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Review

Advancements and Challenges of Ammonia as a Sustainable Fuel for the Maritime Industry

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Abstract: The maritime industry needs sustainable, low-emission fuels to reduce the environmental impact. Ammonia is one of the most promising alternative fuels because it can be produced from renewable energy, such as wind and solar. Furthermore, ammonia combustion does not emit carbon. This review article covers the advantages and disadvantages of using ammonia as a sustainable marine fuel. We start by discussing the regulations and environmental concerns of the shipping sector, which is responsible for around 2% to 3% of global energy-related CO_2 emissions. These emissions may increase as the maritime industry grows at a compound annual growth rate of 4.33%. Next, we analyze the use of ammonia as a fuel in detail, which presents several challenges. These challenges include the high price of ammonia compared to other fossil fuels, the low reactivity and high toxicity of ammonia, NOx, and N_2O emissions resulting from incomplete combustion, an inefficient process, and NH_3 slipping. However, we emphasize how to overcome these challenges. We discuss techniques to reduce NOx and N_2O emissions, co-combustion to improve reactivity, waste heat recovery strategies, the regulatory framework, and safety conditions. Finally, we address the market trends and challenges of using ammonia as a sustainable marine fuel.

Keywords: ammonia; fuel; maritime; combustion

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1. Introduction

The significance of maritime transport has become increasingly pronounced in its contribution to bolstering the resilience of economies to the post-COVID-19 crisis [1], the war between Russia and Ukraine [2], and the constant changes in the market due to the US–China Trade War [3]. In addition, the International Chamber of Shipping (ICS) initiatives encompass endeavors aimed at reducing carbon emissions in the maritime sector, which are about 3% of the global energy-related carbon dioxide (CO_2) emissions [4]. These include continuing discussions within the United Nations International Maritime Organization (IMO) and a groundbreaking proposition from the industry, proposing the establishment of a substantial $5 billion fund to expedite research and development in the field of zero-carbon technologies, among other endeavors [5]. For example, the IMO has set an ambitious strategy for 2023. At the core of this strategy are three key objectives: 1. improving the energy efficiency of new ships to drive down emissions; 2. achieving a minimum of a 40% reduction in emissions per transport work by 2030, measured against the 2008 baseline; and 3. promoting the widespread adoption of zero or near-zero GHG emission technologies, fuels, and energy sources. The target is to have these sustainable solutions account for at least 10% of the industry's energy mix by 2030 [6]. The prevailing circumstances illustrate the existing challenges in the shipping sector.

Within the expansive range of technological and fuel-related options available to ship designers, builders, owners, and operators, anhydrous ammonia has emerged as a prospective marine fuel with the potential for swift market integration and the provision of a zero-carbon solution when considering emissions from tank to wake [7]. Despite the toxic nature of NH_3 and its lower energy density than conventional oil-based fuels, NH_3 exhibits greater favorability than hydrogen (H_2) [8]. The utilization of this technology may be appropriate for prospective implementation in cargo vessels equipped with modified internal combustion engines (ICEs) and low-pressure fuel storage systems.

NH_3 exhibits several advantageous characteristics when used as a fuel. These include a notable power-to-fuel-to-power efficiency [9], a widespread distribution infrastructure, a high-octane rating of 110 RON [10] (gasoline: 92 RON [11]), and a restricted flammability range, enhancing safety by reducing the likelihood of explosions [12]. Nevertheless, burning NH_3 presents several obstacles that can be classified into two main categories: lower reactivity compared to traditional fuels [13] and higher amounts of nitrogenous emissions, including nitrogen oxides (NOx) and NH_3 residuals [14]. The observed poor reactivity of the system leads to a correspondingly low laminar burning velocity (LBV) [15], an extended ignition delay time, a reduced volumetric heat release rate, and increased flame instability. The combustion of NH_3 results in the production of substantial quantities of NOx, mainly through the fuel–NO mechanism, while the levels of unburnt NH_3 remain relatively elevated. Implementing a dual-fuel approach involving blending NH_3 with other fuels at different proportions can address several challenges, such as improving combustion reactivity and reducing NOx and greenhouse gas (GHG) emissions [16].

Currently, most ships use internal combustion engines that run on petroleum products like heavy fuel oil, marine gas oil, and marine diesel oil. These fuels are not sustainable in the long term and contribute significantly to greenhouse gas emissions [17]. To reduce emissions, the industry must find environmentally friendly alternative fuels. One potential solution is NH_3. However, the industry is still in the early stages of experimenting with this fuel, and much research needs to be performed to understand the implications of adopting such fuels. Despite the challenges, companies are planning for decarbonization faster than the current targets established by IMO. This is a positive sign, as it shows that the industry is taking the issue seriously and is committed to making changes. Decarbonization is complex and will require cooperation between ship owners, operators, ports, engine manufacturers, and fuel providers. However, this moment of change should be viewed as an opportunity for bold decision-making. Multiple fuel pathways are available, and the advantages for first movers are significant [17]. Table 1 summarizes the status of the utilization of greener fuels in the maritime sector. As shown in Table 1, NH_3 has advantages and disadvantages compared to fossil and renewable fuels. NH_3 is notable for its low GHG emissions. However, there are significant opportunities for improvement, particularly regarding its cost and handling, since it is a highly toxic substance.

Despite the potential of NH_3 as a fuel to reduce GHG, only a few projects considering NH_3 were funded and implemented. Valera-Medina and his research team [19] led a groundbreaking project funded by FLEXIS, scoping to utilize NH_3 as a carbon-free energy source. They have successfully developed the world's inaugural demonstrator, wherein NH_3 is produced from renewable electricity, stored in a reservoir, and subsequently employed to generate additional electricity [19]. Another example is the ARENA project, which the European Union sponsors, aiming to advance the development of novel materials for a flexible and economically viable power-to-NH_3-to-usage value chain. This encompasses solid oxide electrolyzer cells, catalysts, absorbents, and membrane reactors [20]. A pioneering test engine trial utilizing NH_3 as fuel (for ships) was conducted by MAN Energy Solutions at its Research Centre Copenhagen (RCC) with positive results [21]. The objective of the test was to design and construct a complete two-stroke NH_3 marine engine, representing a noteworthy achievement in the company's endeavors in research and development [21]. Due to the engine's intrinsically poisonous properties, it was imperative to include safety measures, such as constructing a specialized cold chamber to confine NH_3 vapor in case of a potential leakage [21]. The engine's design incorporates many features from the company's dual-fuel portfolio, including double-walled piping and system ventilation. The company intends to conduct additional testing on many factors, including heat release, ignition, safety, pilot-oil energy portion, NOx emissions, and N_2O emissions. The company expects to complete its first NH_3 engine by 2026, operating on a commercial vessel [21].

Table 1. Comparison of alternative marine fuels [18].

Energy Source	Fossil (without CCs)					Bio	Renewable (C)		
Fuel	**HFO + Scrubber**	**Low Sulfur Fuels**	**LNG**	**Methanol**	**LPG**	**HVO (Advanced Biodiesel)**	**NH_3**	**H_2**	**Fully Electric**
High-priority parameters									
Energy density	5	5	4	4	4	5	3	2	1
Technological maturity	4	4	4	3	3	5	2	2	1
Local emissions	2	2	4	4	4	2	3	5	5
GHG emissions	1	1	(B)	2	2	4	5	5	5
Energy cost	5	4	5	3	4	2	1	1	(D)
Capital cost	4	5	4	4	4	5	4	1	5
Converter storage	5	5	3	4	4	5	4	1	1
Bunkering availability	5	5	4	3	3	2	2	1	2
Commercial readiness (A)	5	5	5	4	4	3	2	1	(E)
Other key parameters									
Flammability	5	5	5	3	5	5	4	1	5
Toxicity	5	5	5	3	5	5	1	5	5
Regulations and guidelines	5	5	5	4	3	5	3	1	4
Global production capacity and locations	5	5	5	4	4	2	3	3	1

(A) It considers the technology maturity and fuel availability. (B) GHG benefits of liquefied natural gas (LNG), methanol, and liquefied petroleum gas (LPG) will rise in direct proportion to the amount of bio or synthetic energy carrier use as a drop in fuel. (C) The NH_3, H_2, and fully electric results were only shown for renewable energy sources because they are the only long-term solution that could help reduce carbon emissions in shipping. The results will be detrimental if fossil fuels are used for production without carbon capture and storage (CCS). (D) Large regional differences. (E) Needs to be looked at case by case, not applicable for deep-sea shipping. HFO (hydrofluoroolefin), CCS, and HVO (hydrotreated vegetable oil). 5 = excellent, 4 = good, 3 = fair, 2 = poor, and 1 = bad.

Ongoing efforts are also being made with four-stroke engines [22] that can be fueled by NH_3. The Wärtsilä engine's modular design gives ship owners and operators a high degree of flexibility, allowing them to optimize their operations while reducing emissions. The system can use fuel sources such as diesel, LNG, gas, or liquid biofuels with a carbon-neutral impact [23]. Furthermore, it can be enhanced to accommodate forthcoming carbon-free fuels as they become accessible. The engine above represents the inaugural utilization of NH_3 as a fuel within the Wärtsilä engine lineup. The engine complies with IMO Tier III standards (it gives an overview of the rules that govern NOx emissions and talks about ways to control them, the money involved, and the problems that affect the business as a whole) when utilized in conjunction with natural gas and diesel fuels, provided that it is equipped with the Wärtsilä NOx Reducer emissions abatement system [23]. The system provides extended durations of operation without the need for maintenance and allows for dry-docking plans, with a time between overhauls (TBO) reaching a maximum of 32,000 h [23]. The engine is equipped with a very durable and effective turbocharging mechanism, a self-adaptive proportional, integral, derivative (PID) control system, and the ability to make optional modifications to accommodate extreme cold or hot climates [23].

Azane Fuel Solutions, a Norwegian NH_3 bunkering business, is designing a zero-emission bunker vessel and working with US-based Amogy to test its NH_3-to-power technology. The alliance seeks to supply ships worldwide with zero-emission NH_3 [24]. Amogy Inc. has passed technological verification with Lloyd's Register, a primary maritime and offshore classification and compliance services provider. The procedure assesses new technologies' maturity and hazards. Lloyd's Register approved Amogy's NH_3-to-power system (NH_3 feed, reactor module, adsorber module, fuel cell module, air, and combustion exhaust), a significant milestone for maritime use [25].

On the other hand, Guangzhou Automobile Group (GAC) from China has just unveiled a novel internal combustion engine that runs on NH_3 and is employed in the shipping and trucking industries. This novel method signifies a distinct endeavor to investigate alternate propulsion technologies beyond traditional ICE systems while not fully transitioning to battery electric vehicles (BEVs). The company's utilization of NH_3 in automotive applications has garnered attention and showcased its dedication to environmentally friendly alternatives worldwide [26].

As an H_2 carrier, NH_3 exhibits promising potential for achieving carbon neutrality in engines. However, it is important to acknowledge several limitations associated with its utilization, such as its relatively low laminar burning, its tendency to produce significant nitrogen oxide emissions, and the safety issues related to transporting and storing NH_3, among others. Therefore, this article comprehensively analyzes the accomplishments and issues associated with using NH_3 as a sustainable marine fuel. Moreover, this study aims to enhance the understanding of NH_3 viability as a substitute fuel and encourage investigation and development endeavors to overcome the obstacles that have been highlighted.

2. The Shipping Industry's Current Challenges

The manufacturing industry, technical advancements, and customer preferences have all contributed to the emergence of several challenges in international shipping, including taxing situations, supply chain disruptions, the impacts of political and market fluctuations, maintenance requirements, and, recently, increasing fuel expenses and environmental concerns [27]. International shipping ambitions have increased with the IMO's GHG Strategy revision in 2023, where the new targets are a 20% reduction in emissions by 2030, 70% by 2040 (relative to 2008 levels), and net-zero emissions by 2050. From 2024, the EU will include shipping in its Emission Trading Scheme (EU ETS) and demand well-to-wake GHG emissions (Fuel EU Maritime) from 2025 [28]. Figure 1 illustrates the temporal progression of CO_2 emissions from global maritime transportation, spanning 2000 to 2022. The graph illustrates the IMO revision of its greenhouse gas strategy in 2023, shown by the orange line. It also presents a prospective scenario with an annual growth rate of 1.675% in emissions, depicted by the gray line [29].

