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Review

Sustainable E-Fuels: Green Hydrogen, Methanol and Ammonia for Carbon-Neutral Transportation

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Abstract: Increasingly stringent sustainability and decarbonization objectives drive investments in adopting environmentally friendly, low, and zero-carbon fuels. This study presents a comparative framework of green hydrogen, green ammonia, and green methanol production and application in a clear context. By harnessing publicly available data sources, including from the literature, this research delves into the evaluation of green fuels. Building on these insights, this study outlines the production process, application, and strategic pathways to transition into a greener economy by 2050. This envisioned transformation unfolds in three progressive steps: the utilization of green hydrogen, green ammonia, and green methanol as a sustainable fuel source for transport applications; the integration of these green fuels in industries; and the establishment of mechanisms for achieving the net zero. However, this research also reveals the formidable challenges of producing green hydrogen, green ammonia, and green methanol. These challenges encompass technological intricacies, economic barriers, societal considerations, and far-reaching policy implications necessitating collaborative efforts and innovative solutions to successfully develop and deploy green hydrogen, green ammonia, and green methanol. The findings unequivocally demonstrate that renewable energy sources play a pivotal role in enabling the production of these green fuels, positioning the global transition in the landscape of sustainable energy.

Keywords: alternative fuels; decarbonization; sustainable transport; e-vehicles; carbon-neutral transportation

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1. Introduction

During the Anthropocene era, our actions have significantly shaped the earth, leading to issues such as environmental contamination, changes in weather patterns, and the extinction of numerous species. The global need for energy continues to increase, primarily due to population growth, improved quality of life, and the industrial development of emerging nations [1]. In 2019, total global primary energy provision reached 4410 million tons of oil equivalent (MTOE) [2]. The International Energy Agency (IEA) forecasts a 50% surge in worldwide energy requirements by 2030 [3]. At present, fossil fuels satisfy more than 95% of this significant energy requirement, and their utilization leads to global warming and environmental contamination. To tackle these problems, a promising approach is replacing fossil fuel-based energy sources with renewable, carbon-neutral alternatives in the energy sector [4]. One pivotal solution in the transport sector is the advancement of internal combustion engines capable of operating on environmentally friendly fuels like green hydrogen, green ammonia, or green methanol [5]. This shift can decrease the release of greenhouse gases, alleviate global warming, and confront climate change.

In sustainable energy, the pursuit of green hydrogen, green ammonia, and green methanol has emerged as a promising avenue for curbing carbon emissions. Publication trends on green fuels in the recent decade, i.e., 2013–2023, were obtained using the Scopus search tool. The results were obtained using the keywords "green ammonia," "green hydrogen," and "green methanol," and are presented in Figure 1 (Scopus.com). Overall, the number of publications is increasing continuously, though the yearly increase is regular.

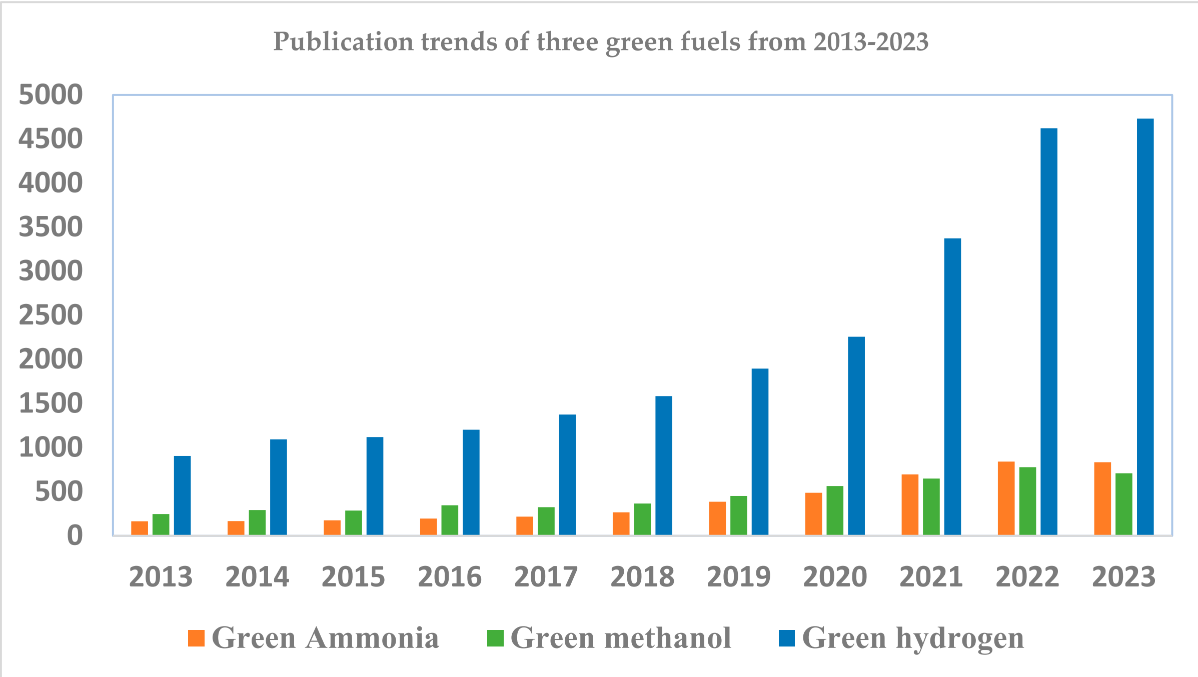

Figure 1. Comparative analysis of the literature on green hydrogen, green ammonia, and green methanol during 2013–2023 (Source: Scopus.com).

Hydrogen represents a unique zero-carbon energy carrier akin to electricity. Hydrogen is hailed as a carbon-neutral fuel of the future, particularly in the form of green hydrogen. This thriving market is presently valued at more than USD 100 billion and is expected to grow substantially, reaching an impressive USD 2.5 trillion by 2050 [6]. Hydrogen production methods vary and can include natural gas, steam, coal, biomass conversion, electrolysis powered by renewable electricity, or virtually any other energy source. Each method has its distinct carbon-emissions profile.

After production, hydrogen can be transported as a compressed gas via trucks or pipelines, moved in liquid form by trucks, or even converted into ammonia for further transportation [7]. This adaptable gas finds primary applications in oil and gas refining; ammonia and methanol production; steel manufacturing; transportation; and numerous other industrial processes.

Ammonia production entails the synthesis of hydrogen and nitrogen via the Haber–Bosch process. After synthesis, ammonia can be conveyed through gaseous pipelines or transformed into a liquid state for transportation via trucks, barges, or ships. Ammonia is primarily employed in producing fertilizers, with secondary applications in oil and gas refining and in manufacturing specialty chemicals. The carbon intensity of the resulting ammonia largely hinges on the type of hydrogen employed, which can range from gray to green and beyond. A noteworthy trend is the commitment of significant ammonia producers to reducing carbon emissions by transitioning to green hydrogen as a feedstock.

Projections indicate that approximately 15% of the global ammonia market will be supplied with green hydrogen by 2030 [8].

Methanol production accounts for 11% of the annual hydrogen production. The process involves introducing a mixture of carbon monoxide and hydrogen, known as syngas, into a reactor. The chemical reaction for methanol synthesis is $CO + 2H_2 \rightarrow CH_3OH$. This reaction occurs under high-temperature conditions, typically between 400 and 600 degrees Fahrenheit, and at pressures ranging from 600 to 1700 pounds per square inch. Presently, methanol is predominantly utilized to produce alternative fuels and olefins. However, ongoing research is exploring the potential to convert green hydrogen into methanol, as it offers a more robust and transportable form of energy storage [9].

The critical industrial drivers of green hydrogen, green ammonia, and green methanol include climate goals, the imperative for energy-efficient storage, industrial decarbonization, and the initiative toward carbon-neutral transportation [10].

1.1. Literature Review and Research Gap

Based on several literature reviews, a recent study meticulously examined three distinct E-fuels—power-to-methane ($PtCH_4$), power-to-methanol ($PtCH_3OH$), and power-to-ammonia ($PtNH_3$)—and drew insights for clean energy transition [1]. Another study extensively explored the green fuel pathway, emphasizing the decarbonization of the shipping sector through environmentally conscious production methods of hydrogen, ammonia, and methanol [5]. In another study, an in-depth analysis focusing on key considerations such as emissions, supply, safety, and storage, tailored explicitly for achieving zero-emission shipping, was conducted [7]. Furthermore, the crucial role of carbon-neutral fuels in steering toward a net-zero future was also discussed [10].

However, despite the wealth of information drawn from multiple references, a comprehensive comparative analysis of green hydrogen, green ammonia, and green methanol is lacking in the current literature. Notably, characteristics/color codes; production and storage methods; applications; challenges; opportunities; and cost analysis of these green fuels are underrepresented in the reviewed literature. This gap in the literature underscores the need for further research to address these aspects comprehensively, enabling an adequate understanding of the comparative merits and drawbacks of these E-fuels in achieving sustainable and efficient transportation.

1.2. Novelty Statement

This research makes a significant contribution to the body of knowledge, ensuring a comprehensive understanding of all facets (production processes, potential costs, and sustainability challenges and opportunities) within the green hydrogen, green ammonia, and green methanol production domains. By doing so, it aims to deliver essential insights and scientifically sound information to scholars, decision-makers, and stakeholders for informed decision-making.

1.3. Objectives of this Study

Given the research gaps described above, the objectives of this study are threefold:

- This study investigates the various methods of producing green hydrogen, green ammonia, and green methanol from renewable sources.
- This study also aims to evaluate the application potential and cost-effectiveness of green fuels in transport sectors.
- Furthermore, this study examines the challenges and opportunities that may influence adopting and deploying green hydrogen, green ammonia, and green methanol technologies.

The present research aims to offer strategic insights into diverse E-fuels that can pave the way for a sustainable future in transportation.

2. Overview of Green Hydrogen

On a global scale, hydrogen consumption was approximately 120 million metric tons in 2020, and this is projected to increase to 530 million metric tons annually by 2050. The worldwide production is about 75 million metric tons of pure hydrogen annually, accompanied by an additional 45 million metric tons of hydrogen as part of a gas mixture [11,12].

