sustainable chemistry

Review

Ammonia Can Be Currently Considered One of the Best Green Energy Allies

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Abstract: Ammonia can be considered a relevant compound in the future energy sector, playing a significant role as an energy carrier, storage, or carbon-free fuel. However, the production of this molecule has a high energy demand, and the use of natural gas, which is not free of controversy due to the accidental leakage into the atmosphere produced during extraction and the fact that it is a nonrenewable source, contributes to increasing greenhouse gas emissions. Reducing the process's energy demand and carbon footprint will be essential to making ammonia a clear alternative for a carbon-free economy. Given the vast research in ammonia production and handling, this gas seems to be the logical step forward in the evolution of the energy sector. However, the current uncertainty in the global market requires cautiousness in decision making. Several factors may impact economic growth and human welfare, thus needing a careful assessment before making any transcendental decisions that could affect worldwide energy prices and raw material availability.

Keywords: economy decarbonization; alternative fuels; CO_2 emission reduction; engines

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Citation: González, R.; Gómez, X. Ammonia Can Be Currently Considered One of the Best Green Energy Allies. *Sustain. Chem.* **2024**, *5*, 163–195. https://doi.org/10.3390/suschem5020012

Academic Editors: Francesca Deganello and Jan-Willem Bos

Received: 15 March 2024
Revised: 13 June 2024
Accepted: 16 June 2024
Published: 19 June 2024

1. Introduction

The aim of the European Commission of reaching an economy based on net-zero greenhouse emissions by 2050 [1] may probably be an overly optimistic objective understood from the perspective of great concerns regarding high CO_2 concentration levels reached in the atmosphere and recent extreme climatic events experienced worldwide. However, the amount of energy needed to maintain industrial activity, employment, and healthcare is globally increasing despite efforts to attain higher process efficiency and reduce energy consumption. Two significant trends can be observed: one is the almost steady demand of European, and North and Latin American countries, and the other is the increasing energy demand of Asian, Pacific, African, and Middle Eastern countries [2], with oil, gas, and coal being the main energy sources.

Efforts in reducing CO_2 emissions and increasing compliance with environmental measurements should keep pace with the country's economic resources without affecting population wellbeing. Thus, Nigeria has experienced a great population increase and showed an energy demand of 167 Mtoe (millions of tons of oil equivalent) with a population of 213.4 million inhabitants by year 2021, which is in contrast to countries such as Saudi Arabia with a population of 35.6 million and an energy demand of 254 Mtoe [2].

The focus on reducing CO_2 emissions is usually set on fossil sources and their replacement by renewable energy. Reducing the usage of fossil fuels is contradictory to social development since energy consumption is expected to increase along with overall economic development unless a change in energy structure is accomplished along with improvements in energy efficiency [3]. However, the solution is not simple. Renewable energies, such as wind and solar technologies, have an intermittent nature with low reliability under standalone configuration, thus requiring an excessive overdimension of installations [4,5]. To these disadvantages should be added the fact of the reduction in energy efficiency experienced by solar panels due to adverse climatic conditions, such as humidity, high temperature, and dust accumulation [6,7] and the effect of extreme climatic events, requiring special measures that allow grids with high penetration of wind power to withstand hurricane damage [8].

Great efforts are being made to increase energy efficiency and economic circularity, thus favoring the reuse of materials and waste valorization. However, several factors need to be considered when assuming a circular economic model, such as material dispersion, low quality of wastes, process feasible integration, and energy demand associated with treating recycled components [9]. The transition to decarbonizing the economy must cope with a global increasing energy demand and attain a gradual substitution of fossil fuels with alternative fuels. Alexander and Floyd [10] described an optimistic view of the economic transition, indicating that adapting to climate change via deep decarbonization may be challenging but manageable if negative emission technologies are implemented. Their approach uses fuel substitution, nuclear power, and carbon capture and storage. Ye and Tsang [11] proposed a similar starting point, reporting a feasible timeline for decarbonizing the ammonia synthesis process, which also involves capturing CO_2 and subsequent process transformation by introducing hydrogen derived from electrolyzers and electricity production from renewable sources.

One important matter to carefully evaluate is the fact that decarbonizing the economy is costly, and although several technological alternatives are available, not all of them are mature enough to consider that a fast and smooth transition can be made in a relatively short period. Currently, fuel substitutes and electrification bring an unavoidable increase in production costs, which the producer cannot assume and, if translated to the consumer in full, may cause excessive market distortion. In a globalized market, producing goods at higher prices may cause consumers to decant their preferences for more affordable products from other regions despite being produced from higher-carbon-footprint manufacturing lines.

It should be taken into account that not all process or fuel alternatives may be directly linked to a decrease in energy intensity. An example of this feature is the production of hydrogen. This carbon-free gas has become the preferred green fuel due to the exclusive emission of water from combustion reactions and the high energy contained per unit of mass. However, the current production of hydrogen comes from fossil sources. Steam methane reforming (SMR) presents an energy demand of 10.84 kWh/kg H_2, while the production of H_2 from water electrolysis, which seems to be more environmentally friendly, requires even more energy (48 kWh/kg H_2) [12]. A similar situation is found when implementing carbon capture and storage: CO_2 capture, compression transportation, and further transformation will undoubtedly raise energy consumption [13].

The present document examines the feasibility of using ammonia as a fuel for energy production and as a complementary alternative fuel in road transport. The production process and combustion features of ammonia, when used with various fossil fuels and biofuels, are discussed. The emphasis is placed on the advantages of ammonia as an alternative fuel to be used in turbines and internal combustion engines (ICEs). This feature may help expedite the move towards a decarbonized economy.

2. Materials and Methods

The present review was carried out by using the following specific keywords for selecting proper references: for the section dedicated to alternative fuels, keywords were associated with the specific fuel analyzed, making preference for the newest published manuscripts. A survey of gray literature was also performed to obtain information regarding current commercial technologies. The subsequent sections regarding ammonia production and energetic valorization in engines used the following keywords: “ammonia production” AND “renewable energies”, “ammonia combustion” AND “alternative fuel” OR “gas turbines”, “spark ignition engines”, “compression ignition engines”. Preference was given to manuscripts published during the last ten years, except for relevant historical information.

3. Alternative Fuels

3.1. Hydrogen

Hydrogen may be considered the energy carrier of the future, and the concept of developing a hydrogen economy dates back to the 1970s by assuming hydrogen would replace fossil fuels, transforming transport and industrial sectors [14,15]. Since then, several authors have used this term and analyzed the feasibility of this approach [16,17]. Nevertheless, storage and delivery problems are still yet to be solved. Transporting and storing hydrogen requires a significant amount of energy to increase density, and there are no feasible solutions yet capable of attaining compact and lightweight storage [18].

Technological development attained in recent years has been astonishing. GE turbines are currently capable of operating with mixtures of hydrogen–methane at a low 5% content and up to 100% hydrogen capability [19] for stationary energy production. Airbus has announced a fuel cell engine and combustion engine development program to run these units using hydrogen as the main fuel [20,21]. Toyota introduced the Mirai model into the market in 2015, a pure-hydrogen-powered vehicle. However, the preferential institutional support for electric vehicles, high price (EUR 75,600 [22]), and difficulties of installing hydrogen gas stations set this technological pioneer in a standby position, waiting for a change in mobility trends.

Practical solutions regarding hydrogen handling, storage, safety measurements, and reliable supply seem to be a step behind. Kurien and Mittal [23] listed problems found when implementing hydrogen as an alternative fuel, including low volumetric density, embrittlement of engine components, safety concerns regarding onboard storage, and practical limitations associated with hydrogen production from water electrolyzers. The list of challenges is extensive, and even with an optimistic view, it is difficult to believe that hydrogen would become a viable option in the short term.

3.2. Biodiesel and Alcohols

Alternative fuels such as biodiesel and alcohols may also be considered suitable allies in decarbonizing the economy and the transport sector. Biodiesel can be obtained from the transesterification reaction of vegetable oils with alcohols or from hydrotreatment, with this later process resulting more interesting in terms of fuel quality (higher calorific value and greater chemical stability) [24]. Petroleum refining companies have succeeded in attaining biodiesel production from hydrotreatment of vegetable oils (HVOs) such as CEPSA and NESTE, among others [25,26], showing compatible characteristics with conventional diesel and better performance regarding pollutant emissions [27]. However, biofuel production must ensure that indirect land use change (ILUC) effects are carefully evaluated [25]. A guarantee should be given so that adverse impacts that may be expected by substituting land use for human and animal feed stocks into biofuel production are avoided.

A similar effect may also be associated with the ethanol production from sugars and cereals. Although ethanol derived from cellulosic substrates is considered a promising technology since it prevents these undesirable effects, various technical difficulties regarding high production costs and low yields have prevented the industrial deployment of this technology. As a result, several commercial plants remain idle or on hold until these issues are resolved [28]. The cultivation of cellulosic biomass for producing ethanol may add CO_2 emissions to the balance, which may not always be easy to quantify due to the changes in land use (LUC) associated with the transformation of land use in the same region or a different region far from the local ethanol production activity [29]. Figure 1 shows a schematic representation of different alternative fuels currently available which can serve as allies in the decarbonization of the energy and transport sector.

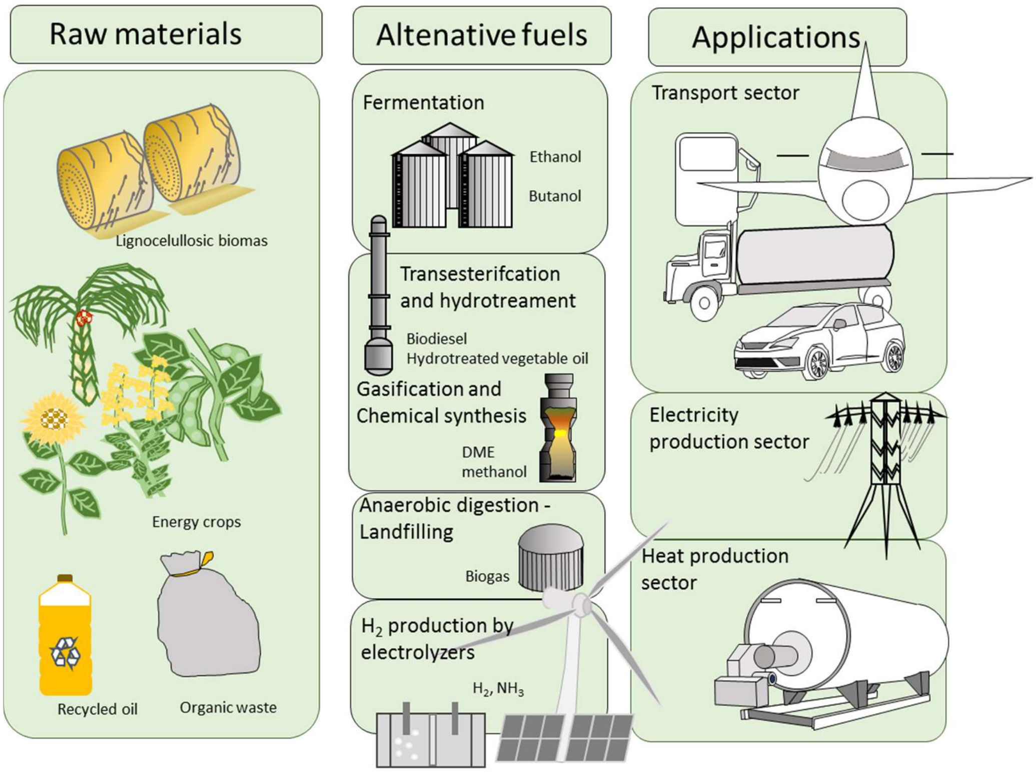


Figure 1. Schematic representation of different process currently available at commercial and precommercial scale which can aid in decarbonizing the energy and transport sector.

