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Review Article

Green hydrogen-based E-fuels (E-methane, E-methanol, E-ammonia) to support clean energy transition: A literature review

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HIGHLIGHTS

- An overview on recent advances of renewable power to fuel technologies.
- Power-to-methane (PtCH4), power-to-methanol (PtCH3OH) and power-to-ammonia (PtNH3).
- Green hydrogen production, carbon capture and storage, and CO_2 hydrogenation.
- Energy input, conversion process, efficiency, fuel produced, and application.
- Role of power to fuel technologies for the decarbonization of energy sector.

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ABSTRACT

Renewable power-to-fuel (PtF) is a key technology for the transition towards fossil-free energy systems. The production of carbon neutral synthetic fuels is primarily driven by the need to decouple the energy sector from fossil fuels dependance which are the main source of environmental issues. Hydrogen (H_2) produced from water electrolysis powered by renewable electricity and direct carbon dioxide (CO_2) captured from the flue gas generated by power plants, industry, transportation, and biogas production from anaerobic digestion, are used to convert electricity into carbon-neutral synthetic fuels. These fuels function as effective energy carriers that can be stored, transported, and used in other energy sectors (transport and industry). In addition, the PtF concept is an energy transformation that is capable of providing services for the balancing of the electricity grid thanks to its adaptable operation and long-term storage capacities for renewable energy surplus. As a consequence, it helps to potentially decarbonize the energy sector by reducing the carbon footprint and GHG emissions. This paper gives an overview on recent advances of renewable PtF technology for the e-production of three main hydrogen-based synthetic fuels that could substitute fossil fuels such as power-to-methane ($PtCH_4$), power-

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to-methanol ($PtCH_3OH$) and power-to-ammonia ($PtNH_3$). The first objective is to thoroughly define in a clear manner the framework which includes the PtF technologies. Attention is given to green H_2 production by water electrolysis, carbon capture & storage (CCS), CO_2 hydrogenation, Sabatier, and Haber Bosch processes. The second objective is to gather and classify some existing projects which deal with this technology depending on the e-fuel produced (energy input, conversion process, efficiency, fuel produced, and application). Furthermore, the challenges and future prospects of achieving sustainable large-scale PtF applications are discussed.

Contents

Introduction

Currently, world energy consumption is nearly 20 TW and current CO_2 concentration is nearly 400 ppm. Approximately, 2/3 of the world population is living under the poverty line and there is a strong correlation between access to power and mitigation poverty. Hence, jumping the poverty line vindicates the creation of an additional 10 TW, but at zero CO_2 emission. Today, most of the energy requirements are met through conventional fossil fuels (coal, crude oil and natural gas) that account for about 80% of the world's primary energy consumption [1]. Estimates reveal that these conventional sources will be fully exploited in the next few decades because of their high extraction and low replenishment rates [1]. This depletion of fossil fuels in the near future with the high-energy demand and energy crisis such as the Russia-Ukraine Conflict leads to the increase in the energy prices. Furthermore, their excessive use causes destruction to the environment, increases greenhouse gases (GHG) emissions and hence contributes to climate change. In an attempt to attain the climate goals of the Paris agreement (COP21), countries have set serious strategies to mitigate GHG emissions in order to restrict the increase in the global average temperature to below 2 °C above pre-industrial levels [2]. Therefore, the need for decarbonizing the power sector is urgently needed through the transition to clean and ecofriendly renewable energy sources.

In this context, electrification can be a potential solution that promotes the reduction of GHG emissions produced from transportation, buildings, and industrial sectors, depending on the resources used to generate electricity. It was reported that the United States (US), for instance, generates about 70% of electricity using zero or low carbon fuels (36% from nuclear energy and renewables, and 35% from natural gas), that releases minimal carbon dioxide compared to fossil fuels [3]. As a consequence, utilizing electricity as a source of fuel directly results in lower levels of carbon dioxide emissions than does utilizing fossil fuels as a source of fuel.

The electrification approach is expected to continuously increase in transportation, buildings, and industrial sectors. However, it has limitations for some applications such as aviation, heavy load vehicles and marine transport; as electrification can hardly be implemented due to their high energy needed and the low volumetric energy densities of batteries [4]. In such cases, electricity needs to be transformed into other forms of energy. Based on the technology or system considered, electricity can be directly implemented (e.g., battery electric vehicles (BEVs)) or is converted into other versatile energy carriers that can be stored, transported and used in multiple forms of energy sectors [5,6]. This has resulted in the emergence of the relatively new term referred to as Power-to-F (PtF), which has been gaining popularity over the past few years for the ever growing number of applications and their broad diversity [3–10]. As the name implies, PtF is about converting power (electricity) into carbon-neutral synthetic fuels that could replace fossil fuels-based products. The term "power" refers to the electricity generated from renewable sources (Solar, Wind, Hydro, Biomass, Geothermal). The term "F″ refers to the produced synthetic hydrocarbon fuels that can be very diversified such as power-to-gas (PtG), power-to-liquid (PtL), and power-to-fuel. These synthetic fuels are called "electro fuels" or "e-fuels" that are derived from captured carbon dioxide or separation of nitrogen from the air in a reaction with hydrogen produced by water electrolysis [11].

The core of PtF concept is Hydrogen (H_2) gas, termed as power-to-hydrogen (PtH_2), which is considered as the main intermediate for converting power to hydrogen-based synthetic fuels. Most hydrogen is currently derived from natural gas using steam reforming of methane [12]. In comparison with this conventional method for hydrogen production, the generation of e-Hydrogen (green hydrogen) from water electrolysis powered by renewable electricity such as hydro, wind or solar power, has minimal GHG emissions when splitting water into hydrogen and oxygen. Therefore, it is regarded as a green energy carrier and a sustainable fuel that can be used in transportation, gas industry, heating, power generation and is essential for the manufacturing of chemicals such as ammonia and methanol [13].

The production of fuels from hydrogen using captured carbon dioxide as a sustainable and affordable carbon source promotes the production of less carbon intensive fuels. Carbon dioxide can be directly captured from air (DAC) or captured from diverse sources of flue gas such as power stations and industrial streams (e.g., iron, steel and cement industries), and transportation. In addition, to be renewable and sustainable, CO_2 can be also obtained from renewable sources including biomass combustion and biogas production through anaerobic digestion processes [14].

The adoption of renewable PtF technologies enables energy transition by strengthening the potential for storing excess and unutilized renewables (solar, wind, hydro etc.) with long-term storage options in addition to grid balancing to match the supply of energy to demand, solve its intermittency and increase the supply security [15]. Hydrogen, for instance, is a good example for storing excess energy. The surplus renewables use electricity to produce hydrogen by the electrolysis of water, and then the produced hydrogen can be stored using different energy storage technologies (compressed gas, liquid hydrogen, and metal hydrides). The production peaks of renewables can be stored during periods when demand is low and electricity tariff is inexpensive, and then returned back to the grid when demand is high and more energy is required, when electricity is expensive or when renewable energy is unavailable [16].

PtF provides an avenue for producing hydrogen-based synthetic fuels and chemical feedstock such as methane, methanol, ammonia, diesel, gasoline and jet-fuel, with a low capital-intensive decarbonization pathway to foster the reduction of CO_2 emissions related to the energy sector [9]. PtF technologies with sector coupling are considered as a bridge to closed CO_2 cycles and low carbon infrastructures [6]. The injection of renewable energies to cover an ever-larger share of the world's electricity needs helps to decarbonize a substantial proportion of the electricity supply. The major constraint of sector coupling is to extend it to the energy-intensive sectors of transport, heating, cooling, agriculture and heavy industries [17].

A large number of research papers have been published in literature in the last decade discussing PtX or PtF concept [5,8,9,18]. Some researchers have investigated power-to-gas [19–22] and power-to-liquid [15,23] providing an overview of various pilot, lab and demonstration projects that are already available mainly in Europe. Others focused on socio-technical-economic assessment of PtX [4,24], alternative fuels and their applications [25], demand side management (DSM), e-production and electricity storage [7]. This work highlights the major research progress on e-fuels production generated from renewable energy sources using captured CO_2, Nitrogen, and green hydrogen. The article offers an assessment of only three possible E-fuels addressing PtF demonstrations that focus solely on power-to-methane (PtCH4), power-to-methanol ($PtCH_3OH$) and power-to-ammonia (PtNH3 These PtF technologies are discussed and analyzed covering the general trends, conversion paths and methods and remaining unknowns. In addition, non-exhaustive existing projects and recent published papers that have been implemented lately are reviewed and discussed. The challenges related to the development and implementation of PtF technologies such as the cost of green hydrogen production, sustainability (water availability for hydrogen production), and scalability of the system (large capacity Electrolyzer - MW to GW) are also discussed in this paper.

Methodology – renewable power to fuels (e-fuels or PtF)

This section discusses the major stages of producing renewable e-fuels generated from renewable electricity, green hydrogen, CO_2 capture, and Nitrogen separation from air. The three main stages are power generation, feedstock, and conversion process; e-fuels type and characteristics; and applications. Fig. 1 presents a schematic of a general overview of renewable PtF technology. The plant location can be suitable depending on the availability of energy sources such as solar, wind, geothermal, hydro, and water source. Thus, it is important to inspect the site's physical characteristics before the design and operation phase in order to take necessary safety measures that affect the performance of the plant. Furthermore, the infrastructures of renewable energy sources need also to be considered as well as its economics.