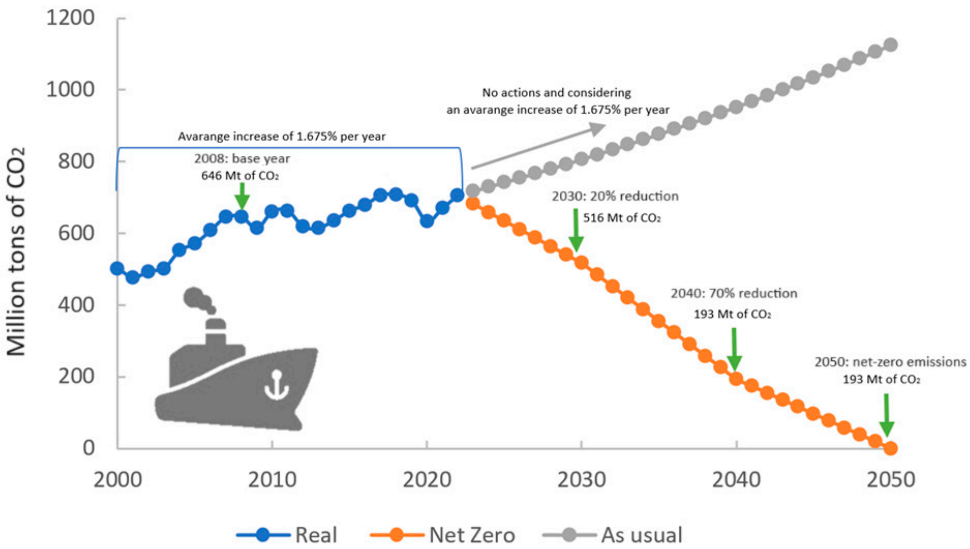

Figure 1. International shipping and future scenarios [28,29].

Alternative fuels exhibit the potential to serve as fuel sources that can effectively address the environmental issues associated with the combustion of fossil fuels [30]. There are now 92,776 operational ships, with around 0.58% (535) utilizing alternative fuels, including LNG, LPG, methanol, and H_2 [31]. Regrettably, the official order book does not currently include ships fueled by NH_3. Nevertheless, there exist multiple demonstration projects. Table 2 presents data on the current fleet of ships utilizing alternative fuels, as well as the number of ships that have been commissioned for future deployment.

Table 2. Growth of alternative fuel ships [31].

	LNG		LPG		CH_3OH		H_2		Ships with Scrubbers
Year	**In Operation**	**On Order**	**In Operation**	**On Order**	**In Operation**	**On Order**	**In Operation**	**On Order**	
2015	63	0	0	0	1	0	0	0	243
2016	82	0	0	0	8	0	0	0	312
2017	99	0	0	0	8	0	0	0	387
2018	124	0	0	0	8	0	0	0	740
2019	157	0	0	0	12	0	0	0	3178
2020	186	0	3	0	12	0	0	0	4362
2021	247	0	21	0	15	0	0	0	4581
2022	355	0	52	0	24	0	0	0	4807
2023	431	110	74	40	28	2	2	5	5095
2024	431	290	74	55	28	33	TBD	TBD	5230
2025	431	431	74	76	28	76	TBD	TBD	5246
2026	431	504	74	95	28	137	TBD	TBD	TBD
2027	431	534	74	99	28	172	TBD	TBD	TBD
2028	431	539	TBD	TBD	28	176	TBD	TBD	TBD

TBD = to be defined.

Furthermore, the data showcase the number of vessels equipped with scrubbers, which accounts for 5.65% of the total number of ships now in operation [31]. Scrubbers function as facilities for CCS. The operational feasibility of implementing scrubbers on a big container vessel can be achieved by incorporating a CO_2 storage capacity of 4000 m^3 on board. This setup allows for the dumping of CO_2 twice during each trip from Asia to Europe, resulting in an annual capture rate of 70% of the emitted CO_2. If the rise in energy consumption associated with the process of capturing remains below 15% and if the expenses related to unloading, transporting, and securely storing do not exceed USD 40 per metric ton, the implementation of onboard CCS may present a viable and economically competitive solution for achieving decarbonization objectives [28].

The Maritime Forecast to 2050 highlights slow progress in the decarbonization of the shipping industry [28]. However, IMO's updated greenhouse gas strategy and EU ETS are expected to expedite the pursuit of net-zero emissions objectives. The necessity of collaboration arises in the context of future fuel supply, infrastructure, and investment decisions. According to the report, by 2030, the maritime industry will need 30–40% of the global carbon-neutral fuel supply [28]. This undertaking is expected to be challenging due to competing sectors vying for the same resources. Therefore, it is necessary to consider energy efficiency for operational energy-saving techniques, including speed reduction and route optimization, where artificial intelligence on board vessels and fleets can produce substantial operating savings. The decarbonization of transportation with liquefied H_2 and NH_3 appears promising. However, decarbonization will be costly for stakeholders, shipowners, and governments; so, additional costs may require new contractual arrangements to reach consumers along the value chain. Therefore, the influence of regulatory change and stakeholder pressure will significantly affect the parameters that define commercial operations, underscoring the importance of making prudent decisions with long-term implications [28].

2.1. Ongoing Projects and Companies Developing Technology

The collaborative research framework aims to investigate the safety evaluations of ships using NH_3 fuel, the bunkering process, the fuel specifications, and the resulting net CO_2 emissions. This endeavor will include the participation of NH_3 producers, international organizations, port authorities, and regulators. Table 3 describes some advancements in recent years [32].

Table 3. Ammonia as a maritime fuel—recent advancements.

Players	Project	Description	Year	Ref.
Azane	Zero-emission NH_3 bunker vessels	It has successfully created an innovative bunker vessel design that produces zero emissions.	2023	[24]
Amogy Inc.	Successful completion of technology verification	NH_3-to-power system for maritime uses.	2023	[25]
	NH_3-powered semi-truck	Amogy Inc. effectively conducted trials on its inaugural NH_3-powered semi-truck, which produced zero emissions, by integrating its proprietary technology into John Deere tractors and drones.	2023	[33]
GAC	Trumpchi E9 NH_3	The first passenger vehicle in its class to utilize NH_3.	2023	[26]
ABS	Technology trends	ABS, a major technology company, has built a base for the marine industry to adapt to the digital world and switch to sustainable operations, leading to a net-zero carbon path and a sustainable future.	2022	[34]
Navigator Gas	AiP	DNV, a classification society, has given Navigator Holdings Ltd. preliminary approval for its company, Navigator Gas LLC, to build a gas carrier that runs on NH_3. DNV and the Norwegian Maritime Authority approved the design based on the unique features code (GF NH_3).	2021	[35]
Anglo American	Biodiesel as a maritime fuel	Anglo American tested sustainable biodiesel on a hired capesize ship from Singapore to South Africa. Biodiesel from Singapore's food and beverage waste cooking oil reduces CO_2 emissions by 5% compared to 100% traditional marine fuel.	2021	[36]
Class NK		ClassNK is a ship classification society. The society is expanding its ship-related activities and services to protect human life, property, and the marine environment at sea.	2023	[37]
DVN	Maritime Cyber Priority 2023	The new global report, Marine Cyber Priority: Staying Secure in the Era of Connectedness by DNV, examines shifting marine cyber security attitudes and practices.	2023	[38]
	Maritime Forecast 2050	It gives maritime stakeholders valuable insights into how to make decisions in their decarbonization journey.	2023	[39]
	Transport transition	DNV forecasts primary fuel, electrical, and infrastructure changes in marine, aircraft, and road transport during the next 30 years. Even though 78% of road travel is electrified, these sectors account for 25% of emissions and will climb to 30% by 2050.	2023	[40]
Equinor		The corporation is investing in offshore wind and rebuilding its shipping fleet. Dual-fuel LPG and LNG propulsion are being introduced aboard LPG carriers, shuttle tankers, and Aframax/LR2s.	2023	[41]

Table 3. *Cont.*

Players	Project	Description	Year	Ref.
Global Maritime Forum	What now, from ambition to action	The 2023 Global Maritime Forum Annual Summit brings together leading maritime voices and others to address the possibilities and challenges that will define global seaborne trade.	2023	[42]
ITOCHU	NH_3-fueled ships	Develop propulsion systems and hulls to introduce NH_3-fueled ships under Japan's leadership by 2028.	2021	[43]
	Bunkering safety for NH_3-fueled ships	ITOCHU promotes NH_3-powered container ships.	2023	[44]
K Line, Itochu, NS United	NH_3-powered ship project	NEDO, Kaiun Kaisha, and Mitsui E&S Machinery will collaborate with the players to introduce NH_3-powered vessels by 2028, using NH_3 as a marine fuel for propulsion systems and hulls.	2021	[45]
MAN Energy Solutions	Dual-fuel two-stroke engines	MAN Energy Solutions is developing research engines based on highly adaptable combustion engines for LNG, LPG, ethane, methanol, and carbon-free NH_3 for the marine energy transition and significant ship propulsion.	2023	[46]
Nihon Shipyard	Co-Firing test using a cutting-edge NH_3-fueled engine	NYK, Japan Engine Corporation, IHI Power Systems, and Nihon Shipyard launched the project in October 2021 to create naval vessels using local NH_3-fueled engines. IHI Power Systems tested a coastal vessel 280 mm bore four-stroke NH_3 marine engine in April 2023. All demonstration equipment did not leak NH_3 during operation or shutdown, and dinitrogen monoxide and unburnt NH_3 emissions were almost nil.	2023	[47]
Nordic Innovation	NoGAPS	The study concludes that technical and regulatory permissions for an NH_3-powered vessel do not prevent the launch of M/S NoGAPS. Green H_2 can produce NH_3, a zero-emission fuel. Creating and convincing investors and operators of a business strategy is the most complex challenge.	2021	[48]
Ube Industries		Ube Industries, Japan's biggest NH_3 manufacturer, will study maritime NH_3 fuel supply and onshore facilities.	2021	[49]
Uyeno Transtech	Korean NH_3 bunker vessel design	Japanese cooperation and the Korean Register's Approval in Principle for an NH_3 bunkering vessel are helping the Korean shipping sector accept NH_3 as a marine fuel.	2020	[50]
Vopak Singapore		Vopak Singapore may extend its NH_3 infrastructure for low-carbon electricity and bunker fuel.	2022	[51]

Table 3. *Cont.*

Players	Project	Description	Year	Ref.
Wärtsilä	First NH_3 conversion project	Wärtsilä and Norwegian ship owner Eidesvik Offshore ASA have agreed to convert an offshore supply vessel (OSV) to an NH_3-fueled combustion engine. The world's first NH_3-only project seeks to operate with minimal ignition fuel. The upgrade will allow the vessel to use 70% NH_3, lowering CO_2 emissions. Both companies support industrial decarbonization. Since 2003, Eidesvik has supported ecological technologies by using LNG fuel in its fleet. The EU-funded ShipFC project will equip the Viking Energy platform vessel with a 2 MW green NH_3 fuel cell.	2021	[52]
	NH_3 2–4	Wärtsilä leads EU-funded NH_3 2- and 4-stroke engines.	2022	[53]
Jera, Mou, Yara		Yara Clean NH_3 and Bunker Holding Group inked an MOU to boost the maritime fuel market for clean NH_3.	2023	[54]

2.2. Regulatory Landscape and Safety Concerns

Highlighting the significance of innovation and caution is crucial in addressing the risks of NH_3 as a marine fuel. The toxicity of the substance necessitates the implementation of safety and health regulations. In the maritime setting, distinct difficulties arise, such as restricted space and the absence of external assistance. To ensure safety, it is necessary to conduct thorough risk assessments that identify potential leak points and failure scenarios. It is necessary to establish exposure limits and alarm systems by considering the concentrations of toxicity and flammability. Strategically positioning gas detectors in hazardous areas is necessary to prevent prolonged and immediate exposure. Safety measures, including fuel preparation areas and tank connection spaces within the machinery space, are essential for safety [55].

Another concern with NH_3 is corrosion since it causes financial and safety risks. Liquefied NH_3 is typically stored at ambient temperature, at −33 °C under atmospheric pressure, or at intermediate temperatures and pressures. Tanks for anhydrous NH_3 storage are designed to meet specific design codes, such as API 620 R or BS 7777 [56]. Standard materials for atmospheric NH_3 tanks are low-temperature certified carbon manganese steel, impact tested at or near −40 °C. The susceptibility to stress corrosion cracking increases with steel yield strength, with materials with a minimum yield strength (SMYS) between 290 and 360 MPa often used. Compatibility between the weld and base material is crucial for resistance against NH_3 stress corrosion cracking [57].

