Methanol and Ammonia as Emerging Green Fuels: Evaluation of a New Power Generation Paradigm

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Abstract

In the current context of the energy transition, the use of liquid fuels is attracting attention to be used as energy storage, due to the inherent fluctuations of the main renewable energy sources. In addition, these liquid fuels have also been proposed as energy carriers, to introduce renewables in hard-to-electrify applications. Methanol and ammonia emerge as the two most promising green liquid fuels for energy purposes. In this work, a systematic assessment of the transformation of methanol/ammonia into power is performed. Two different routes have been studied: thermochemical (through fuel combustion) and electrochemical (using fuel cells). From a technical analysis, the methanol process reaches the highest efficiency, around 38%. In general, thermochemical processes show better performance in terms of energy efficiency. From an economic perspective, the current costs of the thermochemical route are around $0.3 \notin/kWh$ and $0.6-1 \notin/kWh$ for the electrochemical. Electricity cost are expected to be reduced as process efficiency increases down to values of around $0.1 \notin/kWh$. A progressive introduction of these green liquid fuels will be necessary to achieve a 100% renewable energy system in all areas, guaranteeing the long-term sustainability of the planet.

Keywords: Ammonia, Energy storage, Energy carriers, Green Fuels, Methanol, Power Generation, Renewable Energy

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Highlights

- Green methanol/ammonia are assessed as alternative fuels for power generation.
- Two different routes are analyzed: thermochemical and electrochemical.
- Methanol combined cycle reaches the maximum energy efficiency, around 38%.
- Fuel cells have a higher cost of electricity between $0.6-1 \notin kWh$.
- Further improvements can make these alternative fuels cost competitive.

Abbreviations

AEM	Anion exchange membrane
DAFC	Direct ammonia fuel cell
DMM	Dimethoxymethane
DME	Dimethyl ether
DMFC	Direct methanol fuel cell
HEM	Hydroxide exchange membranes
OME	Oxymethylene dimethyl ethers
PCFC	Protonic ceramic fuel cell
PEMFC	Proton exchange membrane fuel cell
PV	Photovoltaic
RES	Renewable energy sources
SCR	Selective catalytic reactor
SOFC	Solid oxide fuel cell
TRL	Technology readiness level

1. Introduction

1.1. Background

The energy transition is one of the key challenges of society to create a new sustainable energy system to tackle the current environmental problems [1]. The introduction of renewable energy sources (RES) in the energy mix will be essential to achieve the sustainable targets of the different energy sectors (power, heating, mobility, etc.). Bouckaert et al. [2] state that, by 2050, around two-thirds of the total energy supply is expected to come from RES with solar energy being the largest source. In terms of power generation, around 90% of the total production will come from renewables in 2050, making it one of the sectors that will undergo the biggest transformation in the coming years. However, the use of renewable sources involves a major challenge in the operation of the energy system. The two main energy sources of the future will be wind and solar which are inherently fluctuating depending on weather conditions [3]. To guarantee the stability and robustness of the energy system and to ensure demand satisfaction, the use of different storage alternatives has been proposed as an efficient solution [4, 5]. Additionally, energy carriers have been suggested to decarbonize some energy uses that are difficult to electrify, for example, maritime or air transportation [6].

In this context, where energy storage technologies play a major role and the use of energy carriers is required to decarbonize some significant applications, the use of Power-to-X processes emerges as an attractive option [7]. The first and most widespread alternative is the production of hydrogen from renewable electricity [8]. Three areas in which hydrogen will have great potential have been suggested [9]: as an energy storage system when the electricity grid cannot absorb the excess of renewable power, as a way to decarbonize hard-to-electrify sectors, and as a zero-carbon raw material for chemical and fuel industry (fertilizers, steel, efuels, etc.). According to BloombergNEF [10], hydrogen could help to mitigate the most challenging one third of the global greenhouse gas emissions by 2050. One of the main drivers for the implementation of the hydrogen economy is the reduction in the cost of renewable electricity because this item is responsible for around 50% of the total operating cost [11]. A wide range of applications has been proposed for this renewable hydrogen. In transportation, hydrogen has been analyzed in some important sectors such as heavy road transport [12] or maritime applications [13]. The use as an energy storage system is also proposed for grid-scale operation [14] with high potential for seasonal storage. Hydrogen has been proposed as energy carrier to produce it in areas with high availability of renewable resources and transport where it is required [15]. However, the use of hydrogen presents some major challenges such as the low volumetric energy density or its difficult storage and transport conditions of this component [16]. Therefore, other chemicals produced from hydrogen have been proposed under the umbrella of the Power-to-X processes.

The synthesis of other gaseous fuels, mainly methane, has been suggested [17, 18]. Methane is a gas but with an energy density 3 times higher than hydrogen and with easier storage and transportation conditions. Moreover, the existing infrastructure of the natural gas network can be used to handle this energy carrier [19, 20].

A wide range of liquid fuels has also been suggested such as methanol [21], oxymethylene dimethyl ethers (OME) [22, 23], dimethoxymethane (DMM) [24], dimethyl ether (DME) [25], ammonia [26], etc. The main advantage of liquid fuels is the easy storage (they can be used for long-term storage) and transportation due to the high energy density [27]. Some of the most important liquid energy carriers produced

by Power-to-X processes are: methanol [28, 29] and ammonia [30, 31]. The production of these chemicals is widely proposed in the literature with the combination of hydrogen (from water electrolysis) and CO_2 (for methanol) or N_2 (for ammonia). One of the main challenges for the full implementation of these liquid fuels as energy storage systems or energy carriers is their transformation into electricity. Two different routes, thermochemical and electrochemical, have been proposed and are discussed in the following section.

1.2. Literature review

This section presents the main advances in the use of methanol and ammonia as liquid fuels following two different routes: thermochemical and electrochemical. The use of methanol by the thermochemical route has been widely proposed, mainly focused on the use of this chemical for internal combustion engines [32]. This technology seeks to provide a sustainable and efficient alternative to current combustion fuels. However, the scope of this system is not the transformation of methanol into power, therefore, other alternatives should be considered, mainly methanol gas turbines. One of the first studies was developed by Carapellucci et al. [33]. They found that the emissions of different pollutants (NO_x and N₂O) were reduced when feeding methanol and that the levels of CO were the same as those of conventional gas turbines. The use of methanol directly into the combustion chamber might be challenging due to its flammability properties. Hence, methanol decomposition to produce a syngas that is introduced in the combustion chamber is widely extended. Jin et al. [34] proposed a combined cycle based on a gas turbine fed with methanol using this decomposition scheme. The thermal efficiency of the process could be as high as 57.4%. Liu et al. [35] considered the integration of a methanol gas turbine together with solar thermal energy, which is used to decompose the inlet methanol achieving a primary energy ratio of up to 75.42%. Cherednichenko et al. [36] studied the economic profitability and carbon dioxide emissions of a chemically recuperated gas turbine fed with methanol/ethanol varying the water/alcohol ratio to maximize the energy efficiency. At the optimal water to methanol ratio of 3, the gas turbine can increase the efficiency by 4% and reduce tank-to-wake emissions by 80%. These advantages in terms of power generation have been implemented in real operation facilities. For example, the power plant located in Eilat (Israel) has been adapted to use methanol as fuel instead of the previous fuel oil demonstrating a good operational performance [37].