Power-to-Hydrogen (PtH_2)

Power-to-hydrogen is the process of generating hydrogen using electrolysis powered by renewable electricity.

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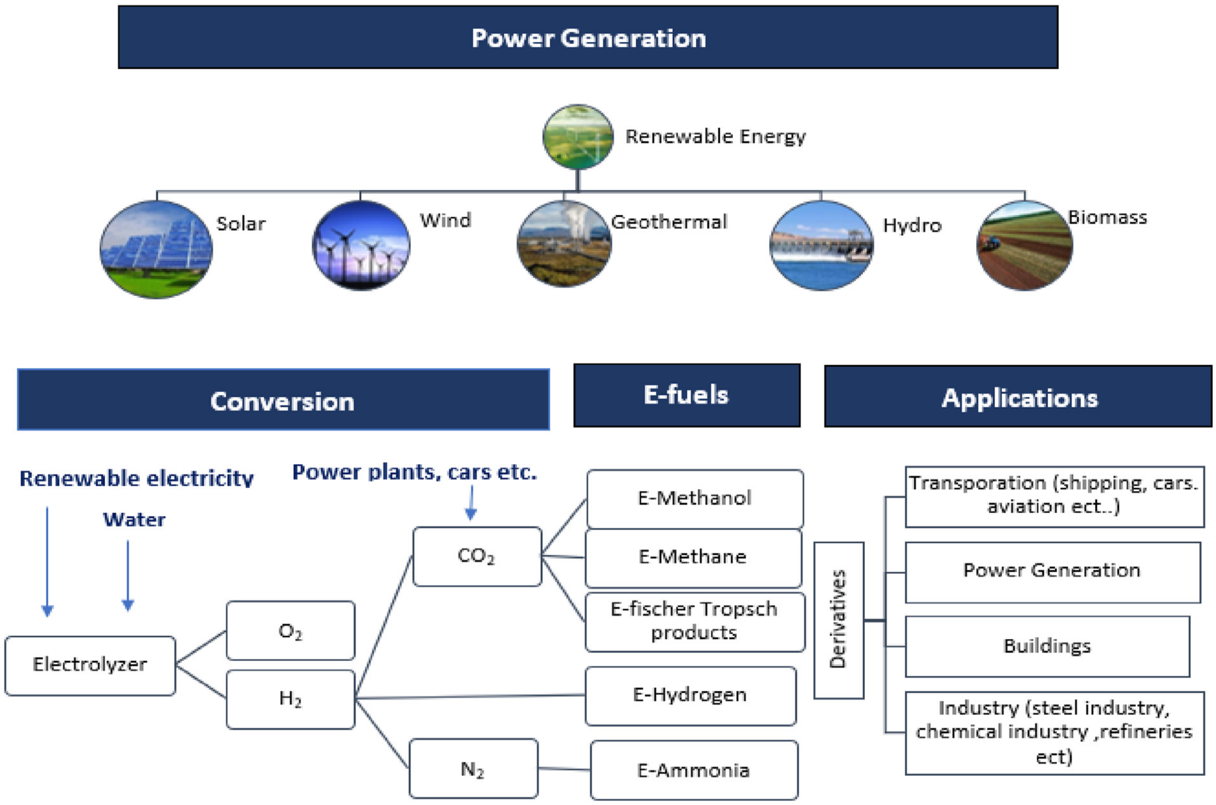

Fig. 1 — A schematic of power to fuel (PtF) process.

Electrolysis plays an important role in the synthesis of renewable hydrogen when electricity is generated from renewable sources (solar, wind, geothermal, hydro etc...). This process is a GHG free and a well-known technology, however it accounts just for about 4% of the total hydrogen production [12]. This is due to a number of barriers that averts the full contribution of green hydrogen in the energy transition including the lack of devoted infrastructure (e.g. transport and storage infrastructure), issues associated to the production stage of electrolysis such as energy losses, lack of value recognition, ensure sustainability and high production costs [26]. Numerous papers have been published discussing green hydrogen production using water electrolysis from solar [27–30], wind [28,31–34] and geothermal energy [35–37].

Water electrolysis is the process of splitting water into hydrogen and oxygen (R1) by applying electrical energy. The electrochemical reactions for an alkaline electrolyzer that occur at the electrodes are given below [38]. The reduction reaction (R2) takes place at the negatively charged electrode (cathode) whereas the oxidation reaction (R3) takes place at the positively charged anode.

$$\text{Overall}: H_2O\ (l) \rightarrow H_2(g) + ½O_2(g) \quad (1)$$

$$\text{Cathode}: 2H_2O + 2e^- \rightarrow 2OH^- + H_2 \quad (2)$$

$$\text{Anode}: 2OH^- \rightarrow ½O_2 + H_2O + 2e^- \quad (3)$$

There are three types of water electrolyzers: Alkaline electrolyzers (AEC), polymer electrolyte membrane (PEM), and elevated temperature solid oxide electrolyzers (SOE). Table 1 presents the main characteristics of the three electrolyzers while other parameters can be found in Refs. [39–42].

AEC is the most mature technology that is commercially available which has been used in chemical industries and in the production of hydrogen at large scale. It comprises two electrodes placed in an aqueous AEC electrolyte (KOH or NaOH) and usually operates at 60–80 °C condition [12]. AEC electrolyzers can work under high pressure (pressurized AEC) or atmospherically (atmospheric AEC) [39]. The advantage of pressurized AEC is that they produce compressed hydrogen that can be directly injected to the grids or used in other further applications without the need to compress it, thus no additional energy input is required (lower energy consumption) [40]. However, they suffer from low efficiency in comparison with atmospheric AEL with low purity level of the produced hydrogen [39]. The main disadvantage of AEC is the high maintenance costs associated to the highly corrosive used electrolytes [39]. PEM electrolyzers, on the other hand, are also gaining market share and have recently received big attention for hydrogen production for their better coupling with dynamic and intermittent electrical systems. PEM electrolyzers use a solid polymer electrolyte operating at a temperature lower than 80 °C. In comparison with AEC electrolyzers, PEM electrolyzers have wider operation range, a shorter response time and higher flexibility [12]. In addition, they are characterized by low density electrolysis and high purity [39] with minimal footprint. The major drawback of PEM is its expensive capital cost compared to AEC due to the

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Table 1 – Comparison between the diverse types of electrolyzers.

Electrolyzer Type	Alkaline	PEM	SOE
Technology maturity	Commercial [39]	Commercial [39]	R & D/Laboratory [39,40]
Operating temperature (°C)	60-80 [40]	50-80 [40,42]	600-1000 [12,43]
Pressure (bar)	<30 [40]	<30 [40]	<30 [40] <10 [43]
Energy consumption (kWh/m^3 H_2)	4.5–7.0 [40]	4.5–7.5 [40]	2.5–3.5 [40]
Cell voltage (V)	1.8–2.4 [40,41]	1.8–2.2 [40,41]	0.95–1.3 [40,41] 0.7–1.5 [42]
Voltage Efficiency (%)	Low efficiency [43] 62-82 [40,41]	Moderate efficiency [43] 67-82 [40,41]	Higher efficiency [43] 81-86 [40,41]
Life span (year)	15-30 [45] 20-30 [40,41]	10-20 [40,41,45]	–
H_2 production rate (m^3/hr.)	<760 [39,40]	Up to ~450 [39] <30 [40]	–
Hydrogen purity (%)	>99.8 [41]	99.999 [41]	–
Capital Cost[1] (€/kW)	620–1170 [42]	1090–1650 [42]	>1560 [42]
Cost of H_2 production (USD/kg)	4-6 USD/kg [46,47]		

[1] Prices for 2020.

utilization of noble metal catalysts [39]. With regard to hydrogen production capacity, AEL electrolyzers generally have large production capacity and a high efficiency whereas PEM electrolyzers have a lower production capacity (<30 Nm^3/h) and a moderate efficiency [43]. The SOE electrolyzer is one of the recently developed types of electrolyzers which is still in the laboratory stage. It uses oxygen ions conducting cells that works at high temperature ranges (600–1000 °C) [43]. The high temperature level lowers the equilibrium cell voltage for SOE compared to AEC and PEM electrolyzers which have a higher cell voltage [39]. This electrolyzer has higher energy efficiency and a high standard thermal and chemical stability [39]. Besides, it consumes less electricity because of the high energy conversion efficiency [44] However, the elevated temperature operation range results to a restricted long-term stability of the cells and fast material degradation [45].

Carbon capture and storage (CCS)

Carbon capture and storage (CCS), also called carbon capture sequestration, is the process of capturing emitted CO_2 and storing it in large sites to avoid its release into the atmosphere. The CCS process involves three main steps: the capture of CO_2, the compression, and the transportation & permanent storage. The two main sources of CO_2 are natural sources and human sources. Natural (anthropogenic) sources comprise ocean atmosphere exchange (42.84%), soil respiration and decomposition (28.56%), respiration of animals and plants (28.56%) and a minor portion of volcanic eruptions (0.03%) [48]. The CO2 can be directly captured by solid and liquid DAC technological approaches. Solid DAC (S-DAC) utilizes adsorbents operating at low pressure and medium temperature (80–120 °C). Liquid DAC (L-DAC) relies on an aqueous basic solution such as potassium hydroxide, that releases the captured CO_2 through a series of units operating at high temperature (300 °C–900 °C) [49]. Apart from natural sources, CO_2 can be also released into the atmosphere by human sources. The flue gases released from fossil fuels power stations (coal, oil and natural gas) accounting for 87%, land use (9%) such as deforestation and agriculture, and other carbon energy intensive industries (4%) such as cement production as well as transportation are all kinds of human activities/sources. Although human sources produce less CO_2 emissions compared to natural sources, human activities have led the atmospheric concentration of CO_2 to rise and has offset the natural balance in the carbon cycle that existed before the industrial revolution. This is because additional co2 is released to the atmosphere without carbon capture.