Identifying and implementing eco-friendly hydrogen production methods is greatly hindered by the requirement for a gradual transformation of national energy systems [13]. Hydrogen-focused decarbonization involves using hydrogen in energy-intensive industrial sectors, including energy, transportation, and the chemical industry, while encouraging its adoption in local markets and everyday utilities [13]. Hydrogen is a promising energy carrier and feedstock that offers a natural-based solution for fuel consumption and its associated environmental impacts [14].

2.1. Color Codes of Hydrogen

The production of hydrogen fuel is possible through diverse primary energy sources. Consequently, these technologies are classified into distinct categories, denoted by different colors, which reflect the production process, the type of energy utilized, and the costs and emissions associated with hydrogen production [15]. These classifications encompass green, blue, aqua, and white hydrogen (referred to as low-carbon hydrogen) alongside gray, brown, black, yellow, turquoise, purple, pink, and red hydrogen (refer to Table 1).

Presently, multiple approaches have been suggested to produce hydrogen in a more environmentally friendly manner [16–18]. Gray hydrogen production entails fossil fuels, primarily through reforming and pyrolysis techniques, with direct CO_2 emissions, and minimal energy costs. In contrast, blue hydrogen, which involves carbon-capture utilization and storage (CCUS), has no direct CO_2 emissions but comes with additional expenses for capturing and storing CO_2 [15]. Hence, the production of green hydrogen through the electrolysis of water (H_2O) is increasingly being recognized as the primary method for future hydrogen production. Presently, hydrogen gas is derived from a variety of sources, both renewable and non-renewable [19]. Renewable sources encompass biomass conversion; water electrolysis; and harnessing wind, solar, hydro, and nuclear energy.

These various methods of hydrogen generation come with their advantages and drawbacks, varying in terms of efficiency and costs [20]. Notably, a significant portion of hydrogen gas is generated through non-renewable means, mainly using the steam reforming of methane (SRM) [21]. Electrochemical water splitting has emerged as a highly promising method for generating hydrogen energy [22]. Hydrogen produced using renewable electricity from solar, wind, biomass, geothermal, and ocean sources is commonly called renewable hydrogen [19,23].

Table 1. Summary of different types of hydrogen and their characteristics [13,15,16,18,24].

Hydrogen	Technology	Feedstock/Energy Source	Products	Emission (kg CO_2/kg H_2)	GHG Footprint	Cost (USD/kg H_2)
Black	Gasification	Coal (Bitumen)	H_2 + CO_2 Released	21.8	High	1.2–2.0
Brown	Gasification	Coal (Lignite)	H_2 + CO_2 Released	20	High	1.2–2.0
Gray	Reforming	Natural Gas	H_2 + CO_2	8.5–10.9	Medium	0.67–1.31
Blue	Reforming + CCUS	Natural Gas + CCUS Coal + CCUS	H_2 + CO_2 CCUS	1–2	Low	0.99–2.05
Turquoise	Pyrolysis	Methane	H_2 + C Solid Carbon	Solid Carbon	Solid Carbon	2.0–2.1
Yellow	Electrolysis	Water + Mixed origin Grid Energy	H_2 + O_2	0	Medium	6.06–8.81

Table 1. *Cont.*

Hydrogen	Technology	Feedstock/Energy Source	Products	Emission (kg CO_2/kg H_2)	GHG Footprint	Cost (USD/kg H_2)
Pink/Violet Purple	Electrolysis	Water + Nuclear Energy	$H_2 + O_2$	0	Minimal	2.18–5.92
Green	Electrolysis	Water + Renewable Energy	$H_2 + O_2$	0	Minimal	2.28–7.39
Aqua	Oxygen injection	Oil sands (Natural Bitumen)	H_2 + Carbon Oxides	Geological storage	-	0.23
White	Fracking	Naturally Occurring	H_2	0	Minimal	-
Gold	Water splitting	Water +direct solar	$H_2 + O_2$	0	Minimal	-

2.2. Green Hydrogen Production and Storage

Green hydrogen refers to hydrogen derived from renewable sources, excluding biomass, and achieves an impressive 70% reduction in greenhouse gas (GHG) emissions compared to fossil fuels. Typically, this implies hydrogen production through water electrolysis, powered by renewable energy sources such as photovoltaic systems or wind turbines [23]. With technological advancements, the definition of green hydrogen has expanded to include considerations of potential greenhouse gas (GHG) emissions, energy-related issues, and other climate impacts linked to the production process. Notably, the electrical energy utilized for water electrolysis is not limited to being exclusively generated from renewable sources. It can also be sourced from the conventional power grid [25]. Three primary technologies exist for producing green hydrogen through water electrolysis: alkaline water electrolysis (AEL), proton exchange membrane electrolysis (PEMEL), and solid oxide electrolysis (SOEL). Among these, alkaline water electrolysis is recognized as a well-established and matured state-of-the-art technology [26]. Proton exchange membrane electrolysis (PEMEL) employs a proton exchange membrane (PEM) in a zero-gap configuration, replacing the liquid electrolyte. This design enables direct contact between the electrodes and the surface of the proton [27]. Conversely, solid oxide electrolysis depends on water vapor electrolysis at elevated temperatures. Operating at higher temperatures reduces the energy demands for the water-splitting reaction and improves the efficiency of converting power into hydrogen [28]. Figure 2 illustrates green hydrogen's production, storage, and end use.

Currently, the available methods for storing hydrogen include cryogenic freezing or liquefaction, compressed gas storage, and chemical storage alternatives like metal hydrides, chemical hydrides, and sorbents [29]. Metal hydrides and MOFs (Metal-Organic Frameworks) are promising materials for hydrogen storage, offering efficient and reversible means for storing hydrogen as a clean energy carrier [30]. Freezing or liquefying hydrogen demands substantial energy input, primarily because hydrogen has a shallow melting point and boiling point. Consequently, solid and liquid storage options may lead to an energy loss of up to 30% due to the significant energy consumption required for hydrogen freezing or liquefaction [31]. Additionally, achieving adequate insulation for such storage can be challenging. On the other hand, compressed hydrogen gas systems offer several advantages, including low energy requirements; cost-effectiveness; quick charge and discharge cycles across a broad temperature range, even under extremely low temperatures; and straightforward operation via a control valve. These systems can currently store pressurized gas within 35 MPa to 70 MPa [32].

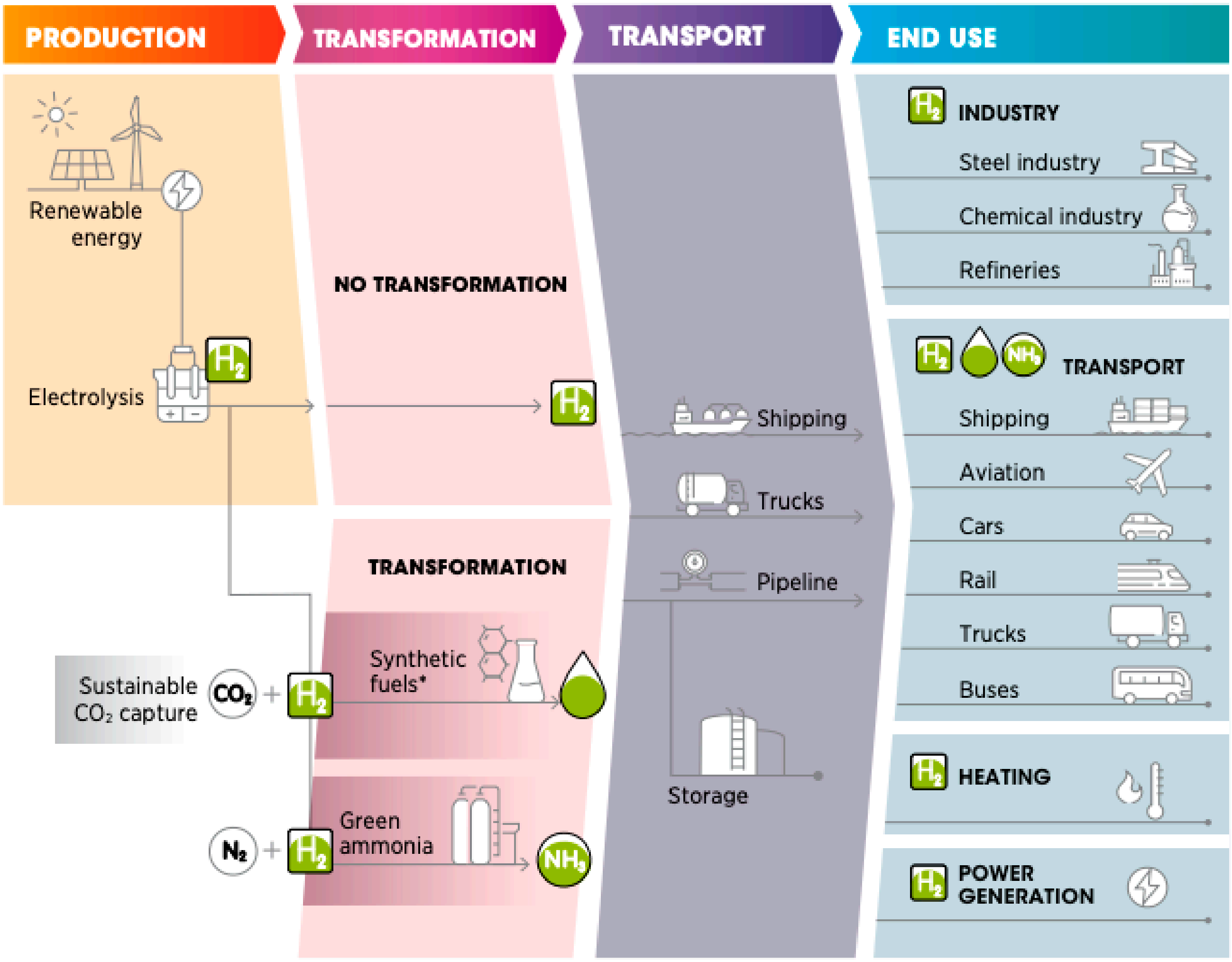

Figure 2. Green hydrogen production, storage, transport, and usage (Source: IRENA (2020), Green Hydrogen: A guide to policy making, International Renewable Energy Agency, Abu Dhabi).