With regard to the methanol transformation using the electrochemical pathway, direct methanol fuel cells (DMFC) can be a suitable option for portable energy resources but larger size is still far from being competitive. Two different technologies have been proposed based on cell configuration: passive (where only passive means are used to introduce/remove the gases) and active fuel cells (where an external means, for instance, a pump are used) [38]. Numerous studies have been developed on several aspects of DMFC in order to address the operating issues, such as methanol crossover, low ionic conductivity at high temperature, limited usage of Pt due to high cost, and low activity catalysts [39]. Alias et al. [40] reviewed both external and internal components used in active systems of direct methanol fuel cells as well as the fuel and product management. They highlighted methanol crossover, mass transport losses, ohmic losses, anodic and cathodic ohmic losses, and activation overpotential as the main challenges in the DMFC development.

In order to improve the overall system performance and the generated power density, it is necessary to optimize each component of a DMFC scheme. Lee et al. [41] employed a 65 cell DMFC stack as an active system to generate 500 W fed with different methanol solutions with concentrations of 0.3-2 M and operating at different temperatures (40-90°C) obtaining efficiencies ranging from 11% to 31%. In order to compare the different modeling approaches for methanol fuel cells, Karaoglan et al. [42] presented a systematic evaluation which includes modeling for a single cell, single-cell testing, and short-stack testing of a DMFC to determine cell performance. The aim of the study was to obtain an in-depth knowledge of the effect of the operating parameters on the DMFC performance using three different characterization methods. They concluded that the voltage of a stack can be obtained by a 1D model or by single-cell tests, instead of testing the stack which is more difficult.

Currently, the catalysts at the cathode of a DMFC based on Pt are the most active and employed; nevertheless, these catalysts present several disadvantages, such as the high cost or the instability due to Pt dissolution. Ercelik et al. [43] studied the effect of introducing titania into Pt-Ru/C electrocatalyst on the performance of DMFCs obtaining a better performance at 80°C and 1 M of methanol yielding a power density of around 705 W/m². Wu et al. [44] analyzed a hybrid system based on the combination of a solid oxide fuel cell (SOFC) and a proton exchange membrane fuel cell (PEMFC) reaching an energy efficiency up to 66.2%. The flue gas of the SOFC contains unreacted fuel components (as CO and H₂) that are sent, after treating the gases, to a PEMFC to increase the energy performance of the process.

Additionally, the combination of different methanol technologies has been proposed. Cocco and Tola [45] proposed a solid oxide fuel cell-micro-gas turbine hybrid power plant fueled with methanol and di-methyl-ether. In this integrated scheme, methanol is first reformed with steam and, after that, fed to the SOFC, which operates at 900°C or 1000°C. Then, the outlet gases are fed to a gas turbine to complete the conversion and produce more energy. The whole system achieves efficiencies of about 67-68% with an outlet power from 500 kW to 700 kW.

Regarding the use of ammonia for power generation, the use of the thermochemical route, and particularly ammonia-based gas turbines, is widely proposed in different recent works [46]. In an early study on ammonia gas turbines, Verkamp et al. [47] concluded that ammonia cannot be used in gas turbine burners designed for hydrocarbon dues due to unstable combustion. Addition of hydrogen from partial decomposition of ammonia could provide more stable operation. The low cost of fossil fuels limited further ammonia studies until recently [48]. Most current studies analyze ammonia as co-fuel with hydrogen [49] or methane [50] to address the low burning velocity fuel and to be able to use the current industrial devices without major technology development.

Li and Li [51] identified the low burning velocity and the NO_x emissions as the major challenges in the implementation of ammonia gas turbines. They studied the effect of cofiring NH_3/H_2 fuel mixture on the NO_x emissions at various combustor operating parameters. The equivalent ratio in the rich-burn stage is the key element in terms of NO_x emissions. Secondly, longer residence time and higher NH_3/H_2 ratio also reduce the NO_x formation. Valera-Medina et al. [48] studied the suitability of using a 70% NH_3 -30% H_2 blend in a gas turbine. Their results showed the future potential of this mixture to be introduced in these units with a significant reduction in CO_2 emissions. However, the current efficiencies are low, and further improvements are required to achieve an ammonia combustion with low NO_x emissions and high cycle efficiencies. In ammonia combustion, hydrogen leaves the combustor, therefore, a hydrogen recovery section could be an interesting option in order to increase the performance of the system. Keller et al. [52] proposed to burn the unreacted hydrogen of a combined-cycle gas turbine in a heat-recovery steam generator increasing the energy efficiency and reducing the NO_x emissions with this integrated system.

Different ammonia fuel cell technologies have been proposed to convert ammonia into electricity using the electrochemical pathway [53]. Some of the most important ones are solid oxide fuel cells (SOFC), protonic ceramic fuel cells (PCFC), hydroxide exchange membranes (HEM), etc. [54]. These devices have been particularly proposed for small-scale and/or portable applications. Two main approaches have been suggested for using ammonia as green fuel in a fuel cell. The first one is to use ammonia as a hydrogen carrier. Therefore, the first step is to decompose ammonia into H₂ in a catalytic reactor. Next, the generated hydrogen is introduced into a hydrogen fuel cell [55]. However, the most promising alternative is the use of direct ammonia fuel cells (DAFCs) [56].

For low-temperature applications, alkaline anion exchange membranes (AEM-

DAFCs) are attracting attention as an efficient alternative. Extensive research has been carried out on the identification of suitable electrocatalysts for the anode and cathode of DAFCs and the development of alkaline polymeric membranes with high ionic conductivity and low swelling. The remaining challenges are mitigating chemical degradation of the membrane, ammonia crossover, and water management during fuel cell operation, thus requiring a durable membrane and a suitable water control method for DAFCs [57]. Zhao et al. [54] conducted a techno-economic study on a hydroxide exchange membrane (HEM-DAFC) prototype fueled by a NH₃-KOH mixture in order to study the possibility of its employment in transportation achieving a peak power density of 135 mW/cm² at 80°C. However, substantial improvements in the performance are still needed for DAFCs to become a competitive power source for transportation applications. Siddiqui and Dincer [58] presented an experimental investigation and performance evaluation of a single-cell and a 5-cell stack fueled by ammonia. A maximum peak power density of 13.4 W/m^2 was achieved in the fuel cell stack at a voltage of 574.2 mV and a current density of 23.4 A/m². Nevertheless, further investigation is needed in order to address the catalyst decay and to avoid ammonia crossover as they affect the fuel cell performance significantly.

Rathore et al. [59] reviewed the state of the art of solid oxide fuel cells (SOFC) using ammonia as fuel. This option emerges as one of the most attractive alternatives, however, the high operating temperature (500-1000°C) of these devices could be a challenge in some real applications. Extensive research is still required to optimize the cell performance or to improve the lifetime of ammonia SOFC.