Once the CO_2 is captured and compressed adequately, it is transported via ships or pipelines in order to be either used as a resource to produce other valuable products or used in other processes or it can be stored deep underground in geological formations [50]. CCS plays a vital role in reducing global warming and climate change by averting the release of CO_2 emissions in the atmosphere. The existing CCS technologies can accommodate 85–95% of the produced CO_2 from a power plant and that can reduce the current emissions by around 80–90% [51,52]. The integration of such system in power plants is an energy intensive process and with an additional energy consumption of 10–40% associated with the CO_2 capture [51].

The need for effective carbon capture methods is essential as society still continues to rely on fossil fuels. The recent technologies for carbon capture and separation techniques including absorption, adsorption, membranes, cryogenic distillation, gas hydrates and chemical looping which are all used for the separation of CO_2 present in the flue gas to be sent for transport and storage and are discussed in details in Refs. [53–55]. Nowadays, the CCS technologies are sorted by the carbon capture timing of the fossil fuel combustion [53,55]. Table 2 shows the differences between the three CCS technologies: post-combustion, pre-combustion and oxyfuel combustion. Post combustion is applied in large-scale fossil-fuel combustion plants where the CO_2 from the flue gas

Table 2 – Main CC technologies: Post-combustion, Precombustion and oxyfuel combustion [55].

CCS Technology	Post-combustion	Pre-combustion	Oxyfuel combustion
Technology maturity	Commercial	Commercial	Under developmental stage
Applications	Commercial and industrial power plants.	Natural gas power plants and process industry.	Appropriate for some types of coal fuels.
Advantages	- Excellent for reconstruction and renovation of already existing power plants that helps in consistent usage. - Matured technology in comparison with other CC technologies.	- Low gas volume - High pressure - High CO_2 concentration - Less energy intensive - Easy CO_2 separation - water combustion is low compared to post combustion	- Uses pure O_2 in combustion which reduces the quantities of nitrogen. - More sustainable and environment-friendly. - No chemical operation is needed. - Easy to capture CO_2 - high efficiency CC
Disadvantages	Low CO_2 partial pressure in flue gas	High energy loss due to sorbent regeneration.	Low net power output.
Capital cost	Excessive cost of system operation.	Integrated gasification combined cycle (IGCC) has an excessive cost compared to a coal plant cost.	Excessive cost of air separation system.

stream is separated after the combustion process, usually using a chemical sorbent process rather than discharging it directly to the atmosphere. The CO_2 is sent to a storage tank whereas the flue gas is released to the atmosphere. This method is a mature technology and currently used in other industrial applications particularly in the food and beverage industry [56]. Compared with other capture methods, post combustion is the most common with an easy adaptation with reference to retrofitting for CO_2 capture from existing coal-fired power plants [57]. In the pre-combustion approach, the method is usually applied in natural gas plants where the fossil fuel is gasified (partially oxidized) at elevated temperature and pressure to produce syngas which consists of carbon monoxide (CO) and hydrogen. The CO reacts with steam (H_2O) in a catalytic reactor to produce CO_2 and additional H_2. The resulting CO_2 is then separated before combustion by a physical or chemical absorption process, and the remaining pure H_2 is used as a fuel in many applications, e.g. gas turbines, engines, fuel cells and boilers etc. [53,56]. This type of technology is characterized by the ease of CO_2 separation because of the high pressure and the high CO_2 concentration being removed in addition to the low consumption of water. All these make it less energy intensive technology although there are some energy losses during the CO_2 capture and the cost of integrated gasification combined cycle (IGCC) is more expensive than the cost of conventional coal combustion plant [55]. The last technology for CCS is the oxy-fuel capture which is still at development stage in which fuel is combusted using pure oxygen instead of air producing a nitrogen-free flue gas without fly ash that contains water vapor and CO_2. Thus, the CO_2 can be easily separated via condensation through cooling to produce pure CO_2 stream [44,58]. This makes oxy-fuel capture more environmentally friendly than post combustion and pre-combustion. Some other advantages of oxy-fuel is the high efficiency carbon capture, high air separation and reduced size equipment [55].

Nitrogen separation from air

Nitrogen, being the main constituent of air, plays a vital role in ammonia production by mixing it with Hydrogen. There are three different technologies that are used commercially for nitrogen generation from air e.g., cryogenic distillation, membrane separation and pressure swing adsorption (PSA). Nitrogen is usually obtained by Cryogenic Air Separation which is viewed as an efficient, mature and economic technology [59]. In the cryogenic technique, nitrogen is separated from air using simple distillation at high pressure and low temperature based on the difference in the boiling points or condensation temperatures of gases. Initially, the ambient air is compressed and cooled to about 10 °C before being passed through filters to remove moisture, dust, oil and other impurities. The compressed air then goes to an expansion engine through heat exchangers where temperature is reduced below the boiling/condensation point (≈ -195.8 °C, 1 atm). Once liquefaction is achieved, the nitrogen fraction is distilled out of the air [60].

In the other hand, the membrane separation process uses hollow-fiber membranes for nitrogen generation. Similar to cryogenic distillation, the ambient air is first compressed and filtered. The compressed air is then channeled through membranes where oxygen, water vapor and other impurities permeate through its side walls. The hollow shape of the membrane helps to increase its surface area for fast permeation. The nitrogen gas stream flows through the center and can be collected in storage tanks. These membrane systems are easier to maintain with a high nitrogen purity ranging from 95 to 99.5%. Besides, they have low-priced operating costs with minor footprint and are applied in small to medium industries [60].

The PSA technology is based on the adsorption and desorption processes by carbon molecular sieves (CMS) for nitrogen separation from air. Once the compressed air is cleaned and dried, it passes through two pressurized vessels that coordinate simultaneously. In the first vessel where the pressure is set 5–10 bar, the unwanted gas oxygen and other gaseous contaminants are absorbed by an adsorbent material such as zeolite, activated carbon; enabling the nitrogen gas to come out to the accumulation tank. The second vessel allows the regeneration through a decrease in pressure via the desorption process where trapped oxygen is released from the sieve material. The PSA ensures continuous repetition of the adsorption and the regeneration processes in the two tanks. This repeated cycle ensure uninterrupted gas generation in a safe and reliable way [60]. The PSA technology is the most common method and often suitable for applications that require high nitrogen purity levels (from 95 to 99.999%). In addition, it is a clean technology and cost-efficient process for producing high purity nitrogen [61].

Review and discussion of E-methanol, *E*-methane, and E-ammonia production processes

E-methanol

One of the notable fuels for power-to-liquid (PtL) technologies is methanol (CH_3OH). Methanol is one of the valuable feedstocks used for the production of many chemicals such as formaldehyde, dimethyl ether, methyl tertbutyl ether (MTBE), acetic acid and many other products such as paints, plastics, building materials and vehicle parts [62]. It is also considered as an excellent solvent and a clean synthetic fuel used in transportation, industrial boilers and cooking, wastewater treatment, electricity production, and also used as a fuel cell hydrogen carrier as well as an alternative carrier for chemical energy [62–64]. At standard ambient conditions, methanol is in a liquid state and it is easy for handling, transportation and distribution [25]. Currently, methanol is generated from fossil fuels (either natural gas or coal) with a global production of 98 million tons (Mt) per year emitting 0.3 gigatons (Gt) of CO_2 annually which accounts for ≈ 10% of the total emissions in the chemical sector. Methanol demand is expected to increase to 500 Mt by 2050 and that results in releasing 1.5 Gt of CO_2 per annum if industries keep relying only on fossil fuels [14].

To decarbonize the chemical sector, it is important to address emissions released from methanol production and to find alternative methods for producing renewable methanol. Methanol is synthesized by the catalytic hydrogenative conversion of carbon dioxide to methanol as per the following reaction [23],

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \quad \Delta H_r = -49.2\ \text{kJ/mol} \tag{4}$$

The catalytic reaction is exothermic that operates in ranges of temperature and pressure of 200–300 °C and 50–100 bar, respectively with a H_2:CO_2 ratio of 3:1 with the presence of the copper/zinc oxide based catalyst [65].

The production of Methanol can come from various carbonaceous sources including natural gas, coal, biomass, by-products as well as carbon dioxide captured from industrial flue gases or direct air capture [66]. Fig. 2 presents a scheme of the main methanol production pathways from different feedstocks. It is clearly noticed that methanol production is still largely based on fossil fuels with about 65% produced from natural gas and the remainder from coal. Only small fraction of methanol is obtained from renewables which accounts for only 0.2% [14,67].