Biodiesel and ethanol have the significant advantage of being compatible with current transport fleet and fuel distribution logistic. This feature enables a smooth transition to a greener transport sector, without requiring significant investments in technological infrastructure. Road transport constitutes the highest proportion of overall transport emissions (76% of all EU’s transport greenhouse gas (GHG) emissions) [30]. Therefore, any technical improvement in this sector regarding increasing fuel economy, fuel substitution, and electrification will significantly reduce CO_2 emissions.

The European car fleet reduced average fuel economy by 36% from 1975 to 2015, simultaneously increasing average vehicle weight and producing more powerful engines [31]. Hybridization has allowed fuel consumption to be reduced even further. Mazda presented in 2021 commercialization of the e-skyactive X (2.0 L) engine with a fuel consumption of 5.6–4.9 L/100 km (NEDC cycle) capable of developing 186 HP at 6000 rpm (Mazda CX-30 model) [32]. Engine manufacturers’ efforts have significantly reduced CO_2 emissions and pollutant levels (particles and NOx). Reducing the average age of the European vehicle fleet (which is 12 years currently [33]) would immediately impact global fuel consumption. This premise may be equally applied to any other country, with this measure having a much greater impact in developing countries (due to their older-vehicle-age fleet [34]), thus becoming a fast and effective solution, since CO_2 emissions are a global problem.

3.3. Electrification of Transport Sector

Electrification of vehicles is currently considered the preferable choice in many developed countries for reducing dispersed emissions and improving air quality. However, a factor that should be carefully analyzed is the current energy mix of countries and the expected introduction of renewable energies in the short term. Electrification of the vehicle fleet may result in a costly and ineffective measure when the energy mix is mainly based on fossil fuels, but even in the case of an energy mix dominated by renewable sources, electrification implies significant changes in infrastructures, fleet vehicle production chains, and installation of a vast network of electric recharge points. The use of synthetic fuels should also be carefully analyzed. If the energy demand for producing these e-fuels is much higher than that needed for producing current fossil fuels, then, as reported by Sacchi et al. [35], the expected emission performance of a fleet based on fossil-fueled hybrid vehicles would be superior.

The introduction into the market of mild hybrid (MHV) and plug-in hybrid electric vehicles (PHEVs) opens an alternative scenario, reducing concerns regarding the extraction of minerals needed for batteries (because smaller batteries are used with these types of vehicles), and a reduced fuel consumption allows an increase in the percentage of biofuels with low cycle GHG emissions [36].

3.4. Biogas, Syngas and Syngas Derivates

Biogas is another attractive fuel that can be derived from landfilling and anaerobic digestion of wastes and energy crops. The process allows the stabilization of highly putrescible material, resulting in environmental benefits by avoiding uncontrolled degradation and the consequent release of methane into the atmosphere [37], as well as avoiding nutrient runoff. However, when energy crops are introduced into the equation, then similar concerns regarding LUC effects must be taken into account to avoid outweighing any potential benefit.

Biogas is composed mainly of methane and carbon dioxide. Upgrading technologies attain a quality similar to that of natural gas, making its introduction into the natural gas grid possible [9]. Thus, biomethane should be considered a natural gas substitute. Nevertheless, the amount of biogas produced in Europe is still small (191 TWh) compared to natural gas imports (3812 TWh) [38,39]. A slow development has characterized the biogas market, although it is expected to increase in the near future. However, the biogas potential extracted from wastes and residual biomass from agri-business may not be enough to provide the whole gas demand of European countries. Therefore, other technologies would need to come into play as it would be biomass gasification of forestry material and lignocellulosic wastes [40]. However, gasification technology has to overcome several challenges regarding syngas cleaning, tar production, and char quality along with inefficiencies caused by biomass transport logistics and energy densification [41,42].

Other alternative fuels that may be also considered are dimethyl ether (DME) and methanol. Both compounds can be either derived from the chemical conversion of syngas or from direct capture of CO_2 and a subsequent hydrogenation process [43,44]. However, although technically feasible, the production of these fuels is costly and to this limitation should be added the challenge of obtaining a green hydrogen stream from renewable sources which further increases production costs.

3.5. Return of Ammonia as Alternative Fuel

Ammonia is again being considered as a suitable alternative fuel that is free of carbon. The early use of ammonia in internal combustion engines (ICEs) dates back to the 1940s due to oil scarcity imposed in World War II, with the first utilization of liquid anhydrous ammonia as fuel in motor buses reported in 1943 [45]. Dimitriou and Javaid [46] reported on the origins of ammonia as fuel, explaining that diesel engines' high fuel efficiency and compatibility with ammonia combustion characteristics will make them play an important role in transforming the transport sector. The main benefits of using ammonia as a dual fuel come from the low degree of changes required in current combustion engines and the feasibility of pollutant abatement with already available catalytic technologies.

A technological transition should be favored. It would be irrational to consider an immediate switch from a fossil-fuel-based economy to a net-zero-emission economy. In contrast to hydrogen, ammonia is a commodity compound used in industrial processes and as fertilizer, with a global production of about 150 MMT (millions of metric tons) [47]. Ammonia is easier to handle, with several years of technical research in distribution and storage. The energy density of ammonia is 12.7 MJ/L at -33 °C [48], whereas liquefied hydrogen has an energy density of just 8.5 MJ/L [49].

The production process of ammonia is well established, with a large-scale capacity that could be easily extrapolated to increase global production based on demand in a much easier way than for other alternative fuels. Concerns regarding the use of fossil fuels in ammonia production may be mitigated with the implementation of carbon capture storage technologies until large-scale production from renewable sources overcomes efficiency and cost constraints.

The use of ammonia as a fuel in engines will endow flexibility to the power sector and is currently considered a net-zero CO_2 emission fuel with great applicability in the long-haul shipping sector [50]. MAN Energy Solutions is developing a fuel-flexible ammonia engine and intends to attain the gradual rebuild of existing maritime engines to allow ammonia as complementary fuel [51]. Toyota presented the GT-89R Marangoni fitted with an ammonia engine system at the Geneva Motor Show of 2013 [52], and the company counts several patents regarding the ammonia engine and hydrogen generator associated with the engine [53,54]. Recently, the Toyota Corporation presented an ammonia engine suitable for passenger cars developed in collaboration with the Chinese car manufacturer GAC [55]. Although environmental concerns may arise regarding NOx levels during ammonia combustion, the technology is expected to meet regulation standards by performing suitable changes in combustion equivalence ratio, combustion chamber pressure, and applying emission control strategies [56].

4. Ammonia Production

Ammonia is one of the chemicals with the highest production worldwide due to its great application in the chemical industry and agriculture. Although it is a gas at room temperature conditions with a pungent smell and corrosive characteristics, there is wide research on its handling [57]. In fact, the strong smell may serve as an alarm, allowing a prompt awareness of leakages and facilitating safety precautions. The high hydrogen content of ammonia (17.7 %wt/wt) and low-pressure liquid state (8.58 bars) make this molecule a suitable hydrogen carrier or an energy storage molecule. Ammonia production can be thought of as a way to transform excess energy from renewables and equilibrate the balance between energy production and demand, a fact that is favored by the vast existing network of available pipelines, thus offering a lower transport cost than that estimated for hydrogen [5,58]. Therefore, the production of this molecule is expected to increase exponentially, with a forecast of 290 million metric tons by 2030 for the production capacity [59]. This value may experience a tremendous rise if expectations in the energy and transport sector are achieved.

The industrial production of ammonia was dominated by the process developed by Fitz Haber in 1908 and industrialized by Carl Bosch thanks to solving material and pressure problems which allowed starting operation in 1913 of the first BASF industrial plant at Oppau site north of Ludwigshafen [60]. Today, Casale S.A. is the leading ammonia company in plant design and revamping (upgrading and retrofitting). Between 1984 and 2021, over 200 ammonia converters were retrofitted by Casale S.A. worldwide, increasing production yield by over 40% and the development of a revolutionary iron-based catalyst called AmoMax®-Casale [61]. Figure 2 shows a schematization of ammonia conventional production.

The catalytic conversion of ammonia from N_2, previously separated from air, requires the production of H_2, which is currently obtained from fossil fuels (natural gas or coal), thus making this process one of the primary candidates for proposing the use of water electrolyzers using renewable energy as power supply. This way, a significant reduction in the carbon footprint is attained. Smith et al. [62] estimated that a wind-powered ammonia process would have a carbon intensity of 0.12–0.53 t CO_2-eq/t NH_3 against a value of 1.5–1.6 estimated for a modern highly efficient methane-fed process [63]. However, the substitution is not so simple and estimation is not so straightforward.