2.3. Properties and Characteristics

Hydrogen, when used as a fuel or as an energy storage medium, has a negligible adverse environmental impact [31]. Moreover, hydrogen is the lightest and most abundant element in the universe, comprising 75% of all matter by mass and an impressive 90% when considering the number of atoms [33]. Hydrogen boasts an exceptional trait as an energy carrier: an impressively high energy density ranging from 120 to 140 megajoules per kilogram (MJ/kg), double that of typical solid fuels [34]. The combination of hydrogen and oxygen releases the highest energy per unit of fuel weight [35]. The heat energy generated from hydrogen combustion is approximately 142.26 kilojoules per gram (kJ/g).

In contrast, petroleum yields a heat energy of 35.15–43.10 kJ/g, and wood produces about 17.57 kJ/g [34]. It is important to highlight that although hydrogen has higher and lower ignition limits and lower ignition energy than gasoline and methane, it also possesses lower explosion energy. Additionally, hydrogen demonstrates lower toxicity levels than gasoline and methane when utilized as a fuel, leading to fewer toxic emissions post-combustion. With a higher ignition temperature and lower flame emissivity, hydrogen is collectively acknowledged as a safer fuel than gasoline and methane. Refer to Table 2 for a breakdown of some of the physical properties of green hydrogen.

Table 2. Properties of green hydrogen.

Property	Green Hydrogen
Chemical formula	H_2
Appearance	Colorless and odorless gas
Molecular Mass	2.0156 g/mol
Melting temperature	−259.2 °C
Density (20 °C)	0.0899×10^{-3} g/cm^3
Boiling point	−252.8 °C
Latent heat of vaporization	446 kJ/kg
Specific gravity	0.070
Thermal conductivity (NTP)	0.1825 W/m-K
Specific heat (kJ/kg-K)	1.44
Octane number, RON	109–114
Cetane number, CN	3
Flash point	−253 °C
Storage pressure and temperature	0.1 MPa, 20 °C

2.4. Application

In the aerospace industry, hydrogen has demonstrated its capacity to serve as an outstanding energy source [33]. For green hydrogen to reach its full potential, it must be adapted for use in majorly polluting industries [33,36,37]. While the green hydrogen industry is still in its early stages, it has already seen the development of five significant applications for this renewable energy source [11,38–40]. It has gained considerable attention for its potential role in achieving low-carbon solutions in transportation industrial decarbonization, particularly within the oil and gas, fertilizer, fuel cell technology, petrochemical, petroleum, metal refining sectors, and also for heat supply across many nations [41].

- Hydrogen feedstocks: Green hydrogen is employed to replace conventional feedstocks, as hydrogen production can be carbon intensive. Green hydrogen is produced using renewable energy, reducing carbon emissions associated with hydrogen production. It facilitates the integration of renewable energy sources into the power system, decreases reliance on imported fossil fuels, and reduces carbon footprint [36].
- Residential and commercial heating systems: Green hydrogen decarbonizes heating systems in residential and commercial settings, where heating contributes significantly to carbon emissions. It can be mixed with natural gas in areas with higher natural gas prices [42].
- Energy storage: Green hydrogen serves as a valuable energy storage option, although early attempts to develop hydrogen-based batteries have seen a decrease in energy efficiency compared to conventional batteries [30].
- Alternative fuel production: Green hydrogen plays a role in producing alternative fuels.
- Fuel cell vehicles: Green hydrogen is used to power these, although it has yet to gain substantial traction in the automotive market. Fuel cell electric vehicles are a transformative development in the energy and transport sector toward achieving a carbon-neutral footprint [43].
- Industrial sector: Green hydrogen is increasingly finding applications in various industrial sectors, notably in the chemical industry for ammonia and fertilizer production, the petrochemical sector for manufacturing petroleum products, and the steel industry, where it is being employed to mitigate its environmental impact. This gas enables changes in industrial processes to make them more environmentally friendly, particularly in response to the ecological challenges faced by the European steel industry. Additionally, ongoing sustainable initiatives aim to substitute natural gas networks with green hydrogen networks for household use, providing households with cleaner sources of electricity and heat while minimizing pollutant emissions [44].

2.5. Cost Analysis

Recent studies suggest that the cost of renewable hydrogen production will need to be halved to be economically competitive with hydrogen produced using fossil fuels [45]. Green hydrogen cost depends on several factors, such as the location (easy/difficult access to green electricity), the production method (e.g., Alkaline Water Electrolyzer (AWE), Proton Exchange Membrane (PEM), Solid Oxide Electrolyzer Cell (SOEC), Anion Exchange Membrane Electrolysis (AEM), photocatalysis), or the capacity and lifetime of the facility; electrolysis efficiency; renewable energy costs; electrolyzer capital costs; operation and maintenance costs; scaling and capacity utilization; infrastructure and transportation; and government incentives, etc. [46]. The current cost range of green hydrogen is about USD 2.28–USD 7.39/kg H_2 produced [18,47]. To decrease the high cost of the electrolysis process, it is necessary to find ideal materials to produce electrolytic cells and establish a large-scale electrolysis supply chain [48].

In the present scenario, improvements in electrolyzer efficiency have led to lower electricity consumption, reducing the cost of hydrogen production. Falling renewable energy prices substantially impact the cost of green hydrogen. As renewable energy costs decrease, green hydrogen becomes more competitive [49]. As electrolyzer manufacturing scales up and technology advances, capital costs are declining. This trend is expected to continue. Proper maintenance and operational practices can help control ongoing costs and maximize equipment lifespan. Large-scale production facilities tend to have lower production costs per hydrogen unit [50]. Efficient use of capacity is essential to cost optimization. It is vital to provide government support and incentives, such as subsidies and tax credits, which can significantly reduce the cost of green hydrogen. The advances in research in this area will result in a reduction in production costs. The price of green hydrogen for commercial use is expected to be reduced by 2030 [11,12].

2.6. Pros and Cons of Green Hydrogen

Green hydrogen, produced through renewable methods, is a promising solution for transitioning to a sustainable-energy landscape. Its primary advantages lie in its potential to significantly reduce greenhouse gas emissions, offering a clean alternative for various industries, particularly transportation and heavy manufacturing. The versatility of green hydrogen in energy storage and its capability to be a key player in decarbonizing industrial sectors make it a frontrunner in carbon-neutrality goals. However, challenges include high production costs, the need for extensive infrastructure development, and the energy-intensive nature of its production process. Table 3 highlights the pros and cons of green hydrogen.

Table 3. Pros and cons of green H_2 [15,51–53].

Pros	Cons
• Eco-friendly power	• Elevated production costs
• Versatile energy carrier	• Infrastructure establishment
• Efficient energy storage solution	• Technical hurdles
• Generates job opportunities	• Competition from other green fuels
• Utilizing excess renewable energy	• Secondary energy carrier
• Decarbonize industries	• Economically not feasible

3. Overview of Green Ammonia

About 1.8% of carbon emissions are released using conventional ammonia [54]. Green ammonia has diverse applications, including as a fertilizer, fuel, energy storage medium, or hydrogen carrier [55]. Produced from renewable energy sources like wind, solar, or hydropower, green ammonia is a sustainable alternative to traditional ammonia derived from fossil fuels. Its adoption can reduce greenhouse gas emissions, enhance air quality, and align with several United Nations Sustainable Development Goals (SDGs) [56]. Green ammonia addresses key SDGs, including zero hunger, affordable and clean energy, industry, innovation, infrastructure, and climate action [57]. A necessary component of fertilizers that increase agricultural yields and food security is ammonia [58].

For agriculture, green ammonia can offer a low-carbon supply of nitrogen [59]. Ammonia is a fuel that may be utilized in manufacturing, transportation, and power generation [60]. Figure 3 presents a schematic diagram of green ammonia production, storage, and transport. Ammonia is a feedstock for several industrial processes, including chemical synthesis, steel production, and refrigeration [61]. These industries' carbon footprints may be decreased, and new technological developments can be made possible via green ammonia. Green ammonia is one of the most promising approaches for reducing carbon emissions from the energy sector and addressing climate change [62].

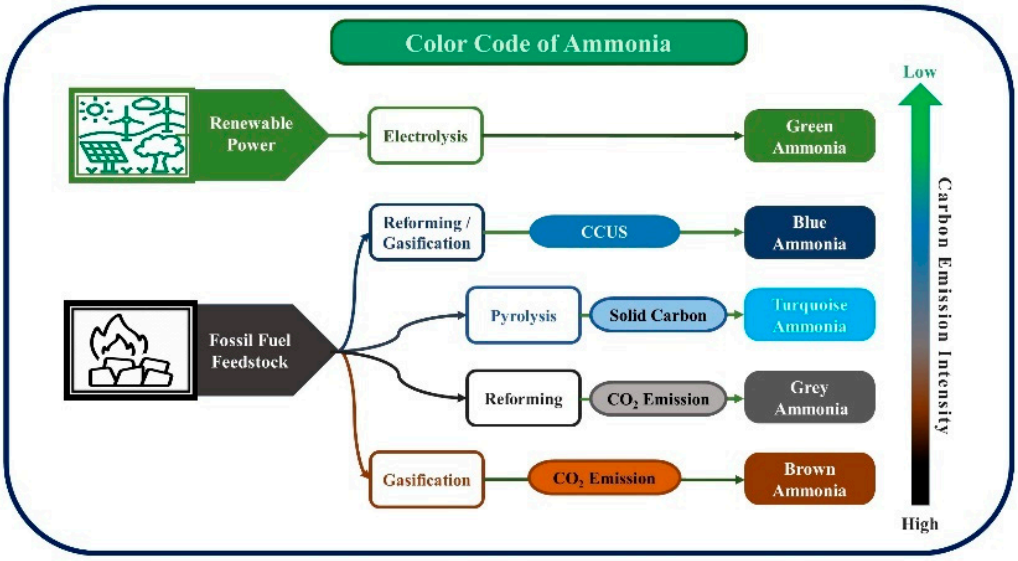

Figure 3. Color codes of ammonia [57,61].

3.1. Color Codes of Ammonia

Ammonia is often associated with color codes to indicate its production methods, which help to distinguish between different ammonia types [57,61]. Commonly recognized color codes include (Refer to Figure 3):

Green ammonia: Produced using renewable energy sources, such as wind, solar, or hydropower, to minimize environmental impact. Ammonia synthesis using renewable power-based electrolysis can achieve about 60–80% less CO_2 emission than gray ammonia, i.e., equivalent to 0.12–0.53 TCO_2. eq/TNH_3 [61].