Methanol can be classified per the amount of the carbon used as low or high carbon and that depending on the feedstock and the conversion route along with associated emissions. As can be seen from Fig. 1, methanol produced from syngas through coal gasification or from natural gas reforming (brown and grey methanol) is considered high carbon intensive. It was pointed out that the methanol produced from natural gas generates lower emissions compared to that through the coal gasification owing to the little impurities of natural gas and its high H/C ratio [68]. However, methanol obtained from renewable sources is considered low carbon intensive (blue and green methanol).

To be considered as 100% renewable, all feedstocks have to originate from biomass, solar, wind, hydro, or geothermal. Renewable methanol (green methanol) can be produced via either bio-methanol or e-methanol pathway. Bio-methanol is obtained from gasification of biomass feedstocks such as forestry, agricultural waste, biogas from landfill, sewage, MSW and paper etc. E-methanol is produced from captured CO_2 and green hydrogen produced from renewable electricity. The captured CO_2 also can be classified as renewable CO_2 which is originated from biomass and from direct air capture (DAC), whereas non-renewable CO_2 is recycled from fossil fuels based industries and power plants [14]. Another way to reduce CO_2 emissions is to inject blue hydrogen into the synthesis of methanol to produce what is called blue methanol. Blue hydrogen is a combination of grey hydrogen and assisted with CCS where hydrogen is produced from natural gas either by steam methane reforming (SMR) or auto thermal reforming (ATR) [17,69]. Such combination and other combinations of different "colors" of methanol facilitates the production of sustainable green methanol to minimize GHG emissions of the process.

According to international renewable energy agency (IRENA) [14], bio-methanol and e-methanol are already being produced worldwide by building prototype and demonstration units. Table 3 presents a non-exhaustive list of existing projects and recent research papers available in literature focusing solely on the field of renewable e-methanol production which investigates CO_2 hydrogenation using green hydrogen powered by renewable energy. Other reference papers and projects also exist that produce methanol without utilizing green hydrogen or produced from biomass. Nevertheless, they are beyond the scope of this work and are not discussed in the following subsections.

One main issue for PtF is the intermittent and discontinuity of electricity which makes the storage of renewable energy sources challenging. Some projects account for a direct supply of renewable energy technologies including wind, solar, geothermal or hydropower farms. However, other projects obtain electricity from the national grid that share a low percentage of renewables. Some European countries had implemented several projects during the last decade, where the demonstrator was connected to the national grid as in Germany, Denmark and the UK [5]. No clear evidence is revealed to which renewable system is favored, neither related to particular electrolyzer type, capacity size, or to a specific

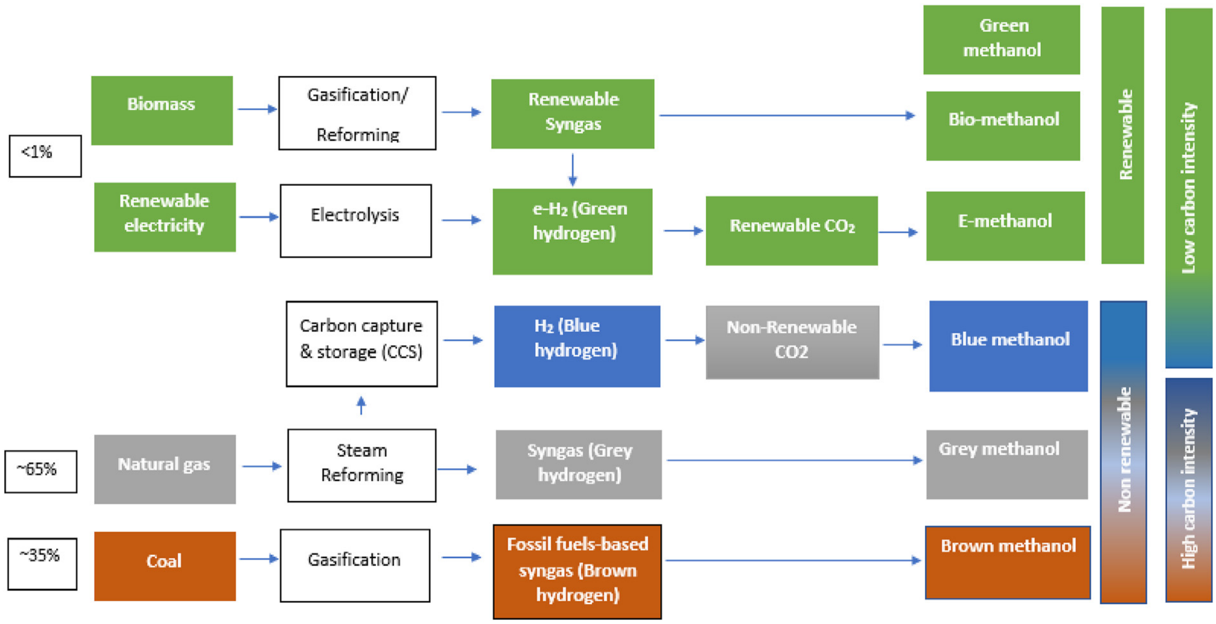

Fig. 2 — Methanol production pathways and their fraction.

country [5]. As can be noticed from Table 3, the majority of renewable sources considered to produce e-methanol came from wind power. This depends on the location since all the projects identified are located in European regions.

It can be observed from Table 3 that AEC and PEM electrolyzers are the most selected electrolyzers with a high percentage of projects accounting for AEC. This is not the same situation for SOE electrolyzers which differs considerably as they are much less mature compared to PEM and AEC systems, even though promising. In addition, SOEC electrolyzers are investigated in a very small percentage of projects with a mere MW installed capacity [18]. Chehade et al. [18] observed similar trends between AEC and PEM within a 5 year interval although AEC is much technically advanced and common technology that was installed first. It can be noticed that the difference between AEC and PEM electrolyzers is not significant, contrary to what is stated in research articles. AEC technology is now the least expensive; though, it is not surprising that PEM can be suitable for PtG processes in the future as PEM cost is expected to be reduced, gaining significant market shares owing to the high partial load range and dynamic behavior. AEC electrolyzers are used for combined heat and power (CHP) purposes whereas PEM electrolyzers are preferred for industrial applications. Some projects are dedicated to two or more applications. For other projects, no such purpose was detected or specified.

With regard to carbon dioxide sources, they differ from project to project. Most projects get carbon dioxide from biogas or biomass plants while others obtain it from industrial power plants.

E-ammonia

Ammonia (NH_3) is a chemical compound that gained significant attention recently as it is considered as an alternative fuel and an effective energy carrier [25]. Ammonia has many usages, but with around 80% of annual ammonia production accounts for the use as agricultural fertilizers [97]. Ammonia is also an important feedstock for the synthesis of some chemicals such as plastics, synthetic fibers and resins, refrigerants and explosives [98]. Like methanol, it can be used as a synthetic fuel in diesel or internal combustion engines and gas turbines [99] and considered as a chemical storage medium for renewable energy [100].

Currently, most ammonia (~98%) is conventionally produced by catalytic steam reforming of natural gas. This accounts for about 1.8% of global CO_2 emissions [101]. Industrially, hydrogen is produced by steam reforming of methane, which is then injected into ammonia synthesis by the Haber Bosch process according to the following reaction:

$$3H_2 + N_2 \rightarrow 2NH_3 \quad \Delta H_r = -91.8 \text{ kJ/mol} \tag{5}$$

The reaction takes place at high temperature (400–500 °C) and pressure (100–450 bar) in presence of iron-based catalysts at Hydrogen to nitrogen molar ratio of 2:1 to 3:1 [102].

Fig. 3 illustrates a schematic of the different power to ammonia existing routes. Like methanol, the production of most ammonia is now obtained from fossil fuels e.g. natural gas, naphtha, heavy fuel oil and coal [102], which is designated as brown ammonia, whereas ammonia produced from fossil fuels with the integration of CCS is termed blue ammonia. In particular, blue ammonia is produced from nitrogen and "blue" hydrogen derived from natural gas feedstock where the by-product CO_2 produced from steam reforming is captured and stored. This leads to a reduction in climate impact compared to the grey ammonia. Green Ammonia is produced with net zero emissions from water electrolysis or biomass-based hydrogen. Our focus in this paper is e-ammonia which is exclusively produced from nitrogen and green hydrogen. The three main techniques to separate nitrogen from air are discussed in Nitrogen separation from air. Once nitrogen is separated from air, it is mixed with green hydrogen

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Table 3 – Power to Methanol production.