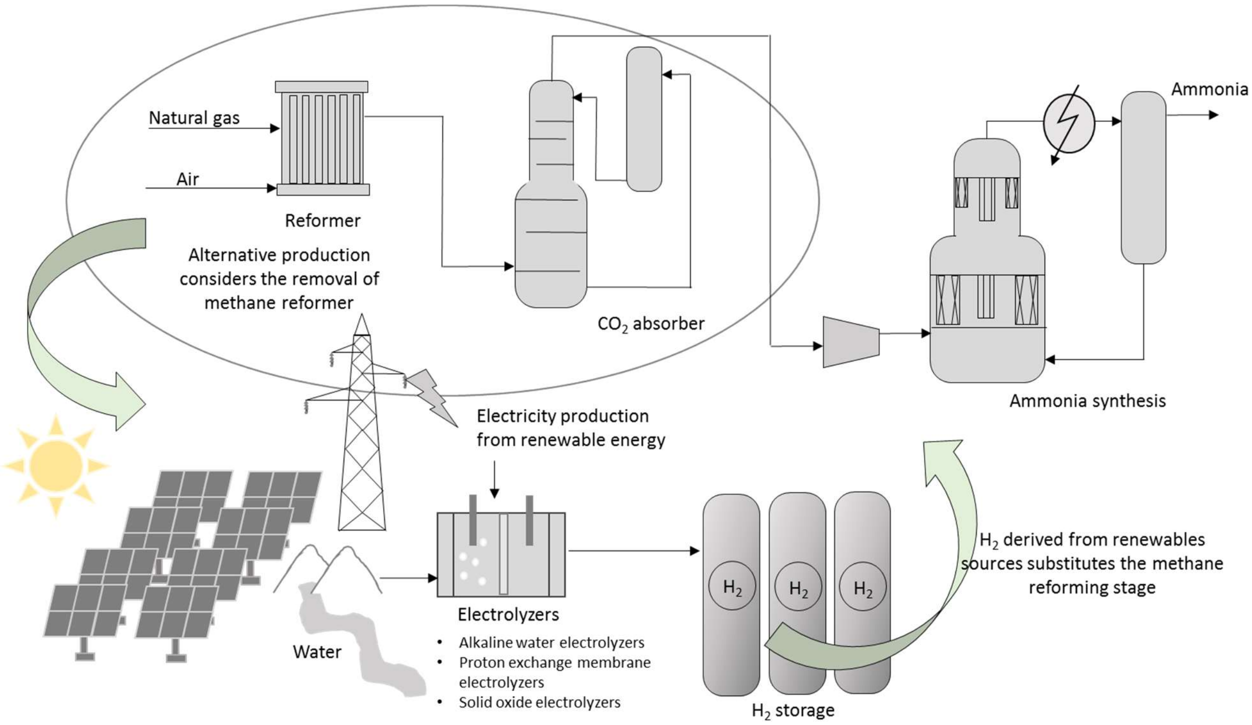


Figure 2. Representation of the ammonia production process. Methane is used in a reformer unit to produce hydrogen. CO_2 and other trace compounds are removed prior to reaching the catalytic converter. The methane reformer can be substituted by electrolysis units.

The industrial market of water electrolyzers is dominated by alkaline water (AWE), proton exchange membrane (PEM) electrolyzers operating at low temperatures, and solid oxide electrolyzers currently under development, with high operating temperatures [64]. AWEs are preferred against PEM electrolyzers given their high installation costs and lower service life of the latter [65]. Companies offering commercial units, such as Nel hydrogen (Oslo, Norway) [66], offer atmospheric AWE with a production of 1.2 t H_2/day and power demand of 2.2 MW (3.8 kWh/m^3 (STP) H_2), whereas McPhy Energy Italia Srl (San Miniato, Italy) [67] offers modules producing hydrogen at 30 bar with a consumption of 4.65 kWh/m^3 (STP) H_2. Additional energy is needed to increase H_2 pressure to the Haber–Bosch process (200–400 atm) and the availability of enough power from renewable source is also needed to guarantee a reliable supply.

Electrolyzers present several drawbacks which need an urgent solution. Inefficiencies in electrolyzer performance are associated with low load (25–45% of rated load), favoring the diffusion of hydrogen into the oxygen container, creating safety concerns regarding the explosive nature of the mixture [68]. The flammability limits of the pure H_2–O_2 mixture are much wider than those expected for H_2–air mixtures, and the problem is aggravated with pressure increase. Fluctuations in renewable energy production would affect performance, leading to start–stop cycles. After shutting down electrolyzers, a reverse current phenomenon associated with redox reactions of the electrodes is observed, causing severe degradation (irreversible oxidation of cathodes), and adversely affecting the service life of electrocatalysts [69,70].

Chau et al. [71] performed a study regarding different hydrogen production technologies evaluating safety, efficiency, and infrastructure, concluding that the SMR process was the most desirable technology. Even if becoming fully optimistic by considering that solutions will be available in the short term regarding safety measurements that allow for technology scale-up, the challenges are still enormous. As an example, the ammonia plants of Fertiberia are expected to reduce their carbon footprint by introducing green hydrogen derived from the use of renewable energy. The plant located at Puerto Llano

(Spain) has a capacity of producing 200,000 t/year, and the company intends to install 200 MW electrolyzers which will obtain electricity from photovoltaic panels [72]. The intermittent nature of solar power and variations in irradiance and temperature deeply impact the reliability of electricity production [73]. Thus, the increase in renewables in the energy mix inevitably comes with a concomitant risk of uncertainty due to the intrinsic dependence on sun irradiance and daily climatic conditions. An equivalent amount of energy as backup is then necessary to cover for unavoidable low/null energy production periods. A similar feature can be ascribed to wind power, causing an overdimensioning of the power supply system. Therefore, interconnection with an electrical grid is needed as a warranty of steady energy supply to ensure electrolyzers' energy requirements. The availability of other electricity sources, such as nuclear or large-scale energy storage systems, guarantees energy supply regardless of the intermittency of renewables.

An additional issue is water supply and quality. The water demand for electrolyzers is high, requiring pure water with low ion contents and low impurity levels. However, water scarcity and water distribution are among the greatest environmental concerns. During the past years, the global population faced changes in rain distribution patterns with extreme drought and flood episodes. This trend is expected to be maintained or even aggravated, requiring extraordinary measures to manage water availability for human consumption and ensure food supply due to the possible scarcity that will be probably faced in certain regions due to depletion of water reservoirs and incapacity of recharging [74,75]. Based on this scenario, it does not seem right to consider the production of H_2 as a feasible option in regions characterized by water scarcity problems.

Using seawater or wastewater would offer a great advantage to the process since it avoids the treatment and transport of high-quality water to the hydrogen production site. Unfortunately, the presence of anions, such as chloride and bromide, and cations (Na, Ca, Mg) creates a severe decrease in performance [76]. El-Shafie [77] reviewed the technical barriers regarding the use of water sources other than pure water. These authors reported that the presence of organics increases cathode fouling rates, halide oxidation reactions occur under the presence of anionic impurities (chloride and bromide) instead of the oxygen evolution reaction [78], and cationic poisoning causes a complete electrolyzer failure. Therefore, finding a practical solution to all these problems seems far away, so the immediate alternative to overcome these difficulties may be the use of desalinated water.

The energy demand for water desalination is about 3.2–4.5 kWh/m^3. However, water desalination for human consumption is considered a costly option and too intensively energy-demanding [79]. Based on the previous statement, it does not seem appropriate to think that the use of desalinated water would be an adequate solution for H_2 production, particularly if 9 t of water are required to produce 1 t of H_2 [80]; in contrast, it is considered an unadvisable choice for meeting water human consumption demand. Despite this controversy, this alternative is being categorized as a feasible option by several authors based on the currently high costs of hydrogen production systems [81–83].

It should be remembered that many current hydrogen projects are receiving public funds as an incentive for facilitating technological penetration. The objective should be to pursue economically viable activities along with climate protection. As a result, the costly installation and energy-intensive nature of the hydrogen production process should not be overlooked, and any additional equipment included in the process should not contribute to increasing the already high energy demand.

Saygin et al. [84] analyzed the energy demand of the ammonia-producing process. These authors indicated that the rise in oil and gas prices directly affected that of fertilizers since most of ammonia plants are based on the SMR process and are incapable of assuming such an increase in feedstock and energy prices, generating a curtailment in European production. The increase in ammonia prices also had a negative impact on food production consequently rising food prices. The interconnection between fuel prices and the economy is a factor that needs careful assessment. At its beginning, the Ukrainian war caused a great disruption in the cereal market; this, along with an increasing trend in inflation and oil prices, created food security risks [85].

The future increase in ammonia prices may be caused by a greater implementation of green ammonia production worldwide given the higher cost of this technology [86] or because of a higher demand if ammonia is used either as a hydrogen carrier or alternative fuel. Therefore, a careful deployment of green ammonia technology is necessary to avoid adverse perturbations in the food supply chain. An interesting review of the industrial ammonia production using water electrolysis was performed by Rouwenhorst et al. [87]. These authors described the expansion of the process in different countries, highlighting the relevance of the Lougi Casale process, indicating that the main factor for the installation of these plants was the availability of cheap hydropower electricity for producing hydrogen. The lower costs of fossil-fuel-based plants and better scale-up of electrolyzer-based ammonia plants led to a shut-down, with the only plant still operating located in Cuzco, Perú (Cachimayo plant, Enaex) [88].

Alternatives Routes for Producing Ammonia

Alternatives to the Haber–Bosch process for ammonia production are electrocatalytic, photocatalytic, and biocatalytic ammonia synthesis. Other technologies include plasma catalysts and nonthermal plasma methods; in this latter case, an electric discharge generates the ionization stage [88–90]. However, commercial ammonia production is still dominated by the SMR due to the multiple difficulties associated with installation costs, energy demand, and process efficiency of the different alternatives.

In the case of electrochemical synthesis, the process can be carried out at different temperature ranges using liquid electrolytes, molten salts, composite membranes, and solid-state electrolytes [80]. These methods allow ammonia synthesis through nitrogen reduction (NRR), nitrogen oxide reduction (NORR), and nitrate/nitrite reduction (NtrRR). In some of these electrochemical processes, water is used as a source of protons and electrons as reducing agents, with the reaction taking place under ambient temperature and pressure conditions, directly using electricity and, thus, offering a sustainable strategy for ammonia production [91,92]. However, N_2 is thermodynamically very stable under ambient conditions; thus, binding and subsequent activation to initiate conversion stages into ammonia becomes a great challenge [93]. A schematization of the different technological pathways for producing ammonia is presented in Figure 3, where the most commonly studied configurations are summarized.

The direct reduction of nitrogen by electrochemical synthesis follows the equation:

$$N_2(g) + 6H^+ + 6e^- \rightarrow 2NH_3(g) \quad (1)$$

The ammonia formation reaction has a higher potential than the hydrogen evolution reaction ($2H^+ + 2e^- \rightarrow H_2(g)$), thus compromising process efficiency. In addition to the low efficiency and high stability of the N_2 molecule, its limited solubility in water is another factor that adversely affects the process [94], along with the high energetic costs due to the low faradic efficiencies of different catalysts [95,96], and the low stability and activity of some catalysts which degrade rapidly [97]. Even with theoretical faradic efficiencies of 100%, the energy consumption is 8.5 MWh/t, close to that of the Haber–Bosch process (9.5–10.5 MWh/t) [98]. Catalysts of different materials are being investigated to improve production, faradic efficiency, and inhibit the hydrogen evolution reaction [99,100].