Blue Ammonia: Generated using a combination of conventional ammonia production methods with CCUS technologies to reduce carbon emissions. It has an emission factor of 0.22–0.95 TCO_2. eq/TNH_3, which is 56% higher than green ammonia [57,61]

Gray ammonia: Produced through traditional methods using steam methane reforming without carbon capture or using renewable energy sources, producing higher carbon emissions. The commercial Haber–Bosch ammonia synthesis using methane as a feedstock emits about 1.5–1.6 TCO_2.eq/TNH_3 [61].

Brown ammonia is produced using hydrogen generated from coal gasification. The carbon intensity of the coal-based Haber–Bosch process is high at about 3.75 T CO_2.eq/TNH_3 [61].

3.2. Green Ammonia Production and Storage

The production of green ammonia is a process that involves using renewable energy sources to make ammonia from water and air without emitting any carbon dioxide [63]. The Fritz–Haber process, also known as the Haber–Bosch process, produces ammonia from nitrogen and hydrogen gases. It is one of the most important industrial processes in the world, as ammonia is used to make fertilizers, explosives, and other chemicals. The production, storage, and transportation steps of green ammonia are illustrated in Figure 4.

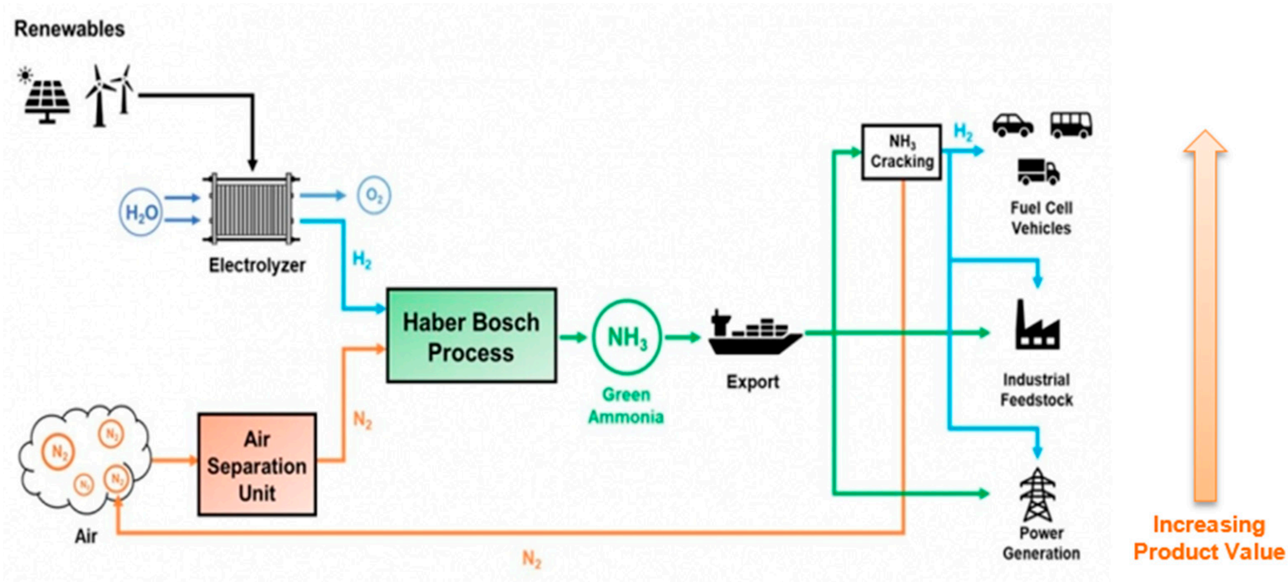

Figure 4. Production, storage, and transportation of green ammonia (Source: Particle and Catalysis research lab, UNSW Australia).

The first step is producing green hydrogen from water electrolysis using solar, wind, or hydropower electricity. Hydrogen gas is obtained from natural gas (mainly methane) by steam reforming and water–gas shift reactions. Water electrolysis is a process that splits water molecules into hydrogen and oxygen gas by passing an electric current through water. The hydrogen gas is then collected and purified.

The second step is to produce nitrogen, separated from the air by an air–separation process. Using fractional distillation and liquefaction, nitrogen gas is taken from the atmosphere. Air–separation is a process that uses low temperatures and high pressures to separate the different gases in the air, such as nitrogen, oxygen, argon, and carbon dioxide. The nitrogen gas is then collected and purified. The gases are then mixed in a ratio of 1:3 by volume, which corresponds to the stoichiometric ratio of the reaction [64].

The third step is to produce green ammonia from green hydrogen and nitrogen using the Haber–Bosch process [65]. The nitrogen and hydrogen gases react in the presence of a metal catalyst at a high temperature and pressure to produce ammonia. The catalyst is usually iron with some additives, such as potassium hydroxide, to increase efficiency. The reaction occurs in a reactor at about 400–450 °C temperature and 200–300 atm pressure. The reaction is reversible and exothermic, releasing heat, and can proceed in both directions. Within the reaction mixture is the presence of ammonia and a substantial amount of unreacted nitrogen and hydrogen. The unreacted nitrogen and hydrogen are recycled back into the reactor to maximize resource efficiency. Following this, the mixture undergoes cooling and compression, condensing ammonia gas into a liquid state. The liquefied ammonia is then prepared for storage or transport [61]. The chemical representation for the reaction is as follows: Nitrogen gas (N_2) reacts with three molecules of hydrogen gas (H_2) in equilibrium to produce two molecules of ammonia gas (NH_3).

The Fritz–Haber process is based on the principles of chemical equilibrium and Le Chatelier's principle. These principles help to determine the optimal conditions for maximizing the yield of ammonia [56]. Some of the factors that affect the yield are:

Temperature: According to Le Chatelier's principle, lowering the temperature will favor the forward reaction, which is exothermic. However, reducing the temperature will also decrease the reaction rate, as it depends on the kinetic energy of the molecules. Therefore, a compromise temperature range of about 400–450 °C is employed.

Pressure: According to Le Chatelier's principle, increasing the pressure will favor the forward reaction, as it reduces the number of moles of gas. However, increasing the pressure will also increase the cost of equipment and energy. Therefore, a compromise pressure of about 200–300 atm is used.

Catalyst: The catalyst does not affect the equilibrium position but increases the reaction rate by providing an alternative pathway with lower activation energy. The catalyst also helps to prevent side reactions that may reduce the yield of ammonia. The Fritz–Haber process is an example of how industrial chemists use their knowledge of chemistry to design efficient and sustainable strategies for producing valuable substances.

Ammonia is a gas that can be stored differently depending on its amount, temperature, and pressure [66]. Ammonia can also be stored as a liquid under high pressure or solid under very low temperatures. These also require more energy and equipment to maintain the storage conditions. Small amounts of ammonia, such as in household products, can be stored in an appropriate container and kept out of the reach of children. They should also be stored away from heat, flames, and incompatible substances like acids or chlorine. Large amounts of ammonia, such as in industrial plants or distribution terminals, can be stored in atmospheric tanks operating at low pressure and low temperatures. These tanks are usually made of steel and insulated with perlite or other materials to prevent heat loss. These tanks have different designs and safety features to prevent leaks or spills of ammonia. There are different types of atmospheric tanks, such as single-wall, double-wall, or double-wall double-integrity tanks. However, these methods are less common and more expensive than atmospheric storage [67]. Ammonia storage is subject to various standards and regulations to ensure the safety and environmental protection of workers and the public. It should also include a fire-rated chemical storage building, a risk assessment, and an emergency response plan.

3.3. Properties and Characteristics

Natural ammonia (NH_3) takes the form of ammonium salts. Storing and transporting ammonia is simpler than hydrogen, as it possesses an energy density of 18.6 MJ/kg [68]. The purest form of ammonia (NH_3) is called anhydrous NH_3, and is colorless and odorous. Ammonia has a low freezing point of −77.73 degrees Celsius, which makes it a good fuel for extremely cold settings [68]. It is also an excellent hydrogen transporter, containing 1.5 mol of hydrogen per mole of ammonia, or 107 kg of hydrogen per cubic meter of liquid ammonia [68]. Because ammonia is lighter than air and very soluble in water, it reduces the risk of fire or explosion and helps contain spills [69]. Table 4 presents the properties of green ammonia [68,70,71].

Table 4. Properties of green ammonia [68,70,71].

Property	Green Ammonia
Chemical formulae	NH_3
Appearance	Colorless
Molecular weight	17 g
Vapor pressure (mm/hg)	7500
Critical temperature (degree Celsius) and critical pressure (bar)	132.41 and 113.57

3.4. Applications

Green ammonia has several potential applications in industry and commercial sectors. Green ammonia can store excess renewable energy in a liquid form that can be easily transported and distributed. It can be converted to electricity using combustion engines, turbines, or fuel cells. Green ammonia can be used differently in fuel cells and combustion processes depending on the engine type and the desired performance [72].

Transport fuel for fuel cell vehicles: Green ammonia can be used as a zero-carbon fuel for vehicles that use fuel cells, such as cars, buses, trucks, or ships. In combustion processes, green ammonia can be used as a substitute or an additive for fossil fuels in internal combustion engines (ICEs) or gas turbines. In ICEs, green ammonia can be burned in spark or compression-ignition engines. In spark-ignition engines, green ammonia can be used as a pure fuel or mixed with hydrogen to improve the flame speed and stability. In compression-ignition engines, green ammonia can be used in dual-fuel mode with diesel, where diesel acts as a pilot fuel to ignite the ammonia-air mixture. Therefore, the combustion of green ammonia requires appropriate modifications of the engine design and operation parameters, as well as effective after-treatment systems.

Fuel cells: Green ammonia can be either directly used in ammonia fuel cells or cracked to produce hydrogen and nitrogen for hydrogen fuel cells. Ammonia fuel cells use a platinum black catalyst to split ammonia into hydrogen and nitrogen and then use the hydrogen to generate electricity and water. Hydrogen fuel cells use a reformer to crack ammonia into hydrogen and nitrogen and then use the hydrogen to generate electricity and water. Both types of fuel cells have the advantage of producing zero-carbon emissions. Still, they also face some challenges, such as the low efficiency of ammonia cracking, the high cost of catalysts, and the safety issues of ammonia handling and storage.

Feedstock for green fertilizer: Green ammonia can make nitrogen fertilizers for agriculture without emitting carbon dioxide. Green ammonia can be produced on-site, where it is needed, using local renewable energy sources and air. This can reduce dependence on imported fertilizers and the associated carbon footprint.