As in the case of methanol, the integration of thermochemical and electrochemical routes has also been investigated. Ezzat and Dincer [60] developed a system fed only with ammonia that combined solid oxide fuel cells and a gas turbine obtaining an overall efficiency of 59% and studied the effect of varying different variables of the process. The fuel cell was fed with hydrogen, produced from ammonia in an electrolytic cell, and the gas turbine with a mixture of the non-reacted hydrogen and ammonia.

Most of the studies presented in this section focus on experimental results at laboratory scale. Just a few of these technologies have been tested on a larger scale, especially the thermochemical routes. This is reflected in the technology readiness levels (TRL) of the different alternatives. For methanol, gas turbines can reach a TRL of 7 [61] and direct methanol fuel cell is currently at commercial scale with a TRL equal to 9 but further research is required for an effective deployment of this alternative [62]. For ammoniato-power technologies, the TRL of direct ammonia fuel cells is around 1-4 and for the ammonia gas turbines around 4-6 [63].

1.3. Aim

Therefore, several investigations have been performed in the field of converting renewable liquid fuels, especially methanol and ammonia, into electricity. Most of these studies evaluate the experimental performance of the power generation device (gas turbine/fuel cell) at laboratory scale. These evaluations constitute the first step in the development of this technology towards a future implementation in the energy system. The next step required to deploy this alternative in real applications is a process scale assessment. This stage is mandatory in order to determine the performance of the entire transformation of methanol/ammonia into power, the optimal operating conditions in real applications, and, also, the economics of the different alternatives to compare them with other proposed systems. Therefore, a systematic evaluation at process scale of this methanol/ammonia to electricity transformation is needed.

In this work, the liquid fuel to power transformation is evaluated from a process design perspective. In particular, the two most promising liquid energy carriers have been considered: methanol and ammonia. To convert these fuels into electricity, two different alternative routes have been suggested: thermochemical using combustion of the fuels and electrochemical based on a fuel cell. The proposed scheme includes all the necessary stages to perform this conversion including the preparation of the raw materials, the power production, and the gas treatment to recover the valuable components and to discharge in a safe and sustainable manner the generated products. The process superstructure is optimized to determine the best operating conditions for methanol/ammonia-to-power transformation. Finally, a technical and economic evaluation is carried out to understand the performance of the process.

The remainder of the work is organized as follows. Section 2 provides a general overview of the different processes involved in this methanol/ammonia to power transformation. Results and discussion are shown in Section 3 including a technical and an economic perspective. Finally, Section 4 draws some conclusions.

2. Process description

There are two possible ways to transform methanol or ammonia into power: thermochemical or electrochemical. In Figure 1, a simplified diagram of the alternatives evaluated to produce power using methanol and ammonia is presented. The main sections of each process are shown in a schematic manner with the common objective of power generation. An equation-based approach is followed to optimize the operating conditions of the fuels to power transformation using an economic objective function. The modeling of the different units is based on first principles, surrogate models, experimental correlations, etc. This modeling approach of the different units involved is presented in the Supporting Information, including also a detailed process flow diagram of each of the alternatives.

2.1. Thermochemical route

2.1.1. Methanol process

The process of converting methanol into power in this case is divided into two main sections: fuel mixture preparation and combined cycle (gas and steam turbines).

For an efficient combustion, a blend of methanol and hydrogen is proposed in the literature improving the methanol combustion itself in terms of burning velocities, flame stability, CO emissions, etc. [64]. The first step is the steam reforming of methanol to produce the necessary hydrogen. In this case, a blend of 85% of methanol and 15% of hydrogen is selected [65], and the reforming takes place in a catalytic reactor. Now, only one outlet stream is obtained, and it is made up of hydrogen, carbon dioxide, carbon monoxide, water, and the unreacted methanol.

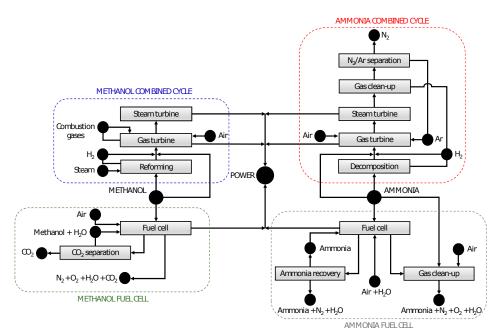


Figure 1: Process superstructure diagram of power production using methanol or ammonia.

This stream is introduced in the second stage, which is the combined cycle that consists of a gas turbine and a steam turbine. In the gas turbine, the inlet gases are compressed, burned, and finally expanded to produce power [60]. In this alternative, not only methanol and hydrogen are combusted in this unit, but also carbon monoxide and the exhausted gases are used to produce steam that feeds the steam turbine to produce power. A part of the exhausted combustion gases is introduced like an inert stream to control the maximum gas turbine temperature (1873 K) due to material limitations of the unit [66]. In contrast to the case of ammonia, the gas treatment is not necessary for this process because there are no valuable components in the combustion gases, and the NO_x concentration does not exceed the environmental limits.

2.1.2. Ammonia process

The process of converting ammonia into power is divided into four main sections: fuel mixture preparation, combined cycle (gas and steam turbines), gas clean-up, and N_2/Ar separation [67].

In this work, a blend of ammonia and hydrogen is used to feed the combined cycle due to the flammability characteristics of ammonia. Ammonia is decomposed in order to produce the needed hydrogen for the fuel mixture [68]. A blend of 70% of ammonia and 30% of hydrogen is selected, according to the features required for ammonia combustion [48]. The decomposition takes place in a catalytic membrane reactor and nitrogen and hydrogen are obtained as products, in addition to the unreacted ammonia. This hydrogen is recovered by an appropriate membrane and used to obtain the NH_3/H_2 fuel mixture. Nitrogen and unreacted ammonia are obtained in the other outlet stream and they can be recycled to the ammonia synthesis stage to reduce the production cost.

The NH_3/H_2 blend is mixed with two streams, the argon one and the air one, to fuel the combined cycle, as in the case of methanol. Argon is introduced to control the maximum temperature in the gas turbine that is limited to 1873 K in this work due to material limitations [66]. This inert component is chosen, rather than carbon dioxide or nitrogen, to maintain the carbon-free operation and not to increase NO_x emissions. The exhausted gases are used to produce steam and generate power in the steam turbine.

After that, the gases have to be cleaned up and some operations are set up. The first one is used to recover the hydrogen from the combustion gases because it is a valuable component. In this study, a selective membrane is used and the separated hydrogen is recycled to the fuel mixture preparation stage. The remaining argon and nitrogen in the combustion gases are separated using cryogenic distillation. The recovered argon is recycled to the gas turbine to be used as inert and the outlet nitrogen can be recycled into the ammonia synthesis process. It is important to note that nitrogen monoxide is not removed since the concentration in the output stream does not exceed the environmental limits set by law.

2.2. Electrochemical route

2.2.1. Methanol fuel cell

The process of converting methanol into power is divided into two main sections: power generation and CO_2 separation.