Location, Company/ project name	Start-up year	Renewable Energy System, Power Input (MW)	Hydrogen production		CO_2 Capture		E-Methanol Production				
			Technology	Production capacity H_2	CO_2 capture source/ Technology	CO_2 capture amount	Operating conditions	Conversion Efficiency (%)	MeOH production	Application	Ref
Iceland, CRI	In operation since 2011	RES	Water electrolysis	-	Geothermal CO2	-	-	-	100,000 ton/y	Largest electrolysis hub and e-methanol plant	[70,71]
China, Dalian Institute of Chemical Physics	2020	Solar PV	AEC Electrolyser 10 MW	1000 m^3/h		-	-	99.5% purity	1000 ton/y	China's 'Liquid Sunshine' project demonstrates PV powered methanol	[71,72]
Sweden, Liquid Wind	2026 (plan for ten facilities by 2030)	RES	Water electrolysis ~140 MW	-	Upcycled industrial CO2	230.000 t/y	-	-	100,000 ton/y	The project plans to supply methanol to the shipping industry. The plant will result in surplus heat which can be used for district heating.	[73] [71]
Australia (Tasmania), ABEL	Schedualed 2025	RES	Water electrolysis	-	Biogenic carbon				200,000 ton/y	Green hydrogen and methanol production facility known as the Bell Bay Power fuels project	[74] [71]
Norway, Swiss Liquid Future/ Thyssenkrupp	-	Hydro	Water electrolysis	-	Captured from a ferrosilicon plant	-	-	-	80,000 ton/y	One of the Largest-scale pilot plant in Norway for carbon capture and the electrolysis-based hydrogen production.	[71,75,76]
Norway, (CRI, FINNFJORD AS and Statkraft AS)	Scheduled 2023	RES	Water electrolysis	-	CO2 captured from the Finnfjord ferrosilicon plant	300.000 tons/y	-	-	100,000 ton/y	The partners seek to capture and convert more than half of its emissions into methanol for fuel and chemical applications.	[71,77]
Canada, Renewable Hydrogen Canada Corporation (RH_2C)	-	Hydro	Water electrolysis	-	Forest-derived biogenic CO2	-	-	-	120,000 tons/y		[71,78]
Belgium, port of Antwerp	2022	RES	Water electrolysis	-	Carbon capture	-	-	-	8000 ton/y	Consortium of 7 players established to build 'power-to-methanol' demonstration plan	[79] [71]
Belgium, the Ghent part of North Sea Port	2024	Offshore wind	Water electrolysis 63 MW	8600 ton/y	Industrial plant	63,000 ton/y	-	-	46,000 ton/y	The North-C-Methanol project aims at a world-class infrastructure to reduce CO2 emissions by 140,000 ton/y and green methanol is used as feedstock for local industry and as fuel for ships and trains.	[71,80]

(continued on next page)

Table 3 – (continued)

Location, Company/ project name	Start-up year	Renewable Energy System, Power Input (MW)	Hydrogen production		CO_2 Capture		E-Methanol Production				
			Technology	Production capacity H_2	CO_2 capture source/ Technology	CO_2 capture amount	Operating conditions	Conversion Efficiency (%)	MeOH production	Application	Ref
Netherlands, consortium Nouryon, Gasunie and four partners	-		AEC Electrolyser 20 MW	3000 ton/y	Carbon capture	-	-	-	15,000 ton/y	The project will reduce emissions by up to 27,000 tons of CO2 per year	[71,81]
Germany, Dow	-	RES	Water electrolysis 280 MW	50,000 ton/y	Gas-fired power plant	330,000 ton/y			200,000 ton/y	- Can be used in chemical processes as well as in shipping traffic and heavy-duty transport. –140.000 ton/y CO2 reduction	[71,82]
Denmark, Danish consortium	2025–2030	Offshore Wind	–	-	from MSW and biomass	-	-	-	50,000 ton/y	-E-methanol is used for shipping.	[71,83]
Germany, Leuna (Total, Sunfire and Franhaufer)	2022	RES	High temperature SOE electrolyser	-	Waste gas stream of Total Raffinerie Mitteldeutschland, Leuna	-	-	-	–	E-CO_2Met – Electricity & CO_2 to Methanol	[71,84]
Germany, group of BSE and IRES	2020	Wind	Water electrolysis	-	Carbon capture	-	240 °C 40 bar	Purity of 99.85%	28 L/d	Plant operation launched in Stralsund (Germany) for converting renewable electricity into bio methanol	[71,85]
Denmark, Danish Consortium (Power2Met)	2020	Wind and solar	Water electrolysis	-	biogas	-	–	–	–	A pilot plant for a complete power-to-methanol plant producing eMethanol by utilizing CO2 and hydrogen.	[71,86]
Germany, MefCO_2	2019	Hydrogenic	PEM, 1 MW	-	Power plant flue gas	-	-	-	1 t/d	The MefCO2 projectaims at Synthesizing methanol from captured CO2 and excess electricity.	[71,87]
Japan, Osaka Mitsui	2009	–	Water photolysis	-	Factories	-	-	-	100 ton/y	–	[71,88]
Case study, Italy	2021	Wind, 10 MW	PEM Electrolyser 30 bars	1502 ton/y	Industrial plant	–	210 °C 80 bars	98% Overall ($\eta_{PTM} = 52.1\%$)	8100 ton/y	Power-to-fuel for sustainable fuel synthesis	[89]
Case study, University of Twente-Netherlands		Wind, 100 MW	AEC Electrolyser, 120 °C, 30 bar 65%	–	DAC Solid amine sorbent	90 kton/y	240 °C 50 bars	$\eta_{PTM} = 51\%$	65 kton/y	Renewable methanol production using water electrolysis and CO_2 capture with methanol cost of 800 €/ton including wind turbine capital cost	[90]

Case study, Italy	RES, 1 MW	PEM Electrolyser 30 bar, 80 °C 68%	19 kg/h	Coal-fired power plant CCS: Amines (MEA)[2] 40 °C, 2 bar	140 kg/h	240 °C 80 bars	96%	97 kg/h	Investigation of economic feasibility of methanol synthesis from H_2 (produced by electrolysis and CO_2	[91]
Case study, Paraguay	Hydro-electric, 172 MW	AEC Electrolyser 80 °C, 30 bar 75%	1 kg/s	Wood pellet Biomass gasification 30 bar, 1000 °C	5.5 kg/s	240 °C 100 bars	–	11.1 kg/s	Performance of a thermo-economic analysis of large-scale methanol production from renewable sources	[92]
Simulation study	Wind, 30 MW	AEC Electrolyser 30 bars 70%	533.2 kg/h	DAC –	3881.7 kg/h	274 °C, 50 bars	Yield 88%	2474 kg/h	A techno-economic analysis of CO_2 hydrogenation to methanol.	[93]
Simulation study	RES	AEC Electrolyser 80 °C, 30 bar	–	Power/cement plant Chemical absorption with amine scrubbing (MEA)	–	250 C, 65 bars	85.7%	98,343 ton/y Purity 99.3%	Valorization of industrially captured CO2 towards methanol	[94]
Case study, (Germany, Italy and China)	RES, 63 MW	PEM Electrolyser 30 bars 68%	1.2 ton/h	Coal-fired power plant Amine-based CCS	8.8 ton/h	80 bars	96%	6.1 ton/h	Performance of a feasibility study for methanol synthesis considering three different economic scenarios	[95]
Simulation study	Solar (UHC-PV[1])	Electrolyser 75%	2000 kg/h	fossil fuel power plant/CCS 90%	–	–	–	9.72 ton/h Purity 99.40%	Methanol production using Ultrahigh Concentrated Solar Cells through hybrid Electrolysis and CO_2 Capture	[96]
Case study, Iran	Solar	AEC Electrolyser 74%	–	Power plants	–	RWGS reactor	–	–	Economic assessment of solar-based hydrogen for methanol production	[45]

[1] Ultrahigh concentrated photovoltaic.

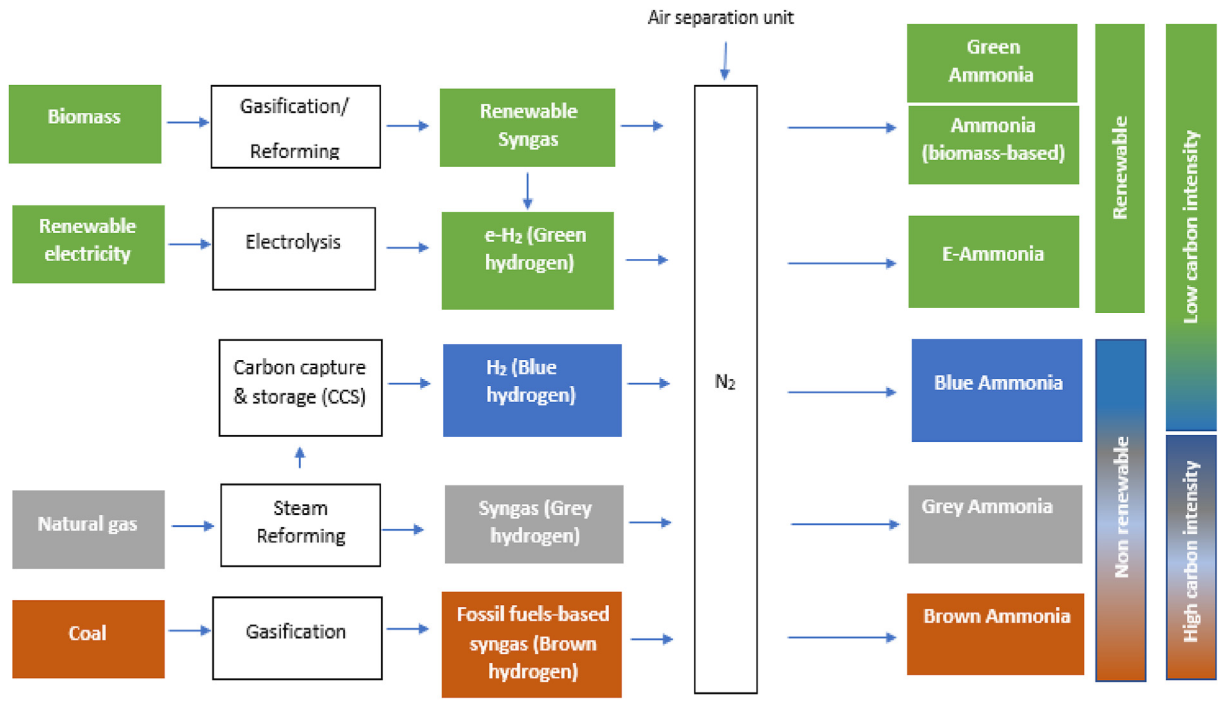

Fig. 3 — Ammonia production pathways.

produced via electrolysis of water powered by renewable electricity. In considering the toxic hazard rating of ammonia exposure, ammonia is a corrosive and a toxic compound with a high vapor pressure at ambient conditions. The National Fire Protection Association (NFPA) rates anhydrous ammonia as a 3 (on a scale of 4) as most serious toxic health hazard and as a 1 (on a scale of 4) as flammable gas [103]. That is, it can have a great burden to human and ecosystem health risks. From an environmental perspective, ammonia leakage into soil, air and water can cause biodiversity losses, eutrophication, air pollution, greenhouse gases emissions and stratospheric ozone loss [104,105]. Thus, all these risks should be considered to effectively minimize and eliminate ammonia hazards.