3. NH_3 Combustion

NH_3 exhibits a notable power-to-fuel-to-power (PFP) efficiency, an extensive distribution infrastructure that is now operational, a high-octane rating ranging from 110 to 130, and a narrow flammability range, reducing the likelihood of explosion hazards [58]. Nonetheless, the process of NH_3 combustion poses several obstacles, including (1) its limited reactivity in combustion, (2) a relatively low LBV, and (3) the production of significant levels of NOx. Several studies have tackled the primary issues associated with the mentioned disadvantages [59]. The following section describes the fundamental characteristics of NH_3 flames and combustion chemistry necessary to comprehend NH_3 combustion in various applications and advance NH_3 combustion technology.

The incomplete combustion of ammonia is a significant environmental concern. This process generates NOx, which is 33 times more environmentally harmful than CO_2 [60].

Additionally, it produces nitrous oxide (N_2O), a greenhouse gas that is 273 times more potent than CO_2 [61]. These pollutants severely threaten the environment and public health, requiring immediate attention. The presence of NO and N_2O in the atmosphere can lead to various environmental issues, such as air pollution, ozone depletion, and the exacerbation of climate change. Addressing this problem is crucial to safeguarding our planet's and communities' health [62]. These gases influence tropospheric ozone and contribute to the formation of pollutants and acid rain [63].

NOx can be formed in combustion through three distinct gas-phase reaction mechanisms: thermal-NOx, fuel-NOX, and prompt-NOx [64]. Thermal-NOx is attributed to a series of oxidation reactions known as the 'Zeldovich mechanism', occurring at higher temperatures (>1300 °C). This process is depicted in Equations (1) and (2).

$$N_2 + O \leftrightarrow NO + N \tag{1}$$

$$O_2 + N \leftrightarrow NO + O \tag{2}$$

When a fuel-rich environment exists, the following reaction also occurs:

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

The precise temperature range at which this oxidation occurs remains a subject of ongoing debate in the literature. The oxidation rate exhibits an almost exponential relationship with the increase in peak flame temperature [65].

Fuel-NOx production is related to volatile-N, and the heterogeneous phase char-N constitutes the primary source of fuel-NOx. Equation (4) provides a simplified equation [66].

$$NH_3 + OH, +NH_2, HNO \leftrightarrow NO \tag{4}$$

The prompt-NOx reaction occurs by CHi-radicals with atmospheric nitrogen in the flame. However, ammonia has no carbon, and so this radical will form when blended with fossil fuels [64,67]. J. Miller and C. T. Bowman [68] proposed a nitrogen combustion mechanism. They attempted to synthesize voluminous data into a consistent and coherent mechanism by which nitrogen compounds react in combustion systems under typical conditions. Even though the reaction mechanism has been validated against experimental data over a relatively wide range of temperatures, pressures, stoichiometries, and fuel types, caution should be exercised when applying the mechanism outside the range of conditions considered. Current advancements in NH_3 combustion have been reviewed, including the reaction, NOx generation mechanisms, mitigation strategies, and how NH_3 addition impacts particulate formation.

For example, Yu Song et al. [69] conducted NH_3 oxidation experiments at high pressures (30 bar and 100 bar) and temperatures spanning from 450 to 925 K under oxidizing and stoichiometric conditions. Under stoichiometric conditions, NH_3 oxidation was sluggish in the investigated temperature range. Under oxidizing conditions, the onset temperature of the reaction was 850–875 K at 30 bars and 800 K at 100 bars, with NH_3 being completely consumed at 875 K. The products of the reaction were N_2 and N_2O, while the concentrations of NO and NO_2 were below the detection limit, even under oxidizing conditions. The data were interpreted using a comprehensive chemical kinetic model. On the other hand, Junichiro Otomo et al. [70] strengthened the Yu Song model by including relevant elementary components like NH_2, HNO, and N_2H_2. Furthermore, the model was used to study the combustion of NH_3/H_2.

N_2O emissions from NH_3 combustion systems are a significant obstacle to the carbon-neutral advantages of using NH_3 as a fuel and hinder its direct application for reducing GHG emissions. The presence of N_2O can be effectively eliminated by increasing the flame temperature or concentration of H atoms. However, the inefficient and incomplete combustion of NH_3 due to factors such as heat dissipation from the flame can lead to increased N_2O emissions [71]. To minimize these emissions, the combustion of NH_3 can be improved by reducing heat dissipation from the flame, co-burning it with fuels with higher heat release rates, and utilizing high-pressure combustion [71]. The success of these measures highly depends on the design of the ICE.

4. ICE Development

Internal combustion engines play a vital role in the power generating and transportation sectors, and optimizing their performance and efficiency is of utmost importance in the pursuit of emission reduction [72]. The fuel supply in engines can be accomplished using injection at the intake manifold or directly into the combustion chamber, a configuration commonly referred to as direct injection (DI) engines [73]. ICEs can be classified into two main categories: spark ignition (SI) and compression ignition (CI). SI engines employ spark plugs as a means of initiating combustion in gasoline [74]. In contrast, CI engines utilize diesel fuel with a notably elevated compression ratio, enabling autoignition during the compression stroke. Compared to SI engines, CI engines exhibit superior thermal efficiency and enhance torque and power production [74]. Nevertheless, diesel engines are associated with elevated NOx and particulate matter emissions, mainly attributed to the increased carbon content in diesel fuel and high combustion temperatures [73]. CI engines exhibit enhanced combustion efficiency and superior performance compared to SI engines [74].

Regrettably, the current market does not offer any commercially available NH_3-powered engines. Nevertheless, there are records of using NH_3 as a fuel for buses. In a paper published in 1945 by Emmeric Kroch, the widespread devastation of oil resources promoted the exploration of other fuel sources, such as NH_3 [75]. Emmeric Kroch concluded that over a year, investigations had been conducted on the viability of utilizing anhydrous NH_3 and coal gas as alternative fuels for internal combustion engines. These investigations revealed promising outcomes, mainly when these fuels are appropriately implemented. When used correctly, this fuel does not result in power loss, corrosion, or elevated levels of lubricating oil consumption. Substituting coal gas with alternative gases or liquids, such as H_2 derived from electric cells and nitrogen sourced from atmospheric air, is viable [76].

Following the conclusion of World War II and the restoration of the oil industry, there was a decline in the interest in NH_3 as an energy source because of its higher cost than fossil fuels, a characteristic that remains true today. However, the need to decarbonize the global economy has recently fueled NH_3's resurgence [73].

Historical documents dating back to the early 1800s prove that NH_3 has been a transportation fuel for over two centuries, as depicted in Figure 2 [30]. Initially, NH_3 was predominantly utilized as a source of energy for compact locomotives and trams [30]. Over time, the technique advanced to incorporate privately owned automobiles fueled by NH_3. An exemplary instance occurred during the early to mid-1900s when NASA's X-15 program employed NH_3 as propulsion technology. Although NH_3 has a lengthy historical background, its utilization as a fuel for transportation has not achieved widespread acceptance.

Nevertheless, recent advancements indicate a potential shift in this situation [30]. The GAC company introduced the inaugural NH_3-powered engine for passenger cars in late 2023. The engine, created by the group's internal research and development center, can achieve consistent fuel ignition with a power output 120 kW and a carbon reduction rate of 90% [33]. This innovation presents a highly effective, dependable, and environmentally friendly gasoline substitute for the automotive sector.

Furthermore, NH_3 is not restricted solely to passenger cars. The maritime sector is investigating the utilization of NH_3 as a fuel source. In 2023, Amogy introduced its NH_3-to-power system specifically designed for maritime applications. The system successfully underwent technology verification conducted by Lloyd's [25]. This achievement is highly noteworthy due to the substantial impact of the maritime industry on global emissions. Employing NH_3 as a fuel has the potential to substantially diminish the industry's carbon emissions and make a valuable contribution to the worldwide endeavor to address climate change.

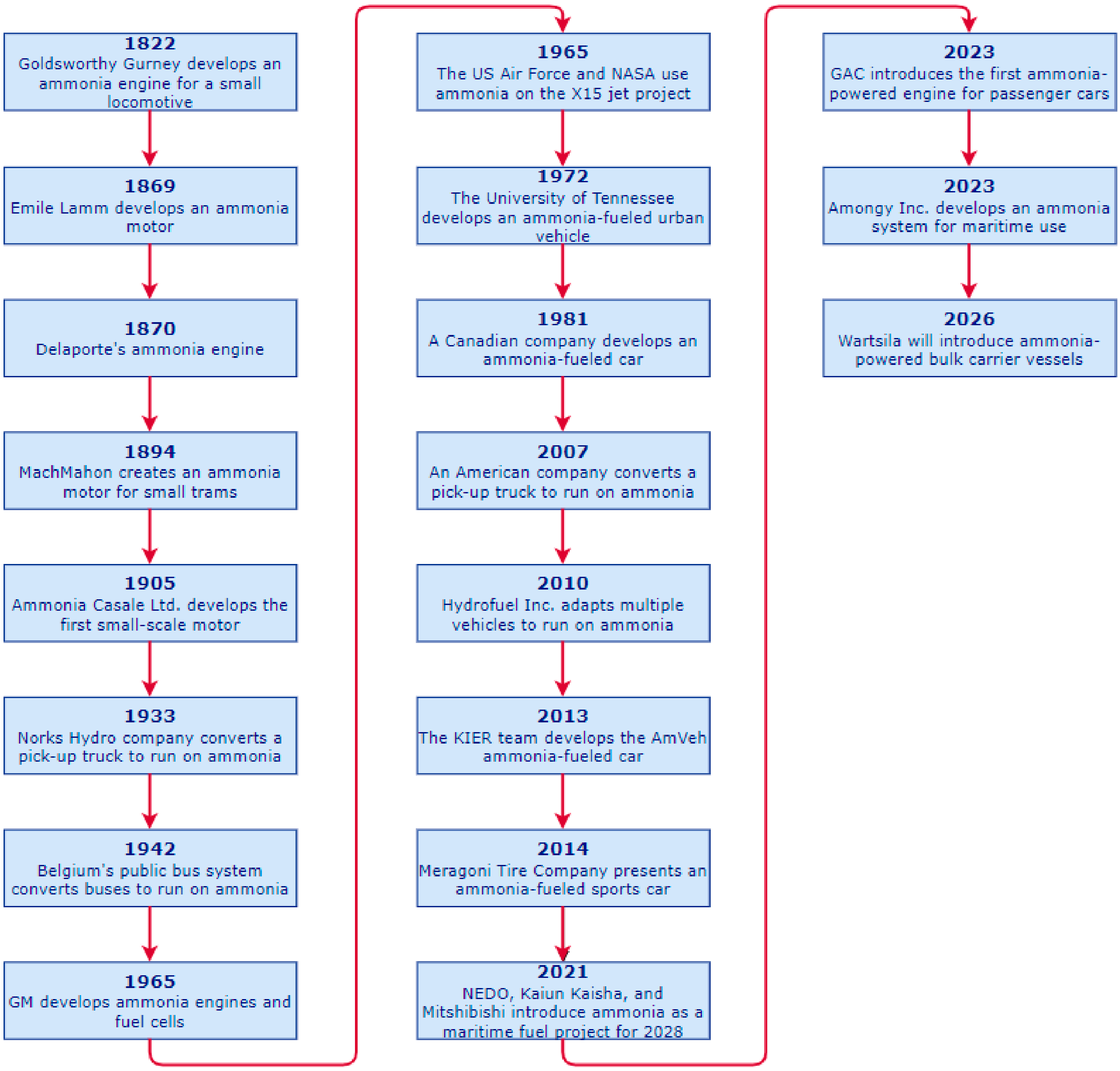

Figure 2. NH_3 in the transportation sector [30].

This section will discuss several key aspects related to ICEs fueled by NH_3. Firstly, it will explore the existing strategies to mitigate NOx and N_2O emissions. Secondly, it will examine the advancements in NH_3 blending with other fuels to mitigate challenges such as low combustion reactivity and low laminar burning velocity. Thirdly, it will delve into waste heat recovery strategies. Lastly, it will provide an overview of the ongoing projects and companies developing this technology.

4.1. Techniques to Reduce NOx

4.1.1. Thermal DeNOx

Thermal DeNOx reduces NO [75] at temperatures lower than 700 °C [77]. It has been used effectively in various boilers and furnaces since 1975 [77]. However, it is still a subject of study because of the significant temperature limitation.

4.1.2. Blending DeNOx

Combining NH_3 with a second reducing agent, such as H_2 or CO, can also reduce NOx. However, the process is unsuitable for many applications due to its temperature sensitivity [77,78]. Furthermore, in the case of sulfur-containing flue gases, there is also the issue of any remaining NH_3 combining with SO_3 downstream of the reaction zone to generate NH_4 and HSO_4, causing fouling [79].