A direct methanol fuel cell is selected to transform methanol into power operating at low temperatures. This fuel cell is categorized as a proton exchange membrane and it is one of the most studied in the literature [40]. In this case, methanol is fed to the anode in liquid form, like an aqueous solution (1 mol/L) [69], and heated up to the operating temperature (333 K) [70]. It is also necessary to heat the air to the operating temperature before being fed to the cathode. The operating pressure of the methanol fuel cell is atmospheric [71]. To produce power, firstly, methanol molecules react with water at the cathode, producing a flow of protons through the membrane and a flow of electrons, but also carbon dioxide. The protons react with the oxygen molecules at the cathode producing water and carbon dioxide. Thus, there are two streams leaving the fuel cell: the first one, at the anode, contains carbon dioxide and unreacted water and methanol, and the second one, at the cathode, containing water, unreacted air, but also carbon dioxide is obtained due to the methanol oxidation at the cathode because it crosses the membrane from the anode [72] and water is obtained due to the electrochemical reaction and its permeation through the membrane [73].

The second stage of this process is the carbon dioxide recuperation because it can be used in the methanol synthesis process. In this work, a flash separation is employed to recover it and water and methanol leaving the unit at the bottom are recycled to prepare the fuel dissolution.

2.2.2. Ammonia fuel cell

The process of converting ammonia into power, in this alternative, is divided into two main sections: power generation and gas clean-up.

An alkaline membrane fuel cell is selected to convert ammonia into electricity which allows operation at a low temperature so as not to decompose ammonia [57]. Before being fed to the anode, the ammonia needs to be evaporated and heated to the operating temperature of the fuel cell (368 K) [74]. Compared to the case of the methanol fuel cell, in this case, in addition to heating the air to the operating temperature, it is necessary to increase its humidity (50%) before being fed to the cathode of the fuel cell [58]. The operating pressure is also the atmospheric [75]. At the cathode, the oxygen and water molecules react electrochemically to produce hydroxyl ions. These anions pass through the anion exchange membrane and react with ammonia molecules at the anode of the fuel cell generating a flow of electrons that produces power. Thus, there are two streams leaving the fuel cell: the first one, at the anode, which contains nitrogen, water, and unreacted ammonia, and the second one, at the cathode, containing unreacted air and water, but also NO_x . This NO_x is produced due to the ammonia oxidation at the cathode because of its permeation through the membrane [54].

The second stage of this alternative is the gas treatment because the NO_x is a pollutant and its concentration exceeds the permitted environmental limits. Therefore, a selective catalytic reactor is used to remove it using ammonia and air [76]. An ammonia recovery system based on condensation is introduced to treat the gases from the anode. The recovered ammonia is recycled to the fuel preparation reducing the consumption of raw materials. Finally, water, nitrogen and a small fraction of the unreacted ammonia leave the facility and can be later used in the ammonia synthesis process.

3. Results and discussion

3.1. Main operating variables

In this section, a brief description of the main operating variables determined during the optimization procedure of each of the fuel-to-power facilities is presented. To compare the results in the case of the thermochemical route, a power production capacity of 100 MW is selected in both ammonia and methanol based facilities (see Table 1). The operating conditions of the decomposition section of each of the fuels are different. Ammonia decomposition operates at higher temperature and pressure than methanol decomposition, 700 K and 10 atm compared to 573 K and 2 atm; nevertheless, the gas inlet velocity is higher in the case of methanol, 3 m/s vs. 1.5 m/s. Since methanol is steam reformed to be decomposed, it is necessary to select the ratio of water to methanol entering the reactor which in this case has a value of 1.5. With these conditions, a reactor conversion of about 97% is reached in both cases. For both, the value of the operating pressure corresponds to the lowest value within the range of this variable in each case. The minimum pressure is selected to reduce the cost of compression. The lower the pressure of the inlet stream of the reactor, the higher the energy efficiency of the system because a smaller fraction of the power production is consumed. Nevertheless, the value of the temperature is different in each case. In the case of ammonia, the lowest value of the operating range is selected to reduce the thermal energy required in this unit. If the thermal energy consumption is lower, the power production is higher because the energy used to heat up the stream is obtained from the outlet gases of the gas turbine. In the case of methanol, the value of the operating temperature corresponds to the maximum value of the operating range. Although the flue gases energy do not provide all the energy needed for the production and heating of steam and for the evaporation and heating of methanol, this value is selected in order to improve the kinetics of the reaction and to make it faster.

Therm	ochemical route		
Variables		Ammonia	Methano
Power	Capacity (MW)	100	100
Inlet flow	Fuel (kg/s)	15.8	13.2
inter now	Air (kg/s)	92.2	99.3
	Capacity (MW) Fuel (kg/s) Fuel (kg/s)	700	573
	Inlet P (bar)	10	2
Decomposition	Inlet v (m/s)	Ammonia Metha (MW) 100 100 g/s) 15.8 13. g/s) 92.2 99. (K) 700 573 (bar) 10 2 m/s) 1.5 3.0 anol ratio - 1.5 on (%) 97.1 96. (bar) 6.8 8.5 on T (K) 1873 187 MW) 171.0 116 (bar) 125 125 (bar) 9.5 9.5 (k) 785.9 1059 (K) 567.1 798 (K) 451.3 670 MW) 23.0 24.	3.0
	Water/methanol ratio	-	1.5
	Conversion (%)	97.1	96.1
	Inlet P (bar)	6.8	8.5
Gas turbine	Combustion T (K)	1873	1873
	Power (MW)	171.0	116.4
	P high (bar)	125	125
	P inter (bar)	35	35
	P low (bar)	9.5	9.5
Steam turbine	T high (K)	785.9	1059.0
	T inter (K)	567.1	798.3
	T low (K)	451.3	670.4
	Power (MW)	23.0	24.7
Direct CO_2 emissions (kg/kg fuel)		0.0	1.4

Table 1: Main operating variables for thermochemical alternatives

For the preparation of the fuel blend, ammonia or methanol, depending on the case, are mixed with hydrogen (produced from the fuel decomposition) and air and, also, with a stream that contains the inert components. For this capacity, it is necessary to feed more ammonia than methanol because the power consumed during the process in

the case of ammonia is more than twice that consumed in the case of methanol due to the facility complexity and the higher pressure in the decomposition section. The characteristics of the combustion on the gas turbine also determine the inlet flows. In the case of methanol, the amount of air fed is higher than in the case of ammonia despite the fact that the amount of fuel fed is lower in the first case. In the case of ammonia, it is necessary to work with O_2 defect, because the concentration of NO_x generated in the gas turbine depends on the ratio between stoichiometric oxygen and actual oxygen. When this ratio is higher, the NO_x emissions are lower and, in this way, the environmental restrictions are fulfilled. Nevertheless, in the case of methanol, these emissions depend on the amount of hydrogen that is fed to the gas turbine. So, in this case, it is possible to work with an excess of air in order to achieve the complete combustion and produce more power. For both cases, the temperature of the combustion of the fuel blend is the same, 1873 K, limited by the upper limit for this temperature due to material limitations. If this value could be raised, the efficiency of the process could be significantly improved. However, the operating pressure is different and, even the fact that in the case of ammonia is lower, the generated power is higher than in the case of methanol. This is because the amount of fuel fed to the gas turbine in the case of ammonia is higher, and this difference is sufficient to generate more power even though the working pressure is lower.

Finally, in both steam turbines, the maximum pressure value of the range of each stage is reached although the steam temperature is different because of the flue gases temperature. As a result, more power is produced in the steam turbine of the methanol facility.