Table 4 displays some of the recent research papers that focus on power to e-ammonia projects which investigate Haber Bosch process by mixing nitrogen and green hydrogen powered by renewable energy. The use of renewable energy depends on the availability of these resources which depends on the location. It can be noticed from Table 4 that the most utilized renewable sources to produce e-ammonia are solar and wind energies. Some countries have high solar irradiation with good environmental conditions; thus, they consider solar energy to assist the development of solar industry. Other renewable sources are wind and hydraulic dams that are used to produce ammonia by Haber-Bosch process. In addition, it is clear from Table 4 that AEC electrolysis is currently an appropriate candidate for hydrogen production being a mature technology with high technical capacity and lower cost. Besides, with rapid development and expected improved performance of electrolyzers, PEM electrolyzers are also expected in the ammonia synthesis process.

Another point that can be discussed is the different applications of ammonia. In general, Ammonia can be used as a chemical feedstock, a clean-burning fuel for transportation, a power generator (Direct combustion - gas turbine and Fuel Cell) and in industrial applications like steel, cement, and fertilizer production. It is noticed that the majority of projects listed in Table 4 produce ammonia for the use as fertilizers, energy carrier and fuel. Ammonia is an excellent alternative fuel and a carbon-free energy carrier that can store hydrogen. This is due to the desirable characteristics of ammonia as it tends to be liquified in moderate conditions and characterized by high amount of hydrogen [59]. Moreover, ammonia storage is relatively easy with already developed distribution infrastructure [25]. Being an energy storage facilitates seasonal balance of supply and demand that enhances infrastructure investment without the need to exploit fossil-fuels for electricity generation [105]. At periods when demand peaks are high or a surplus of renewable energy is available, this excess energy is converted into hydrogen by electrolysis and then into ammonia which is easy to liquify, store and transport. This latter employs renewable energy providing a key solution for large-scale seasonal storage.

The cost of ammonia production depends on the cost of hydrogen. According to a study done by Bartels [106], ammonia is produced with a cost of 3.8 $/kg whereas hydrogen is produced with a cost of 3 $/kg However, Ammonia possesses less costs of pipeline transport and storage compared to hydrogen, and this considers ammonia an effective fuel for energy storage [105]. In particular, storing hydrogen in the form of ammonia for 182 days costs 0.54 $/kg, however, storing hydrogen for 182 days has a cost of 14.95 $/kg [78].

The Abu Dhabi National Oil Company (ADNOC) has planned lately to launch a large-scale "blue" ammonia production plant in Ruwais in UAE with a capacity of 1000 kilotons per annum [107]. This project is an energy transition producing zero carbon fuel -blue ammonia which is obtained from

Table 4 – Power to e-Ammonia production.

Location, Company/ Project name	Startup year	Renewable energy systems	Hydrogen production		N_2 production		Ammonia synthesis (Haber-Bosch process/reactor)				Ref.
			Technology	Production Capacity H_2	N_2 Source	Amount N_2	Operating conditions	Conversion Efficiency (%)	Ammonia production	Application	
Chile, Enaex and Engie	2024–2030	Solar	Water electrolysis, 26 MW	–	–	–	–	–	18,000 ton/y	Considered as a fundamental element to supply the requirements in the blasting processes for the mining industry.	[71,108]
Spain, Fertiberia, Iberdrola	2021	Solar 100 MW, lithium-ion battery	Water electrolysis, 20 MW	–	–	–	–	–	–	100% renewable hydrogen for ammonia and free-emission fertilizers in Puertollano.	[71,109]
Australia, Port Lincoln, (MHI, H2U, thyssenkrupp)	2022	Wind and solar	Water electrolysis, 30 MW	–	–	–	–	–	50 ton/day	–	[71,110]
Western Jutland, Denmark (Skovgaard Invest, Vestas, Haldor Topsøe)	2023	Solar (50 MW) and wind (12 MW)	Water electrolysis	–	–	–	–	–	5000 ton/y	Green ammonia production from renewable power will prevent 8200 tons/y of CO2 from being emitted into the atmosphere. a sustainable fertilizer.	[71,111]
Japan, Tsubame BHB	2022	Wind and Solar	Water electrolysis	–	–	–	–	–	–	-Amino acids, chemical products, fertilizer, electricity.	[71,112]
Rabat, Morocco, Fusion Fuel	2026	Solar	600 MW	31,000 tons	–	–	–	–	183,000 ton/y	Will prevents 280,000 tons of CO2 annually. HEVO Ammonia Morocco is the Morocco's largest announced green hydrogen and green ammonia project to date.	[71,113]
Germany, (HALDOR TOPSOE AND AQUAMARINE)	2024	offshore wind	SOE, 100 MW	–	–	–	–	–	300 ton/day	Can be used as a green marine fuel or as fertilizer.	[71,114]
UAE, AbuDhabi (KIZAD, Helios)	2024	Solar, 800 MW	Water Electrolysis	40,000 ton/y	–	–	–	–	200,000 ton/y	Reduction of CO2 of over 600,000 tons per year.	[71,115]
Saudi Arabia, (NEOM, Air Products, ACWA Power)	2026	Onshore wind, solar	Water Electrolysis	600 ton/day	Air separation using Air Products technology				1.2 million ton/y	The project will mitigate the impact of 5 million tons of carbon emissions per year.	[71,116]
Norway, Varanger Kraft	2025	Wind	Water Electrolysis 125 MW	50 ton/day	–	–	–	–	110,000 ton/y	–	[71,117]
Bell Bay, Australia (Origin)	2025	RES	Water Electrolysis	–	–	–	–	–	420,000 ton/y	Renewables-based ammonia for export, some of the ammonia is used for domestic use.	[71,118]

(continued on next page)

Table 4 – (continued)

Location, Company/ Project name	Startup year	Renewable energy systems	Hydrogen production		N₂ production		Ammonia synthesis (Haber-Bosch process/reactor)				Ref.
			Technology	Production Capacity H_2	N_2 Source	Amount N_2	Operating conditions	Conversion Efficiency (%)	Ammonia production	Application	
Kenya, Maire Tecnimont	2025	Solar, geothermal	Water electrolysis	–	–	–	–	–	550 ton/day	Renewable power-to-fertilizer plant will reduce carbon emission with 100,000 ton/yr compared to a gas-based fertilizer plant	[71,119]
Norway, ExxonMobil, Grieg Edge, North Ammonia, GreenH	–	Norwegian hydro-electricity	Water electrolysis	20,000 ton/y	–	–	–	–	100,000 ton/y	To use ammonia as a low-emission and high-efficiency energy carrier, particularly to ship and store hydrogen over long distances.	[71,120]
Canada, Quebec (Hy2Gen)	2026	Hydropower 200 MW	Water electrolysis	3.2 ton/h	Air Separation Unit (ASU), powered with hydro-electricity	–	–	–	173,000 ton/y	Ammonia is shipped from a deep sea harbor on the east coast of Canada.	[71,121]
AustriaEnergy, Ökowind, Chile	2026	Onshore wind	Water electrolysis	150,000 ton/y	–	–	–	–	850,000 ton/y	Can be used as explosives, fertilizers, Others (e.g. refrigerants).	[71,122]
Australia, InterContinental Energy	2030–2035	Solar, Wind	Water electrolysis	300,000 ton/y	–	–	–	–	990,000 ton/y	Hydrogen is difficult to transport, but is readily converted into green ammonia, which is easier to ship.	[71,123]
Case Study, Italy	2021	Wind 60 MW	PEM Electrolyser 30 bars	1012 ton/year	Industrial air separation unit (ASU)	–	450 °C, 200 bars	95% (Overall: 49.8%)	8510 ton/yr	Ammonia is an excellent hydrogen carrier compared to methanol, as it can store a considerable amount of H_2 in its structure.	[89]
Paraguay, Case study	2019	Hydro-electric 80 MW	AEC Electrolyser 30 bars	1520 kg/h (1.52 tons/h)	air separation unit (ASU)	–	150 bars	96%	200 ton/day (8330 kg/h)	Fertilizer	[124]
Case Study	2013	Wind 3 MW	Water Electrolysis	–	–	–	–	–	2300 ton/yr	Used as fertilizers to maintain the high agricultural production	[125]
UAE, Case study	2018	Solar	AEC Electrolyser	–	Pressure swing adsorption (PSA)	–	–	electricity to NH_3 process efficiency = 43.4%	1700 mt/day	Energy carrier/Storage for UAE region with high solar radiance and saline water sources.	[105]
Chile, Case study	2020	Solar 160 MW	PEM Electrolyser 35 bars	2687 kg/h	Cryogenic air separation		400 °C, 250 bars	97%	15,000 kg/h 99.95% purity	–	[59]
US, Case study	2017	Wind (offshore)	AEC Electrolyser	53.3 tons per day	Cryogenic air separation	246.7 tons/day	450 °C, 150 bars	Power to Nh3 53.8%	300 tons/day	Fertilizer/ fuel	[99,126]
Sweden, case study	2015	Wind 1.65 MW	Electrolyser	–	Pressure swing adsorption	–	350–550 C 100–300 bar	–	628 kg/h (5500 metric tons/yr)	Fertilizer	[127]

nitrogen and "blue" hydrogen resulting from natural gas, with capture and storage of the carbon dioxide by-product.

