upgrading	MeGa-stoRE – Methane Gas storage of Renewable Energy	Lemvig, Denmark	2013–2015	AU, Elplatek, GreenHydrogen, Lemvig Biogas, DTU-Mekanik, AU Herning	[139]
Biogas upgrading	SYMBIO	Denmark	2013–2018	DTU-Environment, SDU, UM, Energinet.dk, Maabjerg BioEnergy	[143,145]
Biogas upgrading	RENOVAGAS	Spain	2014–2016	Enagas, ICP-CSIC, CNH2, FCC-Aqualia, Gas Natural Fenosa, Tecnalia, Abengoa	[146,147]
CO ₂ methanation	Technical assumptions, technology demonstration and results P2G project	Rozenburg, Netherlands	2013–2015	DNV GL, TKI Gas, Stedin, Rotterdam Council, Ressort Wonen	[148,151]
Syngas upgrading	Synthetic methane: a medium for storage and transportation of excess renewable energy	Netherlands	2011–2014	ECN, TU-Delft, Hanze UAS	[153,156,157]
Syngas upgrading	DemoSNG	Köping, Sweden	2011–2015	DVGW-EBI, KIT, KTH, Cortus, Gas Natural Fenosa	[160,163]
CO ₂ methanation	Storage of electric energy from renewable sources in the natural gas grid – water electrolysis and synthesis of gas components	Baden-Wuerttemberg, Germany	2011–2014	DVGW-EBI, EnBW, Fraunhofer ISE, H-Tec, IoLTec, Outotec	[165,167]
CO ₂ methanation	CO ₂ -SNG	Poland	2014–2017	Tauron, CEA, Atmosstat, AGH-UST, IchPW, Rafako, WTT & T Polska	[170,173,174]
CO ₂ methanation	CO ₂ recycling via reaction with hydrogen	Reno, United States	2009	DRJ, RC02 AS	[175,176]
CO ₂ methanation	Pilot- und Demonstrationsanlage Power-to-Methane HSR	Rapperswil, Switzerland	2014–2015	HSR-IET, HSR, Audi, Climeworks, Erdgas Obersee, Erdgas Regio	[177,178]
Biogas upgrading	Kommunale Kläranlagen als Energiespeicher	Emden, Germany	2012–2014	Stadtwerke Emden, BEE, Thalen Consult, ibis Umwelttechnik, GA-Group	[184,185,186]
CO ₂ methanation	CO ₂ Conversion to Methane Project	Rayong, Thailand	2012–2016	Hitachi Zosen, DAE, PTTEP	[188,190]
CO ₂ methanation	Pilot plant – Tohoku Institute of Technology	Tohoku, Japan	2002–2005	Tohoku University, ToITech, Hokudai, DAE, NRIM, MES, Ryoka	[194,195]
CO ₂ methanation	Prototype plant – Tohoku University	Tohoku, Japan	1996	Tohoku University, IMR, ToITech, Hokudai, DAE, NRIM, MES, Ryoka	[194,195]
CO ₂ methanation	EE-Methan from CO ₂	Leoben, Austria	2013–2016	JKU Linz, MU Leoben, TU Wien, Christof Group, Profactor, ÖVGW, FGW	[198,203,204]
Biogas upgrading	OptFuel	Leoben, Austria	2013–2016	JKU Linz, MU Leoben, TU Wien, Christof Group, Profactor, ÖVGW, FGW	[199,204,207]
CO ₂ methanation	P2G Solar Energy Storage RD & D	Golden, United States	2014–2016	NREL, SoCalGas	[209,210]
CO ₂ methanation / Biogas upgrading	RENERG ²	Villigen, Switzerland	2013–2016	PSI, EMPA, ETH Zurich, ZHAW, EPFL	[212,214]
CO ₂ methanation	Catalytic methanation of industrially-derived	Dübenndorf, Germany	2014–2017	EMPA, ZHAW	[218,220]

(continued on next page)

Table 2 (continued)

Process type	Project Name	Location	Period	Institutions	Ref.
Biogas upgrading	CO ₂ SmartCat	Switzerland Dübendorf,	n/a	EMPA, ZHAW, Zeechem, VSG	[217,219]
CO ₂ methanation	HyTech	Switzerland Dübendorf,	2012–2015	EMPA, ZHAW, EPFL, PSI	[212]
CO ₂ methanation	CO ₂ -Methanation of flue gas	Switzerland Brandenburg, Germany	2013–2015	BTU, Panta Rhei, Vattenfall	[222,223,225]
CO ₂ methanation	CO ₂ catalysis, pilot plant - Technikum 1 & 2	Cottbus, Germany	2013–2014	BTU	[225,230]
CO ₂ methanation	GeoEn	Cottbus, Germany	2011–2013	BTU, GFZ, Uni-Postdam	[227,228,229]
CO ₂ methanation	Dual function materials for CO ₂ capture and conversion using renewable H ₂	New York, United States	2013–2015	Columbia University, BASF	[232,233,234]
CO ₂ methanation	Biocatalytic methanation in an anaerobic three-phase system	Cottbus, Germany	2013–2015	BTU-FESPE	[235,236]

*Note: Photo-electrochemical water splitting.

adsorption (PSA) from the EWE Biogas plant. Hence, the α -plant was tested at the current location of the Audi e-gas project, and it was formed a three member alliance [85].

- Power to Gas α -plant with raw biogas (Morbach, 2011): For the first time, the α -plant was operated with raw biogas instead of pure CO₂. It was demonstrated that direct methanation of biogas is technically feasible in a PtG plant. In this stage, Juwi AG joined to the previous partners [85,86].
- Power to Gas α -plant in long period operation with raw biogas (Bad Hersfeld, 2012): This research stage corresponds to a project launched at the Fraunhofer IWES, in collaboration with ZSW. The target was in situ methanation with raw biogas from an agricultural biogas plant located in the Hessian Biogas Research Centre (HBFZ). The α -plant property of ETOGAS was integrated in the already existent infrastructure for long period operation despite the fluctuating raw biogas composition [87].
- Power to Gas 250 kW_e test facility (Stuttgart, 2012–2014): ZSW, Fraunhofer IWES and ETOGAS developed the largest PtG plant of this type at that time [88]. The main objective was to examine and test different fixed-bed reactor technologies for methanation (plate versus tubular reactor construction) [74]. The system is composed by two fixed-bed reactors, with a capacity for 50 l of catalyst. The first one is refrigerated by water, whilst the other by molten salt. Also, there exists a condensation stage between both methanators, and a recirculation of the final gas towards the first reactor [84]. The methane content achieved is 99%, thanks to processing the gas with membrane technology after methanation. Furthermore, the 250 kW alkaline pressure electrolyser was operated in dynamic and intermittent mode, enabling flexible respond to fluctuating solar and wind energy supplies [82].

Its main goal was to reach commercialized PtG systems around 20 MW between 2015 and 2017, with efficiency above 80% thanks to the recovery of the extra thermal heat from methanation [89].

3.2. Electrochaea – BioCat

The Power-to-Gas via Biological Catalysis (P2G-BioCat) project, which was launched in February 2014 [90], aims to develop the world's largest commercial-scale plant for converting biogas into methane through biological methanation [91]. The facility, located in Avedøre (Denmark), will be operated in dynamic mode to demonstrate its ability to provide energy storage services to the Danish energy system [92].

The construction phase began in July 2015 at the Avedøre Wastewater Treatment Plant, and the facility is expected to be operational by April 2016 [93]. The carbon dioxide source may be raw biogas from an anaerobic digester (60% CH₄ and 40% CO₂) or pure CO₂ supplied by a conventional biogas upgrading system [94]. The

hydrogen will come from a 1 MW_e alkaline electrolyser provided by Hydrogenics, which is scheduled to be shipped in early December 2015 [95]. It will be fed with local excess wind power, and the by-product oxygen will be recycled into the wastewater treatment process. Additionally, the heat from methanation will be also integrated, and the final synthetic natural gas produced is destined to be injected into the 4 bar distribution grid [96].

The methanation will be performed in a liquid phase reactor by methanogenic archaea, a single-celled microorganism which has been selectively evolved through survival tests by Electrochaea GmbH. It metabolizes the hydrogen and carbon dioxide to methane in sequential reduction steps in which the 98.6% of carbon is fixed into the product. The archaea works at low temperatures (60–65 °C) and present high tolerance for hydrogen sulfide, nitrogen oxides, ammonia, particles, as well as partial tolerance for oxygen and ethanol [96].

The project has an overall budget of €6.7 million partially supported by the ForskEL-programme (€3.7 million), which is managed by Energinet.dk, the operator of the Danish power and gas transmission grids. The beneficiary consortium is led by the developer of the methanation technology, Electrochaea, and includes the partners Hydrogenics, Audi, NEAS Energy, HMN Gashandel A/S, Biofos A/S, and Insero Business Services [91,92].

The previous research necessary to achieve the current state of development in this project has passed through three relevant phases. Furthermore, Electrochaea participates in two new H2020 projects that has been recently launched following BioCat [97,98]. The three previous research stages and the newly started H2020 projects are summarized in the following:

- Basic research and proof of concept (2006–2010): The scientific basis of the technology was established in The University of Chicago by Dr. Laurens Mets, the inventor of Electrochaea's biocatalyst [86,96].
- Lab-scale 1 kW (2011): Electrochaea successfully tested the biocatalytic capability of archaea using raw biogas coming from the digester of a brewery waste plant located in St. Louis. It contained 30% CO₂, 68% CH₄ and up to 7000 ppm of hydrogen sulfide [99,100].
- Pre-commercial 250 kW (2013): Electrochaea demonstrated the technology in a pre-commercial setting using a 10,000 l non-optimized reactor, a 250 kW PEM electrolyser, and raw biogas [100,101]. The project was operated over 3000 h under realistic market conditions at Aarhus University's Biogas Research Centre in Foulum. It was partially funded with a grant of €0.88 million from the Danish Energy Agency [102], and the partners of the project were E.ON AG, Energie 360° AG, Elektrizitätswerk der Stadt Zürich (EWZ), and NEAS Energy [103].
- POWERSTEP (2015–2018): This project, launched in September 2015, aims to convert wastewater treatment plants in new renew-

able power producers. The concept will be demonstrated in 6 full-scale studies among Austria, Denmark, Germany, Sweden and Switzerland. Different technologies will be implemented, including Power to Gas developed by Electrochaer. The budget amounts to €5.2 million, and is funded with €4.0 million through the H2020 programme [104,105].

- STORE & GO (2015–2019): Up to 19 industrial and academic partners will demonstrate Power to Gas technology in Switzerland, Germany and Italy, for preventing further construction of new power lines. The project began in September 2015 and puts together multiple institutions researching on methanation like the Swiss Federal Institute of Technology in Lausanne (EPFL), the Swiss Federal Laboratories for Materials Science and Technology (EMPA) and Deutscher Verein des Gas- und Wasserfaches e.V. (DVGW) [98,106].

3.3. MicroEnergy – BioPower2Gas

BioPower2Gas is the first Power to Gas plant based in biological methanation that has achieved the commercial status in the world. This has been constructed in a 3 year project located in Allendorf (Germany) that was launched in September 2013. The first injection of SNG into the national gas grid took place in March 2015, and the finishing certification of the plant was obtained in April 2015 [107].

The equipment of the facility has been provided by subsidiaries of the Viessmann Group. The PtG plant is composed by 2×150 kW_e PEM electrolyzers and a H₂ buffer from Carbotech, a 5 m³ biological reactor from MicroEnergy GmbH, and system controls from Schmack Biogas GmbH [107]. Moreover, the biogas can come from the two biogas plants (dry or wet fermentation) that Viessmann owns in the area [108].

The first injection of SNG, into the gas grid, consumed 15 Nm³/h of hydrogen for the methanation process. However, the potential production of the electrolyser is 60 Nm³/h. Furthermore, Viessmann aims to extend the research up to 1,2 MW_e aiming to reduce the specific cost of the entire facility from 10,000 €/kW to 1200 €/kW for the year 2017 [109]. In addition to the Viessmann companies, the beneficiary partners are EnergieNetz Mitte GmbH (network operator), EAM EnergiePlus GmbH (utilities company), CUBE (engineering consultants) and the project coordinator Institute decentralised Energy Technologies (IdE). Moreover, the German Biomass Research Centre (DBFZ) has provided scientific support [110].

Prior the BioPower2Gas project, MicroEnergy led the line of research of Viessmann, which could be resumed in four development stages:

- Lab-scale research: The proof of the concept was performed at laboratory with a 10 l reactor, increasing the methane content of biogas from 60% to 95% [111].
- Biological methanation of pure streams: A biological reactor for the methanation of pure carbon dioxide and hydrogen was installed in Schwandorf (Germany), coupled to a 55 kW electrolyser. The reactor worked at ambient pressure and had an external heat supply to achieve the necessary operation temperatures (40–65 °C). The results showed that the reactor was able to handle a flow 30 times its size [73].
- Methanation of raw biogas (2011): The objective of the project was to upgrade biogas, during its formation inside the digester, through biological methanation. The biogas reactor was supplied with maize and grass, whilst the hydrogen came from a 120 kW_e electrolyser that produced 21.3 Nm³/h. The methanogenic bacteria consumed the hydrogen, which was introduced from the bottom, as it rose in the reactor through the viscous liquid. Thus, the methane content increased from 50% to 75% and it was obtained a SNG flow of 5.3 Nm³/h [73,112].
- Methanation of biogas from wastewater (2013): MicroEnergy

installed a 180 kW_e PEM electrolyser at the wastewater plant of Schwandorf (ZVKSW), in collaboration with the Research Centre for Power Grids and Energy Storage (FENES) from Universität Regensburg [113]. The goal was to study the stability and reaction rate of the biological methanation under real conditions, by introducing the hydrogen (approximately 30 Nm³/h) directly in the digester as in the previous research [114]. The project budget of €1,42 million was partially funded with a €0.53 million grant [115].

3.4. Sunfire – HELMETH

Sunfire GmbH is involved in the HELMETH project (Integrated High-Temperature Electrolysis and Methanation for Effective Power to Gas Conversion), launched in April 2014 with a time horizon of three years. It aims to demonstrate efficiencies above 85% in Power to Gas systems by integrating high temperature electrolysis and CO₂ methanation [116]. Thus, Sunfire continues the research on SOEC technology developed in a prior Power to Liquid project [117,118].

Electrolysis research will be conducted in a 15 kW SOEC [119] working at 800 °C and 15 bar, whilst methanation process will comprise two reactors in series at 300 °C and 30 bar, with intermediate water removal [120] thus producing up to 5.4 m³/h (60 kW). The plant is expected to be constructed by mid-2016 [121], managing partial loads down to 20% [120]. Moreover, first results concerning catalyst show higher conversions and stability by adding composite oxides to the γ-Al₂O₃ substrate [122].

The project consortium is led by the Karlsruhe Institute of Technology (KIT), and formed by Sunfire, Politecnico di Torino (PoliTo), European Research Institute of Catalysis AISBL (ERIC), Turbo Service Torino spa, National Technical University of Athens (NTUA), and DVGW [116]. The budget totals €3.8 million, funded with €2.5 million from the European Union's Seventh Framework Programme [123].

3.5. Haldor Topsoe – El-Oprgraderet Biogas

The El-Oprgraderet Biogas project aims to construct and operate a pilot plant in Foulum (Denmark) that upgrades biogas by consuming hydrogen from a 40 kW_e SOEC electrolyser. The project was launched in June 2013 for three years [124], but no information has been released so far.

The €5.3 million budget was funded with €3.5 million through the EUDP Danish programme. Moreover, although Haldor Topsoe A/S leads the project, the Aarhus University (AU) received the 70% of the grant for constructing the demonstration plant [125]. The rest of the partners are HMN Naturgas I/S, Naturgas Fyn I/S, EnergiMidt, Xergi A/S, Danish Gas Technology Centre (DGC), PlanEnergi.dk, Ea Energianalyse A/S, and Cemtec [126].

During the past years, Haldor Topsoe has intensively researched in SOEC electrolysis for PtG, although in a theoretical perspective in most cases. Moreover, another project was launched in July 2015 for the period 2015–2019. Their timeline of research can be summarized as follows:

- GreenSynFuels (2010–2011): This project analysed technologies for the development of methanol and DME as green synthetic fuels, through techno-economic calculations. The most favored concept was the methanol synthesis based on gasification of wood assisted by hydrogen from a SOEC electrolyser [127]. The budget amounted to 190 k€ and was partially funded by the EUDP Danish programme [128].
- Biogas SOEC (2011–2012): The project studied two upgrading routes based in SOEC electrolyzers: the direct methanation of biogas by adding hydrogen, and the co-electrolysis of biogas with steam to produce CO and H₂ for a subsequent methanation. Furthermore, the presence of sulphur in the biogas supplied to the SOEC was

investigated experimentally [129]. The budget of the project was 180 k€ (67% funded by the ForskNG programme) [128].

- Towards the Methane Society (2011–2012): Haldor Topsoe constructed a three-reactor pilot plant for purifying biogas, which was operated for 1000 h at the Aarhus University. The two first reactors reduced the sulphur content below 0.04 ppmv, and the third removed the remaining traces. Moreover, the hydrogen was supplied prior the entrance of the last cleaning reactor to consume the oxygen contained in the biogas, thus preparing it for the Sabatier reaction. However, no methanation experiments were performed. Furthermore, the El-opgraderet biogas project, which is currently in progress, arose from this research as a second development phase [130]. The budget amounted to 214 k€ [131].
- CO₂ Electrofuels (2011–2013): This project quantified the cost potential of several fuel synthesis (methane, methanol and DME), and elaborated a roadmap for their introduction in the Nordic region [132]. The research was funded by the Nordic Energy Research Programme [133].
- Green Natural Gas (2011–2014): The Green Natural Gas project identified CO₂ and heat sources for methanation based on SOEC, and provided a technology roadmap through cost-analysis [134,135]. Moreover, dynamic properties for SOEC were tested at Haldor Topsoe facilities. The budget amounted to €3.2 million and was funded with €1.7 million through the EUDP programme [136].

Besides biogas upgrading, Haldor Topsoe has launched a new project named SYNFUEL (2015 – 2019) to explore a PtG process in which carbon source comes from syngas. This project aims to be a proof-of-principle of the combination of SOEC electrolysis and oxygen-blow gasification of biomass. Innovation Fund Denmark granted the project with €2.8 million, whose budget amounts to €3.8 million [137].

3.6. Aarhus University – MeGa-stoRE

The MeGa-stoRE (Methane Gas Storage of Renewable Energy) project has developed a proof-of-concept plant for upgrading biogas through catalytic methanation. Aarhus University launched the project in 2013 for two years, inspired by its participation in the Towards the Methane Society project [138]. It was initially located in its Department of Business Development and Technology (AU Herning) for designing and construction, later continued at GreenHydrogen.dk for testing, and finally the equipment was mounted in a container and transported to Lemvig Biogas Amba for operation [139].

The plant comprises a cleaning unit and a methanation reactor. Firstly, a two-step catalytic process purifies biogas and converts contaminants into micronutrients for the digested slurry. Thus, the H₂S content is maintained below 30 ppb. After cleaning, biogas is methanised using bottled hydrogen, in a single air-cooled reactor [139].

The technology was verified in four long-term tests ranging from 15 to 24 h. All the experiments showed stability and final methane contents between 97–99%. The reactor temperature was set to 270 °C, the pressure was kept at 8 bars and the biogas flow rate was 720 L/h [139].

Besides Aarhus University, which was the project manager, five more partners conformed the consortium: GreenHydrogen, Elplatek A/S, Lemvig Biogas, Department of Mechanical Engineering of the Technical University of Denmark (DTU-Mekanik), and AU Herning [139]. The ForskEL programme partially funded the budget of 900 k€ with a 300 k€ grant [140]. Furthermore, DTU-Mekanik has continued the research by launching a pre-commercialisation project called MeGa-stoRE Optimising and Upscaling, for 2015 onward. The budget amounts to €3.5 million, and ForskEL grants the 25% [141]. The new objective is to achieve SNG productions of 10 Nm³/h [142].

3.7. Technical University of Denmark - SYMBIO

Besides the collaborative projects with Aarhus University and Haldor Topsoe, the Technical University of Denmark (DTU) leads the SYMBIO project. This research aims to develop the biogas upgrading through the injection of renewable hydrogen into the anaerobic digester. The project was launched in 2013 with a time horizon of five years [143], although DTU had developed previous research experiences in this topic [144].

The two main objectives of the project are to establish a technical solution for the hydrogen injection, and to evaluate the increment in the biogas produced by a secondary injection of CO₂. However, no results have been released so far [145].

The project consortium is composed by the Department of Environmental Engineering of the Technical University of Denmark (DTU-Environment), University of Southern Denmark (SDU), Energinet.dk, Maabjerg BioEnergy A/S, and the Department of Microbiology and Immunology from the University of Montreal (UM-DMI). The budget amounts to €2.3 million funded with €1.7 million [143].

3.8. Enagas – RENOAGAS

RENOAGAS aims to develop the first Spanish pilot plant for upgrading biogas through methanation. The project was launched in July 2014, and is planned its conclusion by December 2016. Moreover, as final goal, the SNG produced should have enough quality for its injection to the gas grid [146].

The plant will be constructed along 2015 and operated in 2016. A containerized design will be used for delivering the facility to a biogas plant belonging to FCC-Aqualia S.A., which is expected to produce up to 2 Nm³/h of SNG. The pilot will comprise a 15 kW alkaline electrolyser, a modular multichannel reactor with oil-based cooling, and the control systems. The methanator will operate at 25 bar and 275–330 °C with a gas space velocity between 2000 and 20,000 h⁻¹, and the catalysts will be made of Ni or Ru, supported on Al₂O₃ [146].

Enagas S.A., which is the technical manager of the Spanish gas system, leads this project with a consortium composed by the Institute of Catalysis and Petrochemistry (ICP-CSIC), the National Centre for Hydrogen and Fuel Cell Technology (CNH2), FCC-Aqualia, Gas Natural Fenosa, Tecnalia, and Abengoa Hidrógeno. The budget amounts to €1.7 million, and is funded with €1.2 million by the Spanish Ministry of Economy and Competitiveness (MINECO) [146].

Based on the results of this project, it is planned to scale up the system by constructing a 250 kW pilot plant in a second project. Finally, a last stage would build a 5 MW commercial infrastructure [147].

3.9. DNV GL – Power to Gas in Rozenburg

The DNV GL Group has developed the first Power to Gas facility in Netherlands. The project objective was to validate the capability of the PtG technology to regulate power production, by injecting SNG into the gas network. The plant, located in Rozenburg, provides natural gas to 30 nearby apartments [148] since its inauguration in October 2014 [149]. The lab-scale research began in 2011 [150], the project was initiated in 2013 and the final report has been released in 2015 [151].

The facility comprises a 7 kW commercial PEM electrolyser (model Hogen S40), a four-reactor methanation system, and two CO₂ tanks, placed in three individual containers. Four solar panels, on the containers' roofs, partially supply the hydrogen production, whilst the electricity grid provides the remaining demand. Moreover, the carbon dioxide comes from a wholesale distributor [151].

The methanators are made of stainless steel 316 L with a capacity of 1.06 L for each, filled with different commercial catalysts depending on H₂ and CO₂ concentrations. The two first reactors use 11% Ni

catalysts to avoid exceeding the temperature requirements, whilst the third and fourth reactors use 37%w and 54%w Ni contents, respectively. Hence, reactors can work at temperatures between 150–700 °C and pressures below 15 bar, although the best results are obtained at 377 °C and less than 8 bar. Lastly, the entire plant can be started up in approximately 40 min while the electrolyser is completely operative after just 4 min [151,152].

The project emerged from the cooperation between DNV GL, the Rotterdam Council, and Ressornt Wonen, with funding from Stedin (grid operator) and TKI Gas.

3.10. ECN – Synthetic Methane

The Synthetic Methane project analysed the upgrading of syngas, by simulation, under scenarios of energy excess –addition of renewable hydrogen– and energy demand –conventional operation by removing CO₂ excess–. Moreover, a novel sorption enhanced methanation was proposed and tested experimentally [153]. The project was launched in November 2011 [154], and later extended to December 2014 through a complementary work-package regarding SOFC [155].

For the thermodynamic simulation, three methanation configurations were considered: 3-reactor and 2-reactor schemes with recirculation over the first methanator, and 3-reactor scheme with recirculation from the second to the first methanator. Results showed that 3-reactor schemes are preferred. Furthermore, recycling over the first methanator reduces the size required for the following reactors and improves the operational control, although the heat available for external integration diminishes. Additionally, it was found that adding renewable H₂ to the syngas upgrading impacts on the economics rather than on methanation efficiency [156].

The experimental tests were performed at the methanation facility of the Energy Research Centre of the Netherlands (ECN), developed during the prior project Advance Green Gas Technology Development, which was focused on the conventional syngas upgrading (i.e., without renewable H₂ addition). This equipment works at 6 bar with a gas space velocity of 2000 h⁻¹, and comprises one pre-reformer at 340 °C for the conversion of aromatic hydrocarbons, followed by two methanation reactors at 230 °C and 240 °C, respectively [157].

In the proposed sorption enhanced methanation, zeolite 4A is added to the catalyst to simultaneously dehydrate the SNG inside the reactor. Later, water is desorbed through a regenerative process using heat from methanation. Large methane yields were found even at pressures below 10 bar, thus reducing compression consumptions and increasing efficiency [158].

The project was carried out by ECN, Delft University of Technology (TU-Delft), and Hanze University of Applied Sciences (Hanze UAS). The budget amounted to €1.3 million, and it was financed through the EDGaR programme [154].

3.11. DVGW-EBI and KIT – Demo-SNG

The DemoSNG project demonstrated the feasibility of syngas upgrading by developing a new reactor concept based in honeycomb nickel catalyst [159]. The project was launched in 2011 and concluded during 2015 [160].

The pilot plant was installed into a standard container for shipping purposes. Gas Natural Fenosa was in charge of the hydrogen production [161] through PEM electrolysis [162], and KTH Royal Institute of Technology (KTH) of the hot syngas cleaning process (sulphur, nitrogen and ash removal) [160]. Karlsruhe Institute of Technology (KIT) performed the initial tests, and Cortus operated the pilot at their biomass gasification plant in Köping, Sweden [159].

The proposed methanation uses a single reactor that prevents catalyst degradation through an improved temperature control. The heat transfer from the catalyst to the cooling fluid was simplified by immobilising the catalyst on a metallic monolithic structure (honey-

comb). Thus, the process runs below 300 °C [163], and the facility can process up to 14 Nm³/h of raw biogas [160].

KIT coordinated the project. Moreover, DVGW-Forschungsstelle at the Engler-Bunte Institute (DVGW-EBI) participated in the research. KTH, Cortus, and Gas Natural Fenosa completed the consortium. The project was supported by KIC InnoEnergy with €4.5 million [159,161].

Furthermore, DVGW-EBI led a related project between 2011 and 2014 [164], called SEE project (Storage of electric energy from renewable sources in the natural gas grid–water electrolysis and synthesis of gas components). Their research focused on comparing fixed-bed and slurry methanators at lab-scale, besides studying dynamic operation of electrolysers [165].

The Fraunhofer Institute for Solar Energy Systems (Fraunhofer ISE) characterized a 6 kW PEM electrolyser, provided by H-Tec Systems, by simulating realistic load profiles [166]. Outotec studied different catalysts in a single fixed-bed reactor by varying the inlet and reaction temperatures as well as the gas space velocity. The methanator was 73 cm high and 10 cm in diameter, with a 10 cm catalyst layer in the middle. It was fed by selecting the gas composition through different pure gas bottles, achieving up to 70% CO₂ conversions [167]. DVGW-EBI developed slurry reactors filled with liquid property of Ionic Liquids Technologies GmbH (IoLiTec) in which catalyst is finely distributed. This fluid efficiently dissipates the reaction heat, thus enabling an accurate temperature control under fluctuating feed streams. Catalyst particles are suspended by the rising gas bubbles and can be replaced during operation. Finally, Energie Baden-Württemberg AG (EnBW) evaluated the economic viability.

Although the SEE project is already concluded, DVGW-EBI is still improving the slurry methanation process by testing two reactors with diameters of 24.6 mm and 54.5 mm, and height/diameter ratios of 26 and 13, respectively [168]. Furthermore, DVGW-EBI and the KIT are also studying together the combination of the slurry reactor in series with the honeycomb methanation [169].

3.12. Tauron – CO₂-SNG

The CO₂-SNG project (CO₂ methanation system for electricity storage through SNG production) aims to develop a pilot plant for consuming CO₂ from industry facilities [170]. Tauron Group, as leader, launched the project in 2014 [171] and planned the commissioning of the plant for the first quarter of 2017 [172].

The Power to Gas facility will be located in a coal-burning power plant of Tauron, in Poland [172]. The French partners, the Atomic Energy and Alternative Energies Commission (CEA) and Atomstat, have already developed a structured reactor that processes 1 Nm³/h with a 95% conversion rate. The final design will treat up to 25 Nm³/h and is expected to be delivered in mid-2016 [173]. The AGH University of Science and Technology (AGH-UST) select and test the catalyst for the methanation reaction. The Institute for Chemical Processing of Coal (IChPW) is responsible for capturing the CO₂ from flue gas. A portable amine plant developed in cooperation with Tauron through a previous project [172,174] will be used. West Technology & Trading Polska Sp. will integrate the methanation reactor and auxiliary equipment [172], whilst Rafako S.A. will evaluate a potential commercialisation. The project has been funded through KIC InnoEnergy [170].