4.1.3. Homogeneous Charge Compression Ignition (HCCI)

The autoignition phenomenon occurs at a specific temperature and pressure. HCCI utilizes the autoignition principle as an alternative to traditional SI and CI engine technologies [77]. Unlike SI and CI engines, HCCI combustion does not rely on a spark plug or direct fuel injection near the Top Dead Center (TDC) to initiate the ignition process.

In HCCI engines, the fuel and air mixture is homogeneously premixed throughout the cylinder, and the autoignition of the mixture occurs due to the combined effects of compression, temperature, and pressure within the cylinder. This unique combustion process allows for leaner fuel–air mixtures, which can significantly improve fuel economy [80].

One key advantage of HCCI combustion is the lower combustion temperatures compared to SI and CI engines. This reduced temperature range significantly decreases the formation of NOx. The ability to operate with lean mixtures and achieve lower NOx emissions makes HCCI an attractive option for meeting increasingly stringent emissions regulations, considering conventional fuels. Furthermore, the homogeneous mixture preparation in HCCI engines can lead to efficient and complete combustion, further enhancing fuel efficiency. This contrasts the heterogeneous mixture distribution in traditional SI and CI engines, where the fuel–air mixture can be non-uniform, leading to incomplete combustion and increased emissions.

Despite the promising potential of HCCI technology, some challenges need to be addressed. Precise control of the autoignition timing and maintaining a stable combustion process across various operating conditions can be challenging. Researchers are actively exploring multiple strategies, such as advanced engine control systems, alternative fuel formulations, and innovative engine designs, to overcome these hurdles and unlock the full potential of HCCI combustion in modern internal combustion engines.

For example, T. Karthikeya et al. [81] simulated an HCCI engine using n-dodecane. The goal was to reduce NOx emissions. They used swirl motion to improve the convective heat transfer inside the combustion chamber and helped reduce NOx emissions. The findings indicate increased heat transfer rates to the wall with swirl ratios of four and three. The pressure was also increased from 1 to 2 bars, resulting in a heat transfer increase. The maximum NOx reduction was 30% at a swirl ratio of four.

On the other hand, Chenxu Wang et al. [82] studied HCCI running in an ammonia engine. They suggested replacing nitrogen with argon in the fuel–air mixture to improve important factors like the ignition delay time, efficiency, and power. The study was performed with a compression ratio of 19 and an excess oxygen ratio of 3.0, considering a mixture of 79% argon and 21% oxygen. The outputs showed a decrease in the ignition delay time from 700 milliseconds for pure ammonia to just 0.31 milliseconds under the optimized conditions. Efficiency increased from 65.1% to 78.2%, and the power increased by about 20%. However, the researchers also found higher NOx emissions. The higher temperatures during the combustion caused this increase in NOx. Therefore, further research is needed to find an optimal balance between the improved combustion characteristics and the elevated NOx emissions and unlock the full potential of ammonia as a cleaner and efficient fuel source. The findings of Chenxu Wang and his team represent a significant step forward in the ongoing efforts to develop sustainable and high-performance alternatives to traditional fossil fuels.

4.1.4. Premixed Charge Compression Ignition (PCCI)

PCCI introduces fuel early in the intake stroke to establish a homogeneous mixture before combustion [78]. However, PCCI often exhibits lower combustion efficiencies and limited operating ranges, despite its reduced NOx emissions. This is true for conventional fuels. However, this situation can change using ammonia, as in HCCI engines.

Lee and Song [83] conducted a numerical simulation study investigating a novel premixed–charged combustion strategy for ammonia-powered engines. The study was conducted in a simulation environment with a high compression ratio of 35:1 and an intake gas temperature suitable for the combustion of ammonia without the need for a secondary fuel. The proposed PCCI involved a two-stage injection approach during the compression stroke. First, a small pilot injection of ammonia (with an equivalence ratio, ϕ, ranging from 0.1 to 0.3) was used to form a homogeneous lean mixture within the cylinder. The autoignition of this lean mixture led to a gradual increase in the in-cylinder temperature and pressure, creating a favorable environment for the subsequent combustion of the leading ammonia charge.

The researchers found that the pilot injection quantity was crucial in determining the overall engine performance. Increasing the amount of the pilot injection resulted in elevated in-cylinder combustion temperatures. It enhanced the combustion efficiency of the leading ammonia spray, injected shortly after the start of combustion. This two-stage injection approach allowed for better control of the combustion process and improved the utilization of the ammonia fuel, making it a promising strategy for ammonia-powered engines. However, the peak temperature affects the amount of NO produced, which increases NO levels.

The simulation study provided valuable insights into developing an effective combustion strategy for ammonia engines, paving the way for further experimental investigations and system optimization. The ability to operate an engine solely on ammonia without a secondary fuel is a significant step towards adopting ammonia as a sustainable alternative fuel for transportation and power generation applications. However, another NO reduction method is required since the studied NOx reduction using PCCI does not apply to ammonia because the temperature influence significantly impacts NOx production.

4.1.5. Lean Engine Operation

It represents another viable method characterized by a higher intake pressure and smaller equivalence ratios. This technique incorporates boosting devices such as turbochargers or superchargers to maintain power output while employing a leaner air–fuel mixture for improved breathing. The exhaust gas recirculation (EGR) system has been observed to reduce NOx emissions from the engine significantly. According to Soheil et al. [84], the implementation of EGR at rates of 0.05, 0.1, and 0.15 has reduced the maximum NOx emissions by 16%, 31%, and 45%, respectively.

4.1.6. Scrubbing the Exhaust

Scrubbing the exhaust is usually performed with sodium hydroxide or hydrogen peroxide, producing nitric acid recovery. Sodium hydroxide is a standard NOx remediation method, but it can convert assimilated NOx into nitrites and nitrates, causing disposal issues. H_2 peroxide-containing scrubbers effectively remove NOx without contaminants, allowing commercial products like nitric acid recovery. H_2O_2 and nitric acid cleanse nitric oxide (NO) and nitrogen dioxide (NO_2) from industrial sources. The reactions are rapid at temperatures between 30 and 80 °C, requiring approximately 1.75 and 0.37 pounds of H_2 peroxide per pound of NO and NO_2, respectively [85], with the following reactions:

$$3NO_2 + H_2O \leftrightarrow 2HNO_3 + NO \quad (5)$$

$$2NO + HNO_3 + H_2O \rightarrow 3HNO_2 \quad (6)$$

$$HNO_2 + H_2O_2 \rightarrow H_2O \quad (7)$$

Including a scrubbing process implies having a storage tank for the H_2, peroxide, and nitric acid. These components are hazardous, and their storage in maritime transport must be evaluated.

4.1.7. Selective Non-Catalytic Reduction (SNCR)

This technology is a very efficient method for reducing emissions after combustion, and it is extensively utilized in industrial operations globally [86]. The SNCR method deliberately introduces an NH_3-based or urea-based reactant into the furnace at a designated point, where it undergoes a chemical reaction with NOx to produce nitrogen and water vapor [86,87].

SNCR has garnered significant adoption in power plants and several industrial sectors. Presently, the shipping industry is also embracing this technology as a means to adhere to progressively rigorous emissions laws. Retrofitting SNCR systems onto pre-existing ships is a viable and economically efficient approach to mitigating emissions [88]. Figure 3 depicts the efficacy of NOx reduction achieved by employing SNCR technology. There are two reagents present: NH_3 and urea. The indications in the shape of triangles represent NH_3, while the indicators in the shape of circles represent urea. Each of them is assessed in various sectors of the industry. Urea exhibits higher minimum and maximum efficiency levels than NH_3 in cement. However, NH_3 is employed in combusting hazardous waste and sludge rather than urea.

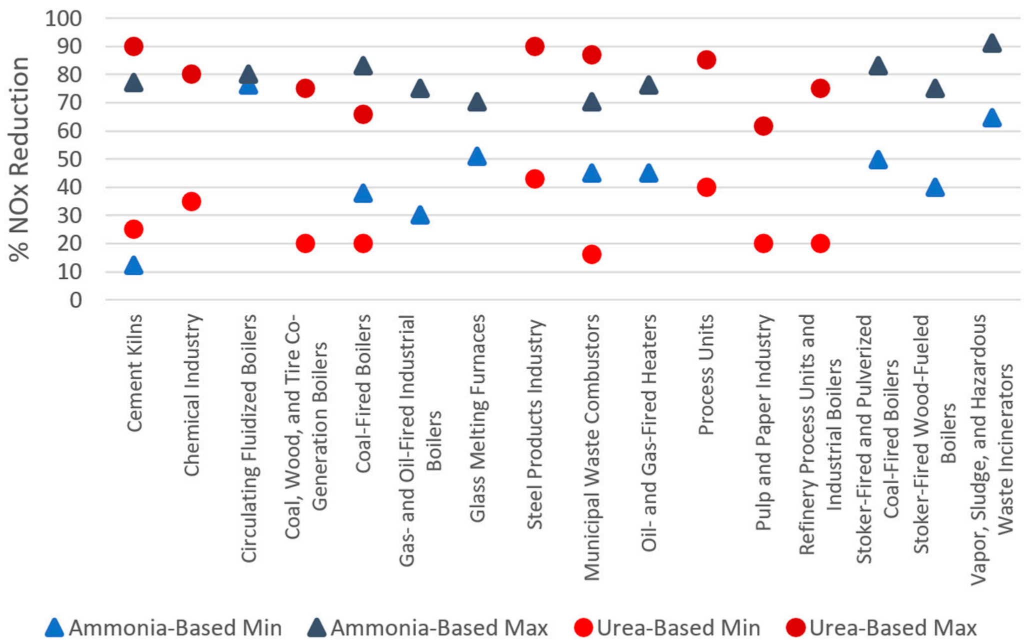

Figure 3. SNCR NOx reduction efficiency by industry and reagent type [86,89,90].

The entire SNCR reactions involving urea and NH_3 with NOx, which encompass both NO and NO_2, can be summarized as follows:

reactions with NH_3

$$2NO + 2NH_3 + \frac{1}{2}O_2 \rightarrow 2N_2 + 3H_2O \quad (8)$$

$$2NO_2 + 4NH_3 + O_2 \rightarrow 3N_2 + 6H_2O \quad (9)$$

reactions with urea

$$2NO + CO(NH_2)_2 + \frac{1}{2}O_2 \rightarrow 2N_2 + CO_2 + 2H_2O \quad (10)$$

$$2NO_2 + CO(NH_2)_2 + O_2 \rightarrow 3N_2 + 2CO_2 + 4H_2O \quad (11)$$

The NOx reduction reaction occurs within a defined temperature range for a chosen reagent. At lower temperatures, the reaction proceeds slowly due to sluggish reaction kinetics. On the other hand, at higher temperatures, the reagent undergoes oxidation, producing extra NOx. The ideal temperature range for NH_3 is between 870 and 1100 °C, with the most effective elimination often happening at 950 °C. The ideal temperature range for urea is between 900° and 1150 °C, with the highest elimination efficiency usually observed at 1010 °C [91,92].

One notable advantage of SNCR is its independence from catalyst use, alleviating the financial burden associated with catalyst procurement, installation, and upkeep. In contrast, the reagent is introduced directly into the exhaust gas flow, undergoing a chemical reaction with the NOx compounds to produce benign nitrogen and water vapor [88].

Nevertheless, some problems are closely linked to implementing SNCR technology. Various elements, such as the engine load, fuel quality, and ambient temperature, can influence the system's efficacy. Furthermore, storing and carrying the reagent on the ship is essential, which adds additional weight and complexity to the vessel [88]. Notwithstanding these obstacles, SNCR is progressively gaining traction as a solution to mitigate ship emissions. Given the ongoing demand on the shipping industry to mitigate its environmental footprint, SNCR is anticipated to be pivotal in attaining this objective.

4.2. Techniques to Reduce N_2O

N_2O is a highly influential greenhouse gas that contributes to both climate change and the depletion of the ozone layer [93]. Research has demonstrated that the generation of N_2O during NH_3 combustion is attributed to two primary reaction pathways [94]:

$$NH_2 + NO_2 \rightarrow N_2O + H_2O \quad (12)$$

$$NH + NO \rightarrow N_2O + H \quad (13)$$

The primary source of N_2O at low temperatures is the first pathway, while at higher temperatures, the second pathway becomes the main contributor. However, the N_2O produced by the second pathway is typically rapidly consumed through reactions with atomic H or thermal dissociation. Therefore, it is considered less concerning than the low-temperature pathway [94].