Other methodologies, such as indirect N_2 reduction using lithium as a mediator, are also being explored, which improves productivity but still presents high energy consumption to compete with the Haber–Bosch process [101]. NO, nitrate, and nitrite reduction have also been proposed as an ammonia production route. NO is a major air pollutant generated mainly from fossil fuel combustion in industrial activities and transport [102]. The NO reduction shows better performance than NRR, since NO is a less stable nitrogen source than N_2. Copper is the most effective metal for catalyzing the reaction, achieving faradic efficiencies above 90% and ammonia production levels comparable to the Haber–

Bosch process [91,103]. However, the low solubility of NO in water requires the use of concentrated or pure NO, limiting its practical application [104].

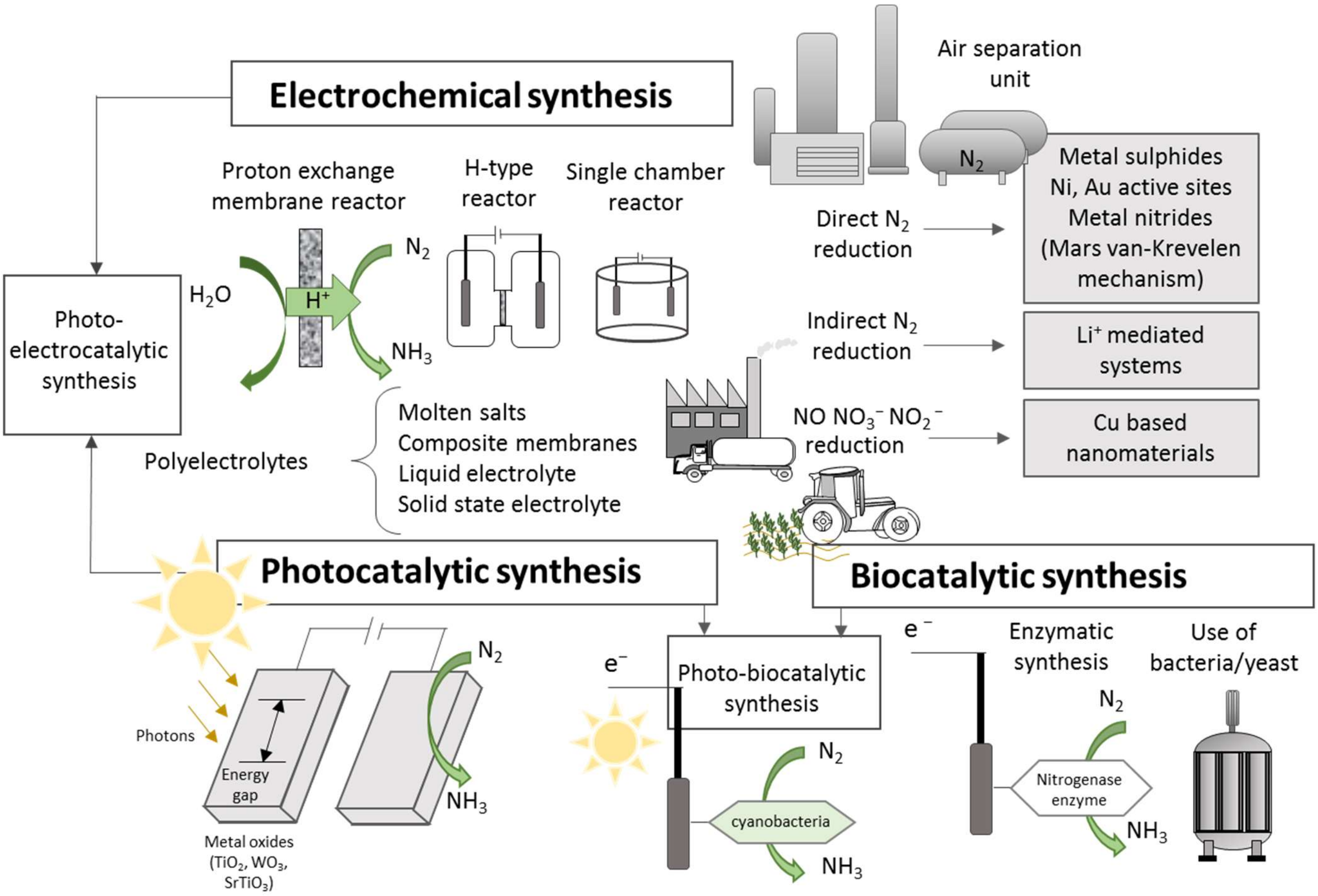


Figure 3. Schematic representation of alternative ammonia production routes.

The electrochemical reduction of nitrates and nitrites to ammonia allows the removal of these pollutant ions, resulting from agricultural and industrial activities, becoming an alternative for wastewater treatment [105,106]. However, the hydrogen evolution reaction is the main secondary reaction at the cathode in this production route, thus also limiting process efficiency [104]. Numerous studies have been carried out with different catalysts and electrolytes [107–109], studying the phenomena at the atomic level to obtain more efficient catalysts. Yin et al. [110] reviewed many of these studies. Although this route presents good current densities and faradic efficiencies, it still presents low productivity [97]. As for its performance under real conditions, almost all tests used synthetic streams, and no studies have been conducted on large-scale treatment of real wastewater, where its long-term performance and techno-economic evaluation should also be considered [104].

Other processes currently under study involve the photocatalytic and biocatalytic processes. In the first case, energy is provided by a light source. Photons transport the energy needed for electrons to surpass the energy gap of the semiconductor. Electrons can migrate and participate in reactions (nitrogen reduction or hydrogen formation), leaving behind valence holes where water is oxidized to O_2 and H^+ [111,112]. In the second case, the process attempts to mimic the biological synthesis of ammonia using nitrogenase enzymes (commonly containing MoFe protein), focusing the interest on artificially supplying electrons to the catalytic protein [113,114]. However, the stabilization of the enzyme shows extreme difficulties, and production and purification costs seem too excessive to consider the process a feasible alternative to the traditional Haber–Bosch process [115]. Other biological alternatives consider the conversion of protein wastes using bacteria or yeast or new hybrid systems combining photocatalysis and cyanobacteria [116,117].

5. Use of Ammonia as Alternative Fuel: Ammonia Combustion

The search for alternative fuels complying with characteristics regarding carbon dioxide emissions and renewable sources has set the focus on carbon-free molecules. The immediate candidate to think of is hydrogen, but given the difficulties of attaining adequate volumetric densities at a reasonable cost, the attention has moved forward to hydrogen-rich molecules such as methane and ammonia. In the case of methane, this gas may be produced from the biological degradation of wastes under anaerobic conditions, or by the Sabatier process using syngas derived from biomass or CO_2 absorbed directly from the atmosphere. The Sabatier reaction requires a special nickel-based catalyst and a source of hydrogen, transforming 1 mole unit of CO_2 into methane by the use of 4 mole units of hydrogen [118,119], making the process complex, with only one plant built until now. The e-gas Audi plant was built in Werlte, Germany, and uses CO_2 derived from an anaerobic digester, thus complying with the requirement of producing synthetic methane from renewable sources [120]. The plant was transferred to Kiwi AG and recently acquired by Hy2Gen [121].

Given the scarce research in producing synthetic methane at an industrial scale, synthetic ammonia production seems a better option if a fast transition to a carbon-free economy is to be achieved. Ammonia has a higher energy volumetric density than hydrogen, although combustion properties are poor compared to hydrogen and methane, with poor ignition and flame propagating behavior [122]. The range of flammability limits is narrower than that of methane or other hydrocarbons, and the flame speed is just 7 cm/s, whereas this value is in the range of 35 to 100 for conventional fuels and biofuels, reaching values as high as 291 for hydrogen [123]. Ammonia's lower energy content per unit mass impacts combustion characteristics by releasing a lower amount of energy in the reaction zone and thereby reaching lower flame temperatures. This affects reactivity because a lower concentration of radicals is present in the flame front [124].

Despite these previous characteristics, ammonia has been proposed as a complementing fuel in ICEs to decrease the use of fossil fuels since the absence of carbon in its molecular structures avoids releasing greenhouse gas emissions. The poor combustion performance can be compensated by introducing modifications in engines to attain either neat ammonia combustion or its use as a dual fuel. The transition to a decarbonized economy may be faster if an important reduction in fossil fuel consumption is achieved by using suitable and available substitutes that have a proven track record of large-scale production and handling. ICEs commonly used in the power generation and transport sector can be classified as compression ignition, spark ignition, and gas turbines. The different operating characteristics of these engines translate into special features and combustion requirements. Thus, different techniques are necessary to adapt engines and attain a suitable performance when using mixtures of ammonia and conventional fuels. Figure 4 shows the main types of engines used in the electricity production and transport sectors.

Compression ignition engines require a fuel with a high cetane number to allow the combustion chamber to reach a high compression stage, attaining the mixture's autoignition by the associated temperature increase. In this system, direct injection of fuel is carried out once the air has been fully admitted into the cylinder and once the piston is closed to reach the top dead center position. On the contrary, spark ignition engines require a spark plug to initiate fuel–air mixture ignition (see Figure 5). Traditionally, in these later systems, the admission of fuel and air takes place in a premixed mode prior to the cylinder's intake ports. Modifications in fuel injection have been implemented in current modern engines, with many counting with direct or stratified fuel injection. These modifications were introduced to improve fuel use efficiency and reduce combustion temperature to lower NOx emissions. Two examples are homogenous charge compression ignition (HCCI), in which the mixture enters the cylinder, achieving a full homogenous state prior to autoignition, and premixed charge combustion ignition (PCCI), where a partial premix is created, allowing for fuel stratification before combustion. Thus, this concept may be classified as being between conventional combustion and HCCI [125].