3.13. Desert Research Institute – CO₂ recycling via reaction with hydrogen

In 2009, the Desert Research Institute (DRI), with financial support from RCO2 AS, built a lab-scale reactor to demonstrate the feasibility of catalytic methanation. The system was installed in a portable trailer in Reno, United States [175].

A cylindrical vessel, made of 304 L stainless steel, acted as reactor; it was 16.5 cm long, with an outer diameter of 88.9 mm and a wall thickness of 4.6 mm. The catalyst packed bed (PK-7R Haldor Topsoe)

occupied 0.55 L, i.e. a length of 10.9 cm. The gas flowed from top to bottom, and two thermocouples monitored the catalyst temperature [175]. A 5 kW PEM electrolyser, supplied by solar panels and wind turbines [176], produced high purity hydrogen (99.999%), at 13.8 bar, that was stored in four tanks with a total capacity of 0.1 kg. Lastly, the carbon dioxide source was a gas mixture of 2% CO₂ in N₂, thus allowing various experimental conditions without excessive temperature rises. In fact, two 400-W band heaters had to be installed in the reactor to achieve the operating temperatures [175].

The optimal operating conditions were studied by varying the H₂:CO₂ ratio, the catalyst temperature and the space velocity. They found a maximum 60% conversion of CO₂ in the range 300–350 °C, using a H₂:CO₂ ratio of 4, and a 10,000 h⁻¹ space velocity [175].

3.14. HSR-IET – Power-to-Methane HSR

The Institute for Energy Technology of the Hochschule für Technik Rapperswil (HSR-IET) has built and put in operation the first Swiss Power to Gas facility, located in Rapperswil. The Pilot- and Demonstrationsanlage Power-to-Methane HSR project focuses on developing simulation models and plant designs through experimentation for assessing the future role of Power to Gas in the Swiss energy supply [177]. The project started in November 2014, the plant opened in February 2015, and the final report should have been released in December 2015 [178].

The developed plant is an upgrade of the 25 kW prototype that ZSW operated in 2009 in collaboration with their spin-off ETOGAS [178]. The hydrogen is produced with renewable energy provided by the local power company Elektrizitätswerk Jona-Rapperswil AG (EWJR) [179], until a 50 m² photovoltaic panel is installed. Moreover, the CO₂ is captured from air, producing up to 4 kg/day [180]. In addition, for first time a Power to Gas plant will integrate the methanation heat in an ambient-CO₂ absorption process [178].

The facility has a maximum output of 1 Nm³/h of methane, which is finally compressed for a filling station (20 h are needed to fill up a car tank) [178]. After 500 h of operation, results show an efficiency of 35% without accounting the CO₂ capture consumption –chemical energy contained in the compressed SNG per unit of electrical energy consumed in the facility [181].

Besides the HSR-IET, the consortium is formed by Audi, Climeworks, Erdgas Obersee, Erdgas Regio, and EWJR [178].

Thanks to the development of a pilot plant, the HSR-IET also participates in other two projects by providing experimental data and operating experience: Renewable Methane for Transport and Mobility (RMTM), and SCCER Storage project. The RMTM project focuses on the application of PtG technology through techno-economic assessment of its entire value chain [182]. It started in October 2015, with a time scope of three years and budgeted for €1.0 million. The Paul Scherrer Institute (PSI) is performing a life cycle analysis of the HSR-IET's PtG facility to quantify the environmental impact [183].

3.15. HS Emden/Leer-EUTEK – Power to Gas in Emden

The Emden Institute of Environmental Engineering of the Hochschule Emden/Leer (HS Emden/Leer-EUTEK) evaluated the suitability of a wastewater treatment plant as CO₂ supplier for Power to Gas. The project was launched in 2012 and developed during two years [184], including experimental research at lab-scale [185].

A facility was dimensioned during the project, comprising a 312 kW electrolyser and an isothermal reactor at 335 °C with a SNG production of 59 m³/h [185]. As a result, it was announced the construction of a pilot plant in the wastewater treatment plant of Emden [186], although no information about it progress has been released so far.

HS Emden/Leer-EUTEK led the project formed by the partners Stadwerke Emden GmbH, Bau- und Entsorgungsbetrieb Emden (BEE), Thalen Consult, ibis Umwelttechnik GmbH, and Gesellschaft

für Abwasserberatung und Management mbH (GA-Group) [184]. The budget amounted to 185 k€ and was funded with 125 k€ by the Ministerium für Wissenschaft und Kultur (MWK) through the European Regional Development Fund (ERDF) [187].

3.16. Hitachi Zosen – CO₂ Conversion to Methane Project

CO₂ Conversion to Methane Project, launched in 2012, aims to develop industrial PtG and construct the first facility in Thailand [188]. They proposed, as main application, to convert CO₂ generated during extraction of natural gas from natural reservoirs [189].

The first phase of the project has been performed using tubular reactors of 5 m long, with a H₂ conversion of 99.3% operating at 200 °C [190]. The process employs ceramic catalyst based on zirconia-samarium, with nickel as active material, which was developed by Hashimoto et al. through previous research [191]. Thus, results have allowed the simulation and design of the plant that will be built in Thailand, with a methane production of 1000 Nm³/h [188,192], between 2014 and 2016 [190]. Moreover, hydrogen will be produced by alkaline electrolyzers [193] fed with desalinated seawater [191,192].

The partners cooperating in this research are Hitachi Zosen Corporation, Daiki Ataka Engineering Co. –a subsidiary of Hitachi– and PT Exploration and Production Public Company Limited (PTTEP) –a Thai petroleum corporation– [191]. However, this project could not be possible without the research carried out by Hashimoto et al. in two prior projects since their technology is employed [194]:

- Prototype plant (1996): The Tohoku University developed the first worldwide Power to Gas prototype, located in the roof of its Institute for Materials Research (IMR). The facility comprises two reactor in series with an intermediate water removal [5], an electrolyser fed by a photovoltaic cell, and a CH₄ combustor from which CO₂ is recycled [194].
- Pilot plant (2002–2005): The prototype research was continued by the installation, in 2003, of an industrial pilot plant in the Tohoku Institute of Technology (TohTech). It produced up to 4 Nm³/h of H₂ and 1 Nm³/h of CH₄ [194]. This second project was funded through a 3-year grant for developing revolutionary technologies within the Millennium Projects framework [195].

3.17. JKU Linz-EI – EE-Methan aus CO₂ and OptFuel

The Energy Institute of the Johannes Kepler University Linz (JKU Linz-EI) participates in four connected projects for developing an entire Power to Gas system in Austria [196]. Wind2Hydrogen (2014–2016) built a 100 kW pilot plant with 12 PEM electrolyzers [197], EE-Methan aus CO₂ (2013–2016) develops catalytic methanation [198], OptFuel (2013–2016) focuses in biological methanation [199], and Underground Sun Storage (2013–2016) studies the storage of the generated gas [200,201].

The main goal of EE-Methan aus CO₂ project is to develop a ceramic honeycomb catalyst adapted to industrial CO₂ sources for increasing lifetime a 10% with respect to commercial catalysts [202]. For testing, a methanation pilot plant was built in the University of Leoben consisting of three reactors in series with intermediate cooling. The operating window allows inlet temperatures up to 350 °C and pressures between 1 and 20 bar, with a maximum flow of 3 Nm³/h [203,204]. Secondary objectives imply conditioning product gases by using membrane technology, environmental assessment and economic evaluation [205].

The second methanation project, OptFuel, focuses on hydrogen production through fermentation and on the purification requirements for its later conversion into methane. Minor goals as cost assessment and life-cycle analysis are also included [206]. The experimental methanation research is also performed at the pilot plant of MU Leoben, thus studying the potential of combining biological and

chemical processes [204,207].

The consortium of the methanation projects is completed by the Vienna University of Technology (TU Wien), the Austrian Association for Gas and Water (ÖVGW), the Association of Gas and District Heating Supply Companies (FGW), Profactor GmbH, and the Christof Group. Moreover, the budgets amount to 780 k€ and 850 k€ for EE-Methan aus CO₂ and OptFuel, respectively [207,208].

3.18. SoCalGas – P2G Solar Energy Storage

The Southern California Gas Company (SoCalGas) is promoting Power to Gas in the United States with the first demonstrative project of the country that includes methanation. It is focused in enabling higher penetrations of solar power generation through its storage in the natural gas network. The project is located in Golden, Colorado, and scheduled from September 2014 to March 2016 [209].

The research takes place in the laboratories of the National Renewable Energy Laboratory (NREL), where a 150 kW electrolyser produces hydrogen under simulated photovoltaic profiles. The CO₂ is transformed through biological methanation by single-cell methanogens in a liquid media reactor. Then, the product gas is used to produce electricity in a fuel cell [210].

The project is a joint research between SoCalGas, NREL and Electrochaepa with a total budget of 900 k\$ equally co-funded [97,209]. In the future, SoCalGas intends to construct a pre-commercial demonstrator of 1 MW [210].

3.19. Paul Scherrer Institute – RENERG²

The RENERG² project (Renewable Energies for Future Energy Supply) focuses on transferring renewable energy surplus to mobility sector, studying electrolysis, methanation, combustion fundamentals, refueling and economics. The project began in 2013 and will be concluded by the end of 2016 [211,212,213].

Methanation research is conducted by the Paul Scherrer Institute through its bubbling fluidized bed methanator (GanyMeth), commissioned in April 2015 and placed in Switzerland. The reactor bed is 2 m high with a diameter of 21 cm, withstanding pressures between 1 and 12 bar and producing up to 160 kW of SNG [214].

Experiments include dynamic load changes and feed gas variations for acting as a polygeneration of fuel, heat and electricity [212]. First tests utilize bottled gas that will be changed for real gases and a 100 kW PEM electrolyser when available. Expected results concern kinetics, hydrodynamics, catalyst abrasion and heat transfer [214].

The project consortium includes EMPA, the Swiss Federal Institute of Technology Zurich (ETH Zurich), the Zurich University of Applied Sciences (ZHAW), and EPFL. Budget amounts around 240 k€, funded by the Competence Centre for Energy and Mobility (CEEM) [212,213].

3.20. EMPA – catalytic methanation of industrially-derived CO₂

The Swiss Federal Laboratories for Materials Science and Technology study the sorption enhanced methanation, which improves CO₂ conversion by absorbing water in situ through a zeolite-nickel catalyst [215,216]. The process and reactor have been developed throughout three different projects focused on catalyst development (HyTech) [212], biogas upgrading (SmartCat) [217], and CO₂ methanation (Catalytic methanation of industrially-derived CO₂) [218].

Experiments are performed in a stainless steel reactor 45 cm long and 1.8 cm in diameter, operating at 1.2 bar with 13 g of catalyst. The space velocity is 1000 h⁻¹ that corresponds to an output of 1 kW [215,216,219]. Currently, they evaluate the utilization of CO₂ from the cement industry, and the issues of catalyst deactivation due to sulphur compounds, under the framework of the last mentioned project [218]. Moreover, the Laboratoire de photonique et interfaces of the Swiss Federal Institute of Technology in Lausanne (EPFL-LPI) assesses the

production of renewable hydrogen through photo-electrochemical water splitting in a parallel project. Both lines of work belong to a collaborative joint of 5 individual projects that also covers fuel cells development and sustainability analyses (Joint project CO₂ Reduction & Use: Renewable fuels for efficient electricity production) [220].

EMPA has collaborated, throughout methanation projects, with ZHAW, EPFL and Zeochem AG [212,220,221]. The funds for the experimental facility came from the Swiss Federal Office of Energy (SmartCat project) and the SNSF (Catalytic methanation of industrially-derived CO₂ project) [216].

3.21. BTU – CO₂-methanation of flue gas

The Brandenburg University of Technology (BTU) researches on the methanation of oxyfuel CO₂, conventional flue gas, and underground-stored CO₂, besides studying the influence of contaminants like SO_x or NO_x. Their last project (CO₂-Methanation of flue gas), which concluded in October 2015, included a 3 month trial operation at Schwarze Pumpe power plant, in Germany [222,223].

The Power to Gas pilot consists of two parallel methanators which are 153 mm in diameter, 870 mm high and have 15 slots for temperature measurements [224]. Total volume reactor amounts to 30 dm³ and contains up to 2 kg of catalyst (Ni 66%w on Silica/Alumina). The pilot plant works at 350 °C and 10 bar, with an input capacity of 1200 Nm³/day thus producing about 200 Nm³/day of CH₄ [225]. H₂ is supplied from bottles although it was proposed the implementation of a PEM electrolyser in the future [224]. Results show conversions above 80% and selectivity between 90% and 100% [225].

Panta Rhei GmbH and Vattenfall Europe Generation AG joined as partners, whilst the BMWi supported the project with 565 k€ [223,226]. Previously, the Brandenburg University of Technology accomplished three projects concerning lab scale tests and upscaling:

- GeoEn (2011–2013): As part of this project, BTU studied the stability of catalysts against SO_x and NO_x in the context of oxyfuel process [227]. The lab facility consists of a reactor tube, 8 mm in diameter and 100 mm in length, mounted into an oven that supplies homogeneous temperature distribution during reaction. As catalysts, they used NiO supported on silica gel and RuO₂ on alumina. BMBF supported financially the joint research in which also participated the German Research Centre for Geosciences (GFZ) and the University of Potsdam [228,229].
- CO₂ catalysis, pilot plant I & II (2011–2014): During this two-phase project, the BTU upgraded the lab facility into the pilot plant employed later in their research [225,230]. The project was funded with about 605 k€ from the European Regional Development Fund through the Ministerium für Wissenschaft, Forschung und Kultur (MWFK) [231].

3.22. Columbia University – dual function materials for CO₂ capture and conversion

The Columbia University in the City of New York, with financial support from BASF, researches on dual function materials that capture CO₂ from an emission source and convert it to synthetic natural gas in the same reactor and at the same temperature, by using renewable H₂ [232].

The related publications range from 2013 to 2015 covering the process parameters, cyclic stability tests, and kinetic characterization of methanation through a 10% Ru/γ-Al₂O₃ catalyst [233,234], in addition to feasibility studies of the dual function material consisting of 1–11% w Ru and 1–10%w CaO dispersed on γ-Al₂O₃ carrier [232]. As methanator they used a fixed bed glass reactor with an inner diameter of 12 mm at a pressure of 1 atm [234].

Table 3
Technical parameters of PiG projects with catalytic methanation.

Project Name	Reactor	Temperature [°C]	Pressure [bar]	Electrolyser [kWe]	Electrolyser Technology	Efficiency PtG [%]	Output [N m ³ /h]	Methane content [%]	Ref.
Audi e-gas	Isothermal fixed bed	–	–	6000	Alkaline	54	325.0	–	[74,77]
HELMETH	–	300	30	15	SOEC	–	5.4	–	[116,123]
MeGa-store – Methane Gas storage of Renewable Energy	Air-cooled	270	8	–	Bottled hydrogen	–	–	97.0–99.0	[139]
RENOVAGAS	Multichannel	275–330	25	15	Alkaline	–	2.0	–	[146,147]
P2G project	Fixed bed	150–700	8–15	7	PEM	–	–	–	[148,151]
Synthetic methane: a medium for storage and transportation of excess renewable energy	–	230–240	6	n/a	Bottled hydrogen	–	–	–	[153,156,157]
DemoSNG	Honeycomb	< 300	–	n/a	PEM	–	–	–	[160,163]
Storage of electric energy from renewable sources in the natural gas grid – water electrolysis and synthesis of gas components	Fixed bed / Slurry	–	–	6	PEM	–	–	–	[165,167]
CO ₂ -SNG	Structured	–	–	–	–	–	–	–	[170,173,174]
CO ₂ recycling via reaction with hydrogen	Fixed bed	300–350	–	5	PEM	–	–	–	[175,176]
Kommunale Kläranlagen als Energiespeicher	Isothermal	335	–	312	–	–	59.0	–	[184,185,186]
CO ₂ Conversion to Methane Project	Fixed bed	200	–	n/a	Alkaline	–	1000.0	–	[188,190]
Pilot plant – Tohoku Institute of Technology	–	–	–	n/a	Alkaline	–	1	–	[194,195]
Prototype plant – Tohoku University	–	–	–	n/a	Alkaline	–	–	–	[194,195]
EE-Methan from CO ₂	Honeycomb	> 350	1–20	–	–	–	3	–	[198,203,204]
Catalytic methanation of industrially-derived CO ₂	Fixed bed	–	1.2	–	PEC (*)	–	0.1	–	[218,221]
SmartCat	–	–	–	–	Bottled hydrogen	–	–	–	[217,219]
HyTech	–	–	–	–	Bottled hydrogen	–	–	–	[212]
CO ₂ -Methanation of flue gas	Fixed bed	350	10	–	Bottled hydrogen	–	200	–	[223,224,226]
CO ₂ catalysis, pilot plant - Technikum 1 & 2	Fixed bed	–	–	–	Bottled hydrogen	–	–	–	[226,231]
GeoEn	Fixed bed	–	–	–	Bottled hydrogen	–	–	–	[228,229,230]
Dual function materials for CO ₂ capture and conversion using renewable H ₂	Fixed bed	–	1	–	Bottled hydrogen	–	–	–	[233,234,235]

3.23. BTU-FESPE – biocatalytic methanation in an anaerobic three-phase system

The Faculty of Environmental Science and Process Engineering of the Brandenburg University of Technology (BTU-FESPE) has developed an anaerobic trickle-bed reactor for biocatalytic methanation at 37 °C and ambient pressure in a continuous process. Their last prototype includes an electrolyser for H₂ generation and conventional CO₂-pressure cylinders, although it can also enrich a biogas source [235].

The reactor is 141 cm in length and 28.2 cm in diameter, with a total volume of 88 L. It contains a fixed-bed of random packing material with a high specific surface area on which microorganisms can be immobilized and surrounded by gas phase. Then, they are sprinkled with liquid thus creating greater concentration gradients and

improving the driving force for the mass transfer. Results show methane outputs of 98% in a single reactor without necessity for gas recirculation [235].

Once the detailed information has been described for each individual PiG project, the technical information is filtered and presented in the following tables to facilitate the comparison between operation parameters. Table 3 includes those projects in which CO₂ methanation is carried out through a catalytic process.

The projects with a biological methanation stage are gathered in Table 4 where their most relevant technical parameters are summarized.

The projects in Table 2 which are not included in Tables 3 or 4 correspond to those projects whose methanation process is not clearly defined in open literature.

Table 4
Technical parameters of PtG projects with biological methanation.

Project Name	Reactor	Temperature [°C]	Pressure [bar]	Electrolyser [kWe]	Electrolyser Technology	Output [N m ³ /h]	Methane content [%]	Ref.
POWERSTEP	–	–	–	–	–	–	–	[97,104,105]
P2G-BioCat project	Liquid phase	60–65	–	1000	Alkaline	–	–	[90,94,96]
Pre-commercial	Liquid phase	–	–	250	PEM	–	–	[100,102]
Industrial Biogas Test	–	–	–	1	–	–	–	[99,100]
BioPower2Gas	–	–	–	300	PEM	–	–	[107,108,109]
Mikrobielle Methanisierung	–	–	–	180	PEM	–	–	[114,115]
Power-to-Gas im Eucolino	Liquid phase	–	–	120	–	5.3	75.0	[73,112]
Biological methanation of pure streams	–	40–65	–	55	–	–	–	[73]
SYMBIO	Anaerobic digester	–	–	–	–	–	–	[143,145]
OptFuel	–	–	–	–	–	–	–	[199,204,207]
P2G Solar Energy Storage RD & D	Liquid phase	–	–	150	–	–	–	[209,210]
Biocatalytic methanation in an anaerobic three-phase system	Anaerobic trickle-bed	37	1	–	–	–	98.0	[235,236]

4. Conclusions

Because of worldwide renewable energy penetration targets, massive energy storage concepts have taken significance during recent years. Power to Gas seems to tackle this issue not only in terms of energy storage but also in CO₂ utilization. A large number of researchers has revisited PtG technology in the last decade with energy storage purposes to better integrate renewable sources in the system. A remarkable increase in technology deployment in terms of ongoing projects dealing with 3step-PtG processes started after 2010 and currently available information predicts that this period will last, at least, until 2025.

Although the first pilot plant was erected in Japan, the current leadership holds in Europe, mainly thanks to the support of the governments of Germany, Denmark and Switzerland. These experiences combine pilot and demonstration plants whose electrolyser sizes vary from few kW_e (lab-scale plants) to 3×2.0 MW_e (largest existing plant). USA has also contributed to the deployment of the technology with up to four projects since 2009. Data show that the average budgets for demo-plants projects are around one million euro per year in most cases.

Regarding methanation technologies, large projects cover mainly catalytic processes due to its scale up capability, although recently some biological projects also rose up to the MW range. Current pilot

plants prefer biogas as source of CO₂ since the energy penalty associated to carbon capture vanishes. For the same reason, syngas upgrading emerges as a future suitable option. Few others have experienced with more innovative CO₂ sources such as industrial processes, the atmosphere, natural gas extraction processes or wastewater treatment plants.

There is large room for further investigation to address the real potential of this technology as a system for decarbonizing natural gas. Future research must focus on the study of new sources of CO₂ which present low energy penalty and a renewable origin in order to completely close the CO₂ cycle. Furthermore, it must be tackled the current high costs of this kind of systems, and the necessity of optimize the heat management for a possible cogeneration or trigeneration integration that increases the global efficiency of the process.

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Annex A. List of institutions/companies and abbreviations

Abbreviation	Institution
AAU	Aalborg University
AB InBev	Anheuser-Busch InBev NV/SA
Abengoa	Abengoa Hidrógeno
AGH-UST	AGH University of Science and Technology
AgroPark	Agro Business Park A/S
APS	Aqua Plant Solutions GmbH
Arctik	Arctik SPRL
Atemis	Atemis GmbH
Atmostat	Atmostat
AU	Aarhus University
AU Herning	Aarhus University Department of Business Development and Technology

<i>Audi</i>	Audi AG
<i>Avedore-WWTP</i>	Avedore Wastewater Treatment Plant
<i>AVL</i>	AVL GmbH
<i>BASF</i>	BASF
<i>BEE</i>	Bau- und Entsorgungsbetrieb Emden
<i>BFP</i>	Studio Tecnico BFP srl
<i>Biofos</i>	Biofos A/S
<i>BMBF</i>	Federal Ministry of Education and Research
<i>BMUB</i>	Federal Ministry for the Environment, Nature Conservation, Building and Nuclear Safety
<i>BMWFJ</i>	Bundesministerium für Wirtschaft, Familie und Jugend
<i>BMWi</i>	Federal Ministry for Economic Affairs and Energy
<i>BTU</i>	Brandenburg University of Technology
<i>BTU-FESPE</i>	Faculty of Environmental Sciences and Process Engineering of the Brandenburg University of Technology
<i>BWB</i>	Berliner Wasserbetriebe
<i>Carbotech</i>	Carbotech
<i>CAS</i>	Chinese Academy of Science
<i>CCEM</i>	Competence Centre for Energy and Mobility
<i>CEA</i>	Atomic Energy and Alternative Energies Commission
<i>Cemtec</i>	Cemtec
<i>Chalmers</i>	Chalmers University of Technology
<i>Christof Group</i>	Christof Group
<i>Climeworks</i>	Climeworks
<i>CNH2</i>	National Centre for Hydrogen and Fuel Cell Technology
<i>Columbia University</i>	The Columbia University in the City of New York
<i>Cortus</i>	Cortus
<i>CUBE</i>	CUBE
<i>DAE</i>	Daiki Ataka Engineering Co., Ltd.
<i>DBFZ</i>	German Biomass Research Centre
<i>DBI-GUT</i>	DBI Gas-und Umwelttechnik GmbH
<i>DEA</i>	Danish Energy Agency
<i>DGC</i>	Danish Gas Technology Centre
<i>DNV GL</i>	DNV GL Group
<i>DONG</i>	DONG Energy
<i>DRI</i>	Desert Research Institute
<i>DTU</i>	Technical University of Denmark
<i>DTU-Environment</i>	Technical University of Denmark - Department of Environmental Engineering
<i>DTU-Mekamik</i>	Technical University of Denmark - Department of Mechanical Engineering
<i>DVGW</i>	Deutscher Verein des Gas- und Wasserfaches e.V.
<i>DVGW-EBI</i>	Deutscher Verein des Gas- und Wasserfaches e.V. Forschungsstelle at the Engler-Bunte Institute of KIT
<i>E.ON</i>	E.ON AG
<i>Ea</i>	Ea Energianalyse A/S
<i>EAM EnergiePlus</i>	EAM EnergiePlus GmbH
<i>Eawag</i>	Swiss Federal Institute of Aquatic Science and Technology
<i>ECN</i>	Energy Research Centre of the Netherlands
<i>EDI</i>	Energy Delta Institute
<i>EII Spa</i>	Engineering Ingegneria Informatica SPA
<i>Electrochaea</i>	Electrochaea GmbH
<i>Elplatek</i>	Elplatek A/S
<i>EMPA</i>	Swiss Federal Laboratories for Materials Science and Technology
<i>Enagas</i>	Enagás S.A.
<i>EnBW</i>	Energie Baden-Württemberg AG
<i>Energie 360°</i>	Energie 360° AG
<i>EnergieNetz</i>	EnergieNetz Mitte GmbH
<i>EnergiMidt</i>	EnergiMidt
<i>Energinet.dk</i>	Energinet.dk
<i>Energy Valley</i>	Stichting Energy Valley
<i>EPFL</i>	Swiss Federal Institute of Technology in Lausanne
<i>EPFL-CEN</i>	Energy Centre of the Swiss Federal Institute of Technology in Lausanne
<i>EPFL-IPESSE</i>	Industrial Process and Energy Systems Engineering of the Swiss Federal Institute of Technology in Lausanne
<i>EPFL-LMER</i>	Laboratory of Materials for Renewable Energy of the Swiss Federal Institute of Technology in Lausanne
<i>EPFL-LPI</i>	Laboratoire de photonique et interfaces of the Swiss Federal Institute of Technology in Lausanne
<i>Erdgas Obersee</i>	Erdgas Obersee AG
<i>Erdgas Regio</i>	Erdgas Regio AG
<i>ERIC</i>	European Research Institute of Catalysis AISBL
<i>ETH Zurich</i>	Swiss Federal Institute of Technology Zurich
<i>ETOGAS</i>	ETOGAS GmbH

<i>EWE Biogas</i>	EWE Biogas GmbH & Co. KG
<i>EWJR</i>	Elektrizitätswerk Jona-Rapperswil AG
<i>EWZ</i>	Elektrizitätswerk der Stadt Zürich
<i>FCC-Aqualia</i>	FCC-Aqualia S.A.
<i>FENES</i>	Research Centre for Power Grids and Energy Storage
<i>FFG</i>	Austrian Research Promotion Agency
<i>FGW</i>	Association of Gas and District Heating Supply Companies
<i>Fraunhofer IPM</i>	Fraunhofer Institute for Physical Measurement Techniques
<i>Fraunhofer ISE</i>	Fraunhofer Institute for Solar Energy Systems
<i>Fraunhofer IWES</i>	Fraunhofer Institute for Wind Energy and Energy System Technology
<i>GA-Group</i>	Gesellschaft für Abwasserberatung und Management mbH
<i>Gas Natural Fenosa</i>	Gas Natural Fenosa
<i>GFZ</i>	German Research Centre for Geosciences
<i>GreenHydrogen</i>	GreenHydrogen.dk
<i>Haldor Topsoe</i>	Haldor Topsoe A/S
<i>Hanze UAS</i>	Hanze University of Applied Sciences
<i>HBFZ</i>	Hessian Biogas Research Centre
<i>HIRC</i>	Hydrogen Innovation & Research Centre
<i>Hitachi Zosen</i>	Hitachi Zosen Corporation
<i>HMN Gashandel</i>	HMN Gashandel A/S
<i>HMN Naturgas</i>	HMN Naturgas I/S
<i>HMUELV</i>	Hessian Ministry of the Environment, Climate Protection, Agriculture and Consumer Protection
<i>Hokudai</i>	Hokkaido University
<i>HS Emden/Leer</i>	Hochschule Emden/Leer
<i>HS Emden/Leer-EUTECH</i>	Emden Institute of Environmental Engineering of the Hochschule Emden/Leer
<i>HSR</i>	Hochschule für Technik Rapperswil
<i>HSR-IET</i>	Institute for Energy Technology of the Hochschule für Technik Rapperswil
<i>H-Tec</i>	H-Tec Systems
<i>Hydrogenics</i>	Hydrogenics
<i>ibis Umwelttechnik</i>	ibis Umwelttechnik GmbH
<i>ICHPW</i>	Institute for Chemical Processing of Coal
<i>ICP-CSIC</i>	Institute of Catalysis and Petrochemistry
<i>IdE</i>	Institute decentralised Energy Technologies
<i>IMR</i>	Institute for Materials Research of the Tohoku University
<i>INBIOM</i>	Innovation Network For Biomass
<i>INSA</i>	Institut national des sciences appliquées de Rouen
<i>Insero</i>	Insero Business Services
<i>IoLiTec</i>	Ionic Liquids Technologies GmbH
<i>JKU Linz</i>	Johannes Kepler University Linz
<i>JKU Linz-EI</i>	Energy Institute of the Johannes Kepler University Linz
<i>Juwi</i>	Juwi AG
<i>KIT</i>	Karlsruhe Institute of Technology
<i>KTH</i>	KTH Royal Institute of Technology
<i>KWB</i>	Berlin Centre of Competence for Water
<i>Lemvig Biogas</i>	Lemvig Biogas Amba
<i>Maabjerg BioEnergy</i>	Maabjerg BioEnergy A/S
<i>MES</i>	Mitsui Engineering and Shipbuilding Co.
<i>MicroEnergy</i>	MicroEnergy GmbH
<i>MINECO</i>	Ministry of Economy and Competitiveness
<i>MIT</i>	Massachusetts Institute of Technology
<i>MU Leoben</i>	University of Leoben
<i>MWFK</i>	Ministerium für Wissenschaft, Forschung und Kultur
<i>MWK</i>	Ministerium für Wissenschaft und Kultur
<i>NEAS</i>	NEAS Energy
<i>NGF</i>	Naturgas Fyn I/S
<i>NREL</i>	National Renewable Energy Laboratory
<i>NRIM</i>	National Research Institute for Metals
<i>NTUA</i>	National Technical University of Athens
<i>NU</i>	Northwestern University
<i>Outotec</i>	Outotec
<i>ÖGW</i>	Austrian Association for Gas and Water
<i>Panta Rhei</i>	Panta Rhei GmbH
<i>PlanEnergi</i>	PlanEnergi.dk
<i>PolTo</i>	Politecnico di Torino
<i>Profactor</i>	Profactor GmbH
<i>PSI</i>	Paul Scherrer Institute