From an environmental perspective, a first analysis is introduced based on the direct CO_2 emissions related to the use of methanol or ammonia as green fuels. Methanol is produced through the combination of carbon dioxide and green hydrogen and, during the thermochemical/electrochemical processes, these are transformed into water and CO_2 . These CO_2 emissions are quantified and presented in Table 1. These emissions could be captured and recycled to the synthesis section to avoid the release and use again in the methanol synthesis when the production of methanol and its transformation into power are close. In the case of ammonia, as a carbon-free fuel, no direct CO_2 emissions are involved in the process. Other CO_2 emissions are less significant (such as heating/cooling-related emissions) since the proposed process is self-sufficient from a power perspective.

To compare the results in the case of the electrochemical route, a power production capacity of 1 MW is selected in both ammonia and methanol (see Table 2). Due to the large differences between the processes (thermochemical and electrochemical), it is not

E	lectrochemical route		
Variat	bles	Ammonia	Methano
Power	Capacity (MW)	1	1
Inlet flow	Fuel (kg/s)	0.3	0.2
inter now	Air (kg/s)	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	3.6
	Inlet T (K)	368	333
	Inlet P (bar)	1	1
Operating conditions	Power density (W/cm ²)	53.7	55.6
1 0	Current density (A/cm ²)	Ammonia Methan MW) 1 1 Ys) 0.3 0.2 s) 1.8 3.6 K) 368 333 ar) 1 1 (W/cm ²) 53.7 55.6 (A/cm ²) 0.2 0.2 V) 0.3 0.4 ry (%) 32.8 13.6	0.2
	Voltage (V)		0.4
	Fuel recovery (%)	32.8	13.6
Efficiency (%)		15	23
ect CO ₂ emissions (kg/kg fu	el)	0.0	1.4

Table 2: Main operating variables for electrochemical alternatives

appropriate to compare them with the same production capacity. Thermochemical alternatives can be used for stationary applications with high power requirements, for example, as grid-scale energy storage systems [77]. Electrochemical processes can be introduced in portable devices or, for stationary uses, where the energy consumption is low [78]. Focusing on the electrochemical path, the operating temperature is slightly higher in the case of the ammonia fuel cells, as recommended in the literature [74]. Both fuel cells operate at atmospheric pressure, also as recommended, because pressurization has been found to be clearly detrimental to the overall system efficiency [71]. The amount of fuel fed to the fuel cells is higher in the case of ammonia. Ammonia fuel cells have lower efficiency than methanol fuel cells, so it is necessary to feed more ammonia to obtain the same production capacity. Furthermore, in the case of ammonia, it is necessary to feed an additional amount of fuel to feed the gas treatment stage (around 8% of the ammonia fed to the fuel cell). As for the amount of air to be supplied, it is almost twice in the case of methanol fuel cells due to the stoichiometry of the global reaction taking place, which indicates that the amount of oxygen required is twice that of ammonia.

Regarding the production of power, the power density in both cases is similar but lower in the case of ammonia fuel cells. The current density is lower in the case of methanol fuel cells, but the voltage difference is sufficient to produce a higher power density. Therefore, the number of fuel cells required to produce the same power is higher in the case of ammonia fuel cells. In addition, there is an amount of power that is consumed in the case of the ammonia process in the fuel recovery stage, so the number of fuel cells increases. Finally, it is found that the amount of fuel recovered, with respect to that fed into the system, is higher in the case of ammonia. This difference is easily justified by the difference in efficiency between the two fuel cells, 15% vs. 23%, which means that the amount of unreacted fuel leaving the system is greater in the case of ammonia, so the fuel recovered will be higher.

3.2. Energy performance

The main objective of this work is the evaluation of the transformation of two different liquid fuels (methanol and ammonia) into electricity. In this section, the energy performance of the facility is analyzed for each case. Firstly, the thermochemical alternatives are discussed. In Figure 2, a Sankey diagram is presented to show the energy flows in the thermochemical process in which methanol is used as fuel. The main energy input of the process is the methanol itself introduced as feedstock for this power transformation. In the power generation section, around 35% of the energy of the fuel is transformed into power using the proposed combined cycle. A fraction of this power is used in the fuel preparation section which reduces the overall efficiency of the process. The exhaust gases from the combustion stage contain a significant amount of energy that is used, through heat integration, in the different sections of the facility.

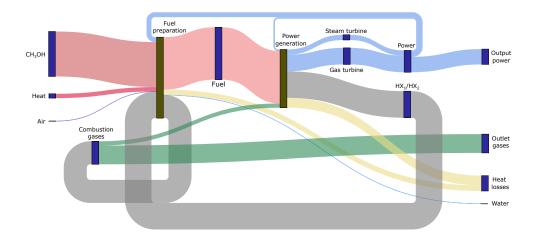


Figure 2: Energy flows for the process based on methanol combustion

For the combustion of ammonia, for the sake of brevity, the diagram with the energy

flows is presented in the Supporting Information (Figure S5). Ammonia is introduced as the main energy input in the fuel preparation section. The recycled hydrogen from the outlet gases is also a significant contribution in terms of energy performance. Around 45% of the energy of the fuel is transformed into electricity in the gas and steam turbines, however, a considerable fraction (about 50%) of this energy is used in the internal operations of the process such as fuel preparation or gas clean-up. Finally, there are three output energy flows of the thermochemical ammonia-to-power process: power, which is the focus of this work, heat losses of the power transformation, and some of the energy that is also contained in the outlet gases of the ammonia decomposition section or in the water removed in the process.

For the electrochemical conversion of methanol into power, the energy flows diagram is presented in the Supporting Information of this work (Figure S6). In this case, the inlet methanol accounts for around 70% of the energy of the inlet fuel to the cell. The recycling of other components, such as methanol itself, from the outlet streams of the fuel cell, is also significant in this fuel preparation section. In the fuel cell, around 15-25% of the energy contained in the fuel is converted into power. A substantial amount of energy is lost due to the heat dissipated in these processes.

Finally, in the case of the electrochemical transformation of ammonia into power, Figure 3 shows the energy flows for each of the stages. In this process, the inlet ammonia is blended with the recycle from the ammonia recovery section mitigating the ammonia losses with the anode gases. Around 90% of the total ammonia is destined for power production and the rest is used in the nitrogen oxide abatement system, in the gas clean-up section. In this fuel cell transformation, only around 10-15% of the energy of the fuel is transformed into electricity in the device.