Industrial energy source: Green ammonia can be used as an alternative to fossil fuels for various industrial processes that require heat or power, such as steel making, cement production, or chemical manufacturing. Green ammonia can be burned in boilers, furnaces, kilns, gas turbines, or combined heat and power systems.

Gas-turbine power plants: Green ammonia can be used as a pure fuel or mixed with natural gas to reduce carbon emissions in gas turbines. However, the combustion of green ammonia also has some drawbacks, such as the low energy density, the high NOx emissions, and the unburned ammonia slip.

Green ammonia is a promising way to decarbonize various sectors of the economy and utilize renewable energy more efficiently. However, challenges and barriers remain to overcome, such as the high cost of green ammonia production, the lack of infrastructure and regulations for green ammonia distribution and use, and the safety and environmental issues related to ammonia handling and storage [73].

3.5. Cost Analysis

Cost analysis of green ammonia production is a critical factor in assessing the economic viability of this sustainable energy carrier [74]. This cost analysis considers various elements, including the capital investment in renewable energy infrastructure, the efficiency of the electrolysis process for hydrogen generation, and the costs associated with the Haber–Bosch synthesis. Additionally, factors such as economies of scale and technological advancements play pivotal roles in determining the overall cost competitiveness of green ammonia. As the world seeks to reduce greenhouse gas emissions and transition to a more sustainable energy future, continuous cost optimization and innovation are essential to making green ammonia a cost-effective and environmentally friendly energy carrier. Production costs of green ammonia vary depending on the technology used, the availability of cheap green energy, and various other factors. Currently, green ammonia is often cheaper than gray ammonia due to the high prices of gas. Nevertheless, production costs are definitely above the long-term average costs of gray ammonia.

Production Cost: The rate at which renewable ammonia plants are currently being announced is closely linked to the speed at which renewable electricity costs decrease. Renewable ammonia may already be cost-competitive with imported fossil-based ammonia in some locations. Today, renewable ammonia production costs for new plants are estimated at USD 720–1400 per ton, which may fall up to USD 310–610 per ton by 2050 [75].

Storage and transport costs: Ammonia fuel must be stored and transported to its destination after production. The additional costs for storage and transportation can significantly influence the overall costs.

Comparative indicative costs: Although specific numbers can vary based on factors like location and technology, it is essential to consider the entire supply chain. For context, coal-derived ammonia costs USD 147–432 per ton, equivalent to USD 0.96–2.83 per gallon of gasoline. In summary, ammonia's cost dynamics involve a trade-off between its carbon-free properties and the expenses associated with its production, storage, and distribution [76].

3.6. Pros and Cons of Green Ammonia

Green ammonia, produced through renewable energy sources, emerges as a promising avenue for sustainable energy applications. Its notable advantages include a significant reduction in greenhouse gas emissions compared to conventionally produced ammonia, aligning with global efforts to combat climate change. Green ammonia's versatility is evident in its clean fuel, energy storage medium, and hydrogen carrier applications, offering multifaceted solutions for various sectors. However, challenges include high production costs, which may limit its widespread adoption, and the need for further infrastructure development. Table 5 highlights the pros and cons of green ammonia.

Table 5. Pros and cons of green ammonia.

Pros	Cons
• Lowers carbon emissions • It improves air quality • Ideal for long-term storage • Produced in decentralized facilities • Reduces dependence on fossil fuels	• It is energy intensive • Complex production that requires advanced technology • Distribution and transportation are challenging • Corrosive and toxic nature • Early development phase • Poses safety risks during handling, storage, and use

4. Overview of Green Methanol

The production of renewable methanol is currently underdeveloped, with less than 0.2 Mt/yr originating primarily from biomass gasification [77]. Methanol, a promising substance for power to liquid systems, has a melting and boiling point at atmospheric pressures of −97.6 °C and 64.7 °C, respectively [78]. Methanol is essential in producing synthetic hydrocarbons in chemical and pharmaceutical industries. In particular, methanol can play a critical role as an energy carrier. Around 90 million tons of methanol is generated annually worldwide [79], with 35% produced from coal gasification (brown methanol) and 65% from steam methane reforming of natural gas (gray methanol). The recommendation of low-carbon fuels for the energy transition by Nobel laureate George A. Olah in 2005 is generating more interest in synthesizing methanol from renewable energy sources [80]. A CO_2-neutral closed-loop system is produced by integrating methanol production into existing facilities like pulp and paper mills or power plants [81].

4.1. Color Codes of Methanol

Like hydrogen and ammonia, methanol has codes associated with its production methods. Color coding, as used in the context of green, blue, gray, etc., is more commonly applied to indicate the environmental impact or sustainability of specific production methods (Refer to Figure 5) [79,80].

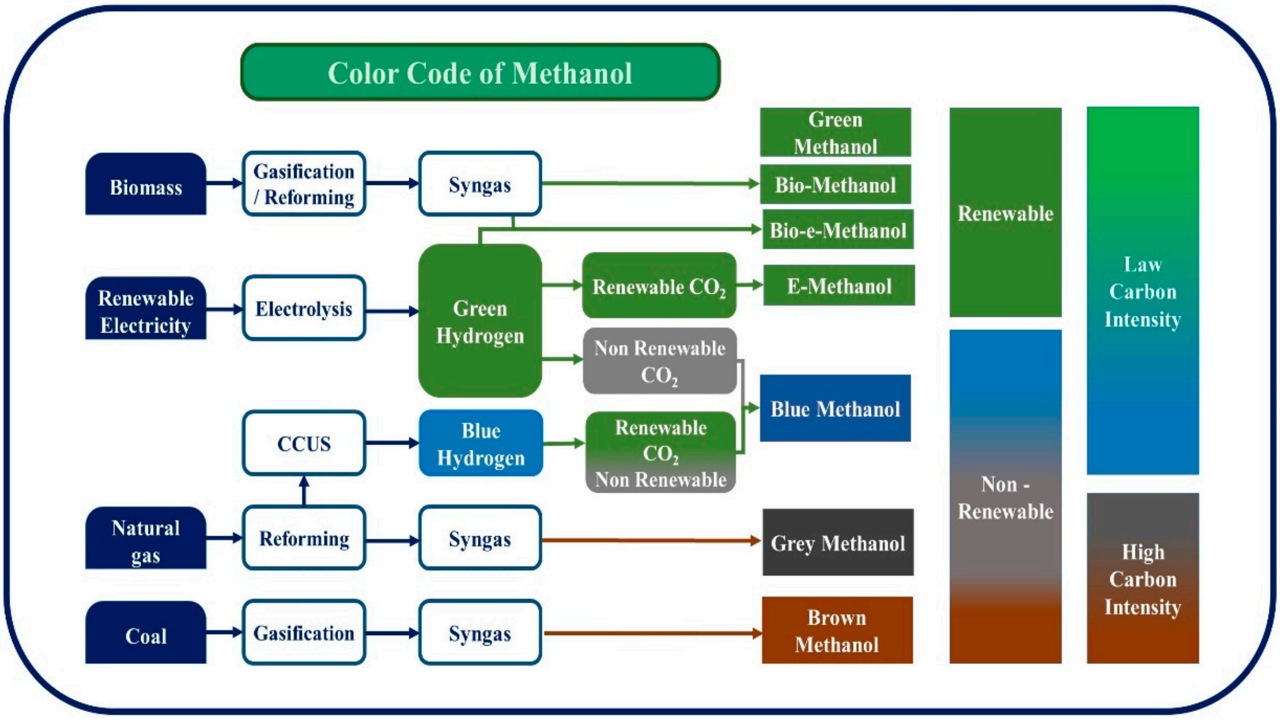

Figure 5. Color codes of methanol [79,80].

4.2. Green Methanol Production and Storage

Producing green methanol involves a chemical synthesis process where CO_2 and hydrogen are combined. Initially, hydrogen is generated using an electrolyzer, and subsequently, this hydrogen undergoes catalytic conversion with CO_2 in a reactor to form methanol. To create green methanol, which is carbon-neutral, hydrogen sourced from renewable electricity is utilized in conjunction with biogenic CO_2 [82]. Biogenic sources of CO_2 encompass a range of sectors, such as the paper and pulp industry, ethanol plants, biomass power plants, waste-to-energy plants, and co-generation plants where biomass serves as a raw material. Biogenic CO_2 for green methanol synthesis is the most sustainable approach with a positive environmental impact. Green methanol fosters sustainable industries by facilitating CO_2-reduced manufacturing and supply chains. Moreover, it can achieve carbon neutrality when employing biogenic CO_2 and renewable electricity. It is essential to note that although industrial CO_2 emissions from fossil fuel combustion in methanol production may not align with the criteria for categorizing methanol as "green", these sources represent the diverse origins of biogenic CO_2. The production process of green methanol is depicted in Figure 6. Yet, the intensifying demand for sustainable fuels, especially in challenging sectors such as heavy industry and transportation, coupled with the increasing reliance on intermittent renewable energy sources like solar and wind, is fostering a keen interest in the production of methanol from renewable electricity, commonly referred to as green methanol [83]. Currently, the most promising technology for substantial commercial growth is CO_2 hydrogenation. This process typically occurs in fixed-bed catalytic reactors under 250–300 °C conditions and 50–80 bar pressure. In water electrolysis, green hydrogen is produced using renewable electricity, and the capturing of CO_2 directly can be facilitated using air or flue gas.

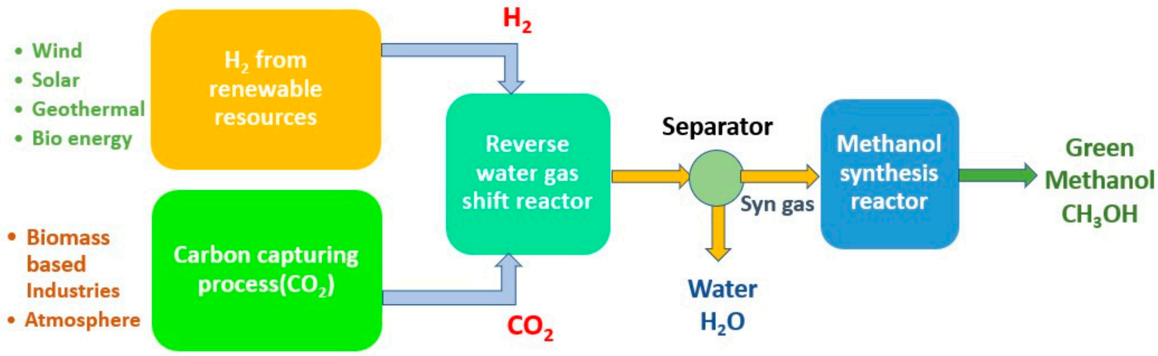

Figure 6. Production process of green methanol using reverse water–gas shift (RWGS) reactor [84].