<i>PTTEP</i>	PTT Exploration and Production Public Company Limited
<i>Rafako</i>	Rafako S.A.
<i>RCO2 AS</i>	RCO2 AS
<i>Regio Energie</i>	Regio Energie Solothurn
<i>RUG</i>	University of Groningen
<i>Ryoka</i>	Ryoka Matthey Corporation
<i>SCCER-HaE</i>	Swiss Competence Centre for Energy Research - Heat and Electricity Storage
<i>Schmack</i>	Schmack Biogas GmbH
<i>SDU</i>	University of Southern Denmark
<i>SFOE</i>	Swiss Federal Office of Energy
<i>SNSF</i>	Swiss National Science Foundation
<i>SoCalGas</i>	Southern California Gas Company
<i>Stadtwerke Emden</i>	Stadtwerke Emden GmbH
<i>Stedin</i>	Stedin
<i>StMWi</i>	Bavarian Ministry of Economic Affairs, Infrastructure, Transport and Technology
<i>Sunfire</i>	Sunfire GmbH
<i>Sustec</i>	Sustec Consulting & Contracting BV
<i>Tauron</i>	Tauron Group
<i>Tecnalia</i>	Tecnalia
<i>Thalen Consult</i>	Thalen Consult GmbH
<i>TKI Gas</i>	TKI Gas
<i>TMLFUN</i>	Thuringian Ministry for Agriculture, Forestry, Environment and Nature Conservation
<i>Tohoku University</i>	Tohoku University
<i>TohTech</i>	Tohoku Institute of Technology
<i>TS-Torino</i>	Turbo Service Torino spa
<i>TU Berlin</i>	Technische Universität Berlin
<i>TU Wien</i>	Vienna University of Technology
<i>TU-Delft</i>	Delft University of Technology
<i>UBA</i>	Umweltbundesamt
<i>Uchicago</i>	The University of Chicago
<i>UM</i>	University of Montreal
<i>UM-DMI</i>	University of Montreal - Department of Microbiology and Immunology
<i>Uni-Postdam</i>	University of Potsdam
<i>Uni-Regensburg</i>	Universität Regensburg
<i>Vattenfall</i>	Vattenfall Europe Generation AG
<i>Veolia</i>	Veolia Deutschland GmbH
<i>Veolia-WT</i>	Veolia Water Technologies AB
<i>Viessmann</i>	Viessmann Group
<i>VSG</i>	Verband der Schweizerischen Gasindustrie
<i>WT & T Polska</i>	West Technology & Trading Polska Sp. Z o. o.
<i>Xergi</i>	Xergi A/S
<i>Zeochem</i>	Zeochem AG
<i>ZHAW</i>	Zurich University of Applied Sciences
<i>ZSW</i>	Centre for Solar Power and Hydrogen Research Baden-Württemberg
<i>ZVKSW</i>	Zweckverband Verbandskläranlage Schwandorf-Wackersdorf

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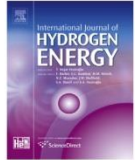
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Power to gas-oxyfuel boiler hybrid systems

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ABSTRACT

One of the main future energy challenges is the management of electrical supply and demand, mainly motivated by the increase of share renewable energy in electricity mix. Thus, energy storage represents a crucial line of research and innovative solutions are currently being proposed. Power to Gas is a technology which stores excess of electrical energy in form of synthetic natural gas through the methanation of hydrogen produced by electrolysis. Methanation requires a source of CO₂ which could be provided from the flue gas of an oxyfuel boiler. A further advantage of this hybridization comes from the supply of the oxygen generated by electrolysis to the oxyfuel combustion. In this study the concept is simulated using Aspen Plus[®] software and the performance of the combined system is analysed through the definition of a size ratio, ξ_{oxy} , that relates the flow of renewable hydrogen produced in electrolyser and the thermal output of the boiler. This variable has allowed defining different ranges of operation for a PtG-oxycombustion hybridized plant. Thus, for ξ_{oxy} of 1.33, the air separation unit required as an auxiliary element for the oxyfuel boiler becomes unnecessary while if this ratio is increased up to 2.29, flue gas is completely consumed in the methanation plant and converted to synthetic natural gas.

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Introduction

The constant increase of the renewable energy share in energy markets brings about the appearance of mismatches between supply and electrical demand which affect to security and stability of the grid [1]. The accommodation of energy production with consumption has become a critical challenge for future society that is being tackled by developing innovative energy storage solutions [2].

The low energy density and limited storage potential of pumped hydroelectric storage, compressed air energy storage,

flywheels and batteries, make Power to Gas technology one promising option to overcome these limitations [3]. PtG converts electricity in synthetic natural gas that may substitute fossil fuels or be injected into the natural gas network which would be used as storage infrastructure [4]. In this way, electric and gas networks would be connected as a unique energy system increasing the flexibility of the energy supply [5].

In a generic PtG system, the conversion of electricity is strictly carried out by an electrolyser which produces hydrogen. The consumption of this gas through Sabatier chemical reaction (Eq. (1)) produces methane and the synthetic natural gas is obtained. The global process is carried out

Abbreviations: ASU, air separation unit; FG, flue gas; LHV, lower heating value; M1, methanator 1; M2, methanator 2; M3, methanator 3; PtG, power to gas; SNG, synthetic natural gas.

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through two consecutive reactions: inverse water-gas shift reaction (Eq. (2)) and CO methanation (Eq. (3)) [6].



Eq. (2) is an endothermic reaction which requires the presence of a catalyst to take place at low temperatures. It promotes conversion to methane in Eq. (3).

Additionally, when the power input to the electrolyser is supplied by renewable energy sources, the obtained SNG will be neutral in CO₂ emissions. The same amount of CO₂ that will be emitted through SNG combustion is required and consumed during its synthesis process.

Different PtG concepts such as hybridization with air separation plants, biogas plants, biomass gasification, sewage plants, fossil power plants or industrial processes have been proposed to obtain the source of carbon dioxide [5]. Two main issues in the PtG systems are the utilization of the residual oxygen produced by electrolysis and the consumption of energy to attain a concentrated stream of CO₂.

Some of the major projects in the world related to methanation (MeGa-stoRE 4.7 MW [7], Erdgas Schwaben 1.0 MW [8], and P2G-BioCat 1.0 MW [9]) upgrade biogas to obtain SNG without previous CO₂ separation, but oxygen from electrolyser do not have a final use. Biomass gasification and sewage plants would solve both issues since oxygen may be used as gasification agent or for the activation of sludge [5]. However, syngas from gasification achieves hydrogen content above 60% and further hydrogen addition is barely needed limiting energy storage potential [7]. Additionally, sewage plants produce poor syngas whose conversion to SNG is relatively expensive. Thus, it is currently preferred to burn this gas in engines for self-consumption [10].

Hence, a suitable option for taking advantage of produced oxygen would be the hybridization of PtG with oxyfuel combustion. In an oxyfuel combustion, a mixture of oxygen and recycled flue gas acts as comburent [11]. Thus, oxygen from electrolyser would reduce the electrical consumption of the required air separation unit, and CO₂ would be taken from the boiler flue gas without extra energy penalty in its separation.

The objective of the study is to determine the global efficiency that would have this hybrid system, the flows of generated SNG and stored CO₂ and other potential variations in the efficiencies of specific elements of the installation as a function of electric power consumption in electrolyser. In addition, the operating ranges for an oxyfuel combustion plant hybridized with Power to Gas technology will be determined highlighting the most convenient size ratios between oxyfuel and PtG plants.

The model and simulation of the proposed concept has been performed under steady state of operation, considering that it will work at full load most part of the year. In Spain, France and Germany, energy loss due to curtailment of wind-generated energy remained under 1% of total wind production during 2010, 2011 and 2012 [11]. Thus, operation of PtG must not be limited to operate with the surplus of electricity from renewable sources. It should be understood as a method for

continuous production of SNG and a sink of CO₂ emissions although the proposed concept may also be applied for energy storage.

Hybrid system description and calculation methods

In this section, a thorough description of the hybrid PtG-Oxyfuel boiler system is presented together with the most important interactions between technologies. The input data to the Aspen Plus® simulation engine as well as the chosen calculation methods are also described. Buchholz et al. investigated the combination of a PtG plant and conventional lignite fired power plant [12]. However, no previous analyses of the combined system PtG and oxyfuel boiler with thermal purposes are found in literature. Thus, the efficiencies of the single elements and the hybrid concept are still to be defined.

Description of the hybrid concept

Fig. 1 illustrates the schematic diagram of the hybrid concept. In order to allow for continuous operation, the system is designed to be fed with a constant power input. A source of renewable energy supplies power to electrolysers which store this renewable energy as hydrogen also producing oxygen as a by-product. This amount of oxygen may partially or completely cover the comburent demand in the oxyfuel boiler, increasing the efficiency of this process since the ASU power consumption is reduced. Additionally, methanation takes place between the flue gas from the oxyfuel thermal plant (basically CO₂ and O₂) and the hydrogen from electrolysis to produce synthetic natural gas.

Besides the heat recovered from the oxyfuel boiler, a significant amount of thermal energy is released from the exothermic reaction in methanators and the intercooling stages in compression trains. This extra available heat could be integrated in external thermal processes or in the hybrid concept itself.

Hybrid system modelling with Aspen Plus®

The proposed scheme for the hybridization between oxy-combustion and PtG technologies has been modelled with Aspen Plus® under industrial conditions for steady state operation and chemical equilibrium. In the following, information on the model of each significant element in the system is presented.

Coal is selected as input material for the oxyfuel combustion process since it represents the most extended fossil fuel for thermal energy supply in industry [13]. The ultimate analysis of coal is presented in Table 1.

Oxyfuel combustion plant

Fig. 2 illustrates a scheme of the model developed in Aspen Plus® for the oxyfuel plant. Fuel and comburent are introduced into the boiler to reach chemical equilibrium by minimizing Gibbs free energy.

Flue gas passes through the heat exchangers where steam is produced reducing its temperature down to 270 °C. This

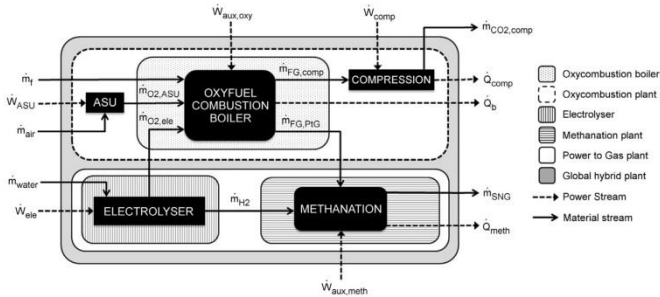


Fig. 1 – Scheme of the hybrid power system.

energy corresponds to the useful output thermal power of the oxyfuel boiler, \dot{Q}_b . Then, flue gas is cooled down to 190 °C to preheat the comburent up to around 150 °C. Once ashes and sulphur compounds are removed, 80% of gas is recirculated to the boiler and the remaining is directed to CO₂ compression stage or to methanation process. Large content of water in the recirculated flue gas must be avoided. Thus, a condensation stage is located prior comburent mixing for oxyfuel applications. The comburent is mainly composed by oxygen from ASU, oxygen from electrolyser and preheated recirculated flue gas. The air separation unit module provides pure oxygen at 15 °C and 1 bar. According to literature, its electrical consumption is assumed to be 190 kWh/tO₂ [14]. The oxygen excess in the boiler is set as 15% and it accounts for the oxygen from ASU and electrolyser.

CO₂ compression stage

The stream of concentrated CO₂ from oxyfuel combustion which is not reused in methanation stage is directed to the compression train to be transported and stored. The train consists of three compressors with pressure ratios of 3.5 and another one with pressure ratio of 3.0, which reaches a final pressure of 111.4 bar. Additionally, there exist four intermediate condensers to remove water, leading to a final CO₂ purity of 94.2%. These intercoolers reduce the temperature of CO₂ stream down to 40 °C.

Electrolyser

The power from a renewable source is modelled as an energy input to the electrolyser module. By varying this input, the amount of produced hydrogen will be modified, and consequently the percentage of flue gas directed to the PtG process,

the flow of generated SNG, and the global hybrid system operation efficiency.

Alkaline electrolyser has been modelled by programming a user-defined subroutine in Aspen Plus®. The inlet electric power and the inlet water stream are the initial variables for the external calculations. This block splits water in two mass flows of pure oxygen and a mixture of hydrogen with unreacted water. Based on literature, the water conversion is assumed to be 99.9% with an electrical consumption range from 4.3 to 4.9 kWh/Nm³H₂ and an outlet temperature of 80 °C [15,16]. These operation conditions leads to an efficiency range of the electrolyser unit, $\eta_{H_2V} = 61.2 - 69.7\%$.

Methanation plant

The proposed scheme of methanation is based on TREMP™ process of Haldor Topsøe, which manages three adiabatic reactors at 30 bar with one recirculation on the first methanator [17]. It makes use of high temperature catalysts to reduce the cooling requirements in the reactors and diminish the recirculated flow while also the extra-thermal energy production can be recovered as high pressure steam [18].

The main target of the methanation plant is to achieve methane molar fractions above 95% in the SNG to inject it

Table 1 – Ultimate analysis of coal for oxycombustion [% w.b.].

C	H	O	N	S	M	Z	LHV [MJ/kg]
66.1	3.6	7.1	1.6	0.6	8.6	12.4	25.4

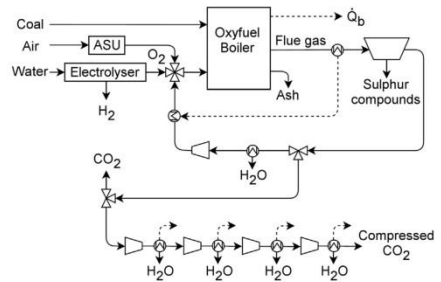


Fig. 2 – Oxyfuel combustion plant model.

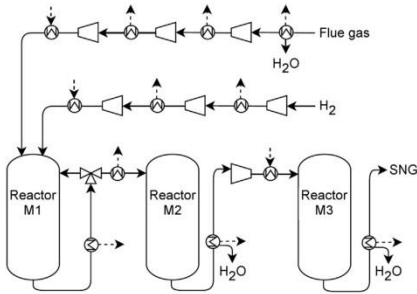


Fig. 3 – Methanation plant model.

into the natural gas network. This threshold concentration corresponds to Spanish legislation for natural gas composition [19]. The proposed configuration, shown in Fig. 3, consists of three adiabatic reactors and an intermediate condensation stage, which operate at 30 bar and temperatures between 250 °C and 550 °C. Reactor blocks (M1, M2 and M3) calculate the composition and temperature of outlet gas streams, at equilibrium state, minimizing Gibbs free energy in an adiabatic process.

The flue gas flow from oxyfuel combustion directed to methanation process is determined by electrical power consumption in electrolyser, and CO₂ and O₂ concentration in flue gas. Since the presence of oxygen in flue gas would poison the catalysts [20], it must be consumed through a controlled combustion with part of the generated hydrogen. A constant H₂:CO₂ molar ratio of 4 has been set at the inlet of the first reactor (Eq. (1)). These two conditions are used to derive Eq. (4) and calculate the percentage of flue gas directed to methanation, ϕ_{FGM} . The last parameter, $\dot{n}_{CO_2, Loss}$, corresponds to the CO₂ lost with water in the condensation stage prior the compression train, which is needed since a large presence of steam inhibits methanation reaction.

$$\phi_{FGM} = 100 \left[\left(y_{CO_2, FG} + \frac{1}{2} y_{O_2, FG} \right)^{-1} \left(\frac{\dot{n}_{H_2}}{4} + \dot{n}_{CO_2, Loss} \right) \right] \quad (4)$$

Both, hydrogen and flue gas are passed through two compression trains with intermediate heat recoveries reaching the operation pressure of the process (30 bar) prior the first methanator. The intercooling temperature is limited to 120 °C since a subsequent preheating up to 300 °C is required [21].

The syngas is cooled down to 300 °C after Reactor 1, M1. Most of the SNG outlet stream is recirculated to maintain the temperature near 550 °C, since the loss of active surface area by atom migration sintering mechanism becomes important above 600 °C [22].

Then, the temperature of the stream is reduced to 250 °C before entering Reactor 2, M2, promoting the upgrade of the syngas. Lower inlet temperatures are typical in second and following methanators of commercial SNG processes like TREMP® [23].

At the exit of Reactor 2 syngas stream is cooled down and steam content is partially condensed to avoid the inhibition of the reaction of methanation. However, it must be taken into account that an excessively low steam molar fraction could generate solid carbon depositions during methanation [6]. In addition, since steam content has been largely reduced, the pressure (30 bar) and temperature (250 °C) must be recovered prior the third methanation step.

The third reactor, M3, also operates without recirculation since sufficiently high pressures favours methane formation. The outlet stream is cooled down to 40 °C to condense steam and reach a purity of methane over 95%.

Definition of partial and global efficiencies

The partial energy efficiencies of the independent elements and the efficiency of the subsystems are defined through the following equations: Eq. (5) corresponds to the boiler efficiency; Eq. (6) defines the efficiency of the oxycombustion subsystem where compression train is included; Eq. (7) presents the efficiency of the electrolyser; methanation plant efficiency is calculated through Eq. (8) and, finally, Eq. (9) expresses the efficiency of the PtG subsystem. These are the ratios between useful energy output and energy input for the different control volumes of the systems established in Fig. 1.

$$\eta_b = \frac{\dot{Q}_b}{LHV_f \dot{m}_f + \dot{W}_{aux, oxy}} \quad (5)$$

$$\eta_{oxy} = \frac{\dot{Q}_b}{LHV_f \dot{m}_f + \dot{W}_{aux, oxy} + \dot{W}_{comp} + \dot{W}_{ASU}} \quad (6)$$

$$\eta_{ele} = \frac{LHV_{H_2} \dot{m}_{H_2}}{\dot{W}_{ele}} \quad (7)$$

$$\eta_{meth} = \frac{LHV_{SNG} \dot{m}_{SNG}}{LHV_{H_2} \dot{m}_{H_2} + \dot{W}_{aux, meth}} \quad (8)$$

$$\eta_{PtG} = \frac{LHV_{SNG} \dot{m}_{SNG}}{\dot{W}_{ele} + \dot{W}_{aux, meth}} \quad (9)$$

Auxiliary work of the methanation plant includes the consumptions of flue gas and H₂ compression trains, and preheating and cooling systems.

The global efficiency of the hybrid plant is given by Eq. (10). Depending on the operation strategy of the system some of the parameters in the equations may be neglected.

$$\eta_{PtG+oxy} = \frac{\dot{Q}_b + LHV_{SNG} \dot{m}_{SNG}}{LHV_f \dot{m}_f + \dot{W}_{aux, oxy} + \dot{W}_{comp} + \dot{W}_{ASU} + \dot{W}_{ele} + \dot{W}_{aux, meth}} \quad (10)$$

Results and discussion

The results obtained in the performed analysis are divided into four main points that are separately discussed: (i) determination of the Power to Gas plant operation point, (ii) study of the operation ranges of the hybrid system, (iii) analysis of

energy efficiencies and (iv) quantification of produced SNG and avoided CO₂.

Operation point of the power to gas plant

Four parameters control the process in the PtG plant; two of them, the initial H₂:CO₂ molar ratio and the inlet temperature to reactors are kept constant. The molar ratio is fixed to preserve the stoichiometry of reaction (Eq. (1)) and the optimal operation temperature for the commercial catalysts [24]. The two remaining variables are the amount of steam condensed in the intermediate condensation stage, and the recirculation in Reactor 1, M1. Recirculation controls operation temperature inside the reactor, producing changes in the equilibrium constants and outlet concentrations; the lower temperature, the more enhanced methanation [6].

Reducing steam content also displaces equilibrium towards methane production. However, there exists a lower limit for steam concentration since solid carbon deposition may occur in the reactors inhibiting the catalysts [6,20]. This limitation points out the existence of a threshold for minimum condensation temperature in the intermediate stage which determines the amount of removed water. The deposition of solid carbon per kilogram of hydrogen produced in the electrolyser is calculated in Aspen Plus® as a function of the condenser temperature and the recirculation in Reactor 1 and illustrated in Fig. 4. The temperature must be set over 125.5 °C to ensure the avoidance of solid carbon deposition for 90% of M1 recirculation; it was kept in 130.0 °C. The specific deposition of solid carbon per unit of kW consumed in electrolyser remains constant for different sizes of electrolyser, since the deposited amount is proportional to the syngas flow and, thus, to the electrolyser power. In Fig. 4, carbon deposition is normalized with respect to the amount of generated hydrogen to avoid the influence of electrolyser efficiency.

The recirculation in Reactor 1 is fixed to achieve a minimum 95% of purity of methane in the final SNG [19]. It should be noted that methane concentration will depend on the composition of oxyfuel boiler flue gas and, therefore, on the type of coal fed to the boiler. In this case, a minimum

recirculation of 79.75% is needed to achieve methane molar fractions above 95% (see Fig. 5). The chosen point of operation recirculates 80.5%, thus, small variations on recirculated stream will not reduce methane content below 95%.

Under these conditions of operation for the Power to Gas subsystem, the molar composition of the obtained SNG is 95.17% methane, 2.48% hydrogen, 1.01% carbon dioxide, 1.00% nitrogen and 0.32% water.

Operation ranges of the hybrid system

The hybridized plant is characterized by a high reutilization of by-products that modifies auxiliary works, available heats and required equipment. Hence, the operation of the entire system will vary depending on the relative amount of energy sent to the electrolyser. The best approach to analyse the performance of the system is to define the ratio between energy contained in the hydrogen produced by electrolysis and net thermal power produced in the oxyfuel boiler. The behaviour of the system keeps constant for a fixed ratio even if scale is modified. Scale effects in the hybrid system would mainly affect heat exchanger network and pressure drop; both may be neglected for the scope of this analysis. The ratio of the hybrid system may be expressed as shown in Eq. (11).

$$\xi_{oxy} = \frac{LHV_{H_2} \cdot \dot{m}_{H_2}}{Q_b} \left[\frac{kW_{H_2}}{kW_{th}} \right] \quad (11)$$

The main benefit of the hybridization between PtG and oxyfuel combustion is to substitute completely or partially the ASU unit with oxygen by-produced in electrolysis. In Fig. 6, the variation of the specific electric power consumption of ASU (\dot{W}_{ASU}/\dot{Q}_b) versus ξ_{oxy} is illustrated. The minimum required ratio between electrolyser and boiler outputs to avoid the ASU is denoted by ξ_{ASU} and a value of 1.33 has been obtained through simulation. The consumption of flue gas at this operation point is 57.9%, and in order to achieve a total utilization of the CO₂ generated in the oxyfuel boiler, a ratio of 2.29 is necessary (denoted by ξ_{CO_2}).

Depending on electrolyser efficiency (61.2–69.7% [15,16]), the specific consumption of electrolysis lie on the range

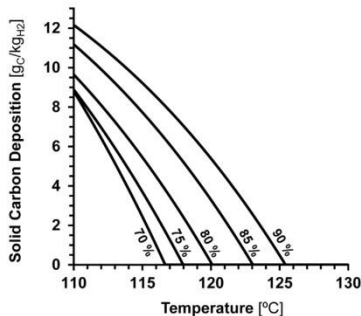


Fig. 4 – Specific deposition of solid carbon vs. condensation temperature and M1 recirculation.

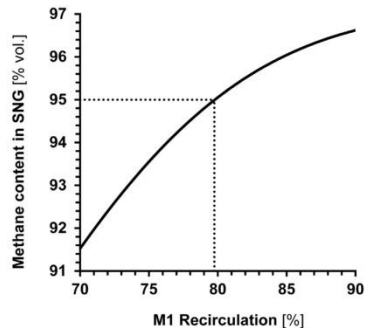


Fig. 5 – Methane molar fraction vs. recirculation.

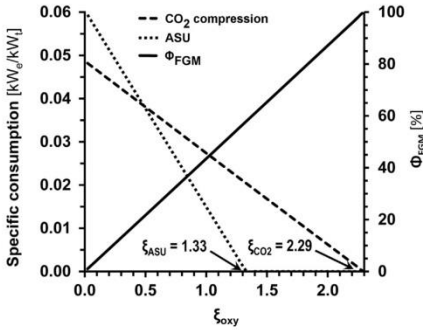


Fig. 6 – Specific consumptions and percentage of consumed flue gas vs. ξ_{oxy} .

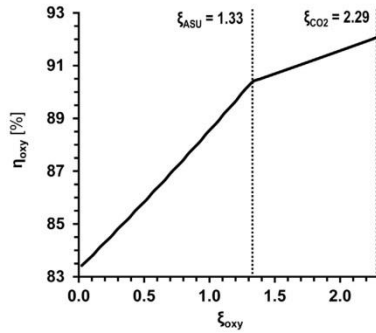


Fig. 7 – Oxyfuel plant efficiency vs. ξ_{oxy} .

1.91–2.17 $\text{kW}_e/\text{kW}_{th}$, for operation point ξ_{ASU} , and between 3.29 and 3.74 $\text{kW}_e/\text{kW}_{th}$ for ξ_{CO_2} .

Auxiliary work on hybrid oxycombustion plant is mainly related to the recirculation of flue gas to the boiler, so it is independent of the electricity supplied to the Power to Gas subsystem, with a constant value of $2.7 \cdot 10^{-3} \text{ kW}_e/\text{kW}_t$. Methanation auxiliary work, $\dot{W}_{aux,meth}$, linearly increases with ξ_{oxy} from zero to its maximum value at ξ_{CO_2} , 0.205 kW_e/kW_t , and it includes compression train (89.8%), preheating (6.0%) and cooling requirements (4.2%).

Analysis of partial and global efficiencies

The efficiencies of the different elements in the hybrid system are calculated from the previously defined equations (Eq. (5)–(9)) and presented in Table 2 together with other relevant ratios for different representative values of ξ_{oxy} .

The oxyfuel boiler operates at constant conditions of comburent excess ratio, temperatures and fuel composition and depends on the size ratio since the sources of oxygen will be different depending on the relative size of electrolyser and boiler. It presents values in the range of 91.6–92.1% for the simulated cases.

However, the energy efficiency of the oxyfuel subsystem increases rapidly while ASU is required since there is a strong reduction of its electrical consumption for larger ξ_{oxy} , Fig. 7. Between ξ_{ASU} and ξ_{CO_2} , the efficiency grows more slowly since only the CO_2 compression stage diminishes its consumption in this range of operation. Above ξ_{CO_2} , neither ASU nor

compression consume power therefore the efficiency of the oxyfuel plant achieves its initial value and remains constant.

In the PtG subsystem, electrolysis efficiency may vary between 61.2% and 69.7% [15,16] depending on the selected technology, whilst methanation performance remains invariable with size ratio since it depends on its design. Hence, η_{PtG} varies from 45.5 % to 51.5 %, depending on electrolyser efficiency.

Finally, the performance of the hybrid plant decreases with ξ_{oxy} since the efficiency of the Power to Gas subsystem is lower than the efficiency of the oxyfuel boiler. Thus, the greater is the share of PtG in the hybrid system; the lower is the hybrid energy efficiency. Fig. 8 illustrates this effect for a range of electrolyser consumption.

The variations in energy efficiency introduced by the electrolysis performance becomes more significant at higher values of ξ_{oxy} , since its influence is larger, whilst at lower ratios it barely affects. At ξ_{ASU} and ξ_{CO_2} , overall efficiency lies between 59.8 and 65.0 %, and 55.5–61.1 %, respectively.

The results obtained in this study may be applied to choose the most convenient sizes and operation ranges for large and small scale of the hybrid system. For small scale facilities (0–100 kW), CO_2 emissions are a less relevant factor and size factors around 1.33 will be operative. Hence, the facility takes advantage of the suppression of ASU necessity without an excessive expenditure for a larger electrolyser. Large scale facilities will be more sensitive to the importance of CO_2 emissions and, in the medium term, they might be regulated with the compulsory installation of carbon capture systems. Under this scenario, the operation range will lie around size

Table 2 – Main parameters and efficiencies of the hybrid system.