The results show the paramount importance of the systematic and holistic analysis of the methanol/ammonia to power transformation in order to determine the energy performance of the system. The production of electricity from these liquid fuels is not an isolated activity focusing only on the power generation section (combined cycle or fuel cell), but requires other fundamental activities, such as fuel preparation or gas cleanup, that can substantially vary the energy yield of the process. Therefore, for a realistic analysis of these power generation alternatives, it is essential to asses the entire process, not only the fuel cells or the gas turbines. In the comparison between thermochemical and electrochemical, the thermochemical processes can provide higher electrical output, however, the process required in the transformation is more complex. The fuel preparation and gas clean-up sections are significant in these thermochemical alternatives, with a substantial power consumption that must be taken into account in the evaluation of power generation. As a summary of the energy analysis of the methanol/ammonia to

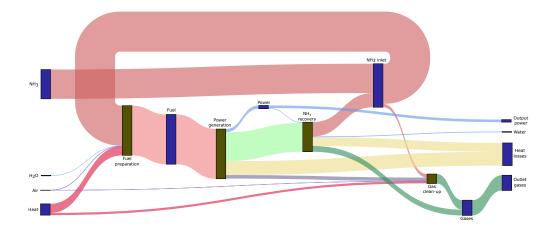


Figure 3: Energy flows for the process based electrochemical conversion of ammonia

power processes, Table 3 includes the main operating energy parameters of the transformation, namely, the energy efficiency, the amount of power that can be produced from one kilogram of fuel, and the exergy efficiency of the process (the Supporting Information file presents more details about the exergy calculations). Two different production capacities have been evaluated: 100 MW for the thermochemical process and 1 MW for the electrochemicals as explained in the previous section due to the different nature of the two alternatives.

The thermochemical alternatives yield a higher energy efficiency than the electrochemical ones. Today, the thermochemical processes are more mature and with the scheme of a combined cycle (gas and steam turbine), it is possible to obtain values of energy efficiency around 35%. However, the electrochemical alternatives are a recent technology, particularly, when methanol or ammonia are used as fuel. The hydrogen fuel cell technology is more developed than the liquid fuels alternatives than are still under an intense research. The average value of efficiency for hydrogen fuel cells is currently around 50-60% [79]. Therefore, further research is required to be able to reach this value for the fuel cells using methanol or ammonia as feedstock. In both cases, thermochemical and electrochemical, methanol technologies show higher energy efficiencies. In the case of the thermochemical route, the process to transform ammonia into power is more complex including the gas clean-up section. Therefore, the internal consumption of energy is more significant reducing the energy efficiency of the entire process. For the electrochemical alternative, the differences in the fuel efficiency are attributable to the configuration of the cell itself. The anion exchange membranes in the case of ammonia show a lower efficiency than the proton exchange membrane fuel cell that is used in the case of methanol. And this in turn determines the energy efficiency of the overall system. Similar results are obtained from the exergy analysis. The introduction of the combined cycle allows for an increase in the exergy efficiency of the thermochemical processes with values of around 30%. This global exergy efficiency is significantly higher in comparison to the scheme where only a gas turbine is introduced [80]. From an electrochemical perspective, the exergy efficiency of the system is highly affected by the energy efficiency of the fuel cell. An expected increase in the current values [81] will improve the exergy performance of these systems with current exergy efficiencies limited to around 15-20%.

Capacity (MW)	Technology alternative	Energy efficiency (%)	Specific energy (kWh/kg)	Exergy efficiency (%)
100	Ammonia combined cycle	33.95	1.768	31.05
100	Methanol combined cycle	38.07	2.122	34.14
1	Ammonia fuel cell	15.00	0.818	14.47
1	Methanol fuel cell	22.99	1.474	23.42

Table 3: System efficiency results for the methanol/ammonia to power transformation

These results obtained in this study can be put in perspective with the results from previous research. For the thermochemical alternatives, Tola and Lonis [82] analyzed a system in which methanol is used as raw material. The energy conversion is based on a gas turbine with the possibility of introducing an organic Rankine cycle. In this assessment, the gas turbine efficiency is in the range of 28-40%, in line with the results of this study. Božo and Valera-Medina [83] analyzed the operation of an ammonia humidified gas turbine reaching an efficiency value of around 40% but excluding the raw material preparation and the gas clean-up section. Keller et al. [52] evaluated the operation of the combined cycle (gas and steam turbines) from a thermodynamic approach using ammonia as fuel resulting in an efficiency value close to 60%. In contrast to these works, in this study, the overall transformation of methanol/ammonia into power is evaluated allowing to provide the global efficiency of the system including all required sections. And this value is obviously lower than the efficiency when only the gas turbine or the combined cycle is considered. For the electrochemical route, Li et al. [84] studied different membranes materials and thickness in direct methanol fuel cells obtaining a range of efficiency between 20.6% and 49.2%. From a modeling perspective, Wang and Sauer [85] showed a reduction of the value of efficiency in DMFC to around 20%. But, if the entire system to transform methanol into power is considered, the efficiency value drops to about 15%. In the same line, Lee et al. [41] analyzed the energy

performance for different methanol concentrations. The energy efficiency of the cell is between 10-30%. For the electrochemical conversion of ammonia, Siddiqui and Dincer [86] evaluated two different fuel cell technologies: anion exchange and alkaline molten. The efficiency value for each technology was 12.1% and 20.6% respectively. For the solid oxide fuel cells, the energy efficiency rises to around 45% [87], but the operating temperature is around 700°C which is unmanageable for a wide range of applications. Therefore, from this analysis, it is possible to conclude that the fuel cells that directly use methanol or ammonia must be improved due to the current low energy performance. Special attention should be paid to the anion exchange membranes for the direct ammonia conversion with a high potential for portable and low temperature applications but with a particularly low efficiency value.

3.3. Economic analysis

In this section, an economic analysis of the different alternatives for transforming ammonia or methanol into power is presented. As a base case scenario, the price of methanol is set to \$518.0/t and the price of ammonia to \$662.9/t [88]. Using the same source for the prices of methanol and ammonia, a fair comparison of both chemicals can be performed in terms of power production. Figure 4 shows the production and capital costs for the thermochemical and the electrochemical routes, respectively. For both cases, different capacities are evaluated to analyze their influence on the profitability of the process, considering the scale for which each route is designed.

Comparing the investment of the thermochemical route alternatives (Fig.4a), it is shown that the capital cost in the case of ammonia is higher than in the case of methanol when both are designed for the same production capacity because of the process complexity. The ammonia alternative has two additional stages compared to the methanol one (both related to the processing of the gases produced), requiring more equipment and raising the investment of the process. Nevertheless, this is not the case for production costs. Both electricity production costs for ammonia and methanol are similar, and it can be seen that the production costs for ammonia are even slightly lower than those for methanol from 100 MW of power production capacity (Fig.4c). This similarity is due to the presence of by-products in the case of the ammonia process and their availability thanks to the additional steps, even if it means that the investment increases. The availability of these by-products means that the raw material item decreases and, therefore, the production costs are lower as it is the most significant item within them. For example, for a facility with a production capacity of 100 MW, capital costs of 377 MM€ and 200 MM€ are estimated for ammonia and methanol, respectively, with approximately the same production cost of electricity of 0.26 €/kWh.