Selective Catalytic Reaction (SCR)

It is an up-and-coming technology for effectively managing and reducing N_2O emissions, and it is tested in nitric acid plants. SCR employs a catalyst to facilitate the decomposition of N_2O into nitrogen gas and oxygen gas [93]. This process exhibits high efficiency and cost-effectiveness when compared to alternative control technologies. For example, the injection strategy of NH_3 [89] and oxygen control [90] can be modified.

Fe-zeolites have been recognized as highly efficient catalysts for the decomposition of N_2O. Zeolites are crystalline aluminosilicates with distinct pore structures and large surface areas, rendering them highly suitable catalysts for various reactions. Fe-zeolites have been discovered to demonstrate a robust N_2O decomposition capability and exceptional stability across various operational circumstances [93].

In its simplest form, the catalytic decomposition of N_2O by NH_3 has been described as follows [95]:

$$N_2O + {}^{*} \rightarrow N_2 + {}^{*}\_O \quad (14)$$

$$2{}^{*}\_O + {}^{*} \rightarrow O_2 + 2{}^{*} \quad (15)$$

$$N_2O + {}^{*}\_O \rightarrow N_2 + O_2 + {}^{*} \quad (16)$$

When NH_3 is injected, the surface oxygen can also be removed as follows:

$$2NH_3 + 3^*\_O \rightarrow N_2 + 3H_2O + 3^* \quad (17)$$

During these reactions, O_2 is not formed. Therefore, N_2O is mainly converted by NH_3, with a proportion of $N_2O/NH_3 \approx 3/2$.

$$3N_2O + 2NH_3 \rightarrow 4N_2 + 3H_2O \quad (18)$$

This overall process involves the interaction between N_2O and NH_3 in the presence of a catalyst, typically a transition metal or a metal oxide. The catalyst plays a crucial role in facilitating the breakdown of the N_2O molecule, which is otherwise relatively stable under normal conditions. The process can be divided into several steps. First, the N_2O molecule adsorbs onto the catalyst's surface, interacting with the active sites. Concurrently, the NH_3 molecule also adsorbs on the catalyst surface, bringing the reactants into proximity. Next, the catalyst mediates the transfer of hydrogen atoms from the NH_3 molecule to the N_2O molecule, weakening the N-N and N-O bonds. This leads to the formation of an intermediate complex, which then undergoes further rearrangement and decomposition. The final step involves releasing the products, typically nitrogen gas and water. The catalyst is regenerated during the process and can continue to facilitate the reaction, allowing for the efficient decomposition of N_2O. Figure 4 depicts the SCR emission system, where the gases from the exhaust duct come to a particle filter and then to a device where NH3 is sprayed to promote the reactions in the zeolite catalyst.

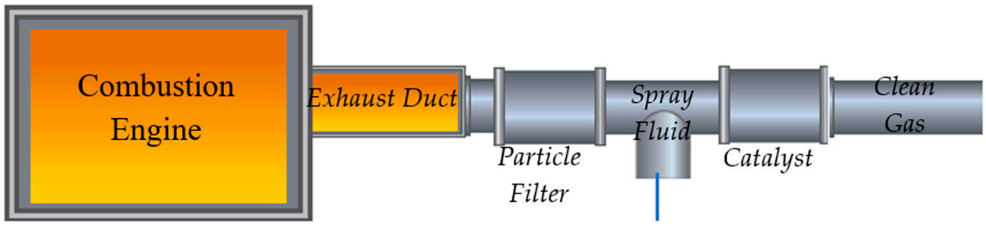

Figure 4. Selective catalytic reduction emission system [95].

4.3. NH_3 Blending with Other Fuels

It is known that NH_3 combustion has low reactivity, and to overcome the limited combustion reactivity, research has been conducted to determine the optimal conditions for NH_3 combustion. For example, Liang et al. propose an H_2 and NH_3 blend, hence the NH_3 combustion using reactivity stratification [96]. Kim et al. proposed impregnating with NH_3 to improve reactivity and other features [97].

According to Cardoso et al. [98], co-firing NH_3 with coal can reduce CO_2 emissions by up to 26% compared to using only coal as fuel. Cardoso contends that when the co-fire fraction of NH_3 is 10%, NOx emissions are the same as when only coal is used for firing. However, when the ratio increases from 20% to 80%, the NOx emissions gradually fall by up to 40%. This situation is because the placement of NH_3 injections significantly impacts NOx emissions, since injecting NH_3 at places further away from the bed surface results in higher concentrations of NOx. Undoubtedly, further research is necessary on the combustion of traditional fuel blended with NH_3 to comprehend and mitigate the production of NOx and enhance the reactivity of the process. Table 4 showcases several research endeavors in this domain.

In contrast to diesel oil, NH_3 has a very slow flame propagation. Its autoignition temperature is also considerably higher, at approximately 630 °C compared to diesel oil's 210 °C [109]. In addition to this disadvantage, according to Kirkeby, the engine for maritime transport must be designed to adapt to the typical performance peaks associated with acceleration. Therefore, the final fuel mixture would consist of approximately 95% NH_3 and 5% pilot fuel, such as marine gas oil [109].

Table 4. NH_3 combustion.

Description	Type	Blend	Ref
Combustion at different temperatures, O_2 equivalence ratios, and NH_3 co-combustion ratios.	Simulation	Char/NH_3	[99]
It describes the limits of turbulent flame propagation and the associated mechanism for solid particle cloud–NH_3–air co-combustion.	Experimental	Solid/NH_3	[100]
It stimulates the combustion of NH_3 with different carbon fuels.	Simulation	CH_4, C_2H_6, C_3H_8, and H_2	[101]
It asses the performance of a free-piston engine generator fueled by NH_3 and methane mixtures.	Experimental	CH_4/NH_3	[102]
It provides experimental and kinetic data for the combustion of Syngas/NH_3.	Experimental	Syngas/NH_3	[103]
It provides experimental data on LBV and an unsatisfactory activation energy (Ea) prediction.	Experimental	NH_3/H_2	[104]
It assesses the adiabatic flame temperature and reactivity of different blends.	Numerical method	$CH_4/H_2/NH_3$	[105]
It investigates the influence of H_2O on NH_3 combustion.	Simulation	H_2O/NH_3	[106]
This study examines how pure NH_3 burns in an optical spark ignition engine when multiple spark ignition spots exist.	Experimental	NH_3	[107]
It assesses the effects of swirl strength on the features of combustion of NH_3/methane.	Numerical method	CH_4/NH_3	[108]

MAN Energy Solutions is implementing dual-fuel retrofits on its MAN B&W low-speed engines, enabling ships to utilize carbon-neutral fuels and substantially reduce emissions. The engine portfolio's modular design enables various refit possibilities for different environmentally friendly fuels. Given that ships typically have a lifespan of approximately 25 years, the sector must undertake decarbonization efforts. MAN PrimeServ, the company's post-sales branch, has successfully carried out 16 conversions to alternative fuels, with the earliest one dating back to 2015. MAN Energy Solutions intends to provide many alternatives for retrofit conversion, encompassing LGN, ethane, LPG, and methanol variations. The company is developing a refit option that utilizes NH_3 as fuel. They aim to ensure vessels can adhere to their five-year docking schedules starting in the first quarter 2025 [110].

Wärtsilä is now working on the development of dual-fuel engines. A four-stroke engine running on NH_3 is Wärtsilä's first commercially available solution for environmentally friendly shipping operations. The Wärtsilä 25 engine platform, unveiled in September 2022, is a marine engine that operates at a moderate pace and has a modular structure. It is a four-stroke engine that can be upgraded and offers a high power output per cylinder. The engine is offered in diesel, dual-fuel LNG, and dual-fuel NH_3 variants. The solution includes the Wartsila NH_3 Release Mitigation System (WARMS), the AmmoniaPac fuel gas supply system, and the Wartsila NOx Reducer (NOR). These work together to treat exhaust gases effectively. The solution design prioritizes safety and efficiency, incorporating an automation system to optimize outcomes. The Wärtsilä 25 NH_3 System can decrease greenhouse gas emissions by more than 70% in comparison to a diesel solution of similar size. This allows it to fulfill the European Union's targets until 2050 and surpass the International Maritime Organization's target for 2040 [111].

N_2O and NH_3 Slipping

Minimizing NOx is an essential prerequisite for the sustainable functioning of NH_3 engines. The selective catalytic reduction process is extensively employed to transform NOx into benign nitrogen and water. Nevertheless, the SCR process can also produce unwanted by-products, specifically N_2O [112].

A significant obstacle in SCR technology is the regulation of NH_3 slip. NH_3 slip is where unreacted NH_3 escapes from the catalyst bed and undergoes reactions with other compounds in the exhaust gas, forming NOX and N_2O. Therefore, releasing NH_3 contributes to global warming as it leads to the formation of N_2O. Hence, producing N_2O through NH_3 slippage is a noteworthy environmental issue that demands attention [112].

It is essential to highlight that N_2O emissions resulting from NH_3 slip are only a concern when NH_3 escapes the SCR system. Therefore, the greenhouse gas effect of N_2O would not remain consistent throughout the entire range of vehicle operation. Nonetheless, the generation of N_2O through the chemical reaction between NOx and NH_3 over the SCR catalyst can happen at any point during the vehicle's operation [112]. Consequently, this process necessitates meticulous attention.

The goal of resolving NH_3 slip from an SCR catalyst is not just preventing NH_3 from escaping into the atmosphere but also achieving the highest possible selectivity of NH_3 oxidation to N_2. Optimizing the SCR process for the maximum reduction of NOx and minimal emission of harmful by-products necessitates a meticulous equilibrium between catalyst design, operating conditions, and system control. By tackling the difficulties associated with NH_3 slip, SCR technology can help diminish emissions from NH_3 engines and advance sustainable transportation.

4.4. Waste Heat Recovery Strategies

Waste heat recovery systems harness the thermal energy dissipated into the environment and convert it into usable electricity, eliminating the need for extra fuel use. Marine boats experience a significant loss of around 50% of their fuel energy to the surrounding environment. However, it is essential to note that this energy has poor quality characteristics owing to its low temperature and limited capacity for power generation. Efficient systems use low-temperature waste heat to achieve optimal performance [113].

The Rankine cycle, a thermodynamic cycle used for converting heat energy into mechanical work, is increasingly used as a waste heat recovery system in marine vessels due to the growing focus on energy efficiency and environmental sustainability. The cycle uses a working fluid to absorb residual heat from the ship's engines, which is then used to generate steam and electricity. This energy can then be used to operate the ship's systems, reducing reliance on diesel generators and conserving fuel resources [114].

One of the primary benefits of the Rankine cycle is its ability to recover waste heat even at lower temperatures, allowing even low-grade waste heat to be captured and transformed into electrical energy. It can be combined with other waste heat recovery mechanisms, such as exhaust gas boilers and heat exchangers, to optimize overall recovery, significantly reducing fuel consumption and emissions [115].

However, the Rankine cycle has some challenges, such as the need for significant physical space and costs for installation and maintenance. Additionally, the system's performance may be influenced by other parameters, such as the working fluid's characteristics and the temperature of the waste heat. Despite these challenges, the Rankine cycle has promising potential for waste heat recovery in maritime applications, offering substantial fuel savings and emissions reductions [115].

The Kalina cycle is a technological innovation designed for waste heat recovery in maritime vessels. The underlying principle of this technology is rooted in a thermodynamic cycle that employs a blend of NH_3 and water as the operational medium. The purpose of the cycle is to efficiently transform the waste heat generated by the ship's engines into energy that can be effectively used [116]. Figure 5 depicts the Kaline cycle. The process begins with a mixture of ammonia and water entering the heat recovery unit. This mixture is then sent to the vapor generator, producing a concentrated, high-pressure, and high-temperature ammonia vapor. The concentrated ammonia vapor is then further heated in the superheater with the ICE exhaust gases, which increases its temperature. This superheated vapor is then sent to the turbine, which expands, transforming the available thermal energy into mechanical energy. The spinning turbine is coupled to a generator, which converts this mechanical energy into electricity. After passing through the turbine, the low-temperature and low-pressure ammonia vapor enters the absorber. The weak and robust solution streams are mixed at a low temperature in the absorber, resulting in a concentrated solution. This concentrated solution is then pumped back to the vapor generator, completing the cycle [116].