ξ_{oxy} [–]	Φ_{FGM} [%]	\dot{W}_{ASU}/\dot{Q}_b [kW_e/kW_t]	\dot{W}_{comp}/\dot{Q}_b [kW_e/kW_t]	$\dot{W}_{aux,meth}/\dot{Q}_b$ [kW_e/kW_t]	η_b [%]	η_{oxy} [%]	η_{meth} [%]
0.00	0.0	0.060	0.049	0.000	91.6	83.4	–
1.00	43.5	0.015	0.027	0.089	92.0	88.5	72.0
1.33	57.9	0.000	0.020	0.119	92.1	90.3	72.0
2.29	100.0	0.000	0.000	0.205	92.1	92.1	72.0

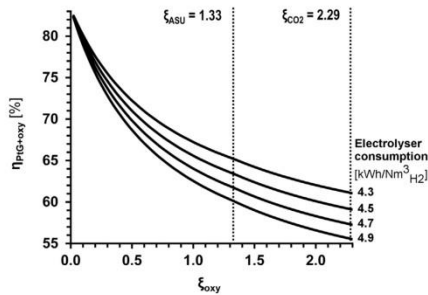


Fig. 8 – Overall efficiency of the hybrid system vs. ξ_{oxy} .

factors of 2.29 since greater size ratios would generate a hydrogen excess and CO_2 lack.

CO_2 emissions and SNG produced

The carbon dioxide produced during oxyfuel combustion can be stored or used in methanation, depending on the size ratio of the system, ξ_{oxy} . When PtG is not included in the system, $\xi_{oxy} = 0$, a flue gas flow of $367.2 \text{ kg}_{\text{CO}_2}/\text{MW}_{\text{th}} \cdot \text{h}$ is sent to compression. This amount linearly diminishes to zero as ξ_{oxy} grows, until it reaches ξ_{CO_2} and produced CO_2 emissions are completely conducted into the methanators. In the intermediate operation point ξ_{ASU} , only $153.9 \text{ kg}_{\text{CO}_2}/\text{MW}_{\text{th}} \cdot \text{h}$ have to be compressed and transported for storage since the rest is processed in methanation stage.

Similarly, specific synthetic natural gas generated increases linearly with ξ_{oxy} . For ξ_{ASU} , $78.5 \text{ kg}_{\text{SNG}}/\text{MW}_{\text{th}} \cdot \text{h}$ are produced whilst the maximum achievable value corresponds to the operational point ξ_{CO_2} , $135.2 \text{ kg}_{\text{SNG}}/\text{MW}_{\text{th}} \cdot \text{h}$. The lower heating value of the SNG produced in the simulated system is $47.7 \text{ MJ}/\text{kg}_{\text{SNG}}$, therefore, the maximum energy that can be stored consuming the carbon dioxide from the oxyfuel combustion is 1.8 MWh per thermal MWh produced in the boiler.

Conclusions

The potential storage of energy by means of PtG hybridization, through the combination of a methanation plant and an oxycombustion coal boiler, has been proposed and analysed. This hybridization takes advantage of the O_2 produced in the electrolyser and overcome the penalty of CO_2 capture required for the Sabatier reaction. It is concluded that represents an interesting option for energy supply and energy storage in a medium term. The parameter used to characterize the system is the size ratio, ξ_{oxy} , which represents the energy contained in the hydrogen produced in the electrolyser divided by the net thermal power produced by the oxyfuel boiler. The results obtained from the Aspen Plus[®] simulation of both subsystems have allowed defining different strategic ranges of operation for a PtG-oxycombustion hybridized plant. Thus, when

$\xi_{oxy} = 1.33$, the ASU becomes unnecessary and CO_2 consumed in methanation reaches the 57.9% of total flue gas from the boiler. If ξ_{oxy} is increased up to 2.29, then flue gas is completely reused and converted to SNG. The continued augmentation of ξ_{oxy} from 0 to 2.29 leads to an increment in oxyfuel combustion plant efficiency, due to the suppression of ASU and CO_2 compression stage consumptions. However, the efficiency of the hybrid system decays with ξ_{oxy} since PtG presents a lower efficiency than oxycombustion process and the increment of PtG share in the system acts as a penalty. The evaluation of the annual plant performance (considering 7000 h/yr operation) reveals that $1493 \text{ t}_{\text{CO}_2}/\text{MW}_{\text{th}}$ and $2570 \text{ t}_{\text{CO}_2}/\text{MW}_{\text{th}}$ could be avoided by the system operated at ξ_{ASU} and ξ_{CO_2} , respectively. The hybridization could also save those CO_2 emissions associated to the ASU electric consumption which corresponds to 422.8 MWh per net MW_{th} of the boiler. Furthermore, through the processing of this carbon dioxide flow, $549.5 \text{ t}_{\text{SNG}}/\text{MW}_{\text{th}}$ and $946.4 \text{ t}_{\text{SNG}}/\text{MW}_{\text{th}}$ would be yearly generated at ξ_{ASU} and ξ_{CO_2} .

Acknowledgements

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Nomenclature

Variables

LHV	lower heating value, kJ/kg
M	moisture
\dot{n}	molar flow, kmol/s
\dot{Q}	thermal power, kWt
R	recirculation percentage in methanation reactors, %
\dot{W}	electric power, kW
y	molar fraction, –
Z	ashes
η	efficiency [%]
ξ_{oxy}	ratio between electrolyser power and boiler net output, kWe/kWt
ϕ_{FGM}	percentage of flue gas directed to methanation, %

Subscripts

air	input air to ASU
ASU	air separation unit
aux	auxiliary consumption
b	boiler
CO_2	carbon dioxide
comp	CO_2 compression train
ele	electrolyser
f	fuel
FG	flue gas
H_2	hydrogen
Loss	losses in condensation phase at point (2c) in Fig. 4
meth	methanation
O_2	oxygen
oxy	oxycombustion plant
PtG	power to gas

PtG + oxy power to gas-oxycombustion hybrid system
 ref reference state
 th thermal energy
 water input water to electrolyser

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Power to Gas–biomass oxycombustion hybrid system: Energy integration and potential applications



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HIGHLIGHTS

- A novel PtG–biomass oxyfuel boiler hybrid system is studied.
- Most suitable potential applications are district heating and industries.
- Available extra thermal energy is integrated to increase overall efficiency.
- Overall efficiency may be increased in a 29.7%.

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ABSTRACT

A promising hybridization which increases the chances of deployment of Power to Gas technology is found in the synergy with oxycombustion of biomass. This study assesses the efficiency of an energy integrated system under different sizes and potential applications. District heating and industrial processes are revealed as the most suitable potential applications for this hybrid technology. Global efficiency of the combined system may be increased through thermal energy integration. The relative increment of efficiency achieved for those designs which avoid the requirement of an air separation unit and for those which completely consumed the generated CO₂, are 24.5% and 29.7% respectively. A 2 MW_{th} district heating case study is also analysed, revealing that 81.2% of the total available heat from the PtG–oxy system could be integrated raising the global efficiency up to 78.7% at the adequate operational point. Further ‘full-fuel-cycle’ analysis will be required prior to decide the interest of the concept under a specific scenario in comparison to other available energy storage technologies.

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1. Introduction

In the mid-term, one of the most promising energy storage technologies might be the Power to Gas (PtG) process [1]. Strictly, renewable electricity is converted to fuel gas by means of electrolysis, storing electrical energy in form of hydrogen. Then, the generated H₂ can be combined with carbon dioxide to produce methane through the Sabatier reaction [2].



The availability of a suitable source of CO₂ is the main limiting factor when assessing the potential of Power to Gas deployment in a region; reducing considerably the geographic location possibilities for this technology [3]. Therefore, the access to a continued carbon dioxide flow to be fed to the PtG process becomes a crucial issue that must be properly addressed.

Biogas plants, waste managers, industries and power plants are the largest CO₂ sources and the most interesting partners for integration with PtG [4]. Nevertheless, attention must be focused on the last two options since their efficiencies will be strongly penalized when the operation of carbon separation technology is accounted.

Biogas is mainly composed by methane (50–85%) and carbon dioxide (15–50%) [5], so a direct conversion of CO₂ without previous separation is possible, avoiding the energy penalty associated to carbon capture. Due to this advantage, some of the major PtG projects in the world perform directly the methanation of the biogas (McGa-store 4.7 MW [6], Erdgas Schwaben 1.0 MW [7], and P2G-BioCat 1.0 MW [8]). Similarly, waste management plants

Abbreviations: 4GDH, 4th Generation District Heating; ASU, air separation unit; DH, district heating; DHW, domestic hot-water; LHV, lower heating value; M, moisture; M1, methanator 1; M2, methanator 2; M3, methanator 3; PtG, Power to Gas; SNC, synthetic natural gas; Z, ash.

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Coal was selected as input material since it represents the most extended fossil fuel for thermal energy supply in industry [14]. However, in order to achieve an entirely renewable system, it has been replaced by biomass (Table 1). The substitution of the fuel in the oxycombustion boiler directly influences on the operation ranges since carbon, oxygen and water contents in the fuel composition differ significantly. Furthermore, the use of biomass implies other technical risks that should be considered in the design of the installation such as structural changes in flames that impose shorter particle sizes in biomass oxycombustion [15] or higher H₂O concentrations inside the combustion chamber [16]. However, the study of these issues are beyond the scope of this paper.

The entire hybrid system has been modelled in Aspen Plus[®] by combining and interconnecting an oxyfuel boiler, a CO₂ storing-compression train, an electrolyser and a methanation plant. The oxyfuel boiler is assumed to operate with 15% of oxygen excess provided by three available sources of O₂, namely, ASU, electrolyser and recirculated flue gas.

The CO₂ train consists of three compressors with pressure ratios of 3.5 and a fourth one with pressure ratio of 3.0, achieving a final pressure of 91.9 bar. To improve the efficiency of compressors, four intercoolers are installed between compression stages for recovering some thermal energy which might be integrated. The temperature of the gas flow is reduced down to 40 °C in every stage, thus removing water too and providing a final high purity CO₂ stream (95.6 vol%).

The electrolyser was modelled by programming a user-defined subroutine in Aspen Plus[®]. Based on literature, water conversion is above 99.9% with an electrical consumption range from 4.3 to 4.9 kWh/N m³ H₂ and an operation temperature around 80 °C [18,19]. The influence of the electrolyser efficiency in the overall performance of the hybrid plant was already studied in a previous work [13]. In this case, the consumption is set on 4.4 kWh/N m³ H₂ ($\eta_{\text{elect,LHV}} = 61.8\%$) since it does not have any influence in the scope of the present study, the available heat by-produced during the process.

Finally, methanation plant is designed to achieve a methane molar fraction above 95% in the final SNG, which corresponds with the threshold concentration in Spanish legislation for injection in the Natural Gas grid [20]. The proposed scheme, shown in Fig. 2, is similar to the original TREMP[®] process of Haldor Topsøe [21]. It manages three adiabatic reactors at 30 bar with an intermediate condensation stage and a recirculation over the first methanator.

To calculate the percentage of flue gas directed to methanation, ϕ_{FGM} , two system conditions must be taken into account. Firstly, a constant H₂:CO₂ molar ratio of 4 is set at the inlet of the reactor M1 according to the stoichiometry of Eq. (1). Then, the presence of oxygen entering the methanator should be avoided since it would poison the catalysts [22]. Thus, it is consumed by a controlled combustion with a small amount of the hydrogen from electrolysis. These two conditions are used to derive Eq. (3). The last parameter, $\tilde{n}_{\text{CO}_2, \text{loss}}$, refers to the CO₂ lost with water in the condensation stage prior the first reactor. Water is removed from the system since a large presence of steam inhibits methanation reaction.

$$\phi_{\text{FGM}} = 100 \left[\left(y_{\text{CO}_2, \text{FG}} + \frac{1}{2} y_{\text{O}_2, \text{FG}} \right)^{-1} \left(\frac{\tilde{n}_{\text{H}_2} / 4 + \tilde{n}_{\text{CO}_2, \text{loss}}}{\tilde{n}_{\text{H}_2}} \right) \right] \quad (3)$$

Table 1
Ultimate analysis of selected energy crop [w.b.] [17].

C	H	O	N	S	M	Z
43.9	5.5	41.6	0.3	0.0	5.5	3.2
Volatile matter			Fixed carbon		LHV (MJ/kg)	
74.0			17.3		17.8	

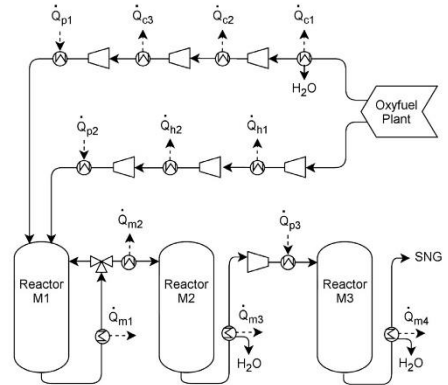


Fig. 2. Methanation plant model in Aspen Plus[®].

Hydrogen and flue gas are passed through compression trains (30 bar) with intermediate cooling stages down to 120 °C for heat recovering. A preheating stage up to 300 °C is also required before the first methanator [23]. Then, the composition and temperature of outlet gas are calculated at equilibrium state, minimizing Gibbs free energy in an adiabatic process.

Due to the loss of active surface area in the catalyst above 600 °C [24], the 80% of M1's outlet have to be cooled (300 °C) and recirculated to maintain the process temperature around 550 °C. Thus, the exothermic energy of the Sabatier reaction can be easily recovered as high pressure steam [25]. This thermal energy and the one from the intercooling stages of compression trains, could be integrated at different temperatures (Table 2) improving the overall efficiency.

Then, temperature of the remaining stream is reduced to 250 °C before entering M2. Lower inlet temperatures are typical in second and following methanators of commercial SNG processes like TREMP[®] since they promote the upgrading of syngas [26]. Later, the steam content in the outlet gas is partially condensed to avoid

Table 2

Available specific energies from CO₂ compression (kW_t/(t_{CO2}/h)), hydrogen compression (kW_t/(t_{H2}/h)), flue gas compression (kW_t/(t_{CO}/h)) and methanation (kW_t/(t_{H2}/h)).

Stream	temperature (°C)	Final temperature (°C)	Available specific energy	Waste energy in condensed water ^a
Q _{p1}	330.8	40.0	159.2	1.7
Q _{c2}	144.7	40.0	33.2	0.2
Q _{c3}	144.4	40.0	28.8	0.2
Q _{c4}	130.6	40.0	23.7	–
Q _{e1}	223.9	120.0	419.4	–
Q _{e2}	279.9	120.0	645.9	–
Q _{c1}	190.0	40.0	90.9	1.1
Q _{c2}	131.7	120.0	3.4	–
Q _{c3}	226.5	120.0	32.0	–
Q _{m1}	539.7	300.0	5826.8	–
Q _{m2}	300.0	250.0	224.7	–
Q _{m3}	380.4	130.0	3485.8	498.8
Q _{m4}	328.7	40.0	1052.4	12.6

^a Energy content of condensed water in the cooling stage, reference 25 °C.

the inhibition of methanation reaction. However, an excessively low steam molar fraction could generate solid carbon depositions [2]. In the studied scheme, the third reactor will not produce solid carbon when the temperature of the intermediate condensation stage remains above 125.5 °C, so temperature at this point is considered to be 130.0 °C.

The third reactor, M3, also operates without recirculation since high pressure favours methane formation. Its inlet stream is preheated to 250 °C and the outlet gas is cooled down to 40 °C to condense steam and reach a purity of methane over 95%.

3. Available thermal energy flows

The different subsystems in the hybrid plant present different cooling needs, from which thermal energy can be recovered for integration purposes. Part of this cooling requirements comes from the storage train in its condensation stages (\dot{Q}_{c1} , \dot{Q}_{c2} , \dot{Q}_{c3} and \dot{Q}_{c4}). Similarly, thermal energy must be extracted from the intercoolers of the hydrogen (\dot{Q}_{h1} and \dot{Q}_{h2}) and flue gas (\dot{Q}_{f1} , \dot{Q}_{f2} and \dot{Q}_{f3}) compression trains. Lastly, in the methanation plant four more energy streams are removed to mitigate the heat released by exothermic Sabatier reaction (\dot{Q}_{m1} , \dot{Q}_{m2} , \dot{Q}_{m3} and \dot{Q}_{m4}).

The available specific energy of each stream, defined as the total amount of thermal energy that must be removed to fulfil cooling requirements (Eq. (4)), is shown in Table 2.

$$\dot{Q}_{ji} = \dot{m}_{ji} \cdot c_{p,ji} \cdot \Delta T_{ji} \quad j = s, h, c, m; \quad i = 1, 2, \dots \quad (4)$$

Depending on the source, heats are normalized with respect to different variables avoiding the influence of ξ_{oxy} . Compression heats are normalized with respect to the inlet mass flows, whilst methanation heat has been divided by the amount of hydrogen produced in the electrolyser. Thus, data of available thermal energy for external integration are valid for every ξ_{oxy} . It should be noted that values of available energy are not comparable for different sub-systems due to the distinct normalization.

As shown in Table 2, there exist several lower limits for the final temperatures due to technical aspects. In the compression train for CO₂ storage and the condensation stage prior the flue gas compression to methanation, the temperature of condensers is set as 40 °C and the cooling process can be carried out with water at ambient temperature. However, the intercooling phases of hydrogen and flue gas compression are limited to 120 °C since a subsequent preheating up to 300 °C is required. In the methanation plant, \dot{Q}_{m1} and \dot{Q}_{m2} streams cannot be cooled below 300 °C and 250 °C respectively, since they are introduced in the reactors and a minimum operating temperature must be ensured. In addition, the heat removed in \dot{Q}_{m3} is limited since an excessive steam condensation in this point will produce solid carbon deposition in the third methanator. Therefore the minimum acceptable temperature for this intermediate condensation is 130 °C. Finally, \dot{Q}_{m4} belongs to a steam condensation stage, which is performed at 40 °C.

Despite all this available energy, only a fraction will be exchanged between hot streams and internal (\dot{Q}_{h1} , \dot{Q}_{h2} and \dot{Q}_{f3}) or external cold streams due to these temperature limitations. In this study, the maximum energy recovery from integration will be defined as useful thermal energy. Furthermore, the waste energy contained in the condensed water that is extracted from the facility is calculated in reference to 25 °C and also included in Table 2.

4. Efficiency definition and potential improvement

The efficiency of the system will be highly influenced by the operational variations that the hybrid plant suffers through the

increment of the ratio ξ_{oxy} . The key operation points for the hybrid system depend on the fuel composition; they are calculated and shown in Fig. 3 for an oxyfuel boiler fed with biomass whose composition has been presented in Table 1.

Depending on the value of the ratio between boiler and electrolyser size, ξ_{oxy} , different strategies of operation may be followed in the PtG–oxycombustion hybridized plant: (i) for a given value, ξ_{ASU} , enough oxygen is produced in the electrolyzers to completely feed the oxyfuel boiler and therefore ASU becomes unnecessary; and (ii) for ξ_{CO_2} , the flue gas flow produced in the oxyfuel combustion is completely reused and converted to SNG.

The results from a previous study of the hybrid PtG–oxycombustion system fired by coal showed the following size ratios for ASU elimination and total CO₂ consumption: $\xi_{ASU} = 1.33$ and $\xi_{CO_2} = 2.29$ [13]. The use of biomass in the boiler allows for reducing the size ratio requirement which avoids the need of ASU since oxygen content in biomass is much greater than in coal. In addition, given the smaller C:H ratio in biomass which limits the amount of carbon dioxide generated in the boiler per kW_{th}, the value of ξ_{oxy} to convert entirely the flue gas is reduced. Nevertheless, those variation in characteristic size ratios as a function of fuel type is beyond the scope of this paper and it is proposed as a further study.

The maximum efficiency of the hybrid system, once the additional available energy streams are considered, can be written down as Eq. (5).

$$\eta_{PtG, oxy} = \frac{\dot{Q}_2 + LHV_{SNG} \dot{m}_{SNG} + \sum_{i=1}^4 \dot{Q}_{e,i} + \sum_{i=1}^2 \dot{Q}_{h,i} + \sum_{i=1}^3 \dot{Q}_{e,i} - \sum_{i=1}^4 \dot{Q}_{m,i}}{LHV_f \dot{m}_f - W_{max, oxy} + W_{ASU} + W_{comp} - W_{ste} + W_{max, meth}} \quad (5)$$

The global efficiency of the system accounts for the chemical energy contained in the synthetic methane and the available heat from the boiler and other sources. In this first approach, the entire available thermal energy from compression trains and methanation are considered useful heat. Fig. 4 illustrates the comparison between the global efficiency of a non-integrated system and a system where complete use of the available heat is accomplished (Table 2). The rest of possibilities, i.e. the partial use of the available heat due to exchanger temperature limitations, will be intermediate curves. In addition, it should be noted that the electrolyser consumption appears in Eq. (5), so the final value of the overall efficiency is actually influenced by the electrolyser performance. However, this effect was neglected since the gap between both limit situations behaves similarly in the possible range of electrolyser efficiency.

It is worthy to note that the system without Power to Gas ($\xi_{oxy} = 0$) still observes an improvement in the global efficiency

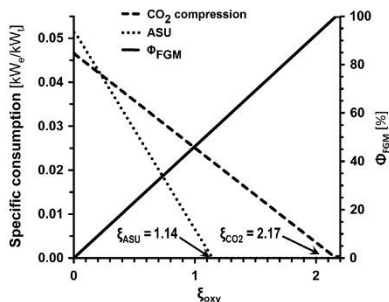


Fig. 3. Specific consumptions and percentage of methanised flue gas vs ξ_{oxy} .

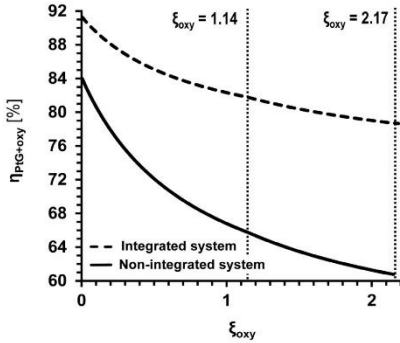


Fig. 4. Hybrid plant efficiency vs ξ_{oxy} (w and w/o energy integration).

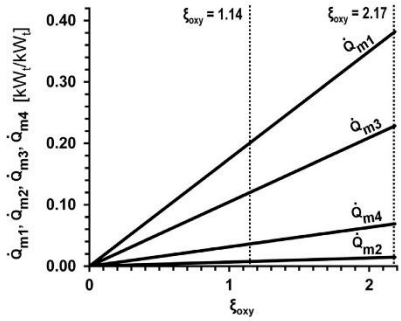


Fig. 6. Available specific heats from methanators vs ξ_{oxxy} .

since the heat from the compression train could be potentially integrated. As the share of PtG increases in the hybrid plant, overall efficiency decreases since Power to Gas presents a more limited performance than the oxyfuel boiler. However, the fall in efficiency is partially buffered thanks to the utilization of the waste energy from different sources, mainly methanation heat.

The available heat from compression trains and methanation are grouped by source (Eq. (6)) and presented in Fig. 5 for illustrating their behaviour against ξ_{oxy} . Furthermore, all of them have been normalized regarding the net thermal output of the boiler for direct comparison. It must be highlighted the difference in order of magnitude between the methanation heat and the other subsystems.

$$Q_j = \sum_i Q_{ji} \quad j = s, h, c, m \quad (6)$$

Data from Table 2 show how the ratio between Q_{ji} for a given j is conserved with ξ_{oxy} . Thus, it can be seen that the 55% of the methanation heat is always released in Q_{m1} (Fig. 6).

5. Potential applications

The final application of the PtG-oxy plant will define the adequate operation point, the required equipment and its suitability. Five generic scales for the concept, based on literature, are

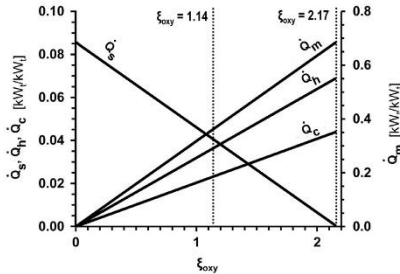


Fig. 5. Available specific heats vs ξ_{oxxy} .

analysed to determine its technical and economic feasibility: households, district heating (DH), industry, biomass power plants and co-firing (Table 3).

Typical household heating consumption in a cold climate region is laid in the range 60–200 kW h/m²/yr [27]. Therefore, assuming 1500 h of operation per year [28], a 150 kW h/m²/yr moderate specific consumption and a 90 m² household, the required boiler power is around 10 kW_{th}.

District heating size distribution varies remarkably from one country to another. In Finland and Denmark, which are northern Europe countries, majority of the DH systems are larger than 10 MW_{th} and rarely smaller than 2 MW_{th}. Moreover, there exist a relevant number of DH facilities with powers higher than 100 MW_{th}. However, in Switzerland (central Europe) the district heating systems are predominantly in the range 1–5 MW_{th} with an important amount of plants even smaller than 1 MW_{th} [29]. Consequently, the percentage of citizens that have access to district heating networks in the two first cases is 50% and 60% respectively, whilst in Switzerland this share drops below 5% [30]. Nevertheless, heat-only boilers for district heating are normally used as backup when peak demands are uncovered [31], so small sizes are more suitable for this scope. Thus, a 2 MW_{th} boiler size would be a representative size for a PtG-biomass oxycombustion hybrid plant used in district heating.

Industry boiler applications and their average capacities can be summarized in five main fields: chemicals (10.0 MW_{th}), paper (31.4 MW_{th}), food (5.9 MW_{th}), refining (33.2 MW_{th}) and metals (9.2 MW_{th}), where typical sizes for each sector have been estimated from United States data [32]. Thus, the average value for an industrial boiler for these five sectors would be around 18 MW_{th}.

Direct combustion biomass plants are commercially available from a few MW_e to 300 MW_e and are the most common form of power generation with this renewable fuel (90% of the biomass used for energy purposes is combusted) [33]. Plants which are compatible with the availability of local biomass feedstock are usually limited to 50 MW_e, whilst those that are supplied by internationally traded biomass may reach 300 MW_e [34]. A 50 MW_e power plant is taken here as a generic case. Efficiency of biomass power plants in the 50 MW_e size range are between 18% and 33% [34], so 26% efficiency is selected as a representative case. Hence, the boiler power that this power plant would need is around 192 MW_{th}.

In the co-firing case, the largest plant has a 4000 MW_e capacity (North Yorkshire, property of Drax Power, 6 × 660 MW_e), whilst

Table 3
Generic applications and characteristics for PtG-biomass oxycombustion at different scales.

Application	Boiler (MW)	ξ_{oxy}	Electrolyser (MW)	SNG (MW)	Technical feasibility	Economic feasibility
Households	0.01	$\xi_{\text{ASU}} - 1.15 \xi_{\text{ASU}}$	0.02	0.01	✓	–
District heating	2	$\xi_{\text{ASU}} - 1.15 \xi_{\text{ASU}}$	3.4–3.9	1.7–2.0	✓	✓
Industry	20	$\xi_{\text{ASU}} - \xi_{\text{CO}_2}$	33.5–63.7	16.8–31.9	✓	✓
Power plant	200	$\xi_{\text{ASU}} - \xi_{\text{CO}_2}$	335–637	168–319	–	✓
Co-firing	1000	$0.8 \xi_{\text{CO}_2} - \xi_{\text{CO}_2}$	2549–3186	1275–1593	–	✓

Note: Electrolyser efficiency 68.1% (LHV).

the following nine larger facilities have a total capacity in the range 1960–2400 MW_e [35]. However, currently the typical direct co-firing plant sizes are between 10 and 1000 MW_e, with a net electric efficiency between 35% and 42% [36]. Thus, the chosen generic case is a 500 MW_e plant with an intermediate efficiency value (38.5%), which would need a 1.3 GW_{th} boiler.

The selection of operation point must be in accordance to the scale of the plant and its final purpose. Hence, small scale installations (households and DH) are not compelled to capture their emissions since the amount of produced CO₂ will not be large enough. Thus, an operation point around ξ_{ASU} would be recommended. In medium and large scale facilities, such as industrial applications or power plants, to avoid greenhouse gas emissions might be mandatory and economically interesting. However, these applications could be operated in a wider range between ξ_{ASU} and ξ_{CO_2} without restrictions given the neutrality in CO₂ emissions of biomass combustion. Contrary, co-firing facilities cannot take advantage of biomass neutral emissions, and they will be compelled to capture their carbon dioxide. Therefore, a range next to ξ_{CO_2} would be the most suitable operation for those applications (Fig. 7).

Once the adequate range of electrolyser size is fixed for each scale, the technical feasibility is determined by the state of the art of the electrolysis technology. Nowadays, electrolysers are commercially available from a few kW_e up to 2 MW_e [37]. Therefore, it may be considered that there is no lower limit but an upper one, which implies that industrial uses are the largest possible applications through the combination of fifteen to thirty units of 2 MW_e size electrolysers. Hence, the next scale steps (power plants and co-firing), would require more than 160 of these electrolysers, so it is assumed that there is not any technical feasibility in these cases.

Finally, the economic feasibility is assessed as a function of the SNG production capacity taken from the results presented in the

final report of the *TKI power-to-gas system analysis project* developed in Rozenburg (Fig. 8) [38].

The amount of SNG generated under each potential application is calculated using the efficiency obtained through Aspen Plus simulations ($\eta_{\text{PtG}} \approx 50\%$). From these calculations it is obtained that the application in households of the PtG-oxy hybrid system would present unbearable capital and operational costs while for larger scales these costs are strongly attenuated.