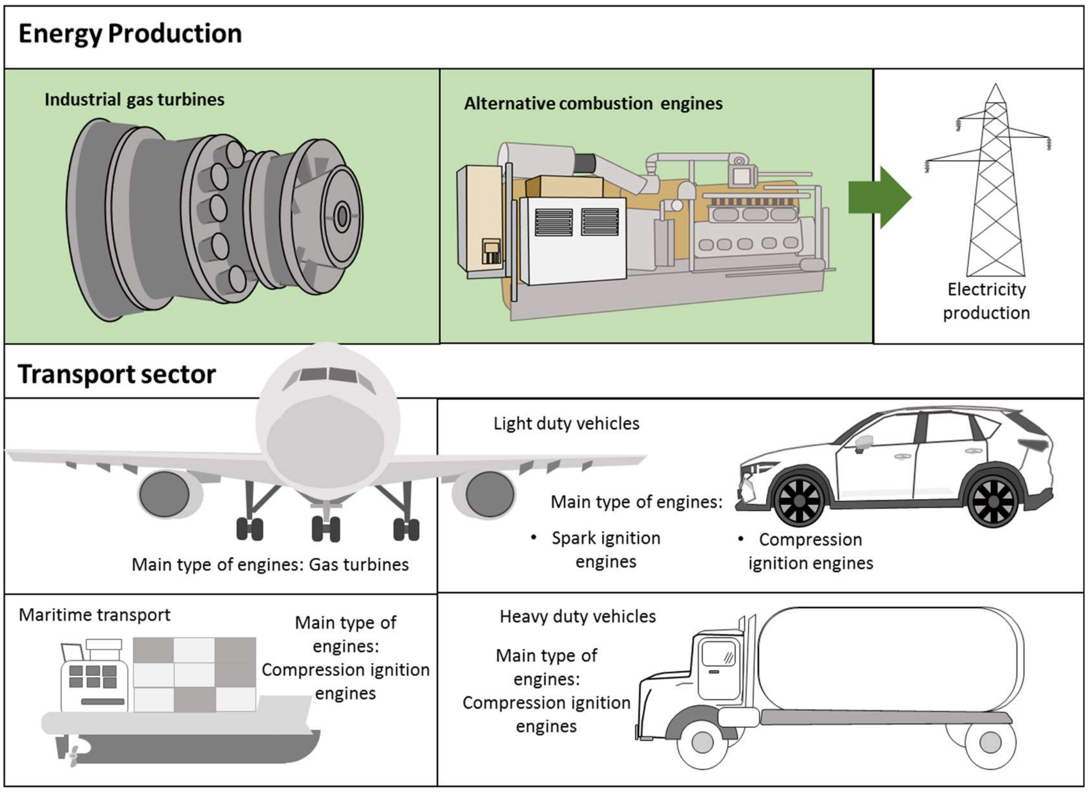


Figure 4. Internal combustion engines used for electricity production and in the transport sector.

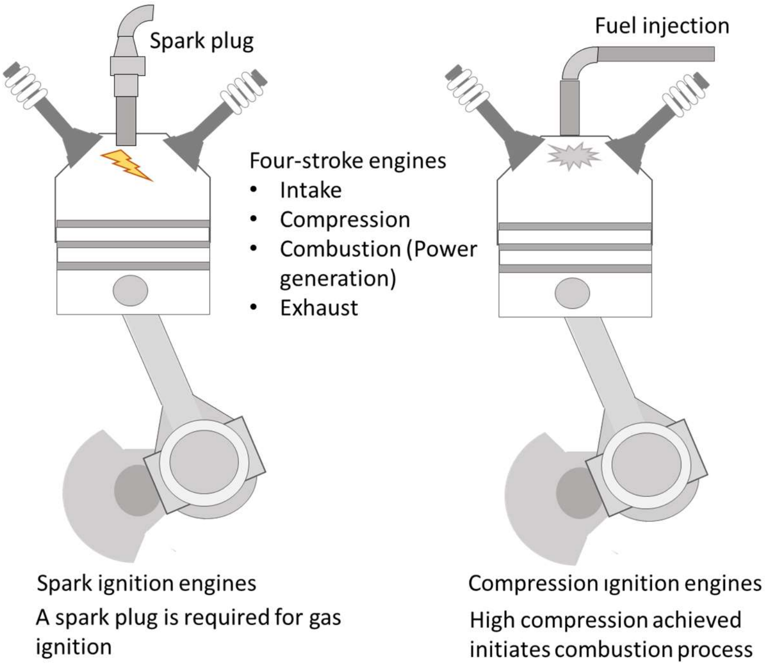


Figure 5. Internal combustion engines: spark and compression ignition engines. Four-stroke engines comprise a cycle of four stages to produce power every two cycles of the piston.

The amount of fuel–air added to a combustion system can be expressed in terms of the equivalence ratio (φ). This parameter gives an idea of the combustion conditions, referencing the stoichiometric point (ratio between the stoichiometric air and the amount of air added). Thus, lean mixtures are defined by values of φ lower than unity due to the addition of excess air. Modifying the amount of air added to combustion allows for controlling temperature and emissions produced. The recirculation of combustion gases also reduces combustion temperature by returning to the reaction zone inert species, creating a quenching effect and acting as a NOx control strategy. Exhaust gas recirculation (EGR) is a common feature of diesel engines and, recently, of new spark ignition engines [126,127]. The different operating concepts in ICEs will need to be adapted based on the combustion characteristics of ammonia. This gas has a high ignition energy (8 mJ for ammonia, whereas propane only requires 0.5 mJ [128]) and low flame speed. Therefore, attaining stable performance under different engine operating regimes will be a challenging work. Several experimental research works deal with the use of ammonia–fuel mixtures of conventional (diesel, gasoline) and alternative fuels (ethanol, biodiesel) [129–131].

The release of pollutants is a characteristic of ammonia combustion, which is a cause of great concern; a higher release of nitrogen oxides and unburnt ammonia in the exhaust may be expected [132]. Combustion of conventional fuels has been extensively studied to reduce the production of NOx emissions. Changes in operating conditions in the combustion chamber have been introduced to lower temperatures and avoid thermal NOx emissions derived from the Zeldovich mechanism [133,134]. Prompt NOx emissions (Fenimore mechanism) are associated with the presence of CH radicals following a different route, where HCN and CN are formed [135]. Additional emissions may be expected from the nitrogen fuel content. Burning under lean fuel conditions, combustion staging, or including a recirculation stream of exhaust gases to create reducing atmospheres are just some examples of the alternatives available for avoiding NOx formation. However, these strategies need additional adjustment and operational modifications when considering the addition of ammonia as a dual fuel.

The presence of nitrogen in the ammonia molecule would make anyone think of extremely high related fuel NOx emissions associated with direct ammonia oxidation. However, the reaction mechanism is complex, and the presence of different intermediary species allows for a window where the production of this undesirable contaminant is mitigated. The overall combustion reaction is the following:

$$4\,NH_3 + 3\,O_2 \rightarrow 2\,N_2 + 6\,H_2O \tag{2}$$

The mechanism of ammonia combustion comprises the presence of HNO and NH as intermediary species participating in NO formation [136]. Nitrogen-related contaminants are high [137] but not as much as one may have inferred from its molecular composition. Shu et al. [138] studied the mechanism of ammonia combustion, reporting that the presence of NH_2 intermediary species plays a fundamental role in autoignition, and its reaction with NO is crucial for the reaction outcome, either increasing or reducing the presence of this pollutant in exhaust gases. Other pathways responsible for NOx formation are those involving HNO and the Zeldovich pathway [139].

Cai et al. [137] reviewed different studies regarding ammonia combustion mechanisms and strategies to mitigate its formation. Operating under fuel-rich conditions, increasing pressure, staging combustion, and steam addition are some of the relevant strategies that have demonstrated success in controlling NOx presence [140–143].

Lean ammonia conditions favor the presence of O/H radicals, which are precursors to the formation of NO contaminants. Thus, lean ammonia flames show peaking NO levels at φ of 0.9, with higher values than those obtained from methane/air flames, but showing a minimum at slightly rich conditions (φ = 1) [144]. The presence of H, OH, and HNO radicals is crucial in the formation of NOx by the following reactions:

$$NO_2 + H \leftrightarrow NO + OH \tag{3}$$

$$HNO + H \leftrightarrow NO + H_2 \tag{4}$$

$$HNO + OH \leftrightarrow NO + H_2O \quad (5)$$

Therefore, adding H_2 to ammonia combustion under lean conditions increases the availability of these radicals in the flame front. On the contrary, increasing the φ over unity values significantly reduces NOx formation because oxygen availability decreases as well as temperature [145].

NO_2 and N_2O are also part of NOx emissions. NO_2 is responsible for smog formation, whereas N_2O is a compound that causes great concern because of its high warming potential (about 300 times greater than that of CO_2) [146]. Therefore, benefits associated with CO_2 emission reduction may be in part mitigated by the release of N_2O or by the adverse effects associated with acid rain. The proportion of N_2O in the global NOx emission is believed to be closely related with incomplete combustion in ICEs, decreasing the yield of N_2O formation with temperature in the 850–1350 K range [147,148].

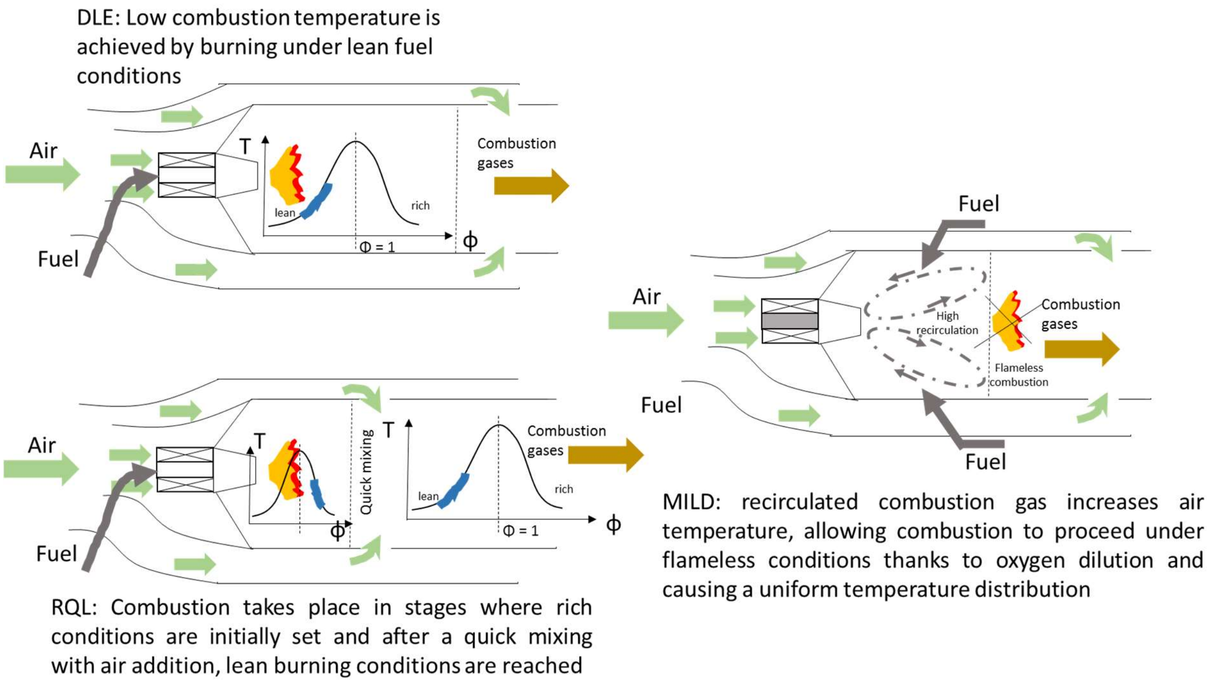
5.1. Gas Turbines

Generating a flame and attaining stable conditions in a combustion chamber can be achieved by the use of different strategies. However, attaining stable performance under different operating conditions with low levels of contaminants was a great challenge, which was only made possible after several years of research and experience. In a very simplistic way, flames can be catalogued as premixed or diffusion types. In the first case, mixing of the fuel and oxidizer is performed prior to reaching the flame front, and the combustion temperature reached corresponds to the φ supplied. The second case refers to the separate supply of fuel and air. Thus, diffusion flames are said to always reach higher combustion temperatures since there is a preference for the flame front to be located at the stoichiometric mixing condition point. Since the diffusion of the fuel and oxidizer to the reaction zone is required, these flames are diffusion-limited, thus explaining their name.