E-methane

Methane (CH_4), also called synthetic natural gas (SNG), is one of the important fuels that can be easily found in nature as it is the major component of natural gas [128]. Although it is one of the most important GHG, It can be used in industrial chemical processes as well as electricity generation by burning it as a fuel in gas turbines or steam generators and touch a large part of our daily lives (ovens, water heaters, kilns, automobiles etc.) [128]. Methane is considered as a cleaner fuel as it generates minimal carbon dioxide emissions compared to other hydrocarbon fuels [129]. Methane has a global warming potential (GWP) value of 28 on a 100-year timescale (GWP100); meaning that a leak of one ton of methane is equal to 28 tons of CO_2 and hence absorbs more heat per molecule compared to CO_2 [130]. The synthesis of methane can be obtained by mixing one mol of carbon dioxide and 4 mol of hydrogen by Sabatier process (R3) which is a linear combination of carbon monoxide (CO) methanation reaction and water gas shift (WSG) reaction [131].

$$4H_2 + CO_2 \rightarrow CH_4 + 2H_2O \quad \Delta H_r = -165\frac{kJ}{mol} \tag{6}$$

The catalytic reaction is highly exothermic and operates at temperature and pressure ranges of 250–400 °C and 5–50 bars, respectively [132]. This process, although is simple and straightforward, requires a large quantity of CO_2 (5.5 kg for each kg of H_2) which is difficult to obtain as CCS systems usually are located far away from renewable plants and that adds the cost of CO_2 transportation [133].

Fig. 4 illustrates the different pathways of methane production. Like methanol and ammonia, most methane is currently produced from fossil fuel-based sources (grey and brown methane) at a low cost. CO_2 hydrogenation (methanation) pathway has been broadly studied for power to methane ($PtCH_4$) demo projects that are already in operation in many countries [8]. The power to e-Methane route is considered renewable and sustainable with lower GHG emissions if hydrogen is produced by water electrolysis using renewable electricity (green e-methane).

E-methane can be obtained by combining electrolysis with methanation in a two-step process. Initially, H_2 is produced by water electrolysis using renewable energy such as solar, hydro and wind power. Then, CO_2 is captured by a CCS plant and hydrogenated in a methanation reactor by Sabatier reaction to produce e-methane. There are already few plants of power to methane using electrolysis and CO_2 methanation, that are in operation (especially in Europe) and other plants that are still being developed.

Table 5 lists some existing projects and recent research papers that focus solely on renewable e-methane production. The Audi e-gas project in Germany, for instance, is the largest PtG plant worldwide that launched in 2013. Three AEC electrolyzers are used to produce hydrogen with a total electrical input power of 6 MW whereas the CO_2 is supplied by a biogas plant. Hydrogen is mixed with CO_2 in a methanation unit to generate renewable synthetic methane that is referred to as Audi e-gas with by-products of only water and oxygen. This e-gas is roughly similar to fossil natural gas and it is distributed via an existing infrastructure to compressed natural gas filling stations [134]. The Audi e-gas plant produces annually about 1000 metric tons, with 2800 metric tons of CO_2 which is

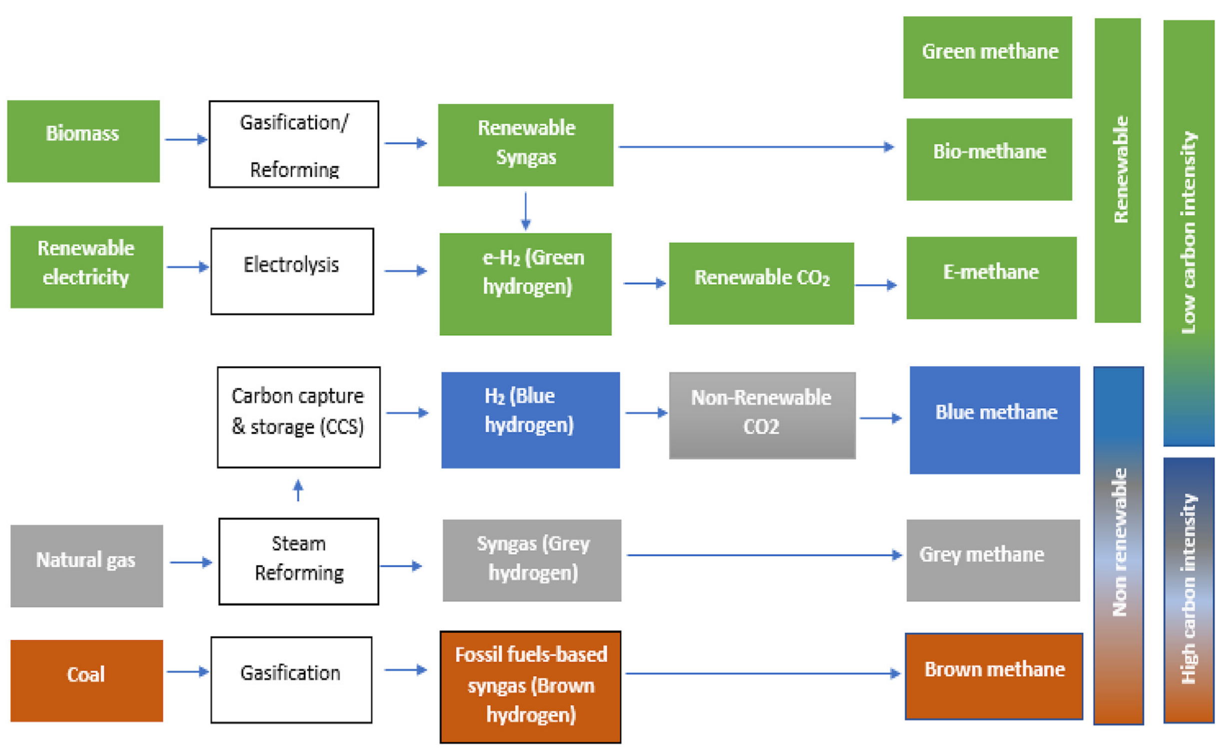

Fig. 4 – Methane production pathways.

Table 5 – Power to E-methane production.

Location, Company/ Project name	Startup year	Renewable energy systems	Hydrogen production		CO_2 production		Methane synthesis (Sabatier process/reactor)				
			Technology	Production capacity H_2	CO_2 capture source/ Technology	CO_2 capture amount	Operating conditions	η_{conv} (%)	CH_4 production	Application	Ref
Portugal, Case study	2014	Hydroelectric 172 MW	AEC Electrolyser 80 °C, 30 bar Eff = 75%	1 kg/s	Biomass (Wood pellet) gasification 1000 °C, 30 bar	5.5 kg/s	270 °C, 10 bars	–	2.2 kg/s	Methane is used to supply natural gas vehicles in Paraguay.	[92] [136]
Case study	2018	RES	AEC Electrolyser 1 KW using carbon/ graphite electrodes	Syngas H_2 = 81.4% CO = 7.7%; CO_2 = 2.0%; O_2 = 8.9%	Syngas produced by Water electrolysis	2.0% of total syngas	125 °C, 1 bar	45%	Selectivity = 97%	Production of syngas and its optimization through a one-step innovative 1 kW prototype of AEC water electrolysis using graphite electrodes.	[129]
Italy, Case study	2013	Hydroelectric 50 MW	AEC Electrolyser 30 bars	–	Carbon capture sequestration	125.5 ton/day	–	–	45.6 ton/day	Thermo-economic study of a hydro-methane production plant	[133]
A German study	2015	Wind 10 MW	Elevated temperature steam Electrolyzer (HTSE), SOEC, 700 °C, 1 bar	1104 tons/year	Biogas	–	–	Overall plant efficiency 38%	5888 tons/yr	A German Study on methane production via HTSE from Wind Energy: Storage and transport of methane is easier compared to H_2. Methane is used as fuel for transport and heat sector.and used as storage medium for the stabilization of the electrical power supply.	[137]
Germany, case study	2014	Wind 6 MW	3 AEC electrolyzers	–	Biogas plant.	2800 metric tons	–	54	1000 metric tons/yr	Audi e-gas plant in Germany is the biggest Power- to-Gas plant worldwide. Operation began in 2013.	[138] [139] [8]

Germany, case study	2017	Wind	AEC Electrolyser 1 MW	–	–	–	–	–	–	Store and go project: Synthetic natural gas (SNG) produced with hydrogen from water electrolysis and CO_2 from renewable sources	[135]
Case study	2019	RES (solar/ wind)	PEM Electrolyser 1 MW	17.6 kg/h	Biomass gasification	66.6 kg/h	–	–	43.8 kg/h	SNG used to produce electricity and heat (e.g., internal combustion engine, gas turbine, combined cycle gas turbine or fuel cells), can be introduced into the gas network or as fuel for transport and as substrate in the chemical industry.	[140]

equivalent to the amount that more than 220,000 beech trees absorbs CO_2 in one year [134]. In a study carried out by Schollenberger et al. [135], SNG was produced in Honeycomb reactor by the addition of "green" CO_2 and "green" hydrogen to the methanation process. However, the study was theoretical to identify the reactor geometry, optimal materials, and boundary conditions.