The significance of the green methanol production process lies in acquiring CO_2 through carbon-capture technologies, either from industrial waste gases or directly from the atmosphere. This approach mitigates additional carbon dioxide emissions and repurposes it as a valuable resource for a novel energy carrier. The synthesis of green methanol, utilizing CO_2 derived from biomass-based industrial flue gas and green hydrogen, holds the potential to establish a carbon-neutral industrial system [85].

The process of methanol synthesis results in the generation of water and waste heat, and these byproducts can be effectively utilized within a closed-loop system for hydrogen production. The recovered waste heat finds application in diverse industrial operations, including but not limited to pulp mills, wastewater treatment, and enhancing overall process efficiency [81].

As a straightforward liquid, green methanol exhibits ease in transportation, storage, and distribution. While it can be stored in tanks, it is essential to avoid compositions involving metals like zinc, aluminum, titanium, or their alloys, as methanol is corrosive to these materials. Since methanol is the smallest hydrocarbon and most reactive alcohol functional substance, caution is needed in its interactions with various polymers, resins, and rubbers. Storing methanol in tightly sealed vessels is imperative to prevent moisture ingress, as methanol is readily miscible with it, and significant moisture concentrations can diminish its combustion qualities when used as a fuel. Like gasoline or jet fuel, green methanol lends itself well to easy transportation and distribution through ships, trucks, trains, and pipelines.

4.3. Properties of Green Methanol

Since green and ordinary methanol are made of the same chemical (CH_3OH), they have many similarities in their traits and features. Green methanol, however, differs from ordinary methanol as it is produced using more sustainable and environmentally friendly techniques. The following are some of the properties of green methanol (Refer to Table 6)

Table 6. Properties of green methanol [86].

Property	Green Methanol
Chemical formula	CH_3OH
Appearance	Colorless liquid
Molecular weight	32.04 kg/kmol
Melting temperature	−97.8 °C
Density (20 °C)	787–792 kg/m^3
Boiling point	64–65 °C
Vapor pressure (at 20 °C)	12.3 kPa
Critical temperature and critical pressure	240 °C, 73.76 bar
Compressibility factor (1.03 bar and 15 °C)	0.224
Specific gravity	0.7915

4.4. Applications of Green Methanol

Due to its clean and versatile character, green methanol, produced from sustainable and renewable feedstock and processes, has many uses in various industries [79]. In sectors like transportation and chemical manufacturing, it can accelerate defossilization.

The following are some of the main uses for green methanol:

- Transportation fuel: Green methanol can be blended with gasoline or diesel or used in its pure form as an alternative fuel for cars [87]. Compared to conventional fossil fuels, it is regarded as a clean-burning fuel that can lower greenhouse gas emissions.
- Power generation: Green methanol may be used in fuel cells to produce energy, making it a dependable and environmentally friendly power source. This use is essential for backup power sources or remote locations.
- Chemical feedstock: Methanol is a valuable chemical feedstock used to create various chemicals and products [88]. Green methanol can be used to produce plastics, adhesives, solvents, and other chemical products, which helps to make industrial operations more environmentally friendly [79].
- Energy storage: Green methanol has the potential to be used as a form of energy storage. It can store excess energy in liquid fuel generated from renewable energy sources, which can be converted back into electricity when required.
- Marine fuel: Methanol is attracting interest as a viable marine fuel in the shipping industry. To comply with increasing environmental standards, such as the International Maritime Organization's (IMO) sulfur and nitrogen oxide restrictions, green methanol can assist in minimizing emissions from ships.
- Cooking and heating: Green methanol can be used as a cooking and heating fuel, substituting conventional solid fuels and lowering indoor air pollution in areas without access to clean and efficient cooking and heating options.
- Carbon recycling: Green methanol is a crucial component of CCUS initiatives because it can be made from carbon dioxide (CO_2) that has been captured. It contributes to carbon recycling and the reduction of carbon emissions.
- Hydrogen storage: Methanol can be used as a carrier for storing hydrogen. It offers a possible method for storing and distributing hydrogen because it is simpler to handle and move than gaseous hydrogen.
- Chemical Industry: Green methanol can be used as a solvent, reactant, or reducing agent in various industrial processes.
- Agriculture: Using methanol as a component in some pesticides, herbicides, and fertilizers can help to promote more environmentally friendly and long-lasting agricultural methods.

Green methanol is an invaluable instrument in the shift to cleaner, more sustainable energy and chemical industries because of its adaptability and environmental advantages. Its uses encourage the integration of renewable energy sources and serve several sustainable development objectives.

4.5. Cost Analysis of Green Methanol

To produce 1000 kg of green methanol, approximately 1400 kg of CO_2, 200 kg of hydrogen, and 1700 kg of water is needed. Around 10–11 MWh of renewable electricity is required to produce 1000 kg of green methanol, a predominant part of which is used for the electrolysis of water [82]. Methanol has a specific gravimetric energy density of 6.2 kWh/kg. The production efficiency of e-methanol, requiring approximately 10–11 kWh of renewable electric energy to produce 1 kg, stands at 56–62 percent. As per the methanol institute and its collaboration with the International Renewable Energy Agency, the anticipated cost for bio-methanol is estimated to range from USD 700 to USD 900 per metric ton, while green methanol's price is expected to be in the range of USD 1200 to USD 1600 per metric ton [9].

4.6. Pros and Cons of Green Methanol

Potential applications of green methanol span from clean fuels to energy storage, enabling diverse industrial sectors to transition to more eco-friendly practices. However, challenges include relatively high production costs, potential corrosion issues with certain metals, and considerations for safe storage due to its corrosive nature. Table 7 highlights the pros and cons of green methanol.

Table 7. Pros and cons of green methanol [89].

Pros	Cons
• Produced from renewable feedstocks	• Gray methanol is cheaper than green methanol
• Easy to store and transport	• Corrosive to metals like titanium, zinc, etc., and plastics
• Biodegradable and soluble in water	• Pure methanol is a poor substitute for diesel
• Produce electricity using fuel cells	• Lower volumetric energy density
• Excellent liquid carrier for hydrogen	• Highly flammable and toxic to humans
• Used in combustion ignition (diesel) engines	• Ingestion could be lethal/lower levels cause blindness
• Lower greenhouse gas emissions (CO_2, SOx, NOx)	• Partial combustion may give rise to pollutants like formaldehyde and formic acid
• Generates lower heat and transfers less heat to surroundings	• Must be stored tightly sealed and kept away from moisture as it is miscible with water
• Methanol fires could be easily extinguished	• Poor lubricant and possesses low vapor pressure at lower temperatures

5. Technical Challenges and Commercial Opportunities

The choice between green hydrogen, green methanol, and green ammonia as the most adequate fuel for the future depends on various factors, including the specific applications, infrastructure, and sustainability goals of a given region or industry. A comparative summary of key characteristics, challenges, and opportunities of green hydrogen, green ammonia, and green methanol is presented in Table 8. Each of these fuels has its advantages and disadvantages:

Table 8. Comparative summary of green hydrogen, green methanol, and green ammonia.

Energy Carriers	Characteristics			Challenges	Opportunities
Green hydrogen		Compressed Hydrogen	Liquid Hydrogen	• High production and storage costs • Low energy density • Large storage and transportation infrastructure • More energy losses during conversion	• Clean and sustainable option • Zero-emission fuel • Wide range of applications • Provides grid stability and resilience • Leakage has less impact
	Temperature	25 °C	−252.9 °C		
	Storage Pressure	69 MPa	0.1 MPa		
	Density	39 kg/m^3	70.8 Kg/m^3		
	Explosive limit in air	4–75% Vol	4–75% Vol		
	Gravimetric energy density	120 MJ/kg	120 MJ/kg		
	Storage method	Compression	Liquefaction		

Table 8. *Cont.*

Energy Carriers	Characteristics		Challenges	Opportunities
Green methanol	Temperature	25 °C	• Energy-intensive and complex production process • Toxic and difficult to handle • Additional infrastructure for end use	• Carbon-neutral fuel • Tool for carbon capture • Higher energy density • Easy to store and transport • Versatile uses
	Storage Pressure	0.1 MPa		
	Density	792 kg/m^3		
	Explosive limit in air	6.7–36% Vol		
	Gravimetric energy density	20.1 MJ/kg		
	Storage method	Ambient		
Green ammonia	Temperature	25 °C	• Distribution infrastructure is needed • Safety concerns in handling and transport • Less energy-efficient process • Regulatory issues	• Potential sustainable fuel • Diverse applications in chemical industry • High energy density by volume • Easily transported and stored • Low storage costs
	Storage Pressure	0.99 MPa		
	Density	600 kg/m^3		
	Explosive limit in air	15–28% Vol		
	Gravimetric energy density	18.6 MJ/kg		
	Storage method	Liquefaction		

5.1. Green Hydrogen

Green hydrogen is a clean, versatile, and environmentally friendly energy carrier. Its integration with renewable energy sources, zero-emission nature, and broad applicability makes it a vital component in plans for achieving sustainability and addressing the challenges of climate change. Moreover, its role in strengthening grid resilience and advancing energy security makes it a key player in the transition towards cleaner and more sustainable energy systems on a global scale [90].

Opportunities:

- Clean and Sustainable Production: Green hydrogen is produced through water electrolysis using renewable energy sources like wind or solar power. This sustainable production process ensures that the hydrogen generated is clean and does not contribute to greenhouse gas emissions [91].
- Zero-emission fuel: When green hydrogen is utilized in fuel cells, it generates electricity with only water as a by-product. This makes it a zero-emission fuel, contributing to a cleaner environment and reducing carbon footprints [92].
- Versatility across sectors: Green hydrogen is an incredibly versatile energy carrier that can be applied across various sectors. It is suitable for transportation, industrial processes, and electricity generation. Its adaptability makes it a valuable solution in diverse applications, aiding the transition towards cleaner energy systems.
- Integration with renewable energy: Green hydrogen is pivotal for the integration of renewable energy sources into the energy mix. It can store excess energy generated from renewables during periods of high production, such as sunny or windy days, and release it when demand is high or during periods of low renewable energy generation. This capability enhances grid stability and helps address the intermittency challenges associated with renewables [93].
- Enhancing grid resilience: Green hydrogen can act as an energy carrier that strengthens the resilience of the energy grid. During periods with surplus renewable energy,

electricity can be used for water electrolysis, producing green hydrogen. This hydrogen can then be stored and utilized during peak demand periods or when renewable energy supply is limited, providing a reliable and stable energy supply.