The previous categorization is far from explaining all complexities taking place during the combustion. Burning fuels with excess air (lean conditions) reduces flame temperature and, thus, NOx emissions, but it also affects flame speed and may create acoustic interactions that adversely affect flame stability. In the case of burning fuels with air deficiency (rich conditions), flame temperature is also lowered, but unburnt hydrocarbons and CO emissions are a concern. Combustion science must deal with reaction chemistry, flow interactions, heat transport phenomena, and acoustic waves, thus explaining the difficulties in attaining stable performance under all possible engine operating regimes.

The use of swirling flow in combustion chambers increases flame stability by creating inner and outer recirculation zones that transport hot products and active radicals back to the reaction region, mixing with the fresh, unburnt mixture, increasing residence time and allowing for the fuel to be consumed [149]. The presence of these zones allows for operation with high inlet flow velocities, although the flame speed of the fuel used may be low. A swirl flow creates a central vortex zone and low-pressure gradient, giving rise to a reverse flow [150] that allows flame anchorage.

The strategies widely applied in gas turbines for attaining acceptable performance regarding combustion efficiency and emission control are dry low emission (DLE), rich-burn, quick-quench, and lean-burn (RQL), and moderate or intense low oxygen dilution (MILD). The first refers to lean burn conditions where low adiabatic flame temperatures avoid NO formation under the thermal mechanism. The reduction in NOx emission is achieved without using water or steam as a heat sink, hence the denomination of dry [151]. The RQL concept is based on the separation of combustion into two clearly distinct zones where rich conditions are initially favored, creating a pool of radicals that are subsequently oxidized in a secondary zone where excess air is sufficiently added, attaining a fast temperature drop and avoiding thermal NOx formation. MILD combustion refers to the recirculation of hot combustion gases, causing an oxygen dilution effect in the reaction zone and, thus, lowering peak temperatures [152]. Figure 6 shows the different operating concepts.



DLE: Low combustion temperature is achieved by burning under lean fuel conditions

RQL: Combustion takes place in stages where rich conditions are initially set and after a quick mixing with air addition, lean burning conditions are reached

MILD: recirculated combustion gas increases air temperature, allowing combustion to proceed under flameless conditions thanks to oxygen dilution and causing a uniform temperature distribution

Figure 6. Operating strategies in gas turbines to achieve low levels of pollutants. DLE: dry low emission, RQL: rich-burn, quick-quench, and lean-burn, and MILD: moderate or intense low oxygen dilution.

Ammonia/air flames are less stable than those of methane under similar conditions, with lower laminar burning velocities, heat release rate, and lower flame temperature [144]. However, combustion of this gas has been possible with success by attaining appropriate hydrodynamic conditions in the combustion chamber. Many industrial applications for energy production use methane in gas turbines. Therefore, there is a great interest in retrofitting current engines to allow for ammonia use, either as a mixture of methane/ammonia or as a single fuel, keeping always in mind that NOx regulation should be fully complied with. Iki et al. [153] studied the performance of a microturbine using methane and mixtures with ammonia and neat ammonia as fuel. Changes in air supply were needed to provide air at higher temperatures and lower flow rates. Staging combustion was also necessary to create two zones (rich–lean) and avoid an excessive production of NOx. Okafor et al. [154] tested single and two-stage (rich–lean) combustion using methane/ammonia mixtures, reporting high NO emissions in the first case but much lower ones in the latter due to the enhanced fuel consumption in the primary zone (where rich conditions are set). The methane/ammonia mixture was characterized by higher flame speed compared to that of neat ammonia flames, a feature that ensured lower NOx production in the secondary zone.

Gubbi et al. [56] performed a numerical study, evaluating the NO emission expected from ammonia combustion by changing combustor pressure and residence time. These authors indicated that current NOx regulation limits can be complied with by changing operating parameters and allowing higher residence time in the combustor. Increasing pressure lowers NOx emissions when using ammonia as fuel since it reduces the availability of O and H radicals [144], and the effect of pressure is just opposite to the behavior obtained when burning conventional fuels [155]. This study opens a door for opportunities regarding the use of ammonia for reducing CO_2 emissions since it is expected that the problem of NO formation will be resolved. However, the increase in pressure also causes a decrease in the laminar flame speed, and the presence of ammonia causes a decrease in temperature and net heat release rate [156], thus requiring modifications intended to attain flame stabilization under such peculiar fuel characteristics.

Rocha et al. [157] also performed a numerical evaluation of ammonia combustion and its emission characteristics by considering the three typical gas turbine operating concepts for keeping low NOx emissions, that is, DLE, RQL, and MILD. Their results indicated that the DLE concept was inappropriate when dealing with ammonia as fuel, whereas RQL and MILD combustion achieved the lowest emissions. The presence of a post-combustion zone at high temperatures enhanced the consumption of NO previously formed by the reaction $NH_2 + NO \rightarrow H_2O + N_2$ [158].

The poor combustion characteristics of ammonia were the main reason for considering the use of more reactive fuels as additives either for starting up the system until steady combustion is attained or using ammonia in dual systems to warrant stable performance at all loading conditions. H_2 has been added as an ignition enhancer to increase the pool of radicals, flame speed, and stability [159,160], but the supplementation of this gas brings along problems associated with storage and handling, along with the use of separate deposits for ammonia and hydrogen. The autothermal cracking of ammonia to release a fraction of hydrogen contained in the ammonia molecule, or the use of catalysts to aid in the thermal decomposition of ammonia, has been proposed as a solution for avoiding the presence of an additional high-pressure container and reducing safety risks.

Regardless of difficulties encountered when attempting to use ammonia as an alternative fuel, several studies have demonstrated that technical advances can overcome combustion inefficiencies observed and reduce the emission of pollutants. Therefore, there is a great interest in considering ammonia as a suitable substitute for conventional fuels and an enabler of the hydrogen economy thanks to its feasible use in power generation and the transport sector (aircraft propulsion and road and marine transport) [161].

Table 1 shows different experimental studies carried out to evaluate the combustion characteristics of ammonia and its performance in gas turbines as single fuel and as dual systems. In these studies, it can be observed that the addition of ammonia under certain operating conditions causes an increase in NO emissions, specifically when working under premixed conditions [162,163] or using a swirl burner [163,164]. Verkamp et al. [128] proposed partial dissociation of ammonia as a method for flame stabilization, achieving stable operation by working only with ammonia as fuel; it was also possible to keep NO emissions under control. Khateeb et al. [164] succeeded in keeping NO emissions under control in a swirl burner under rich operating conditions, thus reducing the risk of backfiring. These studies showed that using ammonia as a fuel in turbines may be possible in the future with certain improvements in the current state of the art.

Table 1. Experimental studies evaluating ammonia combustion characteristics and performance in gas turbines in a single- and dual-fuel configuration.

Fuel	Experimental Characteristics	Main Results	Reference
Ammonia/methane mixtures	Measurement of burning velocity and combustion products using an adiabatic flat flame burner.	Addition of ammonia from 0% to 5% by volume in ammonia–methane mixture. The addition of 4% ammonia resulted in a 10% to 20% decrease in burning velocities. Adding ammonia increased NO concentration.	[165]
Ammonia/methane mixtures	Premixed and nonpremixed counterflow flames: evaluating extinction stretch rate.	Premixed flames under lean conditions were not well predicted for any of the mechanisms studied. However, Okafor's mechanism accurately predicted the extinction stretch rate of nonpremixed flame.	[162]
Ammonia/H_2 mixtures	Flame stability and pollutant emissions using a porous burner.	Addition of ammonia in the fuel blend reduced the flame stability limits and thermal flame thickness. NO emissions decreased under rich conditions.	[166]

Table 1. *Cont.*

Fuel	Experimental Characteristics	Main Results	Reference
Ammonia	Burning liquid and gaseous ammonia.	Partial dissociation of ammonia was considered necessary for attaining stable combustion in conventional gas turbine burners.	[128]
Ammonia/methane; Ammonia/kerosene mixtures	Microgas turbine firing ammonia (50 kW).	NO emission increased with ammonia addition until a certain limit.	[167,168]
Ammonia/methane mixtures	Use of tangential swirl burner. Atmospheric and medium pressure conditions.	Fully premixed injection strategy is not appropriate for optimized ammonia combustion. High flame instabilities can be produced at medium swirl numbers.	[163]
Ammonia/methane mixtures	Microgas turbine (50 kW).	The combustion efficiencies of the NH_3–air combustors ranged from 89% to 96%, increasing the efficiency with the increase in power. Addition of ammonia to a methane-based mixture leads to an increase in NO emission.	[169]
Ammonia/methane mixtures	Laboratory-scale swirl burner.	Ammonia addition reduces flame flash back propensity. Good performance in terms of NO emissions is attained only under rich conditions.	[164]
Ammonia/methane mixtures	T100 microgas turbine (reverse burner). Pilot injector (nonswirl flame). Main injector (premixed flame).	Ammonia addition decreased combustion efficiency. High NOx emissions cancelled any benefit of decarbonization.	[170]
Ammonia	Simulation study: bluff body stabilized nonpremixed turbulent ammonia (NH_3)/air flames using swirling flows. Evaluating the effect of pressure (swirling flames).	Increasing pressure reduces the availability of OH radicals and therefore, limits NO generation.	[171]
Ammonia	Microgas turbine (100 kW). Load range: 40–100%.	Full replacement of natural gas with ammonia was found to reduce electric efficiency by about 0.5 percentage points.	[172]
Ammonia	Gas turbine with heat regenerator.	The addition of H_2 is effective for low NOx combustion with high combustion efficiency. A system of selective catalytic reduction needs to be coupled to the gas turbine system to comply with pollutant emission limits.	[133]
Ammonia	Microgas turbine.	Inclined fuel injection and use of swirler. Two-stage (rich-lean) combustion resulted in high efficiency and low NO emission (42 ppmv) NO emission decreased with pressure increase.	[173]
Ammonia	Small-scale Siemens burner used in the SGT-750 gas turbine. Testing ammonia decomposition degree.	Full and partial ammonia decomposition were tested. When applying partial decomposition, rich conditions were required in the primary zone to avoid the presence of O_2 close to the burner (minimum NOx obtained at φ of 1.1). Increase in pressure reduced NOx formation. When total ammonia decomposition was attained, low NOx levels were measured, but in this case, pressure increase favored NOx emissions.	[174]

5.2. Spark Ignition Engines

ICEs are widely used in the transport sector and power generation. Spark ignition engines are the preferred option in passenger cars, although there was higher efficiency of diesel engines and advancements performed in the last decade regarding particle emission control and NOx production. The diesel scandal damaged public perception towards diesel passenger cars, and political pressures set a regulation preference for gasoline and electric vehicles. Even though diesel vehicles have an equivalent environmental classification in Spain to gasoline and lower CO_2 emission per kilometer, the market experienced a severe drop in sales of this type of vehicle [175].