Challenges and future trends

The use of electro-fuels via Power-to-Fuels (PtF) routes has gained attention for the aim to achieve industrial decarbonization, coupling hydrogen production through water electrolysis combined with a carbon source. However, there are several constraints and limitations that face the PtF concept as it poses new challenges for the synthesis of large-scale plants towards electro-fuels production with direct CO_2-utilization.

Production cost

The main challenge that faces the production of different electro-fuels include the cost of renewable resources related to building and installing facilities, availability of power, infrastructure, safety, transportation, and supply. According to the latest IRENA report, it was reported that the cost of renewable technologies such as wind and solar is continuing to fall significantly, making renewables as the world's cheapest source of power [141]. Renewables are notably weakening the fossil fuels position as the cost of solar projects has fallen 85% in the last decade [141].

Another major concern is the high cost of green hydrogen production which is 2–3 times higher compared to blue hydrogen (produced from fossil fuels with CCS) and grey hydrogen (produced from steam reforming of natural gas) [142]. Generally, the cost of hydrogen production depends mainly on the type of electrolyzer used, its capacity factor which is a measure of what a generation unit is capable of generating, and the cost of electricity generated from renewable sources [46]. As stated in the hydrogen supply report of IRENA [46], the range of the current green hydrogen cost is 4–6 USD/kg in comparison with the cost of grey hydrogen which is about 1–2 USD/kg. To reduce the production cost of green hydrogen, new policy measures and regulations are needed to scale up green hydrogen production such as increasing the capacity size of the electrolyzer to MW and GW (Scalability), reducing its capital and operational costs and enhancing the efficiency. Furthermore, policies should also aim to access renewable electricity to green hydrogen units and to support research and development to improve the performance of electrolyzers and to develop cost effective technologies and enhance safety as a result of applying best practices.

For e-methanol production, it was reported that the current production cost of renewable methanol is significantly higher than that of fossil fuel-based methanol (production price of methanol from natural gas and coal is in the range of 100–250 USD/t). The bio methanol cost is estimated to be between 320 USD/t and 770 USD/t and it can be decreased to the range 220–560 USD/t with lower feedstock cost and with

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process improvements. The cost of e-methanol is directly proportional to the cost of H2 and CO2. The hydrogen price is tightly linked to the cost of renewable electricity generation and the type of selected electrolyzer. It can be emphasized that AEC electrolyzers are currently the cheapest technology and further decreases in both renewable energy and electrolyzers cost is expected in the future. The CO2 price is based on the source of captured CO2 whether it is obtained from biomass, industry, or direct air capture. According to reports published about e-methanol [14], in case CO2 is originated from bio energy with CCS at a cost of 10–50 USD/t, the cost of e-methanol production is projected to range between 800 USD/t and 1600 USD/t. If CO2 is obtained by DAC with a cost of USD 300–600/t, therefore, the range of e-methanol production cost would increase to 1200–2400 USD/t. It is estimated that the cost is anticipated to be reduced to a range between 250 and 630 USD/t by 2050, driven by the expected reductions in renewable energy generation prices in the next years [14].

The same also applies to e-ammonia production cost which is higher than that of fossil fuel-based ammonia (110–340 USD/ton). The range of renewable ammonia production cost is estimated to be between 720 and 1400 USD/ton and it is expected to fall to 310–610 USD/ton by 2050 [71]. The cost of green hydrogen production comprises more than 90% of the total cost of ammonia production. The other small fraction of total cost corresponds to nitrogen purification/separation and the Haber-Bosch process.

Demand

The increased demand for electricity is also a limiting factor for the integration of electro-fuels. As mentioned in earlier sections, electro-fuels can act as potential long-term energy storage carriers and can manage grid-integration of more intermittent renewable energy sources. However, large-scale electro-fuels necessitate an additional demand for electricity. It was revealed by the Swedish energy agency that using electro-fuels would require increasing the current Swedish electricity generation by 60% to meet the demand of the current transport sector in Sweden [143].

Intermittency and fluctuations

Another barrier that needs to be assessed is the intermittency and fluctuations in power output from renewable energy resources (s.t. solar and wind). Therefore, a vigorous electrical grid is needed to be integrated in order to balance the intermittent renewable generation allowing the electro-fuels plants to operate regularly. The development of electro-fuels plants that could handle dynamic fluctuation in electricity power generation from solar and wind energies need to be highlighted.

Conversion efficiencies and losses

The energy losses barrier during storage and transport of both green hydrogen and electro-fuels production needs also to be taken into consideration. Carbon losses are expected during the imperfect processes of hydrocarbon electro-fuels and the different carbon usage pathways. Taking possible measures to reduce such losses need to be taken into account through recycling options and recovery of process surplus carbon [144].

Another constraint, especially for desert regions, is the lack of water availability (sustainability) as vast amounts of water is needed to produce hydrogen via electrolysis. These regions rely primarily on desalinated seawater and ground water for the water supply as the water sources are extremely limited.

As most countries continue their progress in transitioning to clean energy, it is crucial to consider economic, political, and social practices of the transition. Thus, indicating key performance of energy transition (Energy Transition Index) for countries is needed for benchmarking, measuring the success of the actual energy system performance, and fostering effective energy transition initiative. According to the World Economic Forum report [145], this can be done by assessing the performance of the energy systems (security and access; environmental sustainability; economic development and growth); and assessing also the readiness for these countries for effective energy transition (energy system structure; infrastructure and innovative business model; capital and investment; regulation and political commitment; institutions and governance; and human capital and consumer participation). In addition, attention has to be given to research and development and international collaboration between industries, governments, and higher education institutions.

Conclusion

The concept of (PtF) has gained growing interest as it addresses matters concerning carbon neutral fuels production from CO_2 and hydrogen, which promotes the decarbonization of the global economy. This article presents a snapshot of the development of PtF technologies by integrating renewable energy sources with sector coupling using green hydrogen. The paper reviewed the major research progress on synthetic e-fuels production (Methane, ammonia, and methanol) from renewable sources such as solar and wind energy. It summarizes the highlights of research and projects focusing on the main technologies for carbon capture, water electrolysis and conversion routes. Most PtF projects include three main stages: Power generation using renewable energy, water electrolysis for H_2 generation, CO_2/N_2 separation and CO_2 hydrogenation to synthetic fuels (in case of ammonia production, N_2 is used instead of CO_2).

With regard to sustainable H_2 production via electrolysis, which is a key element of PtF technologies, AEC is the cheapest and most mature technology as it is already in its commercial phase at MW scale. PEM electrolysis is suitable for the PtG processes in the near future. It is gaining a high share of the market as its cost is expected to fall in addition to its greater performance with reference to transient operation and good partial load range. SOE electrolysis is promising when coupled with exothermic processes and for CO_2 and water electrolysis. However, it is still in the research and development phase with a promising progress for the integration to commercial level. Scientists have spent a lot of time and effort studying ways to improve the efficiency of H2 generation and electrolyzer while keeping costs low in order to work around PtF limitations. The CO_2 usage for producing e-

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fuels can be derived from anthropogenic CO_2 emissions as well as biogenic sources. Similarly, the excessive cost of CCS technology is also a challenge for the three pathways of carbon capture, i.e., post combustion, pre combustion and oxy-fuel combustion. Thus, CCS technology also needs major developments to attain the market at affordable price. The conversion of CO2 and hydrogen to methanol and methane e-fuels though hydrogenation of CO2 and Sabatier reactions are highly exothermic processes operating at 200–300 C and 250–400 C, respectively. The haber-bosch reaction is used for the production of e-ammonia using N_2 and H_2 at a temperature range of 400–500 C.

In conclusion, considering infrastructure, safety, transportation, and supply, and with anticipated cost reductions of renewable electricity, electrolyzers and CO_2 air capture, the production of synthetic e-fuels like ammonia, methane and methanol is promising as they can function as excellent energy carriers, electricity storage medium, fuels for different fields of applications and feedstock for the chemical industry. The key to meeting the challenge or decarbonizing the global economy is to tackle all the presented barriers and limitations by further research for a successful implementation of PtF technologies.

Declaration of competing interest

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

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