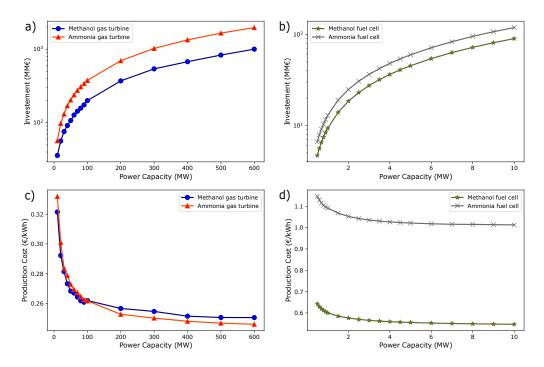


Figure 4: Capital and operating costs: a) capital costs for thermochemical alternatives; b) capital costs for the electrochemical alternatives; d) production costs for the electrochemical alternatives; d) production costs for the electrochemical alternatives

In the case of the electrochemical route (Fig.4b), as in the case of the thermochemical alternative, it can be seen that the investment for the ammonia process is higher. Although the cost of the fuel cell provides the most significant increase in the value of the investment, and its unit price is higher in the case of methanol fuel cells, the investment, in this case, is lower than in the case of ammonia. This is because the ammonia alternative involves a more complex process than methanol, the fuel recovery stage requires more equipment and there is also a gas treatment stage, to remove the nitrogen oxides, which increases the investment. In addition, the ammonia fuel cell has a lower energy efficiency leading to an increase in the number of units for a given power capacity. Nevertheless, in this route, there is a large difference between the production costs of the two alternatives, and it is clear that they are much higher than in the thermochemical route (Fig.4d). As in the other route, the most significant item in the production costs is the cost of the raw materials and they are higher in the case of the ammonia alternative. The price of ammonia is higher than that of methanol [89] and the amount of fuel needed in this case is higher due to the lower efficiency of the fuel cell and the power consumption of the process, so the cost of the raw materials increases, and, consequently, so do the production costs. For example, for a facility with a production capacity of 1 MW, capital costs of 12.9 MM \in and 9.3 MM \in are expected with a production cost of electricity of 1.09 \notin /kWh and 0.60 \notin /kWh for ammonia and methanol, respectively.

These values of the investment and production costs of electricity can be put into perspective with other generation sources. The total investment cost using methanol is about 2250 €/kW and around 3700 €/kW when ammonia is used as fuel in the thermochemical route. These capital costs are comparable with other power generation technologies, for instance, 2353 USD/kW for biomass-based power production or 3991 USD/kW for geothermal energy, or even lower than other electricity renewable production alternatives with storage potential such as concentrated solar power with values of 9091 USD/kW by 2021 [90]. On the contrary, as expected, the investment of the analyzed facilities is higher than the most promising alternatives for renewable power generation, namely solar PV and onshore wind turbines. These generation options show an installed cost of 857 USD/kW and 1325 USD/kW respectively [90]. However, these last ones are non-controllable resources. If the traditional technologies are considered, for instance, the natural gas combined cycle has a capital cost of around 1000 USD/kW and nuclear power generation in the range of 6000-7000 USD/kW [91]. Therefore, the use of methanol and ammonia as fuel for power generation can be competitive to be introduced in electricity production as energy storage technologies to address the fluctuations in renewable resources. These systems can effectively replace traditional more reliable alternatives such as natural gas or nuclear with a reasonable investment allowing for a complete decarbonization of the power sector.

The cost of storage systems based on methanol or ammonia is currently higher than the direct production alternatives. For instance, for the two main renewable energy sources, solar PV panels and wind turbines, the cost of electricity is around 0.05-0.1 €/kWh and 0.1-0.15 €/kWh respectively. Another emerging technology such as biogas has a cost of electricity of around $0.15 \notin kWh$ [92]. If traditional energy sources are included in the comparison, natural gas-based facilities have an average cost of electricity of around 0.22 €/kWh and coal-based plants around 0.1 €/kWh [92]. Finally, a traditional technology with almost zero carbon emissions as nuclear presents a cost of electricity of around 0.07 USD/kWh [91]. These liquid fuels that can be used as energy storage/energy carrier systems have a higher cost of electricity because the energy is first produced from renewable resources, then transformed into these chemicals and, finally, the chemical is transformed back into electricity. However, these energy storage/carrier systems are essential in the future energy scenario due to the inherent fluctuations of the main renewable resources. Therefore, although these technologies result in an increase in cost compared to generation as such, they are necessary to ensure a robust and reliable renewable system.

Some authors have also calculated the cost of electricity for storage systems. Schmidt et al. [14] developed an economic analysis for different technologies for several storage scenarios. Pumped-hydro shows a storage cost of electricity of around 0.2-0.3 USD/kWh for short-term applications. If seasonal storage is introduced, the cost of electricity adds up to 3-4 USD/kWh. Another important technology in energy storage is batteries. For a short-term storage horizon, the cost of electricity is around 0.4-0.6 USD/kWh (with a reduction perspective of up to 0.15-0.2 USD/kWh by 2050). If seasonal storage is required, the cost of electricity from batteries rises to 40-45 USD/kWh (5-10 USD/kWh by 2050). Therefore, the cost of storage is significantly higher than that of direct generation. However, although the use of methanol/ammonia in power generation is expensive like other storage technologies, their use is required in the future energy system due to the variable production of wind and solar-based technologies, particularly, as long-term storage systems where a significant competitive cost is presented, and, also, due to the difficult electrification of some sectors as energy carriers.

3.4. Sensitivity analysis

One of the most important factors influencing the cost of electricity from methanol/ammonia is the price of the feedstock itself. Therefore, an assessment of the impact of the cost of the raw materials on the final cost of electricity is presented. In a renewable energy system, methanol/ammonia will be produced from renewable electricity using the Power-to-X processes [93]. A wide range of methanol/ammonia prices has been proposed. Bos et al. [28] estimated a methanol price of around 800 \notin /t including investment in wind turbines. Hank et al. [29] calculated an average cost of renewable methanol at around $1000 \notin t$ but with values between $600-1400 \notin t$. For the case of ammonia, Cesaro et al. [94] proposed a current average green ammonia price of around 800 USD/t but with values that can exceed 1000 €/ton [95]. However, Powerto-X processes are still under development and significant improvements are expected in the coming years. For example, a reduction in the cost of power generation units is anticipated, mainly in the case of solar PV panels. Or a significant enhancement in the performance of the electrolyzer is expected with better energy efficiency and lower operating costs. All these changes will be reflected in the cost of methanol/ammonia. For example, the cost of methanol could be reduced to around USD 250-630/t by 2050 [96]. Fasihi et al. [97] studied the potential of green ammonia determining an average cost, in 2030, between 370-450 €/t and, in 2050, between 285-350 €/t.

In the previous section, two different methanol/ammonia prices from the same source have been set [88] for the purpose of ensuring a fair comparison of the results. In this section, different prices of methanol/ammonia have been compared to capture the

current and future scenarios for the production of these two chemicals using Power-to-X processes.

In Figure 5, the sensitivity analysis for the thermochemical conversion of methanol is presented. The evaluation is carried out for a range of power capacities between 10 and 600 MW and with methanol prices between 0.2 and $1.4 \notin kg$. Current prices of methanol, around $0.8-1.0 \notin kg$, lead to a cost of electricity of about $0.45-0.55 \notin kWh$. If the future improvements reduce the cost of methanol as expected, the cost of electricity from this renewable chemical can be significantly reduced to values around $0.25 \notin kWh$ or even lower. For the case of the thermochemical conversion of ammonia (Figure S7 in the Supporting Information), the current cost of electricity is around $0.5 \notin kWh$ but, if the future improvements came true, this value could be reduced to promising values around $0.1-0.2 \notin kWh$, even lower than in the case of methanol.