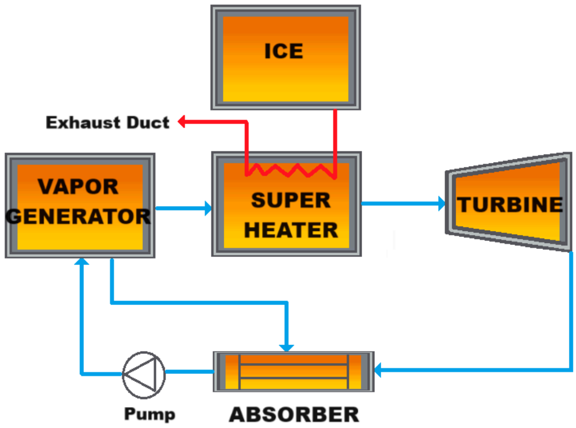

Figure 5. Kalina cycle [116,117].

The use of the Kalina cycle has considerable potential as a technique for waste heat recovery in maritime applications, owing to its superior efficiency compared to other methodologies. This phenomenon may be attributed to the NH_3-water combination's lower boiling point than pure water, resulting in its ability to absorb more heat at a relatively lower temperature. Furthermore, it should be noted that the cycle above can effectively harness waste heat from a broader spectrum of sources [118].

Ships produce substantial waste heat that is often discharged into the surrounding environment. The use of the Kalina cycle in maritime settings is now in its nascent phase. However, it holds significant promise for transforming the recovery and utilization of waste heat. With the progression of research and technological advancements, the Kalina cycle will probably be widely used as a conventional component aboard many vessels in the forthcoming years [118].

The Kalina and Rankine cycles are well-known technologies that can help the maritime industry. The purpose of these cycles is to recover waste heat. So, they can also recover heat in NH_3-powered ships, reducing fuel use and pollution. These cycles can help the shipping industry find a long-term, environmentally friendly answer. As technology improves, they will probably be used more frequently in the maritime business. They are a good choice for shipping companies that want to lower their impact on the environment and make more money because they are efficient and last a long time.

Farhan Yustiarza proposes incorporating a Rankine cycle in the exhaust gas line at the turbocharger outlet, and the cooling water line outlet's air cooler can allow a maritime engine system (Wärtsilä W8L46DF) to recover up to 7.8% of lost energy. This could lead to a decrease in carbon dioxide emissions of 29.2 tCO_2 annually and fuel cost savings of up to EUR 41,300 annually [119]. The maritime business can take a big step toward a more sustainable future if more ships use these cycles.

5. Numerical Models Applied to ICEs Using NH_3

The climate neutrality objectives of the European Union regarding marine transportation consider using mixes of NH_3 and H_2 as a viable substitute for conventional fossil fuel sources. However, as discussed earlier, NH_3 co-firing in current research on the characteristics of NH_3 blends applied to ICEs for maritime transport is limited. More experimental and computational studies are needed to understand the combustion process better and optimize NH_3 co-firing [98].

While many approaches have been used for co-firing NH_3 in coal-fired thermal power plants, research in this domain remains very limited, and more work needs to be performed to explore the potential of NH_3 as a fuel replacement in the maritime sector. However, efforts are continuously made to fill this gap. For example, Fabio Berni et al. [120] provide stakeholders with insights into the efficacy of NH_3-H_2 as a viable alternative to conventional fuels in maritime contexts. The framework has undergone initial testing to facilitate the conversion of an already existing marine diesel engine to use NH_3-H_2 blends. The NH_3-H_2 combination with a composition of 80 mol% of NH_3 and 20 mol% of H_2 is chosen as the optimal solution due to its ability to function without experiencing knock and retain comparable performance to the original blend.

Nevertheless, although the heat transfer remains comparable to diesel, the generation of NOx becomes more pronounced, leading to a noticeable reduction in the engine's operational range. Furthermore, this effort offers practical recommendations to convert current powertrains, explicitly focusing on the suggested diesel engine test case. Additional advancements include enhancing the one-dimensional framework via integrating predictive models, including an enhanced knock model into three-dimensional simulations, refining the ignition model, exploring alternative chemical pathways, and confirming the findings through experimental analysis. The proposed framework can potentially be used in further studies to examine the same engine using pure H_2 in lean circumstances. This would enable the preservation of the original performance of the diesel engine while preventing the appearance of knock and facilitating the estimation of NOx emissions.

In another recent paper [121], researchers used NH_3 in a lean premixed marine engine equipped with a pre-chamber ignition system. The primary emphasis of this study was on examining combustion properties and emissions, specifically unburned NH_3, NOx, and N_2O emissions. The findings demonstrate that the CH_4/NH_3 process can be accurately replicated in simulations, and the augmentation of the H_2 concentration resulting from NH_3 pyrolysis facilitates the development of a jet flame. The research further discovered that the NH_3 component leads to a drop in NOx emissions due to the reduction in unburned NH_3. However, it also causes an increase in N_2O emissions ranging from 0.18 to 0.49 g/kWh. However, NH_3 is a viable alternative fuel option for natural gas marine engines, exhibiting superior thermal efficiency compared to pure NH_3. Researchers have found that blends containing at least 10% CH_4 exhibit increased reactivity.

Additionally, they observed that as the concentration of NH_3 is reduced, NOx emissions decrease due to unburnt ammonia. This suggests that blends with lower ammonia contents are preferable to those with higher concentrations. However, the authors emphasize the importance of further research to control NOx and N_2O emissions, as this will be crucial in assessing the viability of using ammonia/natural gas mixtures as fuel in marine engines. In further investigations, researchers will integrate these discoveries with studies on regulating NOx and N_2O emissions to evaluate the efficacy of using NH_3/natural gas blends in maritime propulsion systems.

Chen Zhang et al. [122] used a zero-dimensional model to numerically analyze NH_3 HCCI combustion within a fluid-phase (FPE) context. This study investigates the impact of piston trajectories on the combustion process. The research revealed that higher values of Ωcomp and Ωexp have the potential to enhance the combustion of NH_3. Additionally, raising the compression ratio (CR) of Ωcomp or Ωexp (piston trajectory) may promote the lean premixed pre-vaporized (LPP) combustion process and reduce exhaust gas emissions. The piston trajectory that yields the highest efficiency and lowest NOx emissions for NH_3 HCCI combustion is characterized by a compression ratio (CR) of 25, an expansion phase duration (Ωexp) of 0.5, and a compression phase duration (Ωcomp) of 0.5. This configuration achieves a thermal efficiency of 58.1% with NOx emissions of 5863 parts per million (ppm). Potential areas for further investigation may include exploring higher operating frequencies, broader air–fuel ratios, and using a computational fluid dynamics (CFD) model.

Jizhen Zhu et al. [123] examine the possibility of reducing NH_3 emissions via low-pressure gas injection in big two-stroke marine engines operating in the dual-fuel (DF) combustion mode. This work also uses CFD modeling and a novel chemical kinetic mechanism to examine the impacts of the NH_3 substitution ratio (ASR) and diesel injection time on the engine's performance and emissions characteristics. The primary findings indicate that introducing NH_3 into the premixed charge effectively hinders the autoignition of the pilot fuel. Additionally, the elongation of the ASR leads to a delay in ignition, generating a more significant number of premixed combustible mixtures of diesel, NH_3, and air. The research also revealed a drop in NOx emissions when ASR remains below 40%. As anticipated, the levels of CO_2 emissions exhibit a consistent reduction as the ASR increases while maintaining the same total fuel energy. The research also identified a trade-off correlation between NOx and N_2O emissions in engines powered by NH_3, wherein N_2O generation occurs at lower temperatures and during the first phases of combustion.

Table 5 presents some numerical models of work on NH_3 combustion.

Table 5. Numerical models of NH_3 combustion.

Description	Blend	Ref.
The research introduces a robust numerical framework utilizing 0D, 1D, and 3D tools for conducting CFD calculations on internal combustion engines powered by NH_3-H_2 mixtures. The model can be improved by incorporating predictive models for knock and emissions, turbulence, and robust chemical mechanisms.	NH_3/H_2	[122]
This paper studies the NH_3/CH_4 flame structure, temperature, and species field. The model can be improved by incorporating robust chemical mechanisms.	NH_3/CH_4	[124]
This research examines the combustion properties of NH_3/H_2/air in various direct-injection combustors, focusing on the impacts of equivalency ratio, H_2 mixing ratio, and emission characteristics.	NH_3/H_2/air	[125]
The research uses dimethyl ether (DME), a highly reactive oxygenated fuel, in combination with NH_3 to address NH_3's low reactivity. The model can be improved by incorporating a more accurate model for NH_2/NO_x.	NH_3/DME	[126]
The paper suggests using a mix of NH_3, coal, and biomass to lower the carbon footprint of coal-fired processes and lower the costs of biomass exploration so that the feedstock supply is not affected, all while making power plants more efficient.	NH_3/coal/biomass	[127]

Extensive research has been conducted to develop numerical models for NH_3 combustion in combination with other fuels. However, further research is needed to comprehensively understand this process's reaction mechanism and kinetics. One of the significant challenges is accurately representing NH_3's turbulence and flame speed when combined with other fuels. Turbulence is a critical factor in the combustion process that affects flame propagation and stability. To create dependable numerical models for industrial use, a precise representation of factors such as the fuel mixture composition, temperature, and pressure conditions is crucial. Despite notable advancements in computer modeling, additional research is required to comprehensively understand the intricate chemical processes and turbulent flame speed involved in this process. Accurate modeling is vital for creating trustworthy numerical models for real-life situations.

6. Regulatory Framework and Safety Conditions

Clean fuel or carbon-neutral propulsion solutions are being developed as the globe struggles with climate change. This has led to promising solutions and new safety problems that must be addressed.

An innovative approach has been created by Zanobetti et al. [128] to evaluate these systems' intrinsic safety performance early. A case study comparing LNG, liquid H_2, and liquid NH_3 safety profiles with marine gas oil (MGO) as a benchmark has provided valuable insights into these technologies' safety profiles. According to the research, LNG technologies perform similarly to the MGO standard in terms of safety. LNG may be a promising and feasible naval fuel source. Unfortunately, liquid H_2's safety performance is hampered by the absence of proven safe storage methods. Liquid H_2 must be researched and developed to be utilized safely and efficiently as a fuel. NH_3 toxicity impacts the safety of liquid NH_3-based applications. This is not impossible, but it emphasizes the necessity for careful design and execution to guarantee the safe usage of these technologies. Overall, the research shed light on these technologies' safety characteristics. The Potential Hazard Index is primarily affected by onboard fuel tanks. This emphasizes the need to build and maintain these tanks safely. Regulations govern certain aspects of the NH_3 supply chain, including its inland production, distribution, storage, and use [129]. Below are listed some of these standards.

6.1. ISO Standards

ISO 8217:2017—Maritime Fuels: It determines maritime diesel engine and boiler fuel needs before regular onboard treatment (settling, centrifuging, and filtering). This document applies to fuels used in stationary diesel engines with the same or equivalent requirements as marine diesel engines [130].

ISO 5771:2008—NH_3 Hoses: It specifies the minimum requirements for rubber hoses for transferring liquid or gaseous NH_3 at ambient temperatures ranging from −40 °C to +55 °C. It is limited to the hoses' and hose assemblies' efficacy and excludes end connectors' specifications [131].

ISO 7103:1982—NH_3 Sampling Technique: The technique involves placing a sample in a clean, dried, and evacuated stainless steel cylinder and filling it with safe water. Never fill the cylinder more than 75% at ambient temperature [132].

ISO 7105:1985—NH_3 Water Determination: The Karl Fischer technique with direct electrometric measurement determines the water content of the residual when ethanediol evaporates a test portion. The procedure applies to items having 50 mg/kg or more water. Diluting the evaporation residue with ISO 4276 anhydrous methanol and titrating an aliquot is best for water concentrations above 1000 mg/kg [133].

ISO 7106:1985—NH_3 Oil Content: Carbon tetrachloride extracts oil from a test amount evaporated at ambient temperature. Evaporating the organic solvent and weighing the residue or measuring the organic phase's absorbance at 3.42 m determines the residue's oil content. Products above 10 mg/kg are gravimetrically measured. Infrared spectrometry is more sensitive for items with oil concentrations above 1 mg/kg [134].

ISO 6957:1988—NH_3 Corrosion Resistance: It specifies an ammoniacal test to identify applied or residual stresses that might induce stress corrosion cracking and material failure in service or storage. The pH value controls the method's harshness. An instructive addendum suggests pH values [135].

ISO 17179:2016—NH_3 Concentration in Flue Gas: It defines the structure and key performance characteristics of automated NH_3 monitoring systems for stationary source emissions, such as combustion facilities using SNCR/SCR NOx control systems (deNOx systems). Performance characterization methodologies are also described. It discusses sampling and sample gas conditioning systems for flue gas NH_3 determination [136].