- Energy security and independence: By producing green hydrogen domestically, regions and countries can reduce their dependence on fossil fuels and foreign energy sources. This enhances energy security and reduces vulnerability to supply disruptions.
- Decarbonizing hard-to-abate sectors: Green hydrogen offers a viable solution for decarbonizing sectors that are challenging to electrify, such as heavy industry, aviation, and maritime transport. Its versatility and ability to replace fossil fuels in these sectors would contribute to global decarbonization efforts [94].
- Global cooperation: Green hydrogen has garnered worldwide attention and collaboration. Many countries invest in research and development to advance their production and applications. This collaborative approach fosters international partnerships and knowledge exchange, accelerating the adoption of green hydrogen.

Challenges:

While green hydrogen offers numerous advantages as a clean and versatile energy carrier, it faces several challenges, including high production costs, efficiency losses, storage and transportation complexities, and the need for innovative solutions to overcome these hurdles. Addressing these disadvantages is crucial for the widespread adoption of green hydrogen and for it to have a role in achieving a sustainable and low-carbon energy future.

- High production costs: One of the primary obstacles facing green hydrogen is its relatively high production costs, particularly when utilizing renewable energy sources for electrolysis. The initial capital investments required for renewable energy infrastructure and electrolysis facilities can be substantial. These high costs can limit the competitiveness of green hydrogen compared to traditional fossil fuels. Reducing production costs through technological advancements and economies of scale is paramount to making green hydrogen more economically attractive [90].
- Efficiency challenges: Electrolysis, the process used to produce green hydrogen, is not 100% efficient. It involves energy losses during the conversion of electricity into hydrogen gas. These efficiency losses can impact hydrogen production's overall energy balance and cost-effectiveness. Therefore, improving the efficiency of the electrolysis process is crucial for making green hydrogen a more viable and competitive fuel option [91].
- Storage and transportation complexities: Hydrogen has a low energy density by volume, necessitating more extensive storage and transportation infrastructure than conventional liquid or gaseous fuels. The need for specialized high-pressure or cryogenic storage tanks and pipelines can add to the cost and complexity of hydrogen transportation. Developing cost-effective solutions for the safe and efficient storage and distribution of hydrogen is a considerable challenge, especially when considering long-distance transport [92].
- Cost of storage: Storing pure hydrogen can be expensive, particularly when considering the need for advanced materials and technologies to prevent leaks and ensure safety. Alternative methods like chemical hydrogen storage or hydrogen carriers have gained attention in response to these challenges. These methods involve storing hydrogen within chemical compounds, which can be more cost-effective and practical for specific applications but may have limitations.
- Intermittency of renewable energy sources: Green hydrogen production relies on a consistent electricity supply from renewable sources like wind or solar power. However, the intermittency of these energy sources can lead to variations in hydrogen production rates, which may not align with demand. This intermittency can impact the stability of the hydrogen supply and necessitate solutions for energy storage or grid integration to ensure a continuous and reliable supply of green hydrogen [93].

5.2. Green Ammonia

Green ammonia holds significant promise as a sustainable and versatile energy carrier. Its potential for carbon neutrality, high energy density, adaptability to existing industrial processes, low storage costs, and vital energy efficiency make it valuable in transitioning towards cleaner and more sustainable energy systems. Moreover, its contributions to reduced greenhouse gas emissions and industrial sustainability underscore its importance in addressing environmental challenges and supporting a greener future.

Opportunities:

- Sustainability and carbon neutrality: Green ammonia is produced by combining green hydrogen and nitrogen, often from the air. This sustainable production process can make ammonia a carbon-neutral or carbon-negative fuel source. When generated from zero-carbon hydrogen, green ammonia emits zero CO_2 during the production and combustion phases. This aligns with global efforts to reduce greenhouse gas emissions and combat climate change [95].
- High energy density for efficient transport and storage: Green ammonia boasts a high energy density by volume, similar to methanol. This characteristic makes it well-suited for long-distance transportation and efficient energy storage. Ammonia can be readily transported using existing infrastructure and stored compactly, addressing the energy storage challenges often faced by renewable energy sources like wind and solar.
- Industrial Versatility: Ammonia is already extensively utilized in the chemical industry. The green version of ammonia can provide a sustainable alternative for these industrial applications. Its versatility extends to producing fertilizers, refrigerants, and other chemical processes. Replacing conventional ammonia with the green variant contributes to reducing the carbon footprint of various industrial sectors [96].
- Low storage costs and good efficiency: Green ammonia exhibits favorable characteristics in terms of storage. It offers very low storage costs, making it economically competitive. Its energy conversion and storage efficiency also enhance its attractiveness as a sustainable energy carrier. These attributes contribute to the economic viability of green ammonia in various applications [97].
- Power-to-X potential: Green ammonia is a critical player in the emerging field of power-to-X technologies. It is a versatile energy carrier that can convert renewable energy into storable and transportable forms. This capability enhances the integration of renewable energy sources into the existing energy infrastructure and supports grid stability [98].
- Industrial Synergies: The widespread use of ammonia in various industries fosters synergies and knowledge transfer. This existing industrial expertise can be leveraged to further develop and optimize the production and utilization of green ammonia, accelerating its adoption.

Challenges:

While offering significant advantages as a sustainable energy carrier, green ammonia faces several challenges, including infrastructure development, safety concerns, energy-intensive production, logistical complexities, and economic considerations. These disadvantages underscore the importance of addressing these issues to fully realize the potential of green ammonia in the transition towards cleaner and more sustainable energy systems.

- Infrastructure development and adaptation: The production and distribution of green ammonia may require the development or adaptation of infrastructure. This includes facilities for production, storage, and transportation. The need for specialized infrastructure can result in initial capital investments and logistical challenges [99].
- Safety concerns: Ammonia, including green ammonia, is toxic, and safety concerns arise during its handling and transportation. Ensuring strict adherence to safety practices and regulations mitigates potential risks. These safety measures are particularly critical in industrial and commercial settings where ammonia is used or transported [100].

- Energy-intensive production: Whether green or conventional, ammonia production can be energy-intensive. Achieving energy efficiency in the ammonia production process is a challenge that needs to be addressed. Reducing the energy intensity of production is not only environmentally desirable but also economically essential in optimizing the cost-effectiveness of green ammonia [98].
- Logistical challenges: When exposed to moisture, especially in the presence of air, ammonia can form ammonium hydroxide, a corrosive substance. This can pose complex challenges for handling, transporting and storing ammonia, especially in large quantities. Adherence to safety regulations, corrosive-resistant infrastructure, choosing appropriate materials, and the use of specialized containers or vessels can mitigate the potential corrosive effects of ammonia. Addressing these complexities is crucial to ensure green ammonia's safe and efficient distribution.
- Economic viability: The development of infrastructure and the implementation of safety measures can add to the overall production costs of green ammonia. A key consideration is ensuring its financial viability and competitiveness with other energy carriers. Factors such as government incentives, market demand, and ongoing technological advancements play a role in determining the economic feasibility of green ammonia.
- Environmental impact of ammonia production: While green ammonia is produced using sustainable methods, the environmental effects of ammonia production, including resource use and potential emissions during the production process, remain a consideration. Minimizing the ecological footprint associated with green ammonia production is an ongoing challenge.
- Ammonia has yet to be broadly accepted as a fuel. There are safety and regulatory issues that need to be addressed. International standards and local regulations must be harmonized to scale up production, bunkering, and the use of ammonia.

5.3. Green Methanol

Opportunities:

Green methanol is an environmentally friendly, versatile, and efficient energy carrier. Its carbon-neutral production, high energy density, and diverse applications make it a key player in transitioning towards cleaner and more sustainable energy systems. Moreover, its role in reducing greenhouse gas emissions, supporting energy storage, and decreasing dependence on fossil fuels positions green methanol as a valuable asset in achieving carbon neutrality and addressing the challenges of climate change.

- Carbon-neutral production: Green methanol can be produced using hydrogen and carbon dioxide (CO_2) captured from the atmosphere or industrial processes. This approach to methanol production is instrumental in achieving carbon neutrality, as it recycles and reuses CO_2, reducing the carbon footprint associated with fuel production. Methanol synthesized from captured CO_2 significantly reduces greenhouse gas emissions [101].
- High energy density: Methanol boasts a higher energy density by volume than hydrogen. This superior energy density makes it a more practical and efficient option for storage and transportation. Methanol can be easily stored and transported using established infrastructure, which is advantageous compared to the challenges associated with the low energy density of hydrogen [101].
- Versatile applications: Green methanol is a versatile energy carrier with diverse applications. It can be effectively used as a clean-burning fuel for internal combustion engines, including vehicles, ships, and power generation. Additionally, methanol is a valuable chemical feedstock, contributing to various industrial processes and applications. Its adaptability makes it helpful in transitioning to sustainable energy systems [100].
- Reduced dependency on fossil fuels: Using captured CO_2 and renewable hydrogen sources, green methanol minimizes the dependence on traditional fossil fuels. It

promotes a circular carbon economy, where CO_2 emissions are repurposed into a sustainable and renewable energy carrier. This not only mitigates environmental impacts but also contributes to long-term energy security.

- Energy storage: Green methanol is a practical option for energy storage. Its higher energy density allows for efficient energy storage, addressing the intermittency challenges often associated with renewable energy sources. This capacity to store excess energy and release it when needed enhances grid stability and supports the integration of renewable energy into the existing energy infrastructure [81].
- Reduction of greenhouse gas emissions: The carbon-neutral nature of green methanol significantly reduces greenhouse gas emissions, offering a clean and sustainable solution for reducing the carbon footprint across various applications. It aligns with global efforts to combat climate change and limit the impact of human activities on the environment [81].