In conclusion, under current conditions only district heating and industry applications seem to be technically and economically feasible for a PtG-biomass oxycombustion hybrid plant. Therefore, these both cases are briefly analysed in the two following sections. However, with a mature PtG technology and a greater electrolyser development, smaller and larger applications could be also suitable.

5.1. District heating

Heating and domestic hot water (DHW) necessities in residential buildings account for 75% of their total energy consumption [39]. A study performed by Carpio et al. [40] shows that the replacement of diesel with biomass, in Spanish residential building heating, leads to CO₂ emission reductions between 82.9% and 95.3%, whilst whether natural gas is replaced, emissions would drop between 77.4% and 93.7%. The proposal of a PtG-biomass oxyfuel boiler for district heating is, thus, well justified.

In 2014, the concept of 4th Generation District Heating (4GDH) was defined. Its main advantage is the increment in efficiency due to the lower distribution temperatures (30–70 °C) [41]. Several 4GDH projects funded by the IEA-DHC research programme have been finalized and other new four projects will be executed during the 2014–2017 period [42]. However, given the fact that the 4GDH approach is still under research, the technical parameters accounted in this study are based on previous district heating generations.

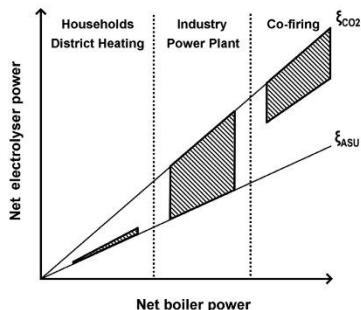


Fig. 7. Map of operation points for different scale facilities.

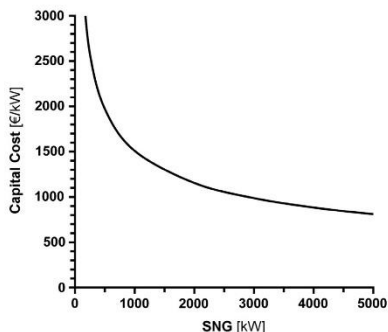


Fig. 8. Capital cost for methanation plants [38].

Table 4

Percentage of available specific heat (Table 2) that is useful in DH systems, and data for the generic case (2 MW_{th} at \dot{c}_{ASU} , Table 3).

	Useful specific heat (%)	Useful heat (kW)	Produced hot-water (kg/h)
\dot{Q}_{s1}	37.5	19.7	118.0
\dot{Q}_{s2}	0.0	0.0	0.0
\dot{Q}_{s3}	0.0	0.0	0.0
\dot{Q}_{s4}	0.0	0.0	0.0
\dot{Q}_{s1}	61.5	17.7	106.1
\dot{Q}_{s2}	75.0	33.3	199.5
\dot{Q}_{s1}	11.1	3.7	22.2
\dot{Q}_{s2}	0.0	0.0	0.0
\dot{Q}_{s3}	63.3	7.5	44.9
\dot{Q}_{m1}	100.0	399.9	2396.3
\dot{Q}_{m2}	100.0	15.4	92.3
\dot{Q}_{m3}	93.9	224.5	1345.2
\dot{Q}_{m4}	43.3	31.3	187.6
Total	81.2	753.0	4512.1

The 3rd Generation DH systems usually are operated at end customer supply temperatures between 80 and 100 °C [43], and pressures above 6 bar [44]. However, hot water transportation from DH plants to end user distribution network is made by transmission networks whose design parameters are more robust. The rigid plastic jacket pipes are the most widely used (140 °C and 25 bar) because of their greater standardization and lower prices [29], so these characteristics are chosen for the present case study.

The waste heat from PtG–biomass oxycombustion plant is recovered in a series of exchangers with a minimum difference of 20 °C between cold and hot streams. Therefore, the lower limit temperature to cool down the hot streams is 160 °C. Under this situation, \dot{Q}_{m1} and \dot{Q}_{m2} will be exhausted, \dot{Q}_{s2} , \dot{Q}_{s3} , \dot{Q}_{s4} and \dot{Q}_{s2} cannot be used, and the remaining heats will be only partially recovered. The useful energy that can be extracted from each point and the amount of water heated to 140 °C and 25 bar are shown in Table 4.

Given the limited amount of GHG emissions in district heating systems, to install a capture and compression facility for the CO₂ is not mandatory. Therefore, the heat recovered from the compression train may compute or not when calculating the efficiency of the system. In Fig. 9 the efficiencies under both scenarios together with the lower and upper limits of the base case (Fig. 4) are represented.

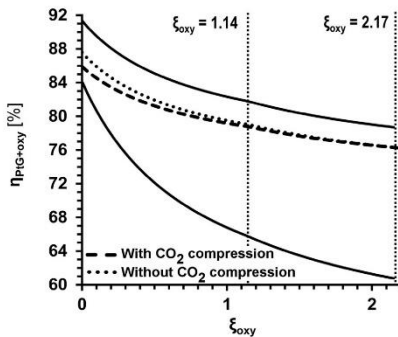


Fig. 9. Hybrid plant efficiency vs ξ_{oxy} (DH application).

Table 5

Requirements for some of the potential uses of steam in paper and chemical industries [45,47,48].

	T_{Steam} (°C)	P_{Steam} (bar)
<i>Paper industry</i>		
Digesting	170.0	7.9
Chemical recovery	144.4	3.1
Bleaching	126.7	1.4
Drying	126.7	1.4
<i>Chemical industry^a</i>		
Distillation	121.1	1.0
Drying	187.8	11.0
Blending	121.1	1.0
Melt compounding	146.1	3.5

^a PVC production case.

Initially, the inclusion of a CO₂ compression stage in the integrated system implies a reduction in the efficiency. However, once the ASU becomes unnecessary this penalty disappears and both systems have barely the same efficiency, because the greater influence of the PtG process against the compression heat.

5.2. Industry

Contrary to district heating application where the target of the produced heat is clear and its technical requirements are fixed, industry applications might be oriented to different final uses in a large range of temperatures. Therefore, a general analysis of industry applications similar to the DH analysis cannot be performed. Nevertheless, some aspects of these potential applications can be highlighted.

Pulp and paper manufacturers, as well as chemical industry, are two of the main medium temperature steam consumers that could take advantage of PtG–oxyfuel systems, since chemical industry employ 47% of their entire energy expenditure for producing steam and paper industry up to 84% [45]. Furthermore, paper manufacturing generates bark and sawdust as by-product that is commonly used as biofuel for producing steam that is self-consumed [46]. Hence, paper mills are one of the best candidates for a big scale PtG–biomass oxycombustion development.

As a summary, some of the main potential uses included in the paper industry and chemical sector, are shown in Table 5, with their corresponding requirements of temperature and pressure.

The strong differences between steam requirements in a specific process together with the availability of multiple thermal energy flows coming from the PtG–Oxycombustion boiler, suggest the utilization of the pinch analysis technique for maximizing the overall net efficiency. There exists huge potential for integration between industry and the proposed hybrid technique and the possibility of greater development through further specific studies.

6. Conclusions

A PtG–Oxycombustion hybrid system which transforms electricity from renewable sources and heat from biomass combustion into carbon-neutral synthetic natural gas has been proposed and analysed. In the light of results, the most adequate applications in which this system could be integrated have also been assessed.

Small scale plants are urged to operate near above \dot{c}_{ASU} since lower CO₂ emissions are normally not compelled to be captured through economic penalties, while for large scale facilities is recommended to operate with size ratios next to \dot{c}_{CO_2} , to ensure the complete conversion of flue gas flow into SNG. Hence, when technical and economic feasibilities of generic cases are evaluated tak-

ing into account these assumptions (Table 3), the most suitable applications for the PtG–Oxycombustion hybrid system are found.

The required size for the electrolyzer size in the cases of power plants and co-firing applications would be too large to be technically feasible, whilst the thermal energy consumption of household are so small that specific cost of the required plant matching the demand would be extremely high. However, district heating and industrial applications requirements lie in an affordable range for the hybrid system.

In addition, extra thermal energy production from methanation and compression trains is quantified to assess the potential increment of global efficiency for these applications. At the operational point ξ_{ASU} , heat integration allows to increase overall net efficiency from 65.7% to 81.8%, whilst for ξ_{CO_2} from 60.7% to 78.7%.

The analysis of a district heating case shows that a 81.2% of the available heat becomes useful for integration at the recommended operational point ξ_{ASU} , so overall net efficiency is increased up to 78.7%. If temperature requirements were lower, as in 4GDH systems, useful heat and efficiency would be even greater.

Further studies are proposed in order to analyse the influence of the type of fuel used in the boiler. First results indicates that oxygen content and C:H ratio produce remarkable modifications in the values of ξ_{ASU} and ξ_{CO_2} , respectively.

Lastly, the boundaries of the system should be extended in order to perform a 'full-fuel-cycle' analysis of the proposed concepts and to estimate the emission factors and losses associated with the power generation. This analysis would allow a realistic assessment of the concept under a specific scenario in comparison to other available energy storage technologies.

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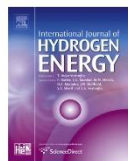
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Future applications of hydrogen production and CO₂ utilization for energy storage: Hybrid Power to Gas-Oxycombustion power plants

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ABSTRACT

Power to Gas (PtG) has appeared in the last years as a potential long-term energy storage solution, which converts hydrogen produced by renewable electricity surplus into synthetic methane. However, significant economic barriers slow down its massive deployment (e.g. operating hours, expensive investments). Within this framework, the PtG-Oxycombustion hybridization can palliate these issues by improving the use of resources and increasing the overall efficiency. In this study we assess the requirements for electrolysis, depending on the size of the oxycombustion plant, the fuel physical and chemical properties and the final application of the hybrid system. Most suitable heat demanding options to implement this PtG-Oxycombustion hybridization are district heating, industrial processes and small combined cycled power plants. The latter case is modelled and simulated in detail and thermally integrated. The global efficiency of this hybrid system increases from 56% to 68%, thanks to avoiding the requirement of an air separation unit and integrating up to 88% of the available heat from methanation in a LP steam cycle.

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Abbreviations: ASU, air separation unit; HEN, heat exchangers network; LHV, lower heating value; M, moisture; Oxy-CC, oxycombustion combined cycle; PtG, power to gas; SNG, synthetic natural gas; Z, ash.

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Introduction

The constant increase of electricity production from intermittent renewable energy sources has brought to light the necessity of deploying energy storage systems. The management of the surplus power generated by these renewable sources is crucial for developing a sustainable power industry. Power-to-gas has been proposed as one of the promising technologies to overcome these issues [1]. PtG technology uses electricity to produce hydrogen by electrolysis, and then combines CO₂ and the produced H₂ to obtain SNG through methanation. This technology widens the range of application of hydrogen as energy vector, and it makes possible to produce a CO₂ neutral fuel by capturing the carbon emissions from an existing source [2,3]. In addition, it allows connecting the electric and gas network for increasing the flexibility of the energy supply.

The PtG process is conceptually explained as follows: renewable electricity is converted to fuel gas by means of electrolysis, storing electrical energy in form of hydrogen. Oxygen is also obtained as by-product from the electrolyser. Then, the generated hydrogen is combined with carbon dioxide to produce methane through the Sabatier reaction (Equation (1)) [4].



The availability of a suitable source of CO₂ can be considered as the main limiting factor for promoting PtG, since it reduces the possible geographic sites for a wide deployment of this technology [5]. Biogas plants, waste managers, energy-intensive industries and power plants are the largest CO₂ sources and the most interesting partners for integration with PtG [6]. However, the energy consumption required to attain concentrated CO₂ streams leads to efficiency penalties that range between 9 and 12 efficiency points [7,8], and the associated costs may vary from 50 to 90 €/tCO₂, depending on CO₂ concentration in flue gas and capture technology [9]. For this reason, some of the largest PtG projects worldwide directly upgrade biogas to obtain SNG without a previous stage of CO₂ separation [10]. However, this kind of concepts makes useless the byproduct oxygen coming from the electrolysis process.

To this context, oxygen may be used as gasification agent or for the activation of sludge in biomass gasification and sewage plants, respectively [6]. Nevertheless, the hydrogen concentration in syngas from gasification may reach values above 60% and further hydrogen addition is barely needed, what limits the energy storage potential [11]. Sewage plants produce poor biogas and its upgrading is relatively expensive. Thus, it is currently preferred to burn this gas in engines for self-consumption [12]. Hence, a suitable option to take advantage of produced oxygen would be the hybridization of PtG with oxyfuel combustion. In oxyfuel combustion, a mixture of pure oxygen and recycled flue gas (mainly CO₂ and H₂O) acts as comburent [13]. The requirement of an air separation unit (ASU) to produce oxygen would be replaced with the electrolyser which by-produces O₂. Thus, the electrical consumption of the ASU would be reduced, and CO₂ would be taken from flue gas without extra energy penalty in its separation. With an adequate size design of the

PtG–Oxycombustion system, the by-produced oxygen from electrolysis could entirely replace the ASU [6,14,15].

This paper deals with some potential applications that include biomass, coal and gas consumption. These applications cover different sizes and technologies but all of them are based on the Oxycombustion-Power to Gas hybridization. Special attention is paid to an advanced oxycombustion combined cycle hybridized with PtG. This technology can achieve higher net electric efficiencies [16] than air-fired coal power plants, so the required capacity of electrolysis to remove the ASU is lower than in other power plants of the same net electric power. Furthermore, methanation produces extra thermal energy that can be useful. Thus, a preliminary heat integration analysis has been also performed and the maximum potential efficiency after heat integration is also determined.

Power to Gas-Oxycombustion hybridizations

As stated above, a suitable option to take advantage of by-produced oxygen is the hybridization of Power to Gas with oxyfuel combustion. During oxycombustion, a mixture of recycled flue gas and pure oxygen is used as comburent instead of air [17]. Thus, the large N₂ content in air is substituted by the combustion products (mainly CO₂ and H₂O), and flue gas can achieve a high carbon dioxide concentration once steam is condensed. Energy penalty associated to this capture process mainly comes from the air separation unit that produces the required oxygen with typical consumptions of 190 kWh/tO₂ [18]. Therefore, by using the oxygen from electrolysis we could suppress the electrical consumption of the ASU, and we would directly obtain pure CO₂ for methanation from flue gas without energy penalties (Fig. 1).

The key variable in the Power to Gas-Oxycombustion hybridizations is the ratio that relates the chemical energy in the hydrogen from electrolysis and the net energy output of the oxyfuel combustion plant, Equation (2) (thermal outputs for boilers, ξ_{oxy} , and net electric outputs for power plants, ξ_{oxy}) [14,19]. The net electrical output accounts for the consumed electricity by the ASU and the auxiliary equipment in the form of Equation (3).

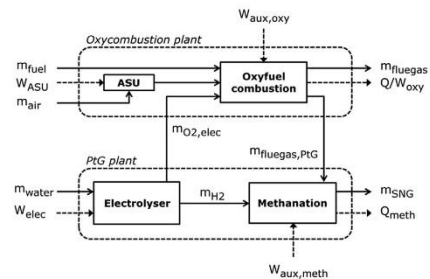


Fig. 1 – Scheme of the hybrid PtG-Oxycombustion concept.

$$\xi_{oxy} = \frac{LHV_{H_2} \cdot \dot{m}_{H_2}}{\dot{Q}_{oxy}} \left[\frac{kWh}{kW_e} \right] \quad \text{or} \quad \xi'_{oxy} = \frac{LHV_{H_2} \cdot \dot{m}_{H_2}}{\dot{W}_{net,oxy}} \left[\frac{kWh}{kW_e} \right] \quad (2)$$

$$\dot{W}_{det,oxy} = \dot{W}_{gross,oxy} - \dot{W}_{air,oxy} - \dot{W}_{ASU} \quad [kW_e] \quad (3)$$

Depending on the size ratio between the electrolyser and the oxyfuel combustion, the byproduced oxygen could cover the oxyfuel process requirements and avoid the air separation unit (situation denoted as ξ_{ASU}). Besides, whenever the installed electrolyser capacity is enough to process the whole flow of flue gas, the size ratio will be denoted as ξ_{CO_2} . The type of fuel used in oxycombustion will modify the values of ξ_{ASU} and ξ_{CO_2} (Fig. 2). Thus, the use of biomass leads to lower values of ξ_{ASU} (1.14) in comparison with coal (1.33) thanks to the greater oxygen content (Table 1). Whilst the smaller C:H ratio of typical biomass fuels also gives minor values of ξ_{CO_2} (2.17) than coal (2.29) due to the less amount of CO₂ produced per generated kWh [19]. The latter effect is more pronounced for natural gas oxycombustion, thus decreasing ξ_{CO_2} (1.29) down to meet with ξ_{ASU} (1.30). Furthermore, despite of the differences between the compositions of natural gas and coal, both of them require for combustion comparable amounts of oxygen per MJ of fuel (2.80 mol_{O₂}/MJ_{fuel} for natural gas, and 2.86 mol_{O₂}/MJ_{fuel} for coal, according to our simulations), what implies similar values of ξ_{ASU} .

It should be noted that $\xi_{CO_2} < \xi_{ASU}$ for the natural gas case, due to second order effects. Since complete combustion of CH₄ is considered and methanation is forced to be stoichiometric, the parameters ξ_{CO_2} and ξ_{ASU} should be equal for natural gas. However, second order effects modify the values of ξ , such as (a) the presence of H₂ in the fuel input (more O₂ required,

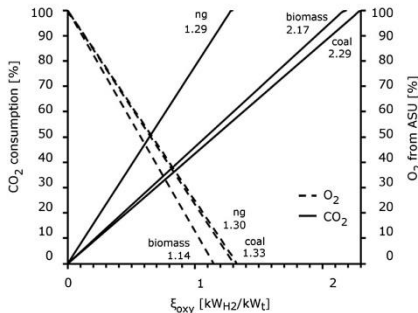


Fig. 2 – Behaviour of ξ_{oxy} for coal, biomass and natural gas.

Table 1 – Ultimate analysis of selected coal and biomass for the study [% w.b.] [14,19].

	C	H	O	N	S	M	Z	LHV [MJ/kg]
Coal	66.1	3.6	7.1	1.6	0.6	8.6	12.4	25.4
Biomass	43.9	5.5	41.6	0.3	0.0	5.5	3.2	17.8

ξ_{ASU} 1), (b) the requirement of an O₂ excess during combustion (more O₂ required, ξ_{ASU} ↑), and (c) the presence of O₂ in the flow of CO₂ that is directed to methanation (more H₂ required, ξ_{CO_2} ↑). These effects almost cancel each other, and makes ξ_{ASU} slightly greater than ξ_{CO_2} .

The type of the power plant also modifies the values of ξ'_{ASU} and ξ'_{CO_2} . Fig. 3 shows the behaviour of ξ'_{oxy} for a subcritical power plant with a LHV efficiency of 38.6% (coal and biomass), and for a combined cycle of 64% LHV efficiency (natural gas) [16]. The greater efficiency of the combined cycle allows reducing the amount of fuel used per kWh produced, and therefore the required oxygen for oxycombustion and the size of electrolysis.

The final application of the PtG–oxycombustion hybridization will define the adequate operation point of ξ_{oxy} and ξ'_{oxy} . Five generic applications are analysed to evaluate its technical feasibility. At small and mid-scale, we consider boilers producing thermal output that is applied to households, district heating, or industrial processes. At big scale, we take the production of electricity by combined cycles for natural gas, and by subcritical power plants for coal and biomass (Table 2).

Small scale installations (households and district heating) are not compelled to capture their emissions since the amount of produced CO₂ is not large enough. Hence, an operation point around ξ_{ASU} would be recommended. In medium scale facilities, such as industrial applications, avoiding greenhouse gas emissions might be economically interesting, so they could operate in the range between ξ_{ASU} and ξ_{CO_2} . Power plants should be compelled to capture their carbon dioxide; therefore, a range next to ξ_{CO_2} would be the most suitable operation for those applications.

The technical feasibility of these applications is strong limited by the high specific cost and the maximum achievable size of electrolysers. Nowadays, electrolysers are commercially available from a few kW up to 2 MWe [20]. Therefore, coal and biomass power plants are prohibitive because they require more than 160 electrolysers. Industry and district heating are the most suitable applications, since they would combine less than 30 units of 2 MWe size electrolysers. In the following

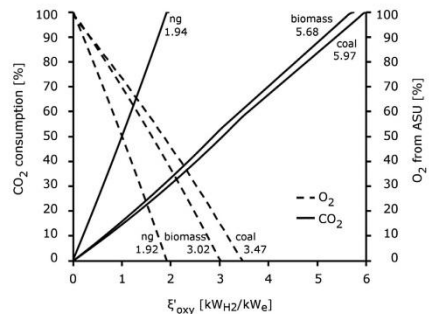


Fig. 3 – Behaviour of ξ'_{oxy} for a subcritical power plant (coal and biomass) and a combined cycle (natural gas).

Table 2 – Generic applications and characteristics for PtG-oxycombustion systems at different scales (electrolyser efficiency 68.1%) [19].

Thermal output					
Application	\dot{Q}_{oxy} [MW]	Electrolyser [MWe]			ξ_{oxy}
		Coal	Biomass	Natural gas	
Households	0.01	0.02	0.02	0.02	$\xi_{\text{ASU}} - 1.15 \cdot \xi_{\text{ASU}}$
District heating	2	3.9–4.5	3.4–3.9	3.8–4.4	$\xi_{\text{ASU}} - 1.15 \cdot \xi_{\text{AST}}$
Industry	20	39.1–67.3	33.5–63.7	39.1–37.9	$\xi_{\text{ASU}} - \xi_{\text{CO}_2}$
Electrical output					
Application	$\dot{W}_{\text{net,ox}}$ [MW]	Electrolyser [MWe]			ξ'_{oxy}
		Coal	Biomass	Natural gas	
Subcritical PP	50	350.6–438.3	333.6–417.0	–	$0.8 \cdot \xi'_{\text{CO}_2} - \xi'_{\text{CO}_2}$
Combined cycle	50	–	–	113.9–142.4	$0.8 \cdot \xi'_{\text{CO}_2} - \xi'_{\text{CO}_2}$

section, we analyse and integrate a small combined cycle power plant as the upper limit case for PtG-Oxy applications.

Power to Gas-Oxycombustion combined cycle model

The operation of a Power to Gas-Oxycombustion combined cycle plant makes sense when we use buffers of H_2 and O_2 to separate the storage periods from the electricity generation (the analysis of storage sizing and management is beyond the scope of this paper, although it becomes essential for economic analysis). Whenever renewable energy surplus exists, the electrolyser starts storing this electricity as hydrogen and oxygen. Contrarily, during the periods of high demand, the electrolyser remains unused, and the combined cycle generates electricity using the stored oxygen for the oxycombustion. Simultaneously, the methanation process combines the hydrogen with the CO_2 emissions of the power plant, what allows generating approximately the same amount of SNG that is consumed. Hence, the final electricity production can be considered as renewable, since methane and carbon dioxide act as the charge and discharged forms of an energy carrier that is continuously recycled. Besides, the exothermal heat from methanation can be integrated as low pressure steam in the steam cycle of the power plant for increasing the overall efficiency.

The hybridization between the combined cycle oxycombustion and the Power to Gas plant has been modelled with Aspen Plus® under industrial conditions for steady state operation and chemical equilibrium. The simulation of both plants is described in detail in the following sub-sections.

Combined cycle power plant

To convert the chemical power of the produced SNG back to electric power, a gas and steam cycles are combined in a single oxycombustion power plant (Oxy-CC). By burning the SNG in pure oxygen, the produced flue gas is rich in CO_2 that can be easily separated from water using a condenser. An overall layout of the power plant is shown in Fig. 4. Pure oxygen, SNG and recycled flue gas are fed to the stoichiometric combustion chamber (BO) where the temperature is raised up

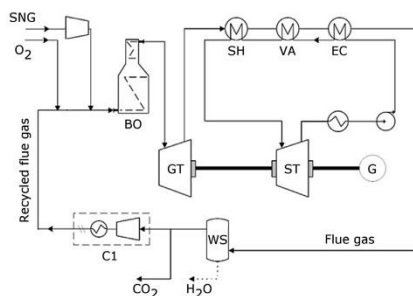


Fig. 4 – Scheme of the oxycombustion combined cycle.

to 1330 °C (see Table 3 for stream details). We assume a complete combustion process and an isentropic efficiency of 90% for all turbines.

The resulting flue gas is then expanded in a Gas Turbine (GT) to atmospheric pressure to produce about 35.7 MWe of electric power. A Rankine cycle is then used to recover the heat from the flue gas. The Steam Turbine (ST) operates at 530 °C and 150 bar and generates up to 13.4 MWe. The used Heat Recovery Steam Generator consists of 3 modules: an Economizer (EC) a Vaporizer (VA) and a Superheater (SH).

The total electric consumption of the Oxy-CC is the sum of the ASU consumption (3.0 MW), the multi-staged compressor of the recycle loop (13.8 MW), and the water pump in the Rankine cycle (0.2 MW). Thus, the total 49.1 MW that the plant is able to generate translates into 31.1 MW of net power, assuming a 98% efficient electric generator (G). This leads to an overall plant efficiency of 55.9% defined as the ratio between the net electric output of the Oxy-CC plant (Equation (3)) where $W_{\text{aux,ox}}$ includes the consumption of the multi-staged compressor of the recycle loop) and the chemical energy contained in the SNG from PtG unit (LHV based). This value is comparable to the efficiency of NGCC power plants with CO_2 capture found in literature [21]. The Oxy-CC produces 5859.1 Nm³/h of CO_2 for methanation with 94.5 mol% CO_2 content.

Table 3 – Main streams of the oxycombustion combined cycle.

	Fuel	Comburent	Flue Gas	CO ₂ to PtG
Stream	SNG	O ₂	Recycled flue gas	CO ₂
T [°C]	40.0	27	382.0	1329.5
P [bar]	26.0	40.0	40.0	40.0
Flow [Nm ³ /h]	5775.9	11210.8	67679.4	84581.4
CO ₂ [%]	0.8	0.0	94.5	82.2
H ₂ [%]	3.5	0.0	0.0	0.0
CH ₄ [%]	95.3	0.0	0.0	0.0
H ₂ O [%]	0.4	0.0	4.3	16.8
O ₂ [%]	0.0	100.0	1.2	1.0

Power to gas plant

The modelled methanation facility is based on TREMP™ process from Haldor Topsøe [22], and consists of three adiabatic stages at about 30 bar with recycling on the first reactor, and a steam condenser after the second one (Fig. 5). The main target is to achieve methane molar fractions above 95% in the SNG, according to the Spanish legislation [23].

The flue gas from the Oxy-CC amounts to 5859.1 Nm³/h at 30 °C and 1 bar. We assume a stoichiometric methanation, so the required amount of hydrogen is 22310.1 Nm³/h. This is calculated by Equation (4) [14] as a function of the total molar flow of flue gas, \dot{n}_{FG} , and its molar concentrations of CO₂, $y_{CO_2, FG}$, and O₂, $y_{O_2, FG}$.

$$\dot{n}_{H_2} = 4 \cdot \left(y_{CO_2, FG} + \frac{1}{2} y_{O_2, FG} \right) \cdot \dot{n}_{FG} \quad (4)$$

This hydrogen comes from alkaline electrolyzers fed with renewable electricity, which have been modelled by programming a user-defined subroutine in Aspen Plus®. The inlet electric power and the inlet water stream are the initial variables for the external calculations. This block splits water in two mass flows of pure oxygen and a mixture of hydrogen with unreacted water. Based on literature, the water conversion is assumed to be 99.9% with an electrical consumption of 4.4 kWh/Nm³H₂ and an outlet temperature of 80 °C [24,25]. These operation conditions lead to an efficiency of the electrolyser unit of 68.1% (LHV basis).

The hydrogen and carbon dioxide are pressurized up to 30 bar prior the methanation plant. At the outlet of both compression trains, the temperature reached allows the removal of any preheating stage before the first reactor. Then, the outlet of Reactor 1 is cooled down to 300 °C, and partially recycled (72.5%) using a blower. The stream directed to the second stage of methanation enters the reactor at 250 °C. After this point, steam content strongly inhibits the methanation reaction; therefore water content is reduced to 12% through a condensation stage and the outlet gas is heated back to 250 °C prior entering the third reactor. Finally, most of the steam at the outlet of Reactor 3 is condensed, and the gas achieves SNG quality (Table 4). In the simulation, the reactor blocks calculate the composition and temperature of outlet gas streams, at equilibrium state, minimizing Gibbs free energy in an adiabatic process. Besides, the pressure drops are assumed to be 3% along the reactors and 2% in the condensation stages.

Energy integration and efficiency

Based on the Power to Gas plant simulation results a heat integration study is conducted in order to find the optimal Heat Exchangers Network (HEN) for heat recovery purposes. The pinch analysis methodology is integrated into the Power to Gas model in order to determine the minimal hot and cold utilities required by the process. Heat fluxes are integrated with a pinch temperature of $\Delta T = 10$ K [26]. The resulting

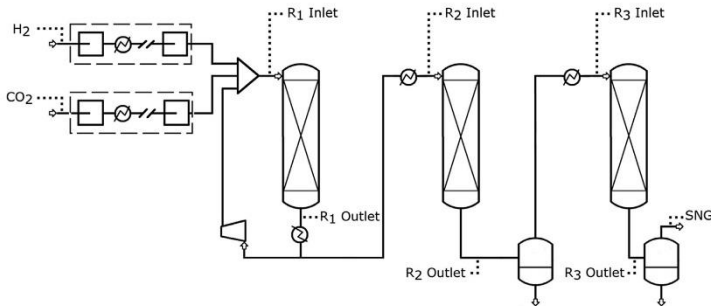
**Fig. 5 – Scheme of the Power to Gas plant.**

Table 4 – Main streams of the Power to Gas plant.