1.4	0.78	0.75	0.74	0.73	0.73	0.73	0.72	0.72	0.72	0.72	0.71	0.71	0.71	0.71	0.71	
1.2	0.69	0.65	0.65	0.64	0.63	0.63	0.63	0.63	0.63	0.63	0.62	0.62	0.62	0.61	0.61	- 0.8
(g) 1.0	0.59	0.56	0.55	0.54	0.54	0.54	0.53	0.53	0.53	0.53	0.52	0.52	0.52	0.52	0.52	- 0.7
CH ₃ OH price (€/kg) 0.8	0.49	0.47	0.46	0.45	0.44	0.44	0.44	0.44	0.44	0.44	0.43	0.43	0.43	0.43	0.42	-0.6 -0.5 -0.4 -0.3
CH ₃ 0.6	0.40	0.37	0.36	0.36	0.35	0.35	0.35	0.34	0.34	0.34	0.34	0.33	0.33	0.33	0.33	-0.3
0.4	0.31	0.28	0.27	0.26	0.26	0.26	0.25	0.25	0.25	0.25	0.24	0.24	0.24	0.24	0.24	-0.1
0.2	0.21	0.18	0.17	0.17	0.16	0.16	0.16	0.16	0.16	0.15	0.15	0.15	0.14	0.14	0.14	
	10	20	30	40	50	60	70 Powe	80 er Capacity	90 (MW)	100	200	300	400	500	600	I

Production cost (€/kWh)

Figure 5: Cost of electricity from methanol via the thermochemical route for different methanol prices and production capacities

When analyzing the electrochemical alternative, in Figure S8 (in the Supporting Information), the results for the methanol fuel cell are presented for a range of power capacities between 0.5 and 10 MW. At current prices, a cost of electricity of around 0.8-1.0 ϵ /kWh is expected. But with the targeted future enhancements, this range can be reduced to around 0.5 ϵ /kWh, approximately half of the initial value. For the case of ammonia, Figure 6 shows that for the current price levels, the electrochemical conversion yields a cost of electricity of around 1.3-1.6 ϵ /kWh which can be reduced to a range of 0.6-0.8 ϵ /kWh in the coming years.

The thermochemical conversion offers better economic performance due to the more

Production cost (Provin)																				
4.1	2.18	2.18	2.16	2.15	2.14	2.13	2.11	2.09	2.08	2.07	2.07	2.06	2.06	2.06	2.06	2.05	2.05	2.05	2.05	
1.2	1.94	1.92	1.91	1.90	1.89	1.88	1.86	1.85	1.84	1.83	1.82	1.82	1.82	1.82	1.82	1.81	1.81	1.81	1.81	
g) 1.0	1.70	1.68	1.67	1.66	1.65	1.64	1.62	1.60	1.59	1.59	1.58	1.58	1.57	1.57	1.57	1.57	1.56	1.56	1.56	
NH ₃ price (€/kg) 0.8	1.45	1.43	1.42	1.41	1.40	1.40	1.37	1.36	1.35	1.34	1.33	1.33	1.33	1.33	1.32	1.32	1.32	1.32	1.32	
N 0.6	1.21	1.19	1.18	1.17	1.16	1.14	1.13	1.11	1.10	1.10	1.09	1.09	1.09	1.08	1.08	1.08	1.07	1.07	1.07	
0.4	0.96	0.95	0.94	0.93	0.92	0.91	0.88	0.87	0.86	0.85	0.85	0.84	0.84	0.84	0.83	0.83	0.83	0.83	0.83	
0.2	0.72	0.70	0.69	0.68	0.67	0.66	0.64	0.62	0.61	0.61	0.60	0.60	0.60	0.59	0.59	0.59	0.59	0.58	0.58	
	0.5	0.6	0.7	0.8	0.9	1.0	1.5	2.0	2.5 Power	3.0 Capacity	3.5 (MW)	4.0	4.5	5.0	6.0	7.0	8.0	9.0	10.0	

Production cost (E/kW/h)

Figure 6: Cost of electricity via the electrochemical conversion of ammonia for different ammonia prices and production capacities

mature technologies and the economics of scale. In the thermochemical conversion, the use of ammonia can reduce the cost of electricity to values below $0.1 \notin /kWh$ in the most favorable scenario, a larger reduction than when methanol is studied. The electrochemical transformation is a developing technology with a worse economic performance at the moment. Particularly, ammonia exhibits poorer results than methanol in these power generation units due to the lower energy efficiency of the ammonia fuel cell. However, this alternative is receiving attention due to the great potential and future improvements can convert this option into a feasible solution from a technical and an economic perspective.

The future energy system is expected to be based on non-controllable renewable energy sources, therefore, energy storage technologies will be essential to ensure the stability and security of the entire system. The two most attractive technologies for this task are batteries (lithium-ion or vanadium redox), for fluctuations in the short-term time horizon, and hydrogen and its derivates, as a seasonal storage alternative. The cost of these storage technologies is highly influenced by the cost of electricity used during the charge of the battery or during the synthesis of hydrogen or its derivatives (such as methanol or ammonia). In the future power system, this cost will be highly influenced by the weather conditions and the demand curve. But, in some periods, there will be an excess of electricity due to favorable weather conditions or lower demand. In this time period, an imbalance between production and demand is expected. And, with renewable technologies, production cannot be adapted to this scenario. Therefore, a noteworthy reduction in the cost of electricity is expected during this time slot and, at this moment, storage technologies have their main niche. For the cost of using methanol or ammonia as energy storage systems, the reduction in the cost of electricity (which could be very close to zero o even negative) involves a significant decrease in the cost of methanol and ammonia from the current levels proposed in this work. Therefore, according to the sensitivity analysis presented, the cost of electricity can reach values around $0.1-0.3 \notin /kWh$ for the thermochemical alternatives and $0.3-0.5 \notin /kWh$ for the electrochemical. Consequently, the high penetration of renewables in the energy system could act as a major driver for the deployment of these storage technologies from an economic perspective. In addition, the storage technologies will be boosted by the energy policy of several governments to develop a robust and reliable energy system.

4. Conclusions

In this work, an assessment of the transformation of two different green liquid fuels (methanol and ammmonia) into power using two different alterantive routes (thermochemical and electrochemical) is presented. From an energy point of view, thermochemical alternatives show a better energy performance than electrochemical ones. The alternative with the highest efficiency is the thermochemical conversion of methanol at around 38%. From an economic perspective, the cost of electricity when methanol/ammonia are used as green fuel depends on the conversion route selected. For the thermochemical alternatives, a cost of electricity of around 0.25-0.3 €/kWh is expected. This value increases considerably for the electrochemical alternatives in which the cost of electricity increases to about $1 \notin kWh$ for the case of ammonia or $0.6 \notin kWh$ for the case of methanol. These values are currently high, but a significant reduction is expected in the coming years due to the improvements in the economy of sustainable methanol/ammonia production and, also, due to the better performance of the energy conversion systems. A sensitivity analysis for a wide range of methanol/ammonia prices and power production capacities is performed showing the possibility of reducing the cost of electricity below 0.2 €/kWh.

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