Challenges:

While green methanol offers environmental advantages, it also faces significant challenges. The complexity of its production process, safety concerns related to its toxicity, the need for infrastructure adaptation, and economic considerations are important factors to address in the ongoing development and adoption of green methanol as an alternative and sustainable energy carrier. Overcoming these disadvantages will be crucial in realizing the full potential of green methanol in the transition toward cleaner and more sustainable energy systems.

- Complex production process: Green methanol typically involves capturing and converting carbon dioxide (CO_2), which can be energy-intensive and complex. The need for CO_2 capture and conversion technologies can increase the overall complexity of methanol production. This complexity may result in higher production costs and energy consumption, potentially offsetting some environmental benefits [85].
- Safety and toxicity concerns: Methanol retains its inherent toxicity even when produced through green and sustainable methods. Safe handling and transportation of methanol are paramount but require meticulous management. The toxicity of methanol presents potential health and safety hazards for workers involved in its production, storage, and transportation. Stringent safety measures and protocols are necessary to mitigate these risks [82].
- Infrastructure adaptation: To fully realize the potential of green methanol, existing infrastructure and technologies must be adapted and upgraded, particularly in the transportation sector. This adaptation process can be time-consuming and costly. Modifications to vehicles, refueling stations, and distribution networks may be necessary to accommodate the use of methanol as a fuel. These adaptations can pose logistical challenges and may slow the widespread adoption of green methanol [9].
- Economic viability: Adopting and scaling green methanol production may face economic challenges. The upfront investments in CO_2 capture and conversion technologies, safety measures, and infrastructure upgrades can result in a significant financial burden. The economic viability of green methanol production is highly dependent on factors such as government incentives, market demand, and the ability to drive down production costs over time [87].
- Resource requirements: The production of green methanol requires resources such as water and renewable energy. The availability of these resources can vary geographically, impacting the feasibility of large-scale production. The sustainable sourcing of these resources is crucial to ensure the environmental benefits of green methanol production [78].

Conventional fuels, derived primarily from fossil sources, have long powered global energy needs but are accompanied by detrimental environmental impacts, including substantial greenhouse gas emissions and finite-resource depletion. In contrast, green fuels, such as green hydrogen, green ammonia, and green methanol, offer a sustainable alternative by leveraging renewable energy sources and carbon-capture technologies. These green fuels present a significant advantage in reducing carbon footprints and fostering a transition to a low-carbon future. However, challenges like higher production costs, limited infrastructure, and technological advancements must be addressed to ensure widespread adoption and maximize positive environmental impact. The shift towards green fuels is crucial in mitigating climate change and achieving long-term energy sustainability. Table 9 provides a summary of conventional and green fuels.

Table 9. Comparative summary of conventional and green fuels.

Conventional Fuels	Vs	Green Fuels
Gasoline, Diesel, LPG/CNG	Types	Green hydrogen, green ammonia, green methanol
Fossilized remains of plants and animals	Origin	Produced from renewable electricity
Millions of years	Time to form	Continuously produced
Very high	Carbon Contents	Virtually none
Limited	Available supply	Abundant
Increase GHG emissions	Long-term outlook	Fewer GHG emissions
Expensive	Cost	More expensive. Will be stabilized with advancements in technology
Well-established production methods	State-of-the-art	Emerging, not yet commercially established
High carbon footprint	Environment	Low carbon footprint
Gasoline: 44–46 MJ/kg Diesel: 42–46 MJ/kg LPG/CNG: 46–51 MJ/kg/42–55 MJ/kg	Calorific value	Hydrogen: 120–140 MJ/kg Methanol: 22.7 MJ/kg Ammonia: 16–20 MJ/kg

5.4. Role in Energy Transition, Decarbonization, and Carbon Neutrality: Future Outlook and Directions

Green hydrogen stands out as an energy source due to its remarkable energy density compared to all other energy carriers. Green hydrogen, green methanol, and green ammonia all offer potential benefits in terms of sustainability and reducing greenhouse gas emissions. However, they also come with various challenges and opportunities. The choice of fuel depends on the specific requirements of the application and the availability of infrastructure and resources. For example, green hydrogen may be suitable for fuel cell vehicles and electricity generation, while green ammonia might be more appropriate for long-haul shipping or industrial processes. Green hydrogen can replace fossil fuels in applications where electrification is not feasible, making it a crucial tool in decarbonizing sectors like steel production and aviation. Green methanol could find applications in the chemical industry and as a transitional fuel for internal combustion engines. Green methanol could be crucial in decarbonizing sectors requiring liquid fuels, such as shipping, heavy industry, and long-range transport. Green ammonia has the potential to decarbonize the fertilizer industry, one of the largest industrial emitters of greenhouse gases, by replacing conventional ammonia production methods based on fossil fuels. In many cases, a combination of these green fuels may be used to meet different energy and sustainability needs, allowing for a more diversified and flexible approach to the future of energy. The choice should also consider local factors, technological advancements, and evolving environmental regulations. Figure 7 provides the commercial status of the studied E-fuels.

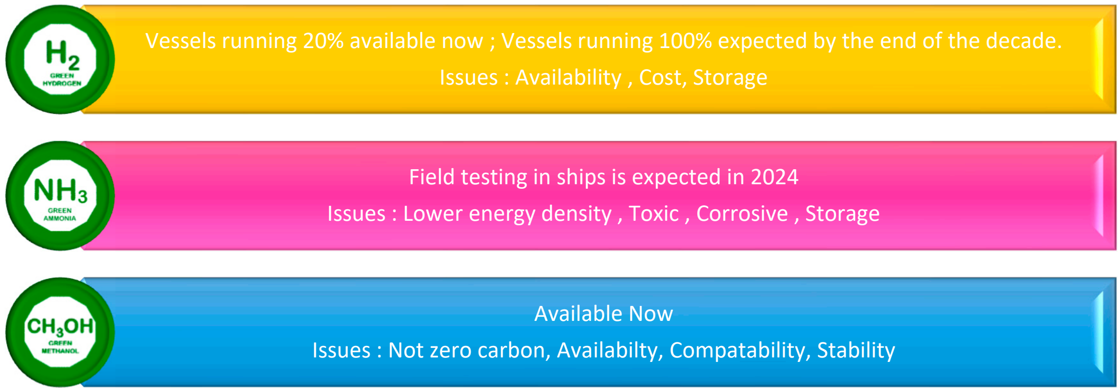

Figure 7. Commercial status of the E-fuels.

5.5. Research Directions and Future Outlook

Research into green hydrogen primarily focuses on reducing production costs, improving efficiency, and developing hydrogen storage and transportation solutions. Innovations in hydrogen-based fuel cells and creating a hydrogen infrastructure are also critical. Research and development on green ammonia is focused on reducing production costs, improving energy efficiency, and developing efficient and safe transport and storage solutions. The role of green ammonia in maritime shipping and long-term energy storage is being explored. Green methanol research focuses on developing efficient synthesis methods, carbon-capture technologies, and sustainable feedstock sourcing. Integrating green methanol into existing fuel supply chains is also an area of exploration.

- Cost Reduction: Significant research is needed to reduce the production costs of these green energy carriers to make them competitive with traditional fossil-based alternatives.
- Infrastructure Development: Developing storage, transportation, and distribution infrastructure for these carriers is crucial for their widespread adoption.
- Policy and Regulations: Governments must implement supportive policies and regulations to incentivize the transition to green energy carriers and ensure their sustainability.
- Sustainability: Ensuring the sustainability of feedstock sources and production methods is essential for avoiding unintended negative environmental impacts.
- Integration: Research should focus on how these carriers can be integrated into existing energy systems and supply chains, providing a seamless transition to cleaner energy.

6. Conclusions

This transition encompasses green methanol, green ammonia, and green hydrogen, each at varying stages of commercial viability. The widespread adoption of these alternative fuels promises to significantly reduce carbon emissions, making it a pivotal strategy in the fight against climate change. However, successfully integrating these fuel types into our energy landscape presents challenges and complexities. The following key conclusions are drawn from this study.

1. Green hydrogen emerges as a crucial alternative fuel for decarbonizing the transportation sector. However, research and development and investment efforts should be focused on enhancing its cost efficiency and 24/7 availability from diverse renewable sources like solar, wind, biomass, geothermal, and the ocean. It is imperative to underscore that the safe handling and deployment of green hydrogen remain pivotal prerequisites for achieving broader adoption within the transportation sector.
2. The production cost of green ammonia, at approximately USD 500 per metric ton, currently stands at two to three times that of conventional ammonia, typically synthesized from natural gas. The present cost of producing green ammonia exceeds that of traditional methods. Nonetheless, with ongoing technological advancements and the

realization of economies of scale, there is an intense anticipation that the cost of green ammonia production will ultimately decrease.

3. Green ammonia stands as a sustainable and environmentally friendly alternative to conventional ammonia. Its broad applications across various industries, including agriculture, pharmaceuticals, and fertilizers, highlight its versatility and eco-friendly nature. Green ammonia possesses the potential to be a pivotal player in driving the transition towards a greener economy. Its adaptability as a vehicle fuel and its capacity to serve as a renewable energy storage medium, particularly for sources like wind and solar power, underscore its significance in advancing sustainable practices.
4. Green methanol is a vital fuel source in many applications to address ever-increasing global energy requirements. These applications encompass automobiles, trucks, marine vessels, boilers, kilns, and other sectors. Furthermore, within the chemical industry, green methanol plays a pivotal role in the production of methanol-to-olefins (MTO), formaldehyde, methyl tert-butyl ether (MTBE), dimethyl ether (DME), and other derivatives.
5. Using green methanol derived from green hydrogen, waste materials, and carbon dioxide captured or sourced from biomass-based industrial flue gas presents a promising avenue for achieving a carbon-neutral industrial system. However, the extent to which green methanol can succeed is closely tied to the maturity and effectiveness of CCUS technologies.
6. Green ammonia, hydrogen, and methanol are promising decarbonization and carbon-neutrality solutions. However, their roles are diverse and complementary in this energy transition. These fuels can complement each other in transitioning to a more sustainable energy future, each finding its niche in various applications and regions.
7. The challenges and opportunities for green hydrogen, green methanol, and green ammonia are interconnected and depend on technological advancements, infrastructure development, safety standards, and economic feasibility.
8. Further ongoing research would make them more cost-effective, efficient, and sustainable, driving the transition towards cleaner and more sustainable energy systems. The success of these fuels will also depend on global efforts to reduce emissions and combat climate change.

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