ISO 21593:2019—Bunkering Liquefied Natural Gas: It specifies the design, minimum safety, functional, marking, interface types, dimensions, and testing procedures for dry-disconnect/connects couplings for LNG hose bunkering systems used on LNG bunkering ships, tank trucks, shore-based facilities, and other bunkering infrastructures [137].

ISO 20519:2021—LNG-Fueled Vessels: The IGC Code does not address LNG bunkering transfer systems and equipment. This agreement covers international and domestic service vessels of any size [138].

ISO/TS 18683:2021—Safety and Risk Assessment of LNG Fuel Bunkering Operations: The risk-based strategy for planning and running the LNG bunker transfer system includes the interaction between LNG bunkering supply facilities and accepting LNG-fueled boats [139].

6.2. American Regulations

ANSI K61.1: Safety Requirements for the Storage and Handling Anhydrous of NH_3 [140,141].

EPA—Clean Air Act (CAA):

General Duty Clause [US Code 7412] [Section 112(r)(1) of the Act]: Facilities that handle highly hazardous substances (such as NH_3) are obliged to evaluate hazards, design and maintain a secure facility, and mitigate the effects of accidental releases [142].

Risk Management Program (RMP) Rule [40 CFR 68]: Facilities with more than 10,000 pounds of anhydrous NH_3 must create a hazard assessment, a protection program, an emergency action plan, and a risk management plan and send it to the EPA [143].

EPA—Emergency Planning and Community Right-to-Know Act (EPCRA):

Emergency Planning [40 CFR Part 355] and Hazardous Chemical Reporting [40 CFR Part 370]: Facilities with 500 pounds or more of NH_3 must report to their Local Emergency Planning Committees (LEPC), State Emergency Response Commission (SERC), and local fire department and comply with emergency planning requirements [144].

Emergency Release Notification [40 CFR Part 355]: Facilities that release at least 100 pounds of NH_3 must promptly notify the LEPC and the SERC. Additionally, CERCLA mandates reporting to the National Response Center [145].

DHS—The Department of Homeland Security (DHS) "Chemical Facility Anti-Terrorism Standards".

The schedule applies to anhydrous NH_3 of more than 10,000 pounds. A careful risk analysis and additional security measures may be required [145].

OSHA (Occupational Safety and Health Administration)

Storage and Handling of Anhydrous NH_3 [29 CFR 1910.111]: It thoroughly describes the NH_3 facility infrastructure, containers, etc. [146].

Process Safety Management (PSM) Standard [29 CFR 1910.119]: NH_3 is listed as a substance with a high hazard potential. Facilities with NH_3 quantities at or above the threshold quantity of 10,000 pounds are subject to numerous requirements for hazard management, such as conducting a process hazards analysis and maintaining the mechanical integrity of the equipment [147].

Hazard Communication [29 CFR]: Requires the evaluation of the potential hazards of toxic and hazardous chemicals and employers' transmission of this information to employees [148].

DOT (Department of Transportation).

Federal Hazardous Materials Regulations [49 CFR 100–180] contain specific highway transport rules for anhydrous NH_3 [149].

6.3. IGC Code

The International Code of the Construction and Equipment of Ships Carrying Liquefied Gases in Bulk (IGC) started on 1 July 1986. SOLAS Chapter VII requires the IGC Code. It applies to ships, even those under 500 gross tonnages, carrying liquefied gases with a vapor pressure above 2.8 bar absolute at 37.8 °C and other chemicals mentioned in Chapter 19. The Code sets international standards for the safe sea transport of bulk liquefied gases and the substances listed in Chapter 19. It regulates ship design and construction and the equipment they should carry to minimize risks to the ship, crew, and environment. Based on current knowledge and technology, the regulations aim to reduce these dangers. Resolution MSC.370 (93) approved the complete IGC Code modifications, which were anticipated to take effect on 1 July 2016 [150].

6.4. IGF Code

The International Code of Safety for Ships Using Gases or Other Low-Flashpoint Fuels (IGF) seeks to provide an international standard for ships operating with gas or low-flashpoint liquids as fuel that the IGC Code does not cover. It is founded on solid naval architectural and engineering principles and the most recent operational experience, field data, and research. The Code addresses all special considerations that must be made when using gas or low-flashpoint liquids as fuel. The purpose of the Code is to establish criteria for the arrangement and installation of machinery for propulsion and auxiliary purposes using natural gas as fuel, which will achieve the same level of safety, reliability, and dependability as new and comparable conventional oil-fueled main and auxiliary machinery [151].

There is no clear framework for using NH_3 as a maritime fuel. Therefore, the above regulations would need to be modified to expand the use of NH_3 as a marine fuel; meanwhile, in the absence of harmonized international rules, class societies can support ship owners through risk-based 'alternative design' approval methodologies [129].

Regional initiatives, such as the EU's 'Fit-for-55' suite of measures, are currently being developed and are expected to provide incentives and impetus for shipping to adopt alternative low- and zero-carbon fuels, such as (green) NH_3, to reduce GHG emissions from shipping [152].

According to techno-economic assessments [129], using NH_3 as a fuel might be encouraged by worldwide and regional GHG reduction rules and market-based policies. O is developing fuel lifecycle analysis guidelines for calculating fuel well-to-wake emissions and considering other technical and market-based measures under which NH_3 and its renewable production pathways would be evaluated [153].

Strengthening the existing regulatory framework could include amendments to the NOx Technical Code and the development of ISO standards.

7. Environmental Impact

Maritime shipping accounts for around 3% of GHG emissions worldwide. Given this significant contribution, it has become crucial for the sector to embrace more environmentally friendly approaches to address the challenges posed by climate change. Based on contemporary statistical data, it has been observed that marine shipping is responsible for an annual emission of around 1056 million tons of CO_2, which may be considered a significant and noteworthy quantity. Consequently, the International Maritime Organization has established aggressive reduction objectives for the maritime sector. The goal for the year 2050 is to achieve a minimum of a 50% reduction in GHG emissions from marine transport compared to the levels recorded in 2008. One possible approach to attain this objective is the use of NH_3 as a fuel source in the marine industry. The absence of CO_2 emissions after burning makes it a clean energy carrier. NH_3, when used as a fuel, primarily emits nitrogen and water, making it a highly suitable contender for mitigating GHG emissions within the maritime sector. Based on empirical research, the extensive use of NH_3 as a fuel source in the marine sector can result in a significant reduction of about 470 million metric tons of CO_2 emissions annually by the year 2050. This substantial decrease has the potential to assist the industry in attaining its lofty goal of reducing greenhouse gas emissions.

Nevertheless, certain obstacles must be overcome before the widespread use of NH_3 as a fuel source in the marine industry. One of the primary concerns is the proper management and storage of NH_3. NH_3 is a toxic gas that has the potential to pose health risks to individuals if mishandled. Consequently, the industry must develop novel safety processes and infrastructure to guarantee the secure handling and storage of NH_3.

The environmental repercussions of NH_3 leaks have been assessed by researcher Samie Parkar [154], leading to many findings. One of the most noteworthy discoveries is that meteorological circumstances have a substantial role in gaseous and liquid NH_3 dispersion. The dispersion of the contaminant may be accelerated by wind and ocean currents, posing challenges in terms of containment and remediation. Nevertheless, there are very few occurrences of the "worst-case" scenario in the event of an NH_3 leak. The most probable situation is a spill resulting from the total rupture of the bunkering line, occurring under circumstances characterized by a low wind speed and atmospheric stability. Although the impact may not be as severe as a storage tank rupture caused by a collision or grounding incident, the implications might still be substantial. The likelihood of an NH_3 leak resulting from a collision or grounding occurrence is low. However, it is crucial to consider the potential occurrence of such an event. In the case of a spill, it is essential to promptly and efficiently install containment procedures to mitigate the potential environmental consequences.

As shown in "The Future of Maritime Fuels 2023" report [155], Figure 6 depicts the forecasted trends for the maritime fuel industry. According to the report, by 2030, H_2 fuels are expected to hold a 9% share of the market, while biofuels will be at 3%, and fossil fuels will still have the majority share at 88%. However, by 2050, the situation is expected to change significantly. H_2 fuels are predicted to have a 64% share, while biofuels and fossil fuels will have an 18% share each.

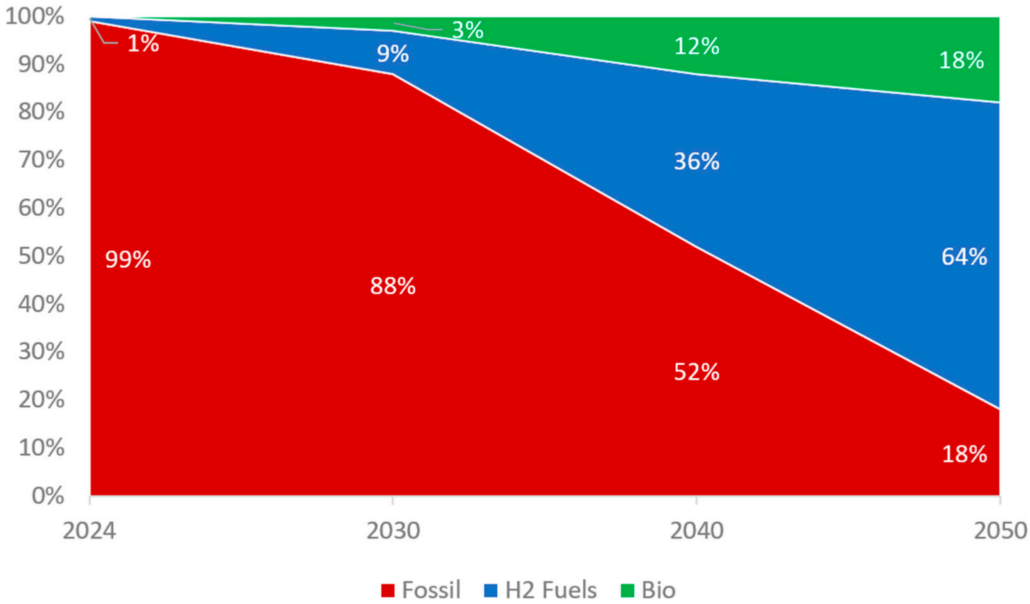

Figure 6. Average trends for scenarios with H_2 fuels.

In general, using NH_3 as a mode of marine transportation entails advantages and potential hazards. Although reducing greenhouse gas emissions may have a substantial effect, it is essential to acknowledge and address the possible environmental consequences while implementing measures to mitigate associated risks. By engaging in this practice, we may actively strive towards achieving a more sustainable future while safeguarding the invaluable ecosystems of our world.

8. Future Outlook

8.1. Market Trends

The maritime freight transport industry is paramount in the global economy, enabling approximately 90% of international trade. Seaborne trade has gained significance due to the increasing demand for goods and commodities. It offers consumers worldwide competitive freight costs and a diverse selection of products. The industry is expected to grow from

USD 381.69 billion in 2024 to USD 471.81 billion by 2029, with a compound annual growth rate (CAGR) of 4.33% during the forecast period [156].

More than 50,000 merchant ships are engaged in international trade, transporting various cargo. The global fleet is registered in more than 150 countries and operated by over a million seafarers representing nearly every nationality. These diligent experts strive to guarantee the secure and effective transportation of goods across the global seas, facilitating businesses and consumers in accessing the necessary products [157].

The maritime sector facilitates international trade by transporting commodities across the Earth's oceans. Dry bulk is the predominant type of cargo transported by sea, with approximately 5250 million tons shipped in 2022 [158]. Dry bulk pertains to commodities conveyed in substantial amounts, such as coal, iron ore, and grain. These materials are commonly transported on specialized vessels called bulk carriers.

In 2022, oil was the second most extensively transported substance by sea, with approximately 3000 million tons [159]. Oil is predominantly transported via large tankers specifically engineered to accommodate massive quantities of liquid cargo. Oil transportation is crucial for maintaining a consistent and reliable energy supply to nations globally. Nevertheless, the transportation of oil carries substantial environmental hazards, including the occurrence of oil spills and pollution.

In 2022, containers carrying various products accounted for 1900 million tons [159], making them the third most commonly transported material by sea. Containerized shipping utilizes standardized shipping containers to transport goods, resulting in a more efficient and cost-effective mode of transportation. This shipping method has transformed global trade, allowing companies to transport goods worldwide swiftly and effectively.