	H ₂	CO ₂	R1 Inlet	R1 Outlet	R2 Inlet	R2 Outlet	R3 Inlet	R3 Outlet	SNG
T [°C]	80.0	30.0	307.7	592.1	250.0	421.9	250.0	366.3	40.0
P [bar]	1.0	1.0	30.0	29.1	29.1	28.2	27.7	26.8	26.3
Flow [Nm ³ /h]	22310.1	5859.1	78318.7	69143.3	18993.7	17579.7	7544.6	7090.9	5756.9
CO ₂ [%]	0.0	94.5	9.9	4.5	4.5	1.6	3.6	0.7	0.8
H ₂ [%]	99.9	0.0	41.3	20.0	20.0	6.3	14.7	2.9	3.5
CH ₄ [%]	0.0	0.0	15.3	24.0	24.0	29.9	69.7	77.3	95.2
H ₂ O [%]	0.1	4.3	32.9	50.8	50.8	62.2	12.0	19.1	0.4
CO [%]	0.0	0.0	0.5	0.7	0.7	0.0	0.0	0.0	0.0
O ₂ [%]	0.0	1.2	0.1	0.0	0.0	0.0	0.0	0.0	0.0

optimal HEN is shown in Fig. 6. In this optimal HEN, part of the heat recovered from the exit of the first reactor is used for internal heating requirements at the inlet of the third reactor (HEX1). The remaining heat is used to generate 24 tonnes of LP steam per hour at 124 °C and 2 bar by using 3 heat exchangers placed at the exit of the first reactor and both ends of the second (HEX2, HEX3 and HEX4).

The heat generated at the exit of the last reactor cannot be efficiently recovered with the considered operating conditions. An external cooling utility is thus used for condensate removal from the final product (e.g. cooling tower).

In order to make use of this generated steam, a low pressure turbine (LP) is introduced into the previous Oxy-CC (Fig. 7). The generated LP steam is mixed to the steam exiting the high pressure turbine (HP) at 2 bar before the second expansion process in the following low pressure turbine (LP). The flow exiting the LP turbine is then separated to retrieve the portion which will be pumped back to the HEN in the Power to Gas plant. This configuration allows to run the oxy-combustion and Power to Gas processes separately if need be.

Thanks to the external heat source for more power generation (heat integration with PtG plant), the new combined cycle is able to produce 53 MW of electric power (near 8% more power). The removal of ASU unit for O₂ generation avoids 3 MW of extra consumption. But the requirement of a new compression train to pressurized O₂ coming from the

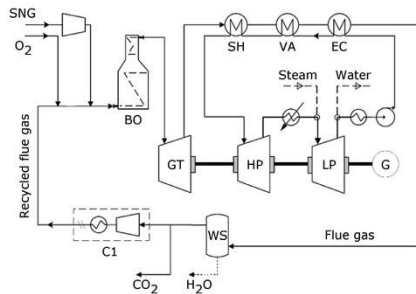


Fig. 7 – Scheme of the oxycombustion combined cycle heat integration.

electrolyser penalizes the system with 2.1 MW. This modification finally leads to a net power generation of 35.8 MW. Thus, the total efficiency of the combined cycle rises by 11.6 points, up to 67.5% (LHV based). Moreover, the performance of the plant could still be further improved by means of an exergy analysis to identify the avoidable losses at fixed design [27].

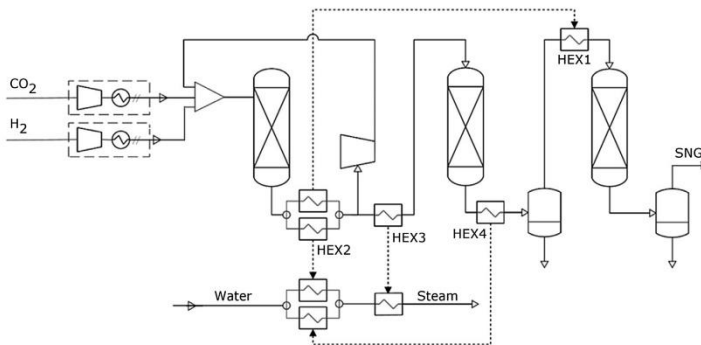


Fig. 6 – Scheme of the Heat Exchangers Network in the methanation plant.

Conclusions

In this study, the PtG-Oxycombustion hybridization that was presented in previous works has been assessed for different types of Oxycombustion plants. These systems store renewable electricity as hydrogen, taking also advantage of the O₂ by-produced during electrolysis to overcome the energy penalty of the ASU in an oxyfuel combustion facility. Later, the O₂ stored can be used to operate the oxycombustion plant and, in addition, the H₂ stored is used in the methanation plant to generate synthetic natural gas. The parameter used to characterize the systems is the size ratio, ξ_{oxy} , which relates the energy contained in the hydrogen from electrolysis and the net output of the oxyfuel combustion plant (thermal output for boilers, ξ_{oxy} , and net electric output for power plants, ξ'_{oxy}). Depending on the value of ξ_{oxy} , the byproduct oxygen could completely feed the oxyfuel process and avoid the air separation unit (ξ_{ASU}), or the hydrogen may be sufficient for processing the whole flow of flue gas (ξ_{CO_2}).

The type of fuel used in oxycombustion modifies the values of ξ_{ASU} and ξ_{CO_2} . Natural gas and coal require comparable amounts of oxygen per MJ of fuel, what implies similar ξ_{ASU} (1.30 and 1.33, respectively), whilst biomass has greater oxygen content, thus reducing ξ_{ASU} down to 1.14. Besides, for smaller C/H ratios, the amount of CO₂ produced per generated kWh is lower, so $\xi_{CO_2,coal} > \xi_{CO_2,biomass} > \xi_{CO_2,natural\ gas}$. The type of power plant also modifies the values of ξ_{ASU} and ξ'_{CO_2} . The lower efficiency of subcritical power plants compared to combined cycles implies increasing the amount of fuel per kWh produced, the required oxygen and the size of electrolysis; therefore, $\xi_{CO_2,SPP} \gg \xi_{CO_2,CC}$.

Five generic applications of the concept have been evaluated, from which industry and district heating result the most suitable options due to their technical feasibility. Small combined cycles are considered as the upper limit for PtG-Oxy applications, whilst subcritical power plants are prohibitive since they require between 330 and 420 MW of electrolysis capacity. Furthermore, a PtG-OxyCC hybrid system has been simulated and thermally integrated with Aspen Plus® software. A total of 88% of the exothermal heat available from methanation is recovered with an optimized heat exchangers network, thus generating low pressure steam that can be introduced in the steam cycle of the power plant. Hence, the absence of ASU unit for O₂ generation and the use of the methanation heat allow increasing the overall efficiency from 55.9% to 67.5%.

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Nomenclature

Variables

LHV	Lower heating value, kJ/kg
\dot{m}	Mass flow, kg/s
\dot{n}	Molar flow, kmol/s
P	Pressure, bar
\dot{Q}	Thermal power, kWt
T	Temperature, °C
\dot{W}	Electric power, kWt
y	Molar fraction, –
ξ_{oxy}	Ratio between electrolyser and boiler outputs, kWe/kWt
ξ'_{oxy}	Ratio between electrolyser and power plant outputs, kWe/kWt

Subscripts

ASU	Air separation unit
aux	Auxiliary consumption
CC	Combined cycle
CO ₂	Carbon dioxide
FG	Flue gas
gross	Gross power
H ₂	Hydrogen
net	Net power
oxy	Oxycombustion plant
O ₂	Oxygen
SPP	Subcritical power plant

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Power to gas-electrochemical industry hybrid systems: A case study



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HIGHLIGHTS

- A novel hybridization of power to gas and an electrochemical industry is proposed.
- This work shows that PtG-Electrochemical hybrid plant is feasible.
- The plant consumes 85% of the available H₂ and 60% of CO₂ emitted by the industry.
- This concept can overcome the economic barriers of erecting a commercial plant.

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ABSTRACT

Several researchers have proposed in literature different Power to Gas (PtG) hybridizations to improve the efficiency of this energy storage technology. Some of the synergies of this hybrid systems are already being tested under real conditions (e.g. PtG-Amine scrubbing, PtG-wastewater treatment) while others have only been studied through numerical simulations (e.g., PtG-oxyfuel combustion). Here, a novel hybridization between Power to Gas and electrochemical industries is proposed for the first time. This PtG-Electrochemical hybridization avoids to implement the typical water electrolysis stage of PtG since hydrogen is already available in the plant. This study thoroughly analyzes the implementation of Power to Gas in a real electrochemical plant that sub-produces hydrogen from the lines of production of chlorine, chlorine, and potassium hydroxide. It is shown that the required carbon dioxide for methanation can be captured from the flue gas of the factory's boilers without additional energy penalty thanks to energy integration. The methanation plant has been designed according to the H₂ and CO₂ availability, taking into account the number of operating hours and the degree of usage of by-products. Results show that this PtG hybridization could operate more than 6000 h per year at large scale concepts (nominal H₂ inputs of 2000 m³/h (NTP)), which represents 2000 h more than pilot/commercial demonstrations of classic PtG concepts. Besides, a detailed economic analysis demonstrates the economic feasibility of the system under current scenarios. It is shown that the capital investment would be recovered in 8 years, generating a 4.8 ME NPV at the end of the project lifetime. Thus, this work presents a suitable way to avoid the subsidy dependency that current PtG research projects have.

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1. Introduction

In 2009, the European Renewable Energy Directive (2009/28/EC) established a global policy to achieve in 2020 a renewable share in the European final energy consumption for at least 20%, together with a 10% share in the field of transport [1]. Beyond 2020, renewables will remain playing a key role since EU countries have already agreed on extending the target up to 27% by 2030.

According to the trends to 2050 from the “EU Reference Scenario 2016”, the share of electricity produced from renewables is expected to grow up to 37.2% by 2020, 43% by 2030, and 53% by 2050 [2].

The intermittent nature of these renewable energy sources (RES) produces mismatches between supply and electrical demand that affect the security and stability of the grid. Typically, generators and system operators can only regulate the 5–10% of the output coming from variable renewable sources (wind and solar). For instance, the degree of regulation in Spain is about 5%, in Sweden 6% and in Germany 7% [3]. Hence, the increase of renewable share in the electricity production mix brings along with fluctuating

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Nomenclature

Variable	Description (units)	
α_i	usage of resource i (%)	$\dot{V}_{H_2, ammonia}$ H ₂ by-production destined to ammonia line ($m^3 \cdot h^{-1}$ (NTP))
v_{Bj}	amount of H ₂ that is present in the buffer at the beginning of hour j (m^3 (NTP))	\dot{V}_{H_2} H ₂ by-production ($m^3 \cdot h^{-1}$ (NTP))
$v_{B,max}$	maximum capacity of the H ₂ buffer (m^3 (NTP))	η efficiency of the electrolysis
v_{ij}	available amount of resource i at hour j (m^3 (NTP))	τ operating hours of the methanation plant (h)
v'_{ij}	used amount of resource i at hour j (m^3 (NTP))	NPV Net Present Value (€)
$V_{H_2, PtG}$	nominal hourly input of the methanation plant (m^3 (NTP))	IRR Internal Rate of Return (%)
		PB pay-back (years)

power that limits the operational predictability and flexibility of the energy system, generating a serious challenge to electrical grid operators. To promote RES deployment, embedding energy storage techniques into conventional power stations and industries result essential to smartly manage renewable intermittent power.

In the last years, Power to Gas (PtG) has been proposed as a very promising and versatile technology to store renewable power surplus. PtG converts electricity into synthetic natural gas via the methanation of CO₂ together with H₂ from water electrolysis [4,5]. This technology widens the application of hydrogen as energy vector, and it makes possible to produce a CO₂ neutral fuel by capturing the carbon emissions from an existing source [6,7]. In addition, it allows the connection between electric and gas network thus increasing the flexibility of the energy supply system. However, significant economic barriers slow down PtG development due to the current high cost of electricity, and the large required investments. These problems could be overcome through hybridizing systems whose synergies increase the global efficiency, improve the resource use, and reduce the investment on new equipment [8].

In 2009, Michael Sterner outlined several configurations that present some synergies depending on the CO₂ source used for the methanation process (biogas, syngas or pure CO₂) [9]. For instance, the use of biogas avoids the necessity of a carbon capture step since biogas is already a mixture of CH₄ (50%–85%) and CO₂ (50%–15%) [10]. Besides, it allows the integration of the methanation heat in the digestion processes. For those reasons, the most recently developed PtG pilot plants prefer biogas as source of CO₂ [11]. In 2015, Electrochaeca commissioned the largest plant worldwide integrating biogas as resource [12], in which a 1.0 MW alkaline water electrolyzer supplies the hydrogen [13]. They aim to integrate both the by-product oxygen and the methanation heat in the wastewater treatment process that generates the biogas [14]. Technical data from this field experience have not been released yet, but previous projects showed that 3000 operating hours were achievable under realistic market conditions [15].

Likewise, syngas from gasification does not require a carbon capture process either, and permits the use of the by-produced oxygen during water electrolysis to carry out oxygen-blow gasification. This type of integration is still under development at lab/pilot scale [11], so there are no studies quantifying the benefits of the integration. The cutting-edge research in this topic is carried out by the Karlsruhe Institute of Technology, which has made some methanation tests with input flows of syngas of 14 m³/h (NTP) [16] in a biomass gasification plant belonging to Cortus, in Sweden [17].

Power to Gas plants that make use of pure CO₂ admit different integration configurations. When amine capture technology is employed, methanation heat may be integrated and used for regenerating the solvent. If oxy-fuel combustion capture technique is used, mass flow integration is possible and the by-produced CO₂ is used as comurent.

The PtG-Amine integration case is the only one that has a commercial experience, the Audi e-gas plant [18]. It uses three alkaline water electrolyzers of 2.0 MW [19] and produces up to 325 m³/h (NTP) of synthetic natural gas [20]. Besides, the plant is qualified for participating in the electricity balancing market [21], and the availability of the renewable energy consumed gives about 4000 operating hours per year [20]. Specific software had to be developed to optimize the thermal management of the waste heat recovered from electrolysis and methanation, to be later supply in the CO₂ removal plant [21,22]. The objective of the manufacturer, ETOGAS, is to reach PtG systems around 20 MW with efficiencies above 80% thanks to the recovery of the methanation heat [23]. Regarding Power to Gas-oxyfuel combustion hybridization, some studies based on simulations can be found in literature. Bailera et al. characterized these kind of systems and proposed district heating and industries as preferred applications [24,8]. Besides, they studied the application of PtG-Oxy hybridization in a combined cycle power plant, and showed that the 88% of the methanation heat can be integrated increasing the global efficiency of the power plant from 56% to 68% [25].

Another hybrid route to store fluctuating power from renewables is the Power to Chemicals concept. Those chemicals that require hydrogen and carbon dioxide for their production (e.g., methanol, ethylene, propylene, and formic acid) act as hybrid storage of energy and CO₂ when H₂ is renewably produced with electricity surplus. In these cases, there is no investment related to the methanation stage of the classic PtG concept, since this stage is substituted with an already existing line of production of chemical products [26]. This kind of hybridization puts together the water electrolysis stage of classic Power to Gas concept with an existing chemical line of production that substitutes methanation (Fig. 1). For instance, the CO2RRECT project produced hydrogen with renewable energy to reduce CO₂ and obtain carbon monoxide, which is later used as precursor of other chemical products [27].

In this paper, we propose for the first time the Power to Gas-Electrochemical industry hybridization, a new type of integration that implements methanation in chemical plants whose lines of production are based on chemical electrolysis. Whenever a chemical electrolytic process generates hydrogen as by-product, it can be integrated in a PtG process (Fig. 1). Thus, the PtG-Electrochemical hybridization avoids implementing the classical water electrolysis stage of PtG since hydrogen is already available in the plant. At the same time, the CO₂ emissions from the electrochemical plant can be used in the methanation process.

The overall objective of the paper is to size a hybrid PtG-Electrochemical plant through its simulation under real operating data from a Spanish factory. The system includes an amine-based CO₂ capture plant, a TREMP methanation plant, and an optimized heat exchanger network to energetically integrate both facilities. The relation between the operating hours of the different subsystems is a key parameter when sizing the Power to Gas plant, and it determines the degree of H₂ and CO₂ utilization, as well as

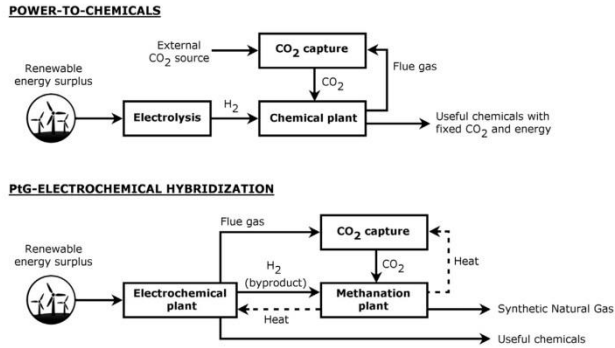


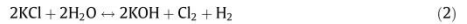
Fig. 1. Comparison between the classical power-to-chemical route and the novel PtG-Electrochemical hybridization.

the size of the required buffer of H₂ to manage the resource. The study concludes with an economic analysis of the proposed hybrid system.

2. Case study: power to gas-electrochemical hybridization

In PtG-Electrochemical hybridizations, the electricity used is no longer considered as consumption in the factory but as stored energy (it should be noted that the conversion of electricity to hydrogen will have lower efficiency than conventional water electrolyzer). This hybrid concept avoids most of the large investment costs (water electrolyzers) and an important part of the operational costs (electricity) associated to classical Power to Gas plants. These costs are removed since hydrogen is directly provided – i.e., by-produced – through other already existing electrochemical processes in the plant. In addition, carbon dioxide could be supplied from the boilers present in the electrochemical plant with low energy penalties thanks to the integration of the heat released in the methanation reaction.

We present here a case study of an existing plant with a significant amount of byproduct hydrogen coming from two electrolytic production lines: sodium chlorate (NaClO₃), Eq. (1), and chlorine (Cl₂) and potassium hydroxide (KOH), Eq. (2).



Currently, both sources of by-produced hydrogen are purified and mixed for further use. The 50% of the produced hydrogen is destined to ammonia (NH₃), the 25% to hydrochloric acid (HCl), and the 20% to hydrogen peroxide (H₂O₂); the remaining 5% are losses (Fig. 2).

The proposed hybridization consists of replacing ammonia production with synthetic natural gas production, since the latter is a more profitable product. In addition, the methanation process could consume CO₂ emissions from a boiler installed in the plant.

The availability of hydrogen in the plant fluctuates following the electricity market in order to operate the chemical electrolysis during the periods of low electricity prices. This operating strategy limits the amount of CO₂ that can be used in every period of time (Table 1). In this sense, January and February present potential CO₂ utilizations below 60%, whilst August usage capability is above 90%. The maximum potential yearly consumption of CO₂ reaches the 68% of total emissions, although this will be limited due to partial load operation restrictions in the methanation plant (periods of

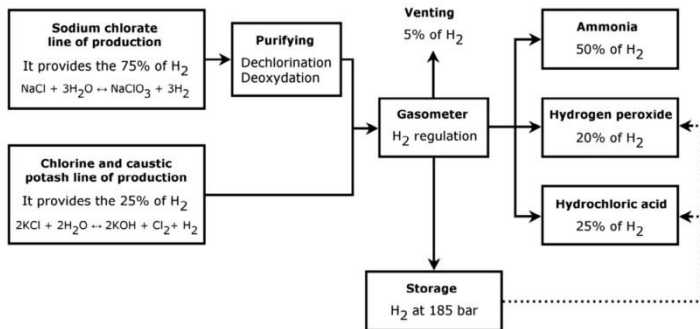


Fig. 2. Scheme of the hydrogen routes in the electrochemical plant.

Table 1
Available H₂, emitted CO₂ and potential CO₂ usable in PtG.

Month	H ₂ available [km ³ (NTP)]	CO ₂ emitted [km ³ (NTP)]	Max. CO ₂ usable [%]
January	1058	512	51
February	1067	465	57
March	1253	457	68
April	1260	466	67
May	1175	446	66
June	1116	312	89
July	949	387	61
August	1670	452	92
September	1179	483	61
October	1303	387	89
November	1078	353	76
December	1007	471	53
Total	14115	5171	68

low H₂ productions) and situations in which there is no enough CO₂ to convert the temporarily available hydrogen.

In this work, we have analyzed the hourly production pattern of H₂ to determine the actual potential of integrating Power to Gas in the selected electrochemical plant, with the aim of simulating the optimal-sized plant and performing a detailed economic assessment.

3. Methodology

The developed study comprises three main issues which have been sequentially approached: (i) the characterization of the hourly distribution of the H₂ availability, (ii) the simulation of the hybrid plant, and (iii) the development of an economic evaluation.

3.1. Evaluation of H₂ availability, and plant sizing

The chemical electrolysis lines of the plant present intensive energy consumptions, so their operations must follow the power market to reduce the operational costs. The electricity price varies among 6 time periods (P1 to P6) that are established by legislation [28,29]. It divides the year in 650 h of P1, 3126 h of P2-P5, and 4984 h of P6 (Fig. 3). Thus, the plant accordingly adapts the holidays and maintenances to mostly operate in Period 6 (the cheapest one), as well as diminishes the production load during periods P1 to P5. Finally, the hourly availability of H₂ along the year is completely defined by also considering the unplanned shutdowns. The operating hours of the electrochemical plant throughout periods P1 to P6 are summarized in Table 2.

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24		
January, February, December (Working days)																									
P6						P2		P1		P2		P1						P2							
16th–30th June, July (Working days)																									
P6						P2		P1						P2											
1st–15th June, September (Working days)																									
P6						P4		P3						P4											
March, November (Working days)																									
P6						P4		P3						P4											
April, May, October (Working days)																									
P6						P5																			
August, national holidays, and weekends																									
P6																									

Fig. 3. Hourly distribution of pricing period [28].

Table 2
Rates of by-production of H₂, and chemical electrolysis parameters, for the six market periods.

	NaCl electrolysis			KCl electrolysis		
	P1	P2-P5	P6	P1	P2-P5	P6
V _{H2} [m ³ /h (NTP)]	0.0	2333.0	3629.1	486.3	689.0	1296.9
V _{H2 ammonia} [m ³ /h (NTP)]	0.0	1166.5	1814.5	0.0	344.5	648.4
h [h/year]	0	1581	4584	570	2846	4584

The largest by-production occurs when both chemical electrolysis lines simultaneously operate at Period 6 (the most economic period) thus giving a maximum of 4926.0 m³/h (NTP) (Table 2). However, only the amount that would be consumed in ammonia can be used in methanation, which is equal to the 50% of the by-produced H₂. In addition, during Period 1 the by-produced hydrogen is very limited due to the high cost of electricity, and it is preferred to entirely dedicate it to the production of Hydrochloric acid and Hydrogen peroxide, instead of ammonia. Therefore, we also consider that during P1 there is no hydrogen available for methanation.

The boiler of the electrochemical plant (the CO₂ source) is operated 24 h per day, except those dates in which the facility is completely closed. Hence, the monthly emissions (Table 1) are equally divided between the operating days, what results in hourly emissions in the range 464–726 m³/h (NTP).

3.2. PtG-Electrochemical hybrid plant model

The proposed hybrid plant has been modelled and simulated in Aspen Plus[®], and then thermally integrated with Aspen Energy Analyzer through the Pinch analysis technique [30,31].

3.2.1. CO₂ capture plant model

Chemical absorption was considered the most suitable technology for CO₂ capture to be integrated in the electrochemical plant. Thus, a MEA absorption facility was designed and modelled in Aspen Plus[®] [32–34]. Fig. 4 shows the CO₂ capture process flowsheet.

Flue gas from the boiler is cooled down to 70 °C before entering the absorber at the bottom (A2). The solvent is introduced at the top of the column (A9). Reactions take place in the absorber with MEA and CO₂ flowing at countercurrent. Vent gas leaves absorber at the top (A10) and a solution of CO₂ and aqueous MEA (rich amine solution) leaves the column at the bottom (A3). Then, the temperature of the rich amine solution is increased from 64 to 80 °C in a heat exchanger (rich/lean exchanger) before entering at the top of the stripper (A11). Steam is required in the MEA regeneration (reboiler) and to separate the solvent and the CO₂. Steam reboiler temperature is limited to 120 °C, in order to prevent high MEA degradation rates and corrosion problems. The lean amine solution (A19) leaves stripper at 103 °C and then goes through the heat exchanger to transfer energy to the rich amine solution flow decreasing temperature down to 87 °C. To achieve a lower temperature before entering again the absorber (A9), an additional cooler is required for reducing solvent temperature to 37 °C. Finally, most of water content in CO₂ flow is removed in the condenser and high purity CO₂ gas flow leaves flash separator (A14).

The amine plant was modelled in Aspen Plus[®]. Besides operation temperature levels [35], some additional assumptions according to a quite conservative scenario were considered to accurately run the simulations [36,37]:

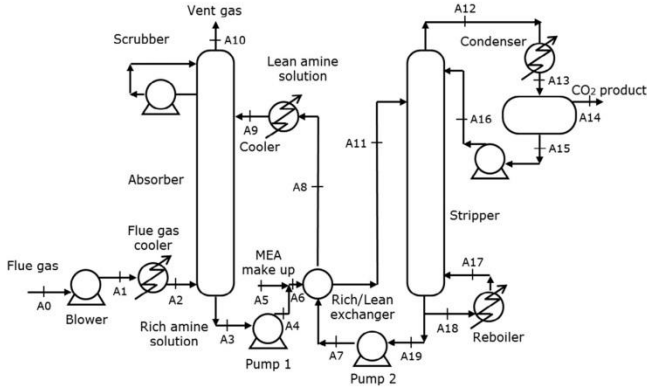


Fig. 4. Scheme of the CO₂ separating amine plant.

- (i) The MEA weight percentage in the absorption solvent was 20% wt.
- (ii) Stripper was designed to require solvent regeneration energy below 6 GJ/t_{CO₂} in any case and to obtain a CO₂ flow with a concentration higher than 94% vol.
- (iii) The amine plant columns were sized to capture more than 90% of CO₂ introduced with the flue gas.
- (iv) The final facility dimension was set according to methanation plant requirements. These values are collected in following section.

3.2.2. Methanation plant model

The proposed methanation scheme is based on TREMP™ technology [38]. It is composed by three adiabatic reactors at 30 bar, a recycling loop in the first reactor, and an intermediate water condensation after the second stage (Fig. 5). Thus, the obtained SNG reaches 95 vol% of methane, as the commercial natural gas that

can be purchased from the Spanish natural gas network [39]. We use adiabatic, catalytic methanation due to its greater scalability and energy integration potential [11].

First, hydrogen (1) and carbon dioxide (2) are pressurized through two multi-stage compressors, what increases the temperature of the gasses up to 300 °C. The outlet gas of Reactor 1 (6) is cooled down to 300 °C and partially recirculated (72%) with a blower (8). The temperature of the remaining flow is reduced to 250 °C prior entering into the next reactor (10). After this second absorption stage (11), water content normally exceeds the 60 vol %, what inhibits the reaction; hence, it is reduced to 13% by condensation (13). Then, the syngas has to be preheated back to 250 °C for the last methanation stage (15). Last, water content is removed again to achieve the required SNG quality. The plant has been simulated in Aspen Plus® considering pressure drops of 0.3 bar at methanation reactors and 0.6 bar at condensation tanks.

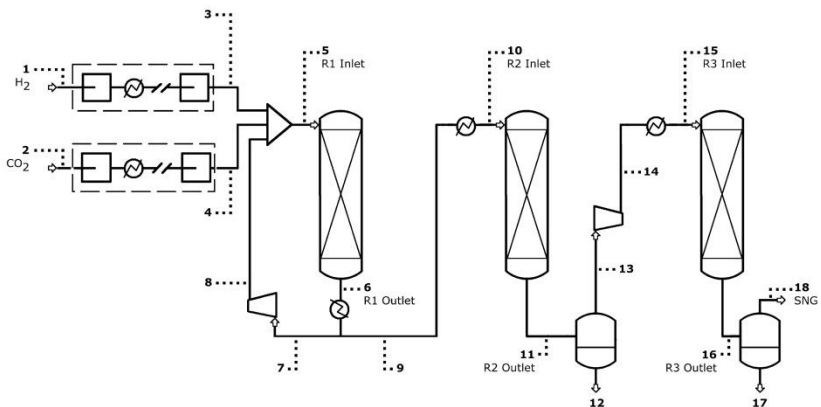


Fig. 5. Scheme of the methanation plant.