Spark ignition (SI) engines can be easily adapted to use gaseous fuels such as natural gas and liquefied petroleum gas (LPG), currently becoming a practical solution for many consumers due to their lower fuel consumption and price. SI engines are also widely used for valorizing biogas since these engines produce electricity and heat recovery concomitantly, which is essential for keeping digestion temperature. When operating under lean burn conditions, NOx emissions are restricted to 400–500 ppm [176,177]. A further reduction in NOx levels, then, requires the use of selective catalytic reactors (SCRs). The main commercial combined heat and power (CHP) engines include Jenbacher®, MWM®, Caterpillar®, MTU®, Waukesha®, and MAN® [178–183], and many of these engines are currently adapted for also using hydrogen as fuel, just as in the case of gas turbines.

Ammonia has been considered a fuel worthy of research by industrial manufacturers regarding its use in gas turbines and compression ignition engines, but this is not the case for spark ignition engines, where the main research is found in academic sites. Early research performed by Cornelius et al. [184] and Starkman et al. [185] already provided a clear insight into the modifications required when using this gas in SI engines, such as the need for increasing compression ratio and using supercharges due to the lower energy content of this molecule, the lower air-to-fuel ratio to attain stoichiometric conditions, and the need for partial ammonia dissociation to release hydrogen (or direct hydrogen addition), which is critical to attain stable performance under different engine loading. Hydrogen enrichment or increased intake pressure may serve as suitable measurements to attain operation with satisfactory combustion efficiency [50,186].

Natural gas engines are more suitable for retrofitting to ammonia–hydrogen operation due to their higher compression ratio and the lower dependence on fuel laminar flame speed of their combustion chamber [187]. However, there is a limit to the addition of hydrogen in the mixture based on the risk of backfire and wall heat losses [188]. Low levels of hydrogen addition allow stability improvement, acting as an ignition promoter and increasing laminar flame speed, but this single factor does not fully explain the improvement in operation achieved [189]. The high octane number of ammonia (130) makes the engine operate under higher compression ratios than the one used for gasoline [190], and the different burning characteristics of hydrogen and ammonia allow for attaining a mixture proportion capable of reaching a similar performance regarding work output to that obtained with gasoline [191]. This approach's main disadvantage is the need for separate fuel storing tanks, making the system too complex for onboard applications. However, in the case of liquid and gaseous supplementary fuels, the technological configuration resembles that of the already tested technology for LPG and petrol passenger cars.

Studies carried out by Grannell et al. [192] using a Cooperative Fuel Research (CFR) engine showed that ammonia could be used in up to 70–30% ammonia–gasoline mixtures, although under idle conditions, the engine needed to be operated with gasoline as single fuel. Ryu et al. [193] indicated that gaseous injection of ammonia is preferred because of the high value of the latent heat of vaporization (1370 kJ/kg) compared with that of gasoline (348.7 kJ/kg), causing a significant reduction in in-cylinder temperature. In addition, the low flame speed of ammonia translates into an increment in combustion duration, thus requiring a greater advancement in spark timing than that applied for typical SI engines [194].

An alternative to avoid using two separate storage fuel systems is to generate hydrogen from the ammonia decomposition. The cracking of ammonia has been studied by several authors [195–197], proposing the use of thermal catalytic reactors that allow reduction in reaction temperature. Catalysts commonly employed contain noble metals (Rh, Ru, Pd, and Pt, among others), but Fe and Ni have also been tested in order to reduce costs and dope the catalyst with rare-earth metals to increase activity, in addition to the use of bimetallic configurations [198,199]. The industrial application of this technology at a large scale was reviewed by Spatolisano et al. [200], analyzing the implications of technology deployment. Many technologies currently developed are still in the experimental stage; thus, information regarding long-term performance, economics, and specific environmental impacts are scarce [201]. Testing at a precommercial stage is necessary for technical maturity before large-scale implementation.

The ammonia cracking reaction is endothermic. Therefore, onboard applications may benefit from using exhaust combustion gases, which can provide the heat needed to release hydrogen, but at the cold start of the engine, external heaters are necessary. Comotti and Frigo [202] proposed using a Ru-based catalyst with electric heaters in the internal section of the reactor, and the outer section used the exhaust gases as heat supply. Their system allowed the use of ammonia as a single fuel in SI engines operating successfully under different loading conditions. One crucial aspect to consider is that when hydrogen is produced from ammonia cracking, the extra amount of N_2 introduced into the cylinder should be taken into account to optimize operating conditions.

Table 2 shows some of the studies carried out using ammonia as fuel in spark ignition engines. The use of ammonia as the only fuel in a spark ignition engine is practically unfeasible due to the difficulty of ignition, low flame stability, combustion efficiency, and power delivery, so dual-fuel configuration seems to be the best option. Using hydrogen as a dual fuel in proportions between 10 and 15% allows for solving these problems [188,189]. The required hydrogen may be obtained from an additional storage tank or the partial dissociation of ammonia; in any case, it is necessary to use systems such as EGR to reduce ammonia and NO emissions [203]. Other fuels have also been evaluated in dual configuration with ammonia. Tutak et al. [204] used DME as a complement to ammonia, allowing stable operation to be achieved. Oh et al. [205] reported that using DME along with methane slightly decreased braking power.

Table 2. Studies evaluating ammonia combustion in spark ignition engines using different ignition promoters.

Fuel	Experimental Characteristics	Main Results	References
Ammonia: Storage using metal complex and partial ammonia reforming for H_2 production	CFR-engine [1]. Compression ratio: 6.23–13.58. Ammonia/H_2 5–100% vol.	Best performance at a fuel mixture of 10 vol.% H_2 with respect to efficiency and power.	[206]
Ammonia–H_2 mixture	4-cylinder 4-stroke SI engine, retrofitted to a single-cylinder by fueling only one cylinder (volume displacement: 399.5 cm^3). Compression ratio: 10.5:1 1500 rpm.	%H_2 addition from 0 to 60%. Stable operation was achieved for NH_3/air stoichiometric condition (0.1–0.12 intake pressure), needing a small amount of H_2 to ensure ignitability and stability. Only mixtures with high H_2 fraction were suitable for lean operation where efficiency was found to be improved. Mitigation strategies for both NH_3 and NOx are required if ammonia is to be considered an acceptable fuel.	[189]

Table 2. *Cont.*

Fuel	Experimental Characteristics	Main Results	References
Ammonia–H_2 mixture	4-cylinder 4-stroke Gasoline Direct Injection-SI EP6 PSA engine. Engine modified to become indirect injection, single cylinder.	10% H_2 addition was required for operation. The highest levels of NO and N_2O emissions were found to be on the lean side. NH_3 emissions were present under rich conditions. EGR [2] reduces NOx.	[203]
Ammonia–H_2 mixture	2.5 L supercharged LPG [3] engine with direct-fuel injection (fuel injection pressures up to 15 MPa). Compression ratio of 10.5.	Stable combustion is impossible under low-load or low-speed operating conditions due to the cooling of the mixture by latent heat and slow combustion. 10% H_2 addition improved performance. However, NOx emissions increased as torque increased with a peak at 200 Nm, whereas ammonia showed minimum values at 160 Nm.	[188]
Ammonia–H_2 mixture	Port fuel injection (PFI) turbo-charged spark-ignition engine, 1.37 L 4-cylinder with compression ratio of 9.8.	15% H_2 (vol./vol.). The engine operated properly between 1500 and 3000 rpm but could not reach 6000 rpm. Maximum engine torque (about 240 Nm) was delivered at 1500 rpm.	[194]
Ammonia–H_2 mixture	Single-cylinder internal combustion engine with a variable compression ratio UIT-85, volume displacement: 652.57 cm^3. Compression ratio: 8:1 and 10:1.	Increasing hydrogen energy content up to 12% in the fuel mixture eliminates ignition instability.	[190]
Ammonia–methane mixture	11 L 6-cylinder heavy-duty turbocharged spark-ignited engine, originally used in city buses using compressed natural gas (CNG) as fuel.	Ammonia addition caused a moderate deterioration in the generation of brake work compared with the case of pure natural gas. Combustion efficiency showed a steep deterioration with the increase in ammonia in the fuel mixture at a lambda of 1.5 because the laminar flame speed is extremely slow at this condition, and the flame temperature is also extremely low; thus, quenching will occur earlier.	[205]
Ammonia–DME mixture	Single-cylinder spark-ignition research engine with a compression ratio of 10 and a constant rotational speed of 600 rpm.	DME was added as a component with higher reactivity to attain stable performance, reducing ignition delay time and combustion duration.	[204]
Ammonia–gasoline mixture	CFR engine: compression ratio of 10:1 and constant speed of 1800 rpm.	The brake-specific energy consumption (BSEC) with gasoline–ammonia was very similar to that with gasoline alone.	[207]
Ammonia–gasoline (E10) mixture	Externally boosted SI research engine (single cylinder) derivative of the MAHLE Powertrain "DI3" demonstrator engine. Volume displacement: 400 cm^3. Maximum speed: 6000 rpm. Compression ratio: 11.33 and 12.39. φ: 1.	Increasing the compression ratio from 11.2 to 12.4 allowed the engine to operate with neat ammonia once a warmed-up state was reached. Under all conditions, the indicated thermal efficiency of the engine was either equivalent to or slightly higher than that obtained using gasoline-only due to the favorable antiknock rating of NH_3 (40% efficiency at 1800 rpm/16 bar IMEPn [4], a 14% improvement over pure E10).	[208]

Table 2. *Cont.*

Fuel	Experimental Characteristics	Main Results	References
Water ammonia solution (WAS)–gasoline mixture	Single cylinder four-stroke air cooled engine (volume displacement: 212 cm^3). Maximum output power of 2.5 kW at 3000 rpm. Compression ratio: 8.5:1.	WAS at 25% ammonia. Mixtures of WAS–gasoline were tested at a range of 5 to 25%. The engine's thermal efficiency was improved but emissions performance (CO, NOx, HC [5]) was not.	[209]

[1] CFR: Cooperative Fuel Research, [2] EGR: exhaust gas recirculation, [3] LPG: liquefied petroleum gases, [4] IMEPn: net indicated mean effective pressure, [5] HC: hydrocarbon.