In 2022, cement and fertilizers, among other dry materials, constituted 1000 million tons [159], ranking as the fourth most extensively transported substance via maritime routes. The total amount of gas, including LNG and LPG, is approximately 500 million tons, whereas chemicals make up 400 million tons [159].

Notwithstanding the difficulties presented by the COVID-19 pandemic, the transportation of these products is experiencing an upward trend, albeit with a minor decline in oil transport in 2020. Nevertheless, following a recovery in the following years, the industry is expected to maintain its growth trajectory. With the growing global interconnectivity, there is a projected rise in the demand for maritime transportation of goods and materials in the foreseeable future.

The United Nations Conference on Trade and Development (UNCTAD) recently published its Review of Maritime Transport 2023 [159], highlighting the need to transition to a decarbonized shipping industry. This call for action comes from a 20% increase in greenhouse gas emissions in this sector over the last decade, attributed mainly to the industry's outdated fleet that primarily operates on fossil fuels.

The report emphasizes the importance of system-wide collaboration, swift regulatory intervention, and substantial investments in green technologies and fleet upgrades. While it acknowledges the need to balance environmental goals with economic needs, the cost of inaction far outweighs the required investments. Therefore, the industry must take concrete steps to achieve sustainability and efficiency.

One such step is adopting digital solutions like Artificial Intelligence (AI) and blockchain. These technologies offer the potential to streamline operations, optimize shipping routes, and reduce emissions. By leveraging AI algorithms to analyze historical data and predict future trends, shipping companies can optimize their fleet and reduce fuel consumption. Conversely, blockchain can improve transparency and accountability by enabling secure and efficient cargo tracking, reducing the risk of fraud and delays.

Despite the challenges posed by global crises, the resilience of the shipping industry remains evident. Maritime trade is expected to grow by over 2% between 2024 and 2028. However, this growth must be accompanied by a commitment to sustainability. The industry must work together to reduce emissions, invest in green technologies, consider green fuels such as NH_3, and adopt digital solutions to create a more efficient and sustainable future. Each of these initiatives has its challenges, and the following section focuses on utilizing NH_3 as a maritime fuel challenge.

8.2. NH_3 Challenges

A significant obstacle is CO_2 emissions linked to NH_3 production since its production accounts for roughly 1.8% of the total global CO_2 emissions [159]. Employing either blue or green NH_3 to mitigate the environmental consequences of NH_3 production is necessary. Blue NH_3 is generated by capturing and storing the CO_2 released during NH_3 production. In contrast, green NH_3 is produced utilizing renewable energy sources like wind, solar, or hydroelectricity. Hence, fostering the advancement and adoption of blue and green NH_3 is imperative to mitigate the maritime sector's carbon emissions.

Using NH_3 as a shipping fuel will necessitate a substantial amount of H_2. The shipping sector is projected to have a more significant impact on the H_2 market in the future, representing 8.3% (31 EJ) of the total H_2 required for a net-zero emissions global energy system or 17.5% (63 EJ) of the total H_2 demand in the pledges scenario outlined in Figure 7 [157].

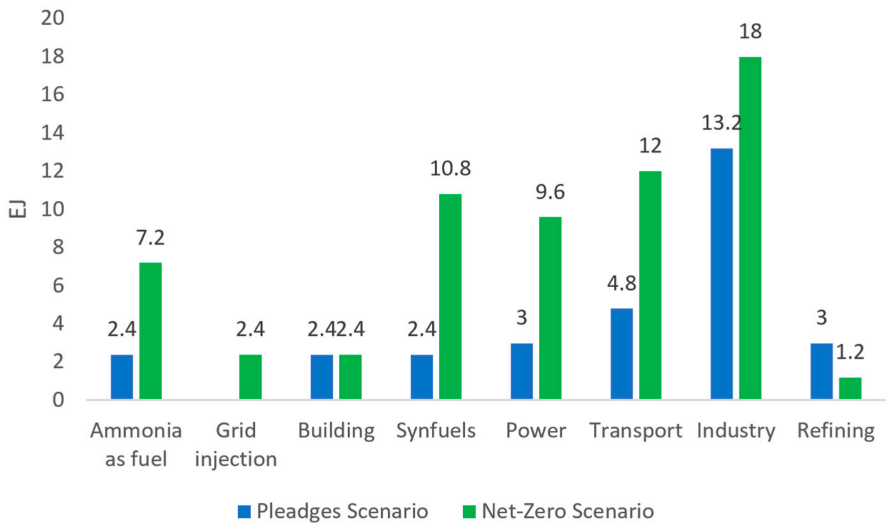

Figure 7. H_2 demand for 2050.

Another obstacle lies in the exorbitant price of NH_3 compared to conventional fuels like methane. NH_3 is significantly more expensive than methane, with a roughly 30 times higher cost. This makes it less attractive to ship owners. To promote NH_3 as a maritime fuel, it is necessary to decrease the cost or for governments to offer incentives to ship owners for transitioning to NH_3. Significant investment in research and development is necessary to decrease the cost of NH_3 production and establish it as a feasible alternative fuel. Figure 8 displays the price history of NH_3. In 2022, there was a sudden rise, peaking at EUR 1312 per ton for Europe.

Moreover, there is presently no turbine accessible in the market that can combust NH_3 for power generation. Although there have been instances where turbines capable of combusting NH_3 have been showcased, implementing a dual turbine that can burn both NH_3 and conventional fuel would incur significant costs. Hence, additional investigations and advancements are necessary to enhance the affordability and accessibility of NH_3 combustion technology for the maritime sector.

NH_3 combustion yields NOx and N_2O, which are 273 times more potent than CO_2 as greenhouse gases. Hence, it is imperative to devise technology capable of mitigating the emissions of NOx and N_2O during NH_3 combustion. A significant research and development investment would be necessary for the technologies that reduce NOx and N_2O emissions, namely, SCR, SNCR techniques, or exhaust gas scrubbing. Minimizing emissions is a paramount concern in the maritime sector. Although these methods successfully decrease detrimental pollutants, it is crucial to acknowledge that they generate other residues like nitric acid, which requires proper management. Ships must be able to store both NH_3 and nitric acid to handle nitric acid effectively. Furthermore, preventing NH_3 from slipping is essential to avoid the production of N_2O, a highly potent greenhouse gas.

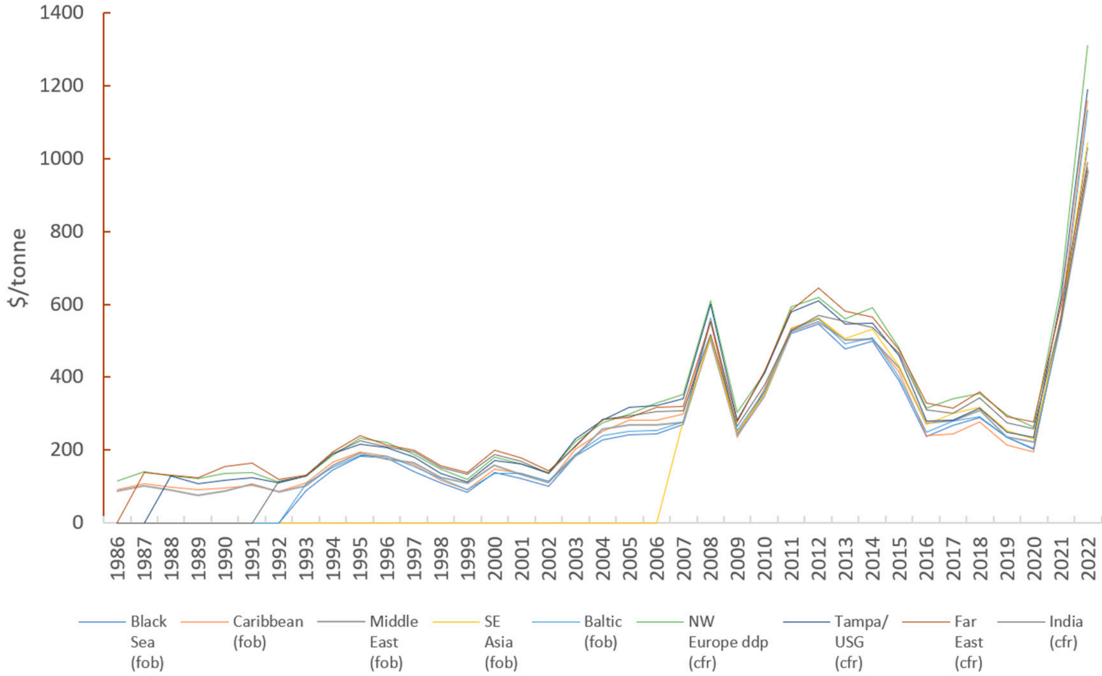

Figure 8. Historic NH_3 prices from 1986 to 2022 [160]. Free on board (FOB) and cost and freight (CFR).

NH_3 is a hazardous and corrosive substance that requires careful handling, and the facilities must be designed to meet specific design codes, such as API 620 R or BS 7777.

On the other hand, a meticulously designed NH_3 supply strategy is crucial for efficiently loading and unloading ships powered by NH_3. This will guarantee a consistent and secure provision of NH_3 and retrofitting ICEs.

To summarize, NH_3 shows excellent promise as a maritime fuel; however, various obstacles must be overcome to fully harness this alternative fuel's potential. Essential measures to mitigate the environmental impact of the shipping industry include advancing blue and green NH_3, optimizing NH_3 production costs, innovating affordable NH_3 combustion technology, and minimizing NOx and N_2O emissions during NH_3 combustion. It is necessary to establish effective protocols for storing and handling NH_3 and to develop a carefully devised supply strategy for ships powered by NH_3.

9. Conclusions

It is increasingly evident that the consequences of greenhouse gas emissions are posing significant environmental, economic, and health challenges. We rapidly approach a critical tipping point, underscoring the urgency to transform our lifestyles and technologies towards clean, eco-friendly solutions. In this context, this review of the recent literature has proposed using ammonia as a promising marine fuel. Ammonia combustion produces no carbon dioxide, making it an excellent candidate to address the maritime industry's environmental impact. However, the article highlights some key challenges that must be overcome to capitalize on ammonia's potential fully. A primary concern is how ammonia is typically produced, which relies heavily on energy-intensive processes fueled by fossil fuels. In this conventional approach, the environmental benefits of using ammonia as a marine fuel are primarily offset by the emissions generated during production. As a result, simply substituting ammonia for existing marine fuels may not be the most effective solution from an environmental standpoint. Fortunately, the landscape is shifting with the emergence of "green" and "blue" ammonia. These innovative production methods leverage renewable energy sources, such as solar and wind power, or incorporate carbon capture technologies to mitigate emissions. These new ammonia variants promise to transform the maritime industry's environmental impact by addressing the supply chain challenges.

Nevertheless, the implementation of ammonia as a maritime fuel faces other hurdles that must be overcome. The high cost of green and blue ammonia, being around 30 times more expensive than methane, is a significant barrier from an economic standpoint. Without government support through regulations and incentives, using ammonia instead of cheaper fuels will not be viable for most applications, particularly in the maritime industry. It is crucial to acknowledge the potential impact on consumers, as the increased cost of marine transport could lead to higher prices for a wide range of products, potentially causing discontent in a society accustomed to more affordable goods. Addressing this economic challenge is a vital first step before delving into the technical complexities of ammonia combustion. One such technical challenge is the emission of NOx and N_2O, which are considerably more harmful to the environment than CO_2 itself, being 33 and 273 times more potent, respectively. The article explores several promising approaches to mitigate these emissions, including adjusting the operating conditions and types of ICEs and incorporating external devices. Temperature is the primary factor influencing these emissions, as their formation increases when temperatures rise above 1300 °C. Therefore, the relationship between temperature and emissions is crucial for controlling and optimizing the process.

Interestingly, recent findings reveal that HCCI and PCCI systems do not provide the same emission reduction benefits observed with traditional fossil. This suggests that using pure ammonia in these advanced combustion systems may not be as effective at lowering emissions as previously thought. External devices, such as scrubbers and SNCR and SCR systems, have shown promising results in reducing emissions when using ammonia as a fuel. Another crucial technical factor to consider is the management of ammonia itself. As a toxic compound, its handling must adhere to strict safety regulations, ensuring the well-being of personnel and the environment.

While ammonia as a marine fuel still faces various challenges that must be addressed, the environmental trends, increasing emissions, and climate change concerns underscore the importance of continued research and development in this field. By addressing the technical and economic complexities and navigating the regulatory landscape, we can pave the way for a more sustainable marine transport sector, contributing a grain of sand to the larger goal of a greener future.

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