4. Results

4.1. H₂ availability and methanation plant size

The hydrogen and CO₂ availabilities (gray area and dashed line in Fig. 6, respectively) have been assessed for the year 2014. These graphs are built from the amount of hydrogen known to be available for each type of hour (Section 3.1, Table 2), taking also into

91.9% respectively. This maximum usage, α_i , is calculated according to Eq. (3), as the sum of the amount that is used in each hour, v'_{ij} [m³(NTP)] divided by the sum of the available amount, v_{ij} [m³(NTP)]. The values of v_{ij} are those presented in Fig. 6 (known data), while $V_{H2,PG}$ stands for the nominal hourly H₂ input of the methanation plant. In the case of the evaluation of the maximum usage, $V_{H2,PG}$ is set at 2462.9 m³ (NTP), which is the available H₂ when both lines of production operate at P6 (Table 2).

$$\alpha_i = \frac{\sum_j v'_{ij}}{\sum_j v_{ij}} \quad i = H_2, CO_2 \quad j = 1, 2, \dots, 8760 \quad (3)$$

$$i = H_2 \begin{cases} v'_{ij} = 0 & \text{if } v_{H2,j} \leq 0.6V_{H2,PG} \\ v'_{ij} = v_{H2,j} & \text{if } 0.6V_{H2,PG} < v_{H2,j} \leq 4v_{CO2,j} \\ v'_{ij} = 4v_{CO2,j} & \text{if } 4v_{CO2,j} < v_{H2,j} \end{cases}$$

$$i = CO_2 \begin{cases} v'_{ij} = 0 & \text{if } v_{H2,j} \leq 0.6V_{H2,PG} \\ v'_{ij} = v_{H2,j}/4 & \text{if } 0.6V_{H2,PG} \leq v_{H2,j} \leq 4v_{CO2,j} \\ v'_{ij} = v_{CO2,j} & \text{if } 4v_{CO2,j} < v_{H2,j} \end{cases}$$

account the planned and unplanned shutdowns that the factory reported for each line of production in 2015 (e.g., 1st January). The right axis of Fig. 6 is adjusted so that the gray area also indicates the corresponding amount of CO₂ required for methanation in each period. Most of the time, the boiler provides enough CO₂ to consume the produced hydrogen through methanation (dashed line, Fig. 6), although the limited emissions during months like November temporarily makes CO₂ insufficient at H₂ peaks (it occurred 1344 h during the year 2014).

These lacks of CO₂ force to set apart some of the available H₂ to maintain the stoichiometry of the methanation reaction. Additionally, there exist periods in which the hydrogen production is too low to reach the minimum operating load of the methanation plant (set at 60% according to literature [4]), so it must be stopped and none of the resources (CO₂, H₂) can be consumed. These two issues limit the maximum potential use of CO₂ and H₂ down to 62.5% and

The size of the hybrid plant was selected taking into account the operating hours (Fig. 7) and the percentage of the available H₂ that is finally used (Fig. 8). We also considered the inclusion of a tank to store the H₂, thus softening the intermittent behavior of the resources. The design criteria to size the facility are a minimum of 6000 operating hours and 85% of H₂ utilization, which give the area hold by the dashed line in Figs. 7 and 8. To reduce economic investment on equipment, we select a small H₂ buffer of 1000 m³ (NTP) and a methanation plant of 6 MW_{H2} input (1998.7 m³/h (NTP)), which leads to 6070 operating hours per year and a 85.9% usage of the available hydrogen. The associated amine plant required to fulfill the requirements of methanation has a nominal output of 500 m³/h (NTP) of CO₂, thus consuming up to the 58.2% of the CO₂ emitted.

The H₂ usage presented in Fig. 8 also follows Eq. (3), but in this case v_{ij} depends on the previous step v_{i-1} and v'_{i-1} , since they

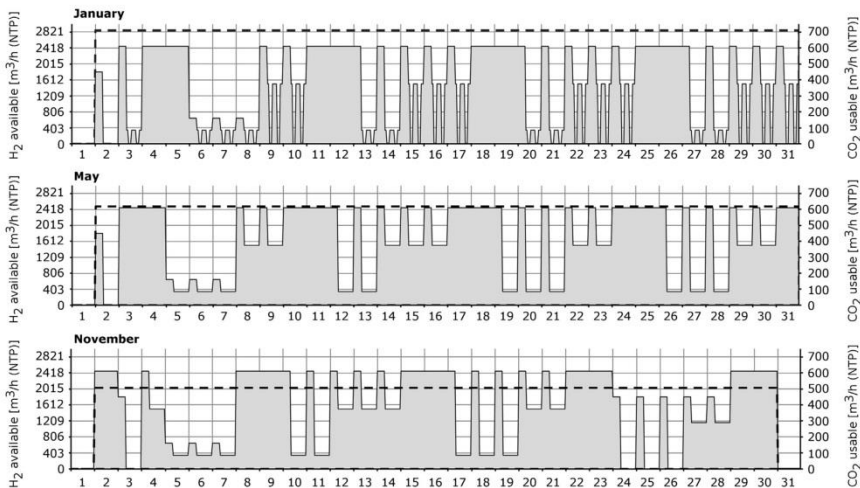


Fig. 6. H₂ (gray area) and CO₂ availabilities (dashed line) for January, May and November.

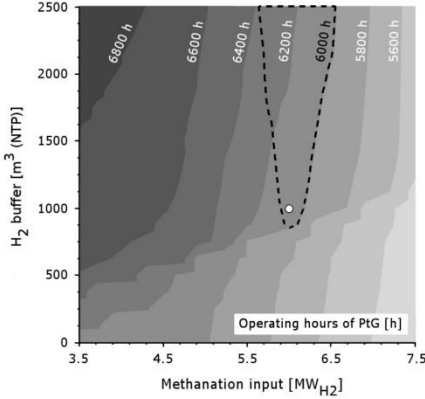


Fig. 7. Operating hours as a function of the methanation size and the H₂ buffer.

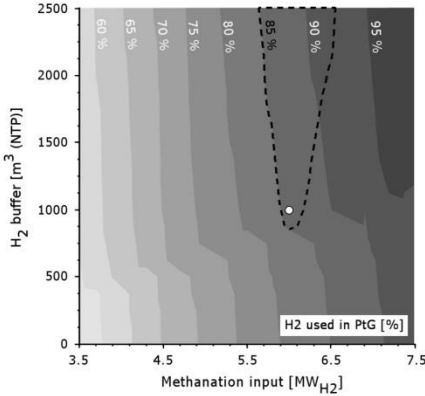


Fig. 8. H₂ utilization [%] as a function of the methanation size and the H₂ buffer.

modify the available H₂ in the buffer $v_{B,j}$. It should be noted that the x-axis determines the value of $V_{H_2,PG}$, and the y-axis sets the value of $v_{B,max}$. The following rules shall be satisfied:

$$\text{for } i = H_2 \begin{cases} v'_{ij} = 0 & \text{if } v_{H_2,j} + v_{B,j} \leq 0.6V_{H_2,PG} \\ v'_{ij} = v_{H_2,j} + v_{B,j} & \text{if } 0.6V_{H_2,PG} < v_{H_2,j} + v_{B,j} \leq 4v_{CO_2,j} \\ v'_{ij} = 4v_{CO_2,j} & \text{if } 4v_{CO_2,j} < v_{H_2,j} + v_{B,j} \end{cases}$$

$$\text{for } i = CO_2 \begin{cases} v'_{ij} = 0 & \text{if } v_{H_2,j} + v_{B,j} \leq 0.6V_{H_2,PG} \\ v'_{ij} = (v_{H_2,j} + v_{B,j})/4 & \text{if } 0.6V_{H_2,PG} \leq v_{H_2,j} + v_{B,j} \leq 4v_{CO_2,j} \\ v'_{ij} = v_{CO_2,j} & \text{if } 4v_{CO_2,j} < v_{H_2,j} + v_{B,j} \end{cases}$$

where $v_{B,j}$ depends on the previous step in the following way:

- If the available hydrogen is below the minimum partial load ($v_{H_2,j} + v_{B,j} \leq 0.6V_{H_2,PG}$), the produced H₂ is stored

$$\begin{cases} v_{B,j+1} = v_{B,j} + v_{H_2,j} & \text{if } v_{B,j} + v_{H_2,j} < v_{B,max} \\ v_{B,j+1} = v_{B,max} & \text{if } v_{B,max} \leq v_{B,j} + v_{H_2,j} \end{cases}$$

- If the available carbon dioxide is enough to consume all the hydrogen ($0.6V_{H_2,PG} < v_{H_2,j} + v_{B,j} \leq 4v_{CO_2,j}$), the buffer is empty $v_{B,j+1} = 0$

- If the hydrogen is enough to consume all the carbon dioxide, but it is necessary to use part of the buffered hydrogen ($4v_{CO_2,j} < v_{H_2,j} + v_{B,j}$), the stored H₂ will diminish

$$\begin{cases} v_{B,j+1} = v_{B,j} - (4v_{CO_2,j} - v_{H_2,j}) & \text{if } 0 < v_{B,j} - (4v_{CO_2,j} - v_{H_2,j}) \\ v_{B,j+1} = 0 & \text{if } v_{B,j} - (4v_{CO_2,j} - v_{H_2,j}) \leq 0 \end{cases}$$

- If the produced H₂ during the hour j is enough itself to consume all the CO₂ ($4v_{CO_2,j} < v_{H_2,j}$), the buffer will store more hydrogen up to its limit

$$\begin{cases} v_{B,j+1} = v_{B,j} + (v_{H_2,j} - 4v_{CO_2,j}) & \text{if } v_{B,j} + (v_{H_2,j} - 4v_{CO_2,j}) < v_{B,max} \\ v_{B,j+1} = v_{B,max} & \text{if } v_{B,max} \leq v_{B,j} + (v_{H_2,j} - 4v_{CO_2,j}) \end{cases}$$

Regarding the operating hours, τ , it is given by Eq. (4):

$$\tau = \frac{\sum_j v'_{H_2,j}}{V_{H_2,PG}} \quad (4)$$

4.2. PtG-Electrochemical hybrid plant

Once methanation plant size was defined, the amine plant was designed according to the CO₂ requirements (496 m³/h (NTP) of CO₂ at nominal output). Table 2 shows the main results obtained from the Aspen Plus simulation of the CO₂ capture plant.

The CO₂ output from the amine plant meets the requirement of the reactors in the methanation plant. A total gas flow of 524.3 m³/h (NTP) is produced from the stripper with a composition of 94.6 vol% CO₂ and 5.4 vol% H₂O. The total auxiliary consumption of the amine plant (14.2 kW) is much lower than the one in the methanation plant. However, heating and cooling demands are significant, especially in the reboiler (1494.3 kW) and in the additional solvent cooler (−937.6 kW).

The simulated methanation plant produces 518.6 m³/h (NTP) of SNG mainly composed by 95.2 vol% CH₄ and 4.1 vol% H₂ (Table 3). The technical data of SNG show that it can be used in typical applications (LHV of 49.8 MJ/kg, density of 0.694 kg/m³(NTP), and Wobbe index of 49.76 MJ/m³). Relevant data of temperature, pressure and flows throughout the methanation plant are presented in Table 4.

The total auxiliary consumption of the methanation plant (513.7 kW) mostly comes from the multi-stage compressors (402.9 kW for H₂, and 105.7 kW for CO₂), while blowers' consumption represents less than 1%. Besides, whenever the plant is operating at full load and simultaneously storing H₂, the hydrogen compressor could require up to 495.6 kW.

The overall cooling and heating needs of the hybrid plant (methanation/carbon capture) are 3675.3 kW and 1533.7 kW, respectively (Table 5). Most of the heat requirement takes place during the desorption stage of the captured CO₂ in the amine plant. Nevertheless, this external heating demand can be suppressed by integrating the streams of both systems (Fig. 9, empty-dot exchangers), what concurrently diminishes the cooling needs down to 2141.6 kW. Moreover, there are remaining cooling necessities with high temperature level (R1 outlet), that allows producing 238.8 kg/h of steam at 180 °C for the electrochemical plant; the remainder energy can be cooled with water since the temperatures

Table 3
CO₂ capture plant simulation results.

<i>Absorber</i>	
Design stages	14
Pressure (bar)	1.0
Top stage temperature (°C)	63.5
Bottom stage temperature (°C)	64.3
Reflux ratio	3.9
Boilup ratio	0.3
<i>Stripper</i>	
Design stages	14
Pressure (bar)	1.0
Top stage temperature (°C)	88.9
Bottom stage temperature (°C)	102.8
Reflux ratio	0.4
Boilup ratio	0.15
Reboiler type	Kettle
Thermal energy demand (GJ/t _{CO2})	5.5
<i>CO₂ product characteristics</i>	
Temperature (°C)	34.0
Pressure (bar)	1.0
Volume flow (m ³ /h (NTP))	524.3
Mass flow (kg/h)	997.5
Mass composition (kg/h)	
CO ₂	974.6
H ₂ O	22.8
O ₂	0.002
N ₂	0.087
MEA	–
Mole fraction (%)	
CO ₂	94.6
H ₂ O	5.4
O ₂	3 ppm
N ₂	132 ppm
MEA	–

Table 4
Molar compositions [%] in the methanation plant.

	H ₂ inlet	CO ₂ inlet	R1 inlet	R1 outlet	R2 outlet	R3 inlet	R3 outlet	SNG
CO ₂	0.0	94.6	9.9	4.3	1.3	3.0	0.2	0.3
H ₂	100.0	0.0	41.5	19.6	6.2	14.3	3.3	4.1
CH ₄	0.0	0.0	15.5	24.5	30.2	69.7	76.8	95.2
H ₂ O	0.0	5.4	32.8	51.1	62.3	13.0	19.7	0.4
CO	0.0	0.0	0.3	0.5	0.0	0.0	0.0	0.0

Table 5
Temperature, pressure and flows in the methanation plant.

Point	Temperature [°C]	Pressure [bar]	Flow [m ³ /h (NTP)]
1	25.0	1.0	1998.7
2	34.0	1.0	524.3
3	305.2	30.0	1998.7
4	287.4	30.0	524.3
5	300.1	30.0	6879.1
6	582.7	29.7	6050.3
7	300.0	29.7	4356.2
8	301.7	30.0	4356.2
9	300.0	29.7	1694.1
10	250.0	29.7	1694.1
11	414.1	29.4	1572.2
12	136.1	28.8	891.0
13	136.1	28.8	681.2
14	141.1	30.0	681.2
15	250.0	30.0	681.2
16	358.0	29.7	643.2
17	40.0	29.1	124.5
18	40.0	29.1	518.6

to reach are not lower than 34 °C (Fig. 9, solid-dot exchangers). The minimum temperature difference between hot and cold streams for the design of the exchanger network is 10 °C.

4.3. Economic analysis

To accomplish the economic analysis of the whole facility, the costs of the main equipment for the three processes were obtained: the amine plant, the methanation plant and the optimized heat exchanger network. Then, total capital investment (CAPEX) was completed including other direct and indirect costs as a percentage of the total purchased equipment. Operating cost (OPEX) includes the production costs, which consist of the O&M, electricity, cooling water, MEA and catalyst renovation. Regarding the economic incomes, two concepts were considered: the Natural Gas (NG) and the additional medium pressure (MP) steam produced in the optimized HEN. This steam is used in the electrochemical industry and hence, can be considered as an input from the network. Meanwhile, natural gas is used in the boiler of the electrochemical plant in order to avoid its purchase from external companies (the selling price would be lower than the purchase price, so thus the income is maximized). The NG price was obtained according to the market (28.99 €/MWh) and the MP steam price was obtained as the NG saving for its generation in conventional gas fired boilers in the baseline scenario (24.64 €/t). Table 6 shows the complete CAPEX and OPEX of the PtG-Electrochemical hybrid plant and the total year incomes of the facility. Some costs regarding the amine plant were included in the HEN disaggregated costs in order not to duplicate equipment costs. Solvent cooler, gas cooler and reflux condenser cooling needs are covered with cooling water and heat exchangers are already included in the HEN (E-112, E-113 and E-114).

Considering previous values, total CAPEX of the facility is 5.13 M€, of which 56% correspond with the cost of the equipment. OPEX is about 0.216 M€/year and total incomes are 1 M€/year. To obtain the Net Present Value (NPV), the Internal Rate of Return (IRR) and the Pay-back (PB) of the investment, a 5% discount rate and a 20 years lifetime were considered. Table 7 shows the economic results for the base case and for different discount rates (see Table 8).

Economic analysis shows positive values that can make attractive the PtG-Electrochemical plant erection. Analyzing the base case scenario (5% of discount rate) it can be observed that capital investment will be recovered in 8 years, generating a 4.8 M€ NPV at the end of the project lifetime with an IRR of 9%. Hence, the present case study avoids the requirement of subsidies to be economically feasible, contrarily to similar PtG research projects that can be found in literature [11]. This is mainly because the H₂ is available in the own industry and no additional water electrolyzers are required. Normally, water electrolyzer represents the highest cost in a PtG facility and it makes very difficult to recover capital investment in a reasonable period of time. Furthermore, the size of the current facility has been carefully chosen after a previous complete analysis of the different processes and taking into account the input gas flows to the methanation plant. In order to extend the economic study, some sensitivity analyses have been performed. Two main parameters were analyzed due to their significant influence on the final revenues of the project: NG price and CO₂ credit price. Firstly, NG price is usually quite unstable and its final value depends on the oil and gas market. In addition, final use of the SNG can be also influenced on the sale price (e.g., transport, gas-fired facilities, NG national network). Regarding CO₂ credit price, there also exists a high uncertainty. Actually, no CO₂ credit revenue has been considered in this study since this particular industry does not have to pay for its emissions. However, if we consider that SNG is fired in the boilers of the chemical facility, CO₂ is always in a loop. It is not emitted since produced CO₂ is the same that is captured and used for SNG production.

In addition, electricity price variation will also have an influence on the cost analysis, especially a change in the pricing system

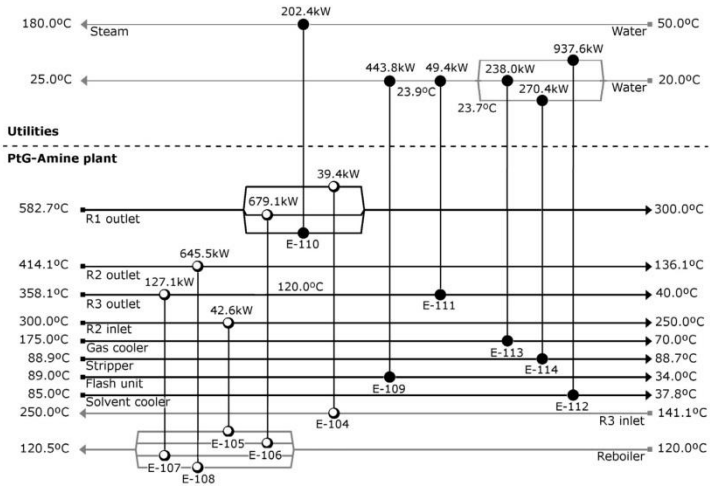


Fig. 9. Optimized heat exchanger network (black lines – hot streams, gray lines – cold streams).

Table 6
Streams of the pinch analysis.

	Stream	T_i [°C]	T_r [°C]	ΔQ [kW]
<i>Amine capture plant</i>				
Solvent cooler (A8)	Hot	85.0	37.8	-937.6
Gas cooler (A1)	Hot	175.0	70.0	-238.0
Stripper condenser	Hot	88.9	88.7	-270.4
Flash unit (A13)	Hot	89.0	34.0	-443.8
Reboiler	Cold	120.0	120.5	1494.3
<i>Methanation plant</i>				
R1 outlet (6)	Hot	582.7	300.0	-920.9
R2 inlet (9)	Hot	300.0	250.0	-42.6
R2 outlet (11)	Hot	414.1	136.1	-645.5
R3 inlet (14)	Cold	141.1	250.0	39.4
R3 outlet (16)	Hot	358.1	40.0	-176.5
<i>Electrochemical plant</i>				
Cold water	Cold	20.0	25.0	1939.2
Steam	Cold	50.0	180.0	202.4

because it will modify not only the OPEX but also the operation hours of the hybrid plant since they directly depend on the billing periods. In any case, this kind of chemical plants based on electrolyzers follow the same operational procedure and their production depends on the electricity price, working at nominal load when electricity prices are low and diminishing production when electricity prices are higher. This pattern is perfectly adapted to the hybrid concept since it also takes advantage of the lower electricity prices periods when the largest by-production of hydrogen occurs.

Figs. 10 and 11 show the influence on economic parameters of both, NG price and CO_2 credit price. The higher NG price is, the more profitable is the investment. It is difficult to predict the evolution of oil and gas fuels, but it is expected a future rise of their prices. For instance, a 15% increase of NG price (from 29 to 33.3 €/MWh) would increase IRR up to 12% with a PB of 6 years and a half achieving very remarkable results for this kind of pro-

jects. The case regarding CO_2 credit price is more complex. The lack of a clear regulation or definitive taxes for these singular facilities make difficult to establish a future price. Nevertheless, 30 €/t CO_2 is a reasonable value for making competitive the most CO_2 capture technologies. With this CO_2 credit price, PB is reduced below 6 years and a half and IRR is increased up to 12.4%.

5. Conclusions

We have proposed a novel PtG-Electrochemical hybrid plant that incorporates methanation as a new chemical line of production, thus rising in value substantial amounts of available byproduct hydrogen, and consuming CO_2 emissions from its own gas-fired boilers. The preliminary analysis shows that the products yielding lower profits, like ammonia, are the most suitable to be substituted. The analysis has been carried out using real operating data of an electrochemical factory.

Table 7
CAPEX, OPEX and year incomes for the PtG-Electrochemical hybrid plant.

Reference	Equipment/process	Cost (€)	Parameter, A	Cost equation (€)
CAPEX				
Direct costs				
Equipment costs				
CO ₂ capture amine plant (total cost, 523486 €)				
[40]	Amine plant	523486	CO ₂ captured (t/h)	$26.094 \cdot 10^6 \cdot (A/408)^{0.855}$
Methanation plant (total cost, 2158644 €)				
[41]	H ₂ compressor	286978	Power (kW)	$26.7 \cdot 10^4 \cdot (A/445)^{0.67}$
	CO ₂ compressor	101916		
	Recirculation blower	10390		
	Blower	6150		
[42]	Reactors	1660500	SNG power (kW)	300·A
[43]	H ₂ storage tank	50614	H ₂ (kg, 30 bar)	563·A
[41]	Catalyst	42097	Catalyst (m ³)	187500·A
HEN (total cost, 179642 €)				
Simulation model				
	E-108	22992	Area (m ²)	Aspen energy analyzer 9016.3 + 721.3·(A) ^{0.8}
	E-113	45716		
	E-109	13459		
	E-114	9912		
	E-112	14981		
	E-104	10546		
	E-106	14894		
	E-110	11276		
	E-111	11822		
	E-105	10135		
	E-107	13908		
Total equipment cost, 2861772 €				
Other direct costs				
[40]	Installation	400648	Total equipment costs (€)	14%·A
	Instrumentation & control	286177		10%·A
	Piping	457884		16%·A
	Electrical	85853		3%·A
	Building	57235		2%·A
	Land	28618		1%·A
Total direct costs, 4178188 €				
Indirect costs				
[40]	Engineering	292473	Total direct costs (€)	7%·A
	Legal expenses	51387		Total CAPEX (€)
	Construction expenses	102774		2%·A
	Contingency	513869		10%·A
Total indirect costs, 960503 €				
Total CAPEX, 5138691 €				
OPEX (€/year)				
[41]	MEA renovation	27679	MEA (t/year)	1520·A
–	Catalyst renovation	6315	Initial catalyst cost (€)	15%·A
–	Waste management	2000	–	–
[28]	Electricity	25512	kWh	Pricing period
[40]	O&M	154161	Total CAPEX (€)	3%·A
Total OPEX, 215666 €/year				
Incomes (€/year)				
	Natural gas	976990	SNG (MW h/year)	28.99 (€/MW h) · A
	MP steam	35716	MP steam (t/year)	24.64 (€/t) · A
Total incomes, 1009706 €/year				
Annual benefit, 794040 €/year				

This work shows that PtG-Electrochemical hybrid plant is technical and economically feasible. The plant can be running more than 6000 h per year consuming more than the 85% of available hydrogen and almost 60% of the CO₂ emitted by the chemical industry. The hybrid plant can achieve a production of 518.5 m³/h (NTP) of SNG and additionally 238 kg/h of MP steam that are used in the industry itself. Since no additional water electrolyzers

and consequently, no further electricity consumption is required, economic analysis yield very remarkable figures. Analyzing the base case scenario (5% discount rate) it can be observed that capital investment will be recovered in 8 years, generating a 4.8 M€ NPV at the end of the project lifetime with an IRR of 9%. Moreover, sensitivity analyses have also shown that these values can be even better if CO₂ credit price or NG price increase in a near term.

Although this is a particular case study, some conclusions can be generalized with the aim of speeding up the deployment of PtG at industrial scale. The present PtG-Electrochemical hybrid technology can overcome the economic barriers of erecting a commercial plant, thus allowing gaining operational experience concerning methanation reactors and their performance with variable H₂ and CO₂ flows. In addition, it is expected that equipment cost can be reduced in a future and this reduction could be achieved faster with more industrial scale facilities.

Table 8
PB, IRR and NPV evaluation for different discount rate.

Discount rate	PB (years)	IRR (%)	NPV (M€)
3.0%	7.3	11.07	6.68
4.0%	7.6	10.00	5.65
5.0%	8.0	8.96	4.76
6.0%	8.4	7.93	3.97
7.0%	8.9	6.92	3.27

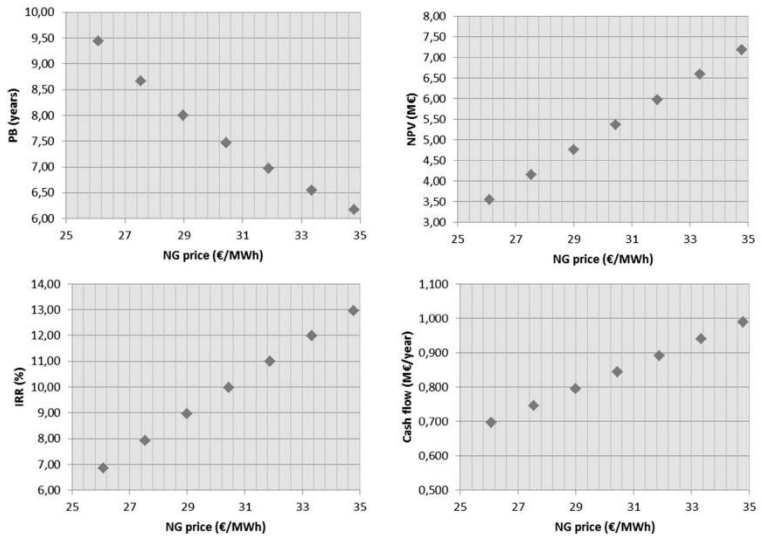


Fig. 10. NG price influence on economic parameters.

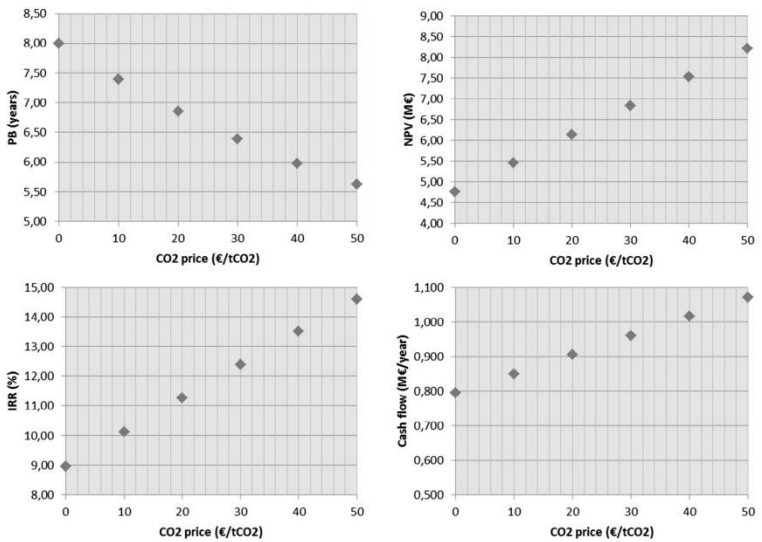


Fig. 11. CO₂ credit price influence on economic parameters.

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4 Summary of the thesis

4 Summary of the thesis

4.1 METHODOLOGY

The overall objective of this thesis was to propose and analyze new configurations of Power to Gas that recycle CO₂ in closed loops, and which can improve the technology in terms of efficiency, utilization of resources and profitability. Secondary tasks included the review of the state of the art of Power to Gas technology, as well as the forecast of the Spanish electricity surplus for the coming decades. The corresponding methodologies of each task clearly differ, so they are presented separately in the following subsections.

Task I: Assessment of expected electricity surplus under future Spanish energy scenarios

The developed model estimates the annual electricity surplus that the Spanish energy system might have in the next decades. This is calculated from the difference between electric production and demand for each day, under different wind generation patterns. The estimation of the electricity demand is based on *The Global Calculator* [42], a tool that models the world's energy, land and food systems to explore future energy scenarios. The electricity production is calculated as the product of the installed power capacity and the operating hours, which are heuristically inferred from the analysis of historical data. Additional restrictions are imposed to validate the feasibility of these scenarios and guarantee the technical consistency. The calculations are performed in Microsoft Excel spreadsheets, and the methodology has been widely explained in section "2.1.1 Future energy scenario model".