5.3. Compression Ignition Engines

Compression ignition engines apply a higher compression ratio and, thus, achieve fuel ignition. Since the fuel is directly injected into the combustion chamber after compression, knock limitations are eliminated, fuel efficiency is high, and fuel consumption can be optimized to provide power. However, the direct injection of the fuel causes diffusion combustion, which translates into high localized temperatures, increasing the emission of NOx and particles. For this reason, it is said that CI engines, although highly efficient, have an emission problem [210]. Fortunately, advances in engine design and emission abatement technologies have guaranteed that post-combustion gases are adequately treated. Exhaust gas recirculation decreases combustion temperature, thus reducing thermal NOx production. Lean NOx trap technology has been developed to trap and reduce NOx compounds under lean operating conditions. Selective catalytic reactors use a nitrogen compound to transform NOx into N_2, and particle filters are incorporated to remove soot [211,212]. Different technological developments have allowed diesel engines to keep playing a fundamental role in energy production and transport. The high energy density of diesel fuel (35.86 MJ/L [213]) makes it the ideal choice for heavy road transport, but it also makes difficult the task of finding a suitable alternative due to the low storage volume needed for onboard applications and the high efficiency reached by these type of engines.

After the initial work of Cornelius et al. [184], Gray et al. [214], and Starkman et al. [215], the studies of Pearsall and Garabedian [216] focused on using ammonia in diesel engines. However, in this case, dual-fuel engines were the best alternative for attaining an acceptable output by controlling ignition thanks to the injection of diesel fuel. Reiter and Kong [217] tested a dual-fuel (ammonia–diesel) engine and reported that NOx emissions did not increase, despite the presence of ammonia, as long as energy substitution attained by ammonia did not reach 60%. However, in a later study, the same authors [218] lowered the ammonia energy supply in the mixture below 40%. Otherwise, NOx emissions would increase significantly due to fuel-bound emissions. These authors also reported high ammonia slip (1000–3000 ppmv) in exhaust gases, which may be regarded as disappointing news for this technology.

The experimental and demonstration works have been extensive in the last decade due to the impact of greenhouse gas emissions and the feasibility of using a noncarbon gas for which industrial technology is already available. Reviews about the use of ammonia as fuel in compression ignition engines have been carried out by Dimitriou and Javaid, [46], Kurien and Mittal [23], and Voniati et al. [219], where it was reported the need to install several after-treatment devices for emission control, and this requirement also limits marine, power generation, and heavy-duty applications. In addition, the formation of N_2O, which has a much greater global warming impact, is one of the main obstacles to surpass when considering the use of ammonia in ICEs [220].

The variety of options currently being considered to reduce CO_2 emissions may add optimism and give hope to a future free of carbon fossil fuels, but it requires significant efforts from researchers and industry. It also comes along with an adverse effect by creating uncertainty regarding the future of the dominant technology and the limited space available in fuel stations and cargo ports since this variety of options also implies having installations for electrification, LPG, hydrogen, ammonia, and methane storage, which has been recently incorporated to the maritime transport sector, thus resulting in an excessive complexity of infrastructure. Space limitations can make it unfeasible for different technologies to coexist. As an example, Imhoff et al. [221] studied the feasibility of implementing ammonia power trains in current vessels, indicating that redesign and reconfiguration efforts are needed but achievable; thus, ammonia-fuel ships may represent a feasible alternative. However, the maritime transport sector needs the certainty that an investment, which may be extremely high, will stay long enough to be worth it. Balci et al. [222] studied critical factors for successfully implementing ammonia as an alternative fuel in shipping. They indicated that adopting green ammonia involves several complexities regarding safety regulation, storage capacity, and reliable renewable energy production, in addition to the evident claim of engine improvements. Resources for increasing research and development may be derived from stakeholders and carbon taxing. The intrinsic concatenation of events will aid in further developing infrastructures; that is, the development of efficient ammonia propulsion engines would aid in reducing operating costs, thus increasing ammonia demand and aiding in the development of port infrastructure.

Table 3 lists different studies dealing with the use of ammonia as fuel in ICEs. The risks of using anhydrous ammonia and pressurization tanks may be avoided if other forms of ammonia are considered. Schönborn [223] proposed the use of water ammonia solution in diesel engines. This way, ammonia can be stored in liquid form under ambient conditions, reducing the risk of vapor ammonia release. The author analyzed the behavior of a diesel engine when injecting a 25% ammonia solution as fuel using numerical simulation. The compression ratio needed to be increased to 27 to attain ignition of the ammonia solution since the high water content creates a dilution effect, making ignition possible only if higher energy is added. However, the dilution effect also allowed a reduction in NOx emissions. Therefore, in addition to facilitating storage, other benefits are associated with this approach, whereas improving ignition may be achievable by adding specific promoters such as hydrogen.

Table 3. Studies evaluating ammonia combustion in compression ignition engines using dual-fuel configuration and ignition promoters.

Fuel	Experimental Characteristics	Main Results	References
Ammonia–diesel mixture	John Deere (Model 4045) multicylinder turbocharged diesel engine. Displacement volume: 4.5 L. Compression ratio: 17.0:1. Engine speed: 1000 rpm. Performance tested under constant engine power and variable engine power operation.	NOx emissions are reduced if ammonia accounts for less than 40% of the total fuel energy. CO and HC [1] emissions were generally higher with the dual-fuel configuration than those of single diesel fuel use for the same power output. NH_3 emission reached 1000–3000 ppmv. Under variable power operation, fuel efficiency was poor.	[218]
Ammonia–diesel mixture	Lifan engine 4 stroke single cylinder. Compression ratio: 16.5:1. Operating conditions: 1200 rpm and full load.	A maximum of 84.2% of input energy can be provided by ammonia. Ammonia reduced CO_2 emissions but also produced N_2O, which has a 298 times greater GHG [2] effect.	[224]
Ammonia–biodiesel mixture	Lifan engine 4 stroke single cylinder. Compression ratio: 16.5:1. Operating conditions: 1500 rpm.	Ammonia-/biodiesel-fueled engine had lower BTE [3] than pure biodiesel at the same operating point. Increasing ammonia in the mixture changes combustion from diffusion to premixed mode.	[225]

Table 3. *Cont.*

Fuel	Experimental Characteristics	Main Results	References
Ammonia–DME mixture	Yanmar L70 V single-cylinder, direct-injection diesel engine. Natural aspiration. Displacement volume: 320 cm^3. Compression ratio: 20.0:1.0. Engine rated speed: 3600 rpm.	The operating range of the engine is reduced when using ammonia. Adding ammonia to the mixture decreases combustion temperature, producing higher CO and HC emissions but much lower soot emissions. NOx emissions increased due to fuel-bound nitrogen. Increasing injection pressure allows the use of mixtures with higher ammonia content.	[226]
Ammonia–DME mixture	Modified Caterpillar 3401 heavy-duty, single-cylinder, four-stroke. Compression ratio: 16.25:1. Displacement volume: 2.44 L. Engine speed: 910 rpm.	The authors proposed split diesel injection as a strategy for improving combustion performance. Lower GHG emissions were achieved than with diesel-only combustion mode.	[220]
Aqueous solution of ammonium hydroxide (NH_4OH) solution (28% ammonia)–diesel	Ford Duratorq CD132 130 PS 4-stroke single cylinder. Displacement volume: 499.56 cm^3.	Aqueous ammonia contributed a maximum of 25% of the total engine load. Increasing this proportion caused higher CO emissions and cycle-to-cycle variability.	[227]

[1] HC: hydrocarbon, [2] GHG: greenhouse gas, [3] BTE: brake thermal efficiency.

Hydrogen has also been widely studied as an ignition promoter when testing compression ignition engines, but also methanol, ammonia nitrite, and diesel fuel (n-heptane in simulation runs) [228–231]. Although modifications in fuel injection strategies are needed, ammonia–diesel dual-fuel engines may reduce CO_2 emissions by 90% and NOx emissions by 70% compared with original diesel engines [232]. Other organic solvents may also be proposed as a liquid phase for storing ammonia without causing detriments in combustion characteristics, such as for the case of water, with methanol being considered a better candidate [233]. Other alternatives proposed the use of spark-assisted ICEs to overcome poor ignition characteristics [234] or changing the injection strategy by allowing the entrance of a small quantity of ammonia that will aid in main fuel ignition, thanks to the precombustion stage during the compression cycle, thus increasing temperature and pressure and facilitating ammonia ignition [235]. Scharl and Sattelmayer [236] studied the presence of diesel-piloted injections and concluded that reliable ignition of ammonia was possible when adding a small fraction of energy as piloted injected fuel (3.2% of LHV based on loading conditions).

6. Conclusions

The aim of a net-zero carbon emission by 2050 is a desirable goal, but this target needs to be carefully evaluated since implications associated with the decarbonization of the economy bring along an increase in costs, which may create market distortions. Several alternatives are currently under development for reducing the use of fossil fuels. However, many of these options result in an increase in process energy demand. Electrification and electricity production from renewable sources aid in achieving decarbonization goals. Impacts regarding mineral extraction, battery recycling, and uncertainty in renewable energy production need careful evaluation. Given the immediacy of the targets, it seems more reasonable to concentrate efforts on well-known and worldwide applied technologies.

Ammonia as an alternative fuel has the main advantage of great research in large-scale production, storage, and handling. Although several aspects regarding emissions need to be addressed, vast research exists in technologies capable of mitigating combustion pollutants. Another matter that may be a cause of concern is the effect of massive ammonia use for other applications besides agriculture. The expected increase in price resulting from the higher costs in production chains caused by the adoption of green hydrogen in the manufacturing process, as well as the pressure induced by growing ammonia demand, are factors that should not be overlooked. These factors can have a significant impact on human wellbeing and the food supply chain.

There is still a long way to go before attaining a feasible solution to decarbonizing the economy. The use of ammonia may be one of them, but in the short term, it seems more reasonable to focus on reducing CO_2 emissions by reducing fuel consumption and optimizing current technologies rather than forcing a complete shift towards electrification of the transport sector, which requires adaptation to a completely different technology, raising costs without the certainty of how production cycles and critical materials will be managed. Electrification can help reduce pollution in some urban regions. However, other alternatives, such as hybridization and current highly efficient combustion engines, can be more effective in achieving a global reduction in emissions by already having global technological deployment.

Author Contributions: Conceptualization, X.G. and R.G.; methodology, R.G.; validation, X.G.; formal analysis, R.G.; investigation, X.G.; resources, X.G.; data curation, R.G.; writing—original draft preparation, X.G.; writing—review and editing, R.G.; visualization, R.G.; supervision, X.G. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Conflicts of Interest: The authors declare no conflicts of interest.

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