Task II: Review of the state of the art of Power to Gas plants

The methodology of Task II consists of thorough literature searches. Scopus was the main tool used, since it is the largest abstract database concerning scientific journals and conference proceedings. Most projects were identified through the Acknowledgement sections of scientific papers, or in journals dedicated to technical news like Fuel Cells Bulletin. Besides scientific manuscripts, additional relevant data was gathered from projects' web pages, official press releases, and annual reports of the involved companies.

Task III and IV: Development of Power to Gas hybrid concepts

According to the level of knowledge of the involved systems, the most suitable methodology for the third and fourth tasks is computer simulation. Specifically, the design and model analysis of the hybrid concepts were carried out using the chemical process simulation software Aspen Plus®.

The developed simulations use the PSRK property method provided by Aspen Plus®. This package is based on the predictive Soave-Redlich-Kwong equation-of-state model. Meanwhile, the Holderbaum-Gmehling mixing rules predict the binary interactions at any pressure, directly provided by the Aspen Plus® database. Besides, it is assumed chemical equilibrium and steady state operation in every simulated process (e.g., methanation, oxy-fuel combustion).

Methanation reactors are modelled with RGibbs units, which calculate the equilibrium of the reaction by minimizing the Gibbs free energy. The combustion of natural gas also uses an RGibbs unit, since all the participants are pure gases. Then, to describe coal and biomass, two nonconventional solid physical property models must be included. These models are based in correlations verified by the Institute of Gas Technology, which use the fuels' proximate analysis, ultimate analysis and sulfur analysis to perform the calculations. The HCOALGEN model calculates the heat of combustion, the standard heat of formation, the heat capacity and the enthalpy of the solid fuels, while the DCOALIGT model is used to calculate their density. The complete procedure to model the combustion of solids in Aspen Plus® can be found in the corresponding manual [163].

In the case of heat integration analyses, these are made with the energy management software Aspen Energy Analyzer, which is included in the Aspen Plus® suite. It allows to design optimal heat exchanger networks based on Pinch analysis methodology, as well as to quantify their capital

cost. In general, the economic evaluation for the rest of the equipment was based on literature data and performed in Microsoft Excel spreadsheets.

4.2 CONTRIBUTIONS

The present thesis is framed in the field of engineering. Main contributions comprise proposals and explorations of innovative solutions to technical issues that hinder the development of novel technologies. In this case, the problems to tackle are the low round-trip efficiency of Power to Gas technology and its required high investment. Previous works from literature approach these issues by researching on different internal configurations for the reactors or by improving the catalyst's performance [13][37]. In this thesis, the main original point is to tackle the problem through the use of synergies with other technologies and processes. This line of research is complementary to the improvements that other authors show in literature about reactors or catalysts. Main contributions are summarized as follows:

- 1) The global 'CO₂ recycling' concept depicted by Hashimoto [55] was applied for the first time to single Power to Gas systems. This allows to avoid the CO₂ emissions of the conventional PtG configuration [14] by means of consuming the SNG in the facility itself, instead of in decentralized applications. This concept makes PtG a valid technology to tackle climate change and overcome CO₂ geological storage.
- 2) Two novel Power to Gas configurations that approach the 'CO₂ recycling' concept were proposed and modeled: Power to Gas-Oxyfuel combustion in power plants, and Power to Gas-Amine carbon capture applied to electrochemical industries. The thermochemical models of each sub-system have been previously used in literature (methanation [164], solid fuel combustion [163], amine carbon capture [165], and Pinch analysis [159]), but their combined application is an original contribution of this thesis to quantify the synergies of the proposed hybrid systems.
- 3) The required size ratios between electrolysis and oxy-fuel combustion to avoid the ASU or/and the CO₂ storage were characterized for three different input fuels (coal, biomass and natural gas). This enabled to establish the most suitable applications for the PtG-Oxycombustion integration.

- 4) A Power to Gas-Oxyfuel combined cycle was modeled and thermally integrated to approach the potential improvement in terms of the round-trip efficiency of the system.
- 5) A model was entirely developed (Annex B) to properly size a methanation plant to be integrated in a chemical industry. It is based on the resource utilization and the yearly-round operation of the chemical plant. This model allows to adapt the PtG-Electrochemical proposal to specific facilities.
- 6) A complete economic analysis of the PtG-Electrochemical integration was elaborated with real data from a chemical company. It was shown that the concept is economically feasible, what may help speeding up the deployment of PtG at industrial scale and overcome the economic barriers of erecting a commercial plant.

Complementary contributions to the core objective are:

- 7) A thorough review that gathers the construction and operation of pilot-, demo- and lab plants concerning Power to Gas technology. Besides, a timeline was built to track the evolution of research lines of different companies and institutions.
- 8) The assessment of expected future renewable electricity surplus in Spain up to year 2050. To this aim, a model of future Spanish electricity demand, production and power capacity was developed.

Besides the research directly related to this thesis, it should be highlighted the participation in the following projects:

- 2014 – “Energy storage through methane. Preliminary analysis of
2015 scenarios with high share of renewable energy in the Spanish electricity market”, funded by Fundación Iberdrola
- 2014 – “Innovative processes: Implementation of Power-to-Gas
2015 technology in the Aragonese Pyrenees”, funded by Dirección General de Industria y de la Pequeña y Mediana Empresa
- 2015 – “Energy storage (Power-to-Gas) and carbon capture integration
2016 in chemical industry with hydrogen production”, funded by Departamento de industria e Innovación Gobierno de Aragón

2017 – “Metano a partir de Energías Renovables y Captura y Utilización de CO₂ en el Sector Residencial, Industrial y Automovilístico”, funded by Ministry of Economy, Industry and Competitiveness

The contributions to international conferences done during the development of the thesis are:

- 2015 Bailera M., Lisbona P., Romeo LM., Analysis of power-to-gas technology with oxyfuel combustion integration. 2nd International Conference on Renewable Energy Gas Technology, 7th-8th May 2015, Barcelona, Spain. Proceedings, pp. 143-144
- 2016 Bailera M., Espatolero S., Romeo LM., Lisbona P., Gracia F., Simón E., Escudero JM., Usón A., Power-to-Gas and carbon capture integration strategies in an electrochemical industry. 3rd International Conference on Renewable Energy Gas Technology, 10th-11th May 2016, Malmö, Sweden. Proceedings, pp. 157-158
- 2016 Bailera M., Romeo LM., Espatolero S., Lisbona P., Reducing energy penalty of oxycombustion through Power-to-Gas hybridization. 1st International Conference on Bioenergy & Climate Change, 6th-7th June 2016, Soria, Spain. Proceedings pp. 241
- 2016 Bailera M., Romeo LM., Espatolero S., Lisbona P., Ferriz AM., Simón J., Bandrés A., Marco P., Power to Gas implementation in the Aragonese Pyrenees. 21st World Hydrogen Energy Conference, 13th-16th June 2016, Zaragoza, Spain. Proceedings, pp. 760-761
- 2016 Bailera M., Romeo LM., Espatolero S., Lisbona P., Future applications of hydrogen production and CO₂ capture for energy storage. 21st World Hydrogen Energy Conference, 13th-16th June 2016, Zaragoza, Spain. Proceedings, pp. 504-505
- 2016 Bailera M., Lisbona P., Espatolero S., Romeo LM., Power to Gas technology in Spanish future energy market. 13th International Conference on Greenhouse Gas Control Technologies, 14th-18th November 2016, Lausanne, Switzerland. Energy Procedia, 114, 6880-6885.
- 2017 Romeo LM., Bailera M., Lisbona P., Peña B., Power-to-Gas and CO₂ capture. Smart storage (& management) of renewable energy. 2^a Conferencia Aportando Valor al CO₂, 9th-10th May 2017, Tarragona, Spain. Proceedings, pp. 91-92

- 2017 Bailera M., Romeo LM., Lisbona P., Espatolero S., Peña B., CO₂ recycling based on 'Power to Gas-Carbon capture' hybrid systems. 9th Trondheim Conference on Carbon Capture, Transport and Storage, 12th-14th June 2017, Trondheim, Norway. Proceedings, pp. 92-93

Additionally, a contribution to a local Doctoral Day was made:

- 2014 Bailera M., Lisbona P., Romeo LM., Power-to-Gas hibridado con oxidación. 6^a Jornada de Jóvenes Investigadores en Física y Química de Aragón, 20 Noviembre 2014, Zaragoza, España. Proceedings, pp. 35

4.3 CHALLENGES AND FURTHER WORK

Roadmaps for further research are essential to valorize the developed work. In this thesis, the core objective was to propose enhanced configurations of Power to Gas able to recycle CO₂ in closed loops.

Regarding the two proposed concepts (PtG-Oxycombustion and PtG-Electrochemical industry), the approach and depth of the analyses were completely different. For that reason, recommendations about further work must be specific for each system.

In the case of PtG-Oxycombustion, it was found that district heating and industry sectors were the most suitable applications. Additionally, it was shown that even a small oxy-combine cycle power plant needs about 100 MW of electrolysis power capacity to be integrated, so an economic analysis may be worthless. Hence, next research stages to continue the characterization of PtG-Oxycombustion option should include:

- To model and simulate a PtG-Oxyfuel boiler applied to district heating. It is highly encouraged to perform a real study case to properly evaluate the benefits of thermal integration.
- To economically evaluate the district heating application under realistic scenarios. Depending on results, it could consider the integration with photovoltaic systems rooftop-mounted on the buildings belonging to the heating network.
- To model and simulate a PtG-Oxyfuel boiler applied to the industry. Recommended sectors are paper or chemical

industries [151]. A real study case is highly encouraged to properly evaluate the heat integration.

- To economically evaluate the industry application of the PtG-Oxycombustion systems.

In the case of PtG-Electrochemical industry hybridization, the developed analysis already included the economic evaluation of the concept. The positive results were found to motivate the extrapolation to other type of chemical plants. Next research stages may include:

- To assess potential chemical lines of production suitable for PtG integration, other than those present in chlorine industry. To model and simulate the most promising options.
- To economically evaluate the new proposals of PtG-Chemical industries. Real study cases are recommended.

Power to Gas is conceived to manage renewable electricity surplus. Hence, variable and transient operation becomes mandatory in further research. Since the technical and economic advantages of the proposed applications have been already analyzed, the characterization of their variable operation arises now as top priority. However, most of the existing methanation kinetic models that can be found in literature have not been validated at industrial conditions [166][167][168].

Among the few authors who developed their own kinetic model, Rönsch et al. [168], Xu and Froment [169] and Zhang [170] are the most relevant. The operating conditions used by Zhang to validate the model are 1-5 bar and 250-360 °C, far from modern industrial methanation plants [170]. Xu and Froment kinetic model was validated at high pressure but the CO methanation step was only validated above 630 °C [169]. Rönsch et al. [168] are the only authors that aimed at developing a kinetic model with wide range of applicability. To that end, they combined different kinetic studies from literature and built a more consistent model. However, minor dimensional errors led to equations not suitable to be used in its published form (probably erratum) [168]. Thus, next research stages regarding this issue would be:

- To validate the kinetic equations developed by Rönsch et al. with experimental data in the desired operating conditions.
- To study how the partial load operation and the transitory periods can affect to thermal integrations and the quality of the SNG produced. Additionally, effects on equipment and auxiliaries should be study (new technical requirements or limitations).

Part of this further research is included in the MERCURIA project, which belongs to the Mechanical Engineering Department of the Universidad de Zaragoza. This project started in January of 2017 and comprises the designing, building and operating of a lab-scale methanation system.

4.4 CONCLUDING REMARKS

The results of this thesis contribute to the development of more efficient applications of PtG technology in terms of utilization of both energy and resources. Power to Gas is attracting a great deal of attention and constitutes one of the most promising candidates in mid-term for massive energy storage and for the decarbonization of sectors based in natural gas. Progress is undoubtedly still required on large scale experimental development, especially for variable operation to follow patterns of electricity surplus. Nevertheless, the novel CO₂ recycling configurations of Power to Gas that were presented in this thesis show an excellent potential to avoid the CO₂ geological storage typically required to make sense of carbon capture technologies. This should increase the interest of Power to Gas and enable its deployment at large-scale, even more when the positive economic results of the electrochemical industry case are considered.

NOMENCLATURE

Variable	Units	Description
α_i	%	Usage of resource i
ΔQ	kW	Exchanged thermal energy
ΔT_{Pinch}	K	Minimum temperature difference between hot and cold streams for the design of the heat exchanger network
ξ_{ASU}	$\text{kW}_{\text{H}_2} \cdot \text{kW}_t^{-1}$	Minimum value of ξ_{oxy} to avoid the ASU requirement
ξ_{CO_2}	$\text{kW}_{\text{H}_2} \cdot \text{kW}_t^{-1}$	Minimum value of ξ_{oxy} to consume all generated CO_2
ξ_{oxy}	$\text{kW}_{\text{H}_2} \cdot \text{kW}_t^{-1}$	Ratio between the chemical energy of the H_2 from electrolysis and the net thermal output of the oxyfuel combustion
ξ'_{ASU}	$\text{kW}_{\text{H}_2} \cdot \text{kW}_e^{-1}$	Minimum value of ξ'_{oxy} to avoid the ASU requirement
ξ'_{CO_2}	$\text{kW}_{\text{H}_2} \cdot \text{kW}_e^{-1}$	Minimum value of ξ'_{oxy} to consume all generated CO_2
ξ'_{oxy}	$\text{kW}_{\text{H}_2} \cdot \text{kW}_e^{-1}$	Ratio between the chemical energy of the H_2 from electrolysis and the net electric output of the oxyfuel combustion
η	—	Efficiency
$v_{B,j}$	Nm^3	H_2 present in the buffer at the beginning of hour j
$v_{B,\text{max}}$	Nm^3	Maximum capacity of the H_2 buffer
$v_{i,j}$	Nm^3	Available amount of resource i at hour j
$v'_{i,j}$	Nm^3	Used amount of resource i at hour j
τ	h	Operating hours of the methanation plant
Φ_{FGM}	%	Percentage of flue gas directed to methanation
CAPEX	€	Capital expenditures
IRR	%	Internal Rate of Return
h	h/year	Operating hours
LHV	kJ/kg	Lower heating value
\dot{m}	$\text{kg} \cdot \text{s}^{-1}$	Mass flow
NPV	€	Net Present Value
\dot{n}	$\text{kmol} \cdot \text{s}^{-1}$	Molar flow
OPEX	€/year	Operating expense
P	bar	Pressure
PB	years	Pay-back
\dot{Q}	kW	Thermal power
$T/T_i/T_f$	°C	Temperature / Initial temperature / Final temperature
$V_{\text{H}_2,\text{PtG}}$	Nm^3	Nominal hourly input of the methanation plant
\dot{W}	kW_e	Electric power
y	—	Molar fraction

Subscripts	Description
<i>ash</i>	Amount of ashes after combustion
<i>ASU</i>	Air separation unit
<i>aux</i>	Auxiliary consumption
<i>b</i>	Boiler
<i>c</i>	Comburent
<i>CC</i>	Combined cycle power plant
<i>comp</i>	Compression
<i>CO2</i>	Carbon dioxide
<i>ele</i>	Electrolyzer
<i>f</i>	Fuel
<i>FG</i>	Flue gas
<i>G</i>	Electric generator
<i>gross</i>	Gross power
<i>H2</i>	Hydrogen
<i>Loss</i>	Leaks in water condenser
<i>m or meth</i>	Related to methanation
<i>net</i>	Net power
<i>o or oxy</i>	Related to oxyfuel combustion
<i>oxyCC</i>	Oxyfuel combined cycle
<i>O2</i>	Oxygen
<i>PtG</i>	Power to Gas plant
<i>PtG + oxy</i>	Power to Gas-Oxyfuel combustion hybrid plant
<i>r</i>	Recirculated stream
<i>s</i>	Sulfur compounds
<i>SNG</i>	Synthetic natural gas
<i>SPP</i>	Subcritical power plant
<i>st</i>	Storage

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Annexes

Annex A

A.1 FORECAST OF ELECTRICITY DEMAND

The trends of electricity demand are calculated based on information provided by *The Global Calculator*. This tool allows to simulate the evolution of various environmental parameters as a function of variables related to the way of living, energy mix, demographics and so.

Table A.1 presents the definition of four scenarios through a large number of variables which lead to different values of the electricity demand yearly increment: + 1.73%/year, + 1.36%/year, + 1.80%/year and + 1.40%/year. Two of them ensure the limitation of global temperature increase up to 2°C by 2100 while the two others do not. The variables which define each scenario are gathered in fifteen categories: travel, homes, diet, transport, buildings, manufacturing, CCS, bioenergy, fossil fuel, nuclear, renewable, food, land use, demographics and emissions after 2050. In order to simplify the quantification of these variables for every scenario, each one may be only varied between 0-4 and each level is properly defined in the cited application (<http://tool.globalcalculator.org/>).

Table A1. Definition of scenarios (variables and levels) related to different electricity demand increments. Global Calculator 2014 version

Variable	Electricity demand increment [%/year]			
	1.73	1.36	1.80	1.40
	2°C increment avoided by the year 2100			
	Yes	Yes	No	No
Travel				
Passenger distance	2.0	2.0	2.0	2.0
Freight distance	2.0	2.0	2.0	2.0
Mode	2.2	2.2	2.0	2.2
Occupancy & freight load	2.5	2.5	2.0	2.5
Homes				
Temperature & hot water use	3.0	3.0	2.0	2.0
Lighting & appliance use	2.3	2.3	2.0	2.3
Building size	2.3	2.3	2.0	2.3
Product lifespan & demand	2.3	2.3	2.0	2.3

Table A1 (Continued). Definition of scenarios (variables and levels) related to different electricity demand increments. Global Calculator 2014 version

Variable	Electricity demand increment [%/year]			
	1.73	1.36	1.80	1.40
	2°C increment avoided by the year 2100			
	Yes	Yes	No	No
Diet				
Calories consumed	2.0	2.0	2.0	2.0
Meat consumed	2.4	2.4	2.0	2.4
Transport				
Electric & hydrogen	3.0	2.0	2.0	2.0
Transport efficiency	3.0	3.0	2.0	3.0
Buildings				
Building insulation	3.0	3.0	2.0	3.0
Temperature & cooking tech.	2.4	3.0	2.0	2.0
Appliance efficiency	2.4	2.7	2.0	2.0
Manufacturing				
Design, materials & recycling	3.0	3.0	2.0	3.0
Iron, steel & aluminum	2.0	2.0	2.0	2.0
Chemicals	2.0	2.0	2.0	2.0
Paper & others	2.0	2.2	2.0	2.0
Cement	2.0	2.2	2.0	2.0
Carbon capture and storage				
CCS (manufacturing)	3.0	3.0	2.0	2.0
CCS (electricity)	3.0	3.0	2.0	2.0
Bioenergy				
Bioenergy yields	1.0	1.0	1.0	1.0
Fossil fuel				
Coal (incl. biomass) / oil / gas	3.0	3.0	3.0	3.0
Fossil fuel efficiency	2.5	3.0	2.0	2.5
Nuclear				
Nuclear	2.0	2.0	2.0	2.0
Renewables				
Wind	3.0	3.0	3.0	3.0
Hydroelectric	2.0	2.0	2.0	2.0
Marine	1.0	1.0	1.0	1.0
Solar	3.0	3.0	3.0	3.0
Geothermal	1.0	1.0	1.0	1.0
Storage & demand shifting	3.0	3.0	2.8	3.0
Food				
Crop yields	2.0	2.0	2.0	2.0
Wastes & residues	1.5	2.0	1.5	1.5
Livestock yields	2.0	2.0	2.0	2.0
Land use				
Land-use efficiency	2.0	2.0	2.0	2.0
Surplus land (forest & bioenergy)	1.5	1.0	1.5	1.0
Demographics				
Global population	2.0	2.0	2.0	2.0
Urbanization	2.0	2.0	2.0	2.0
Emissions after 2050				
Emissions trajectory	2.0	2.0	2.0	2.0

Annex B

B.1 RESOURCE UTILIZATION ADAPTED TO THE INDUSTRY'S OPERATION

The resource utilization, α_i (Equation B1), is calculated as the sum of the amount that is used in each hour, $v'_{i,j}$ [Nm³], divided by the sum of the amount that is available in each hour, $v_{i,j}$ [Nm³]. In the study case presented in section 2.3.2 of this thesis, the values of $v_{i,j}$ are those presented in Figure 28, while $V_{H_2, PtG}$ stands for the nominal H₂ input [Nm³/h] of the methanation plant. When the maximum usage is evaluated, the value of $V_{H_2, PtG}$ in this study is 2462.9 Nm³, which correspond to the available H₂ when both lines of production operate at P6 (Table 16).

$$\alpha_i = \frac{\sum_j v'_{i,j}}{\sum_j v_{i,j}} \cdot 100 \quad (B1)$$

$$i = H_2, CO_2 \quad j = 1, 2, \dots, 8760 \quad \begin{cases} v'_{i,j} = 0 & \text{if } v_{H_2,j} \leq 0.6 V_{H_2, PtG} \\ v'_{i,j} = v_{H_2,j} & \text{if } 0.6 V_{H_2, PtG} < v_{H_2,j} \leq 4 v_{CO_2,j} \\ v'_{i,j} = 4 v_{CO_2,j} & \text{if } 4 v_{CO_2,j} < v_{H_2,j} \end{cases}$$

$$i = CO_2 \quad \begin{cases} v'_{i,j} = 0 & \text{if } v_{H_2,j} \leq 0.6 V_{H_2, PtG} \\ v'_{i,j} = v_{H_2,j}/4 & \text{if } 0.6 V_{H_2, PtG} \leq v_{H_2,j} \leq 4 v_{CO_2,j} \\ v'_{i,j} = v_{CO_2,j} & \text{if } 4 v_{CO_2,j} < v_{H_2,j} \end{cases}$$

When a H₂ buffer is considered (Figure 29), the equation to calculate the resource utilization is the same (Equation B1), with the difference that in this case the used hydrogen in each hour, $v'_{i,j}$, depends on the previous step, $j - 1$, through $v_{B,j}$, the stored hydrogen in the buffer. In Figure 29, the x-axis determines the value of $V_{H_2, PtG}$, and the y-axis sets the value of $v_{B,max}$. The following rules shall be satisfied:

$$\begin{aligned}
 \text{for } i = H_2 \quad & \begin{cases} v'_{i,j} = 0 & \text{if } v_{H_2,j} + v_{B,j} \leq 0.6 V_{H_2,PtG} \\ v'_{i,j} = v_{H_2,j} + v_{B,j} & \text{if } 0.6 V_{H_2,PtG} < v_{H_2,j} + v_{B,j} \leq 4 v_{CO_2,j} \\ v'_{i,j} = 4 v_{CO_2,j} & \text{if } 4 v_{CO_2,j} < v_{H_2,j} + v_{B,j} \end{cases} \\
 \text{for } i = CO_2 \quad & \begin{cases} v'_{i,j} = 0 & \text{if } v_{H_2,j} + v_{B,j} \leq 0.6 V_{H_2,PtG} \\ v'_{i,j} = (v_{H_2,j} + v_{B,j})/4 & \text{if } 0.6 V_{H_2,PtG} \leq v_{H_2,j} + v_{B,j} \leq 4 v_{CO_2,j} \\ v'_{i,j} = v_{CO_2,j} & \text{if } 4 v_{CO_2,j} < v_{H_2,j} + v_{B,j} \end{cases}
 \end{aligned}$$

Where $v_{B,j}$ depends on the previous step in the following way:

- If the available hydrogen is below the minimum partial load ($v_{H_2,j} + v_{B,j} \leq 0.6 V_{H_2,PtG}$), the produced H₂ is stored

$$\begin{cases} v_{B,j+1} = v_{B,j} + v_{H_2,j} & \text{if } v_{B,j} + v_{H_2,j} < v_{B,max} \\ v_{B,j+1} = v_{B,max} & \text{if } v_{B,max} \leq v_{B,j} + v_{H_2,j} \end{cases}$$

- If the available carbon dioxide is enough to consume all the hydrogen ($0.6 V_{H_2,PtG} < v_{H_2,j} + v_{B,j} \leq 4 v_{CO_2,j}$), the buffer is empty

$$v_{B,j+1} = 0$$

- If the hydrogen is enough to consume all the carbon dioxide, but it is necessary to use part of the buffered hydrogen ($4 v_{CO_2,j} < v_{H_2,j} + v_{B,j}$), the stored H₂ will diminish

$$\begin{cases} v_{B,j+1} = v_{B,j} - (4 v_{CO_2,j} - v_{H_2,j}) & \text{if } 0 < v_{B,j} - (4 v_{CO_2,j} - v_{H_2,j}) \\ v_{B,j+1} = 0 & \text{if } v_{B,j} - (4 v_{CO_2,j} - v_{H_2,j}) \leq 0 \end{cases}$$

- If the produced H₂ during the hour j is enough itself to consume all the CO₂ ($4 v_{CO_2,j} < v_{H_2,j}$), the buffer will store more hydrogen up to its limit

$$\begin{cases} v_{B,j+1} = v_{B,j} + (v_{H_2,j} - 4 v_{CO_2,j}) & \text{if } v_{B,j} + (v_{H_2,j} - 4 v_{CO_2,j}) < v_{B,max} \\ v_{B,j+1} = v_{B,max} & \text{if } v_{B,max} \leq v_{B,j} + (v_{H_2,j} - 4 v_{CO_2,j}) \end{cases}$$

Regarding the operating hours, τ , it is given by Equation B2:

$$\tau = \frac{\sum_j v'_{H_2,j}}{V_{H_2,PtG}} \quad (B2)$$

Annex C

C.1 FACTOR DE IMPACTO Y ÁREA TEMÁTICA DE LAS PUBLICACIONES

A continuación se indica el factor de impacto, cuartil y área temática de las revistas en las que han sido publicados los manuscritos que conforman esta Tesis Doctoral. La información ha sido tomada del Journal Citations Reports®, cuyos datos más actual pertenecen al año 2016.

Tabla C1. Revistas en las que han sido publicados los manuscritos que conforman la Tesis Doctoral.

Art.	Revista	Factor Impacto (5 años)	Área temática 1	Área temática 2
ii	Energy Procedia	No indexada (Congreso)	Energy	-
iii	Renew. Sust. Energ. Rev.	9,122	Green & Sustainable Science & Technology (Q1, 2 nd /31 th)	Energy & Fuels (Q1, 5 th /92 th)
iv, vi	Int. J. Hydrog. Energy	3,647	Electrochemistry (Q1, 7 th /29 th)	Energy & Fuels (Q2, 28 th /92 th)
v, vii	Appl. Energy	7,500	Engineering, Chemical (Q1, 4 th /135 th)	Energy & Fuels (Q1, 6 th /92 th)

Annex D

D.1 CONTRIBUCIÓN A LAS PUBLICACIONES

D. Luis Miguel Romeo Giménez, Profesor Titular del Área de Máquinas y Motores Térmicos del Departamento de Ingeniería Mecánica de la Universidad de Zaragoza, y Dña. María Pilar Lisbona Martín, Profesora Ayudante Doctor del Departamento de Ingeniería, Agrícola y Forestal de la Escuela de Ingeniería de la Industria Forestal, Agronómica y dela Bioenergía de la Universidad de Valladolid:

CERTIFICAN,

Que la contribución de D. Manuel Bailera Martín ha sido esencial en las tareas de concepción y diseño de las ideas, realización de los modelos y simulaciones, análisis de los resultados y redacción de los manuscritos de las siguientes publicaciones:

- i Bailera M, Lisbona P. Energy storage in Spain: forecasting electricity excess and assessment of Power-to-Gas potential up to 2050. Energy (2017), Submitted (en 2ª revisión).
- ii Bailera M, Lisbona P, Espatolero S, Romeo LM. Power to Gas technology under Spanish future energy scenario. Energy Procedia (2017), 114, 6880-6885.
- iii Bailera M, Lisbona P, Romeo LM, Espatolero S. Power to Gas projects review: Lab, pilot and demo plants for storing renewable energy and CO₂. Renewable & Sustainable Energy Reviews (2017), 69, 292-312.

- iv Bailera M, Lisbona P, Romeo LM. Power to gas-oxyfuel boiler hybrid systems. International Journal of Hydrogen Energy (2015), 40, 32:10168-10175.
- v Bailera M, Lisbona P, Romeo LM, Espatolero S. Power to Gas-biomass oxycombustion hybrid system: Energy integration and potential applications. Applied Energy (2016) 167, 221-229.
- vi Bailera M, Kezibri N, Romeo LM, Espatolero S, Lisbona P, Bouallou C. Future applications of hydrogen production and CO₂ utilization for energy storage: Hybrid Power to Gas-Oxycombustion power plants. International Journal of Hydrogen Energy (2017), Vol. 42, 19, 13625-13632.
- vii Bailera M, Espatolero S, Lisbona P, Romeo LM. Power to Gas-Electrochemical industry hybrid systems: A case study. Applied Energy (2017), 202, 435-446.

Zaragoza, 15 de Septiembre de 2017



Maria Pilar Lisbona Martín



Luis Miguel Romeo Giménez

This Thesis summarizes the work I developed close together with my advisors and my former workmate Sergio, between 2014 and 2017, under the framework of three research projects concerning Power-to-Gas (PtG) technology. The dissertation covers the thorough analysis of two novel Power-to-Gas hybridizations that improve the technology in terms of efficiency, utilization of resources and profitability. These proposed concepts will help to overcome the current technical and economic barriers of erecting commercial PtG plants, in order to gain operational experience at industrial scale.

Doctoral advisors

Luis Miguel Romeo (Universidad de Zaragoza)
Pilar Lisbona (Universidad de Valladolid)