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Review Article

A REVIEW OF AMMONIA AS A SUSTAINABLE FUEL FOR MARITIME TRANSPORTATION

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ABSTRACT

While the maritime transportation sector plays a critical role in the global economy, it also significantly contributes to greenhouse gas emissions. This study examines the energy efficiency, technical feasibility, and environmental impacts of ammonia as an alternative fuel in maritime transportation. The contributions of regulatory initiatives, such as the IMO's (International Maritime Organization) Energy Efficiency Existing Ship Index (EEXI) and the EU's FuelEU Maritime initiative, in promoting the use of low-carbon fuels to reduce emissions are discussed. The study evaluates the chemical and physical properties of ammonia, challenges associated with its combustion and production processes, with a focus on integrating renewable energy sources for green ammonia production. Findings suggest that ammonia's low reactivity and wide availability make it a promising sustainable fuel. However, overcoming challenges such as combustion difficulties and toxicity will require technological advancements. This comprehensive analysis provides an in-depth perspective on the potential contributions of ammonia to achieving decarbonization goals in the maritime sector, as well as the obstacles that must be addressed.

Keywords: Ammonia fuel, Decarbonization, Maritime, Sustainability, Alternative fuel.

1. INTRODUCTION

Internal combustion engines and other energy conversion systems have significantly contributed to humanity's technological and economic development. Fossil fuels such as oil, coal, and natural gas have served as the primary energy sources for this progress. For decades, internal combustion engines and liquid hydrocarbons have worked as a compatible duo, playing a pivotal role in transportation, power generation, agriculture, and maritime shipping.

Maritime shipping, a crucial component of global transportation, supports the global economy with approximately 127,000 ships and a gross tonnage capacity of 1,600,000 (EMSA, n.d.). Despite its economic contributions, the environmental impact of maritime shipping, particularly concerning carbon dioxide and other harmful emissions, has become a significant concern. These emissions pose a threat to the sector's sustainability and necessitate the search for cleaner energy solutions. Currently, CO₂ emissions from the transport sector account for approximately 24% of global CO₂ emissions, while transport-related greenhouse gases constitute about 14% of global greenhouse gas emissions (Ritchie & Roser, 2024). Therefore, reducing emissions in the transport sector is a critical step in combating climate change.

The International Maritime Organization (IMO) is a United Nations agency that regulates the international maritime shipping industry. The IMO's practices establish an international framework aimed at reducing emissions in the maritime transport sector. To address this challenge, the International Maritime Organization (IMO) has implemented various regulatory measures for newly constructed and operating ships. In 2011, the Energy Efficiency Design Index (EEDI) was introduced for newbuilds, aiming to enhance energy efficiency and reduce emissions through technological solutions. This regulation encourages the adoption of energy-efficient designs in ships and is recognized as a key step toward minimizing the environmental impact of maritime shipping. The EEDI evaluates ships' energy consumption and carbon emissions, promoting the use of low-emission technologies. However, as this regulation applies only to new ships, the Energy Efficiency Existing Ship Index (EEXI) was introduced to assess the energy efficiency of existing vessels. Since 2023, ships of 400 GT and above are required to comply with EEXI standards and meet minimum energy efficiency requirements. These measures aim to enhance environmental sustainability in maritime shipping. In July 2023, the IMO finalized the first update to its GHG strategy. The original 2018 strategy set a target to reduce carbon intensity from shipping by at least 70% by 2050 and to cut total annual GHG emissions by at least 50%, using 2008 as the reference year. The 2023 update significantly enhanced the targets for international shipping, particularly aiming for a 50% reduction in GHG emissions by 2050. The revised strategy sets a 20% reduction in GHG emissions by 2030, with an aspiration to reach a 30% reduction. In the following years, the strategy targets a reduction of 70% by 2040 and 80% by 2040, ultimately aiming for net-zero emissions by 2050 or shortly thereafter (DNV, 2023; Elççek, 2024).

IMO 2020 Rule: Starting from 2020, the sulfur content in fuels used in the maritime industry was reduced to 0.5%. This has significantly reduced SO_x emissions in the maritime sector (Sáez Álvarez, 2021).

IMO 2050 Net Zero Emission Target: The IMO has set the goal for global maritime shipping to achieve net-zero emissions by 2050 (Lee et al., 2024; Lindstad et al., 2023).

Additionally, ships over 5,000 GT are mandated to collect and regularly report energy efficiency data. If a vessel's Carbon Intensity Indicator (CII) rating is deemed inadequate, corrective actions are required from the shipowners. In alignment with climate change mitigation efforts, IMO updated its greenhouse gas (GHG) reduction strategy in 2023, targeting a 70–80% reduction in GHG emissions by 2040 compared to 2008 levels, with the ultimate goal of achieving zero emissions by 2050. Similarly, the European Union has established long-term goals for maritime transport, issuing Directive SEC (2021) 562, which aims to reduce GHG emissions by 90% by 2050 compared to 1990 levels. Achieving these targets necessitates significant reductions in CO₂ emissions from the maritime sector, particularly through improving energy efficiency and promoting the use of renewable and low-carbon fuels, such as hydrogen and ammonia.

The importance of alternative fuels in the maritime sector has been reported in many studies in the literature. Recent researches suggest that alternative marine fuels could reduce CO₂ emissions by anywhere from 20% to 100%, with the exact reduction varying depending on the type of fuel used (Chai et al., 2021; Xing et al., 2021). Many similar studies aim to illuminate how alternative energy sources can play a significant role in reducing carbon dioxide emissions produced by the maritime industry, as well as the potential obstacles that may arise (Rony et al., 2023; Al-Enazi et al., 2021; Wang & A. Wright, 2021).

FuelEU Maritime is a new EU regulation aimed at reducing greenhouse gas emissions from fuels used in the maritime sector by promoting the adoption of renewable and low-carbon fuels. This initiative, a key component of the EU's "Fit for 55" package, outlines comprehensive measures to reduce the greenhouse gas intensity of maritime fuels by 2% in 2025 and up to 80% by 2050. The regulation plans to incentivize renewable and low-carbon fuels while phasing out fossil fuels. Furthermore, by 2030, passenger ships and container vessels at major EU ports will be required to meet their entire energy needs using shore-side electricity. These measures will align the maritime sector with the EU's 2030 and 2050 climate goals, significantly reducing the sector's carbon footprint (Drazdauskas & Lebedevas, 2024).

Ammonia has emerged as a promising alternative fuel for achieving zero-carbon emissions in the maritime sector. Given the need to mitigate the environmental impacts of fossil fuels and curb greenhouse gas emissions, integrating ammonia into maritime transport presents significant opportunities and challenges (Berwal et al., 2021; Herbinet et al., 2022a; Nadimi et al., 2022; Tornatore et al., 2022). This study examines ammonia's potential role in the sector concerning energy efficiency, technical feasibility, and economic sustainability, evaluating the challenges encountered and the benefits it offers. The analysis aims to provide an in-depth perspective on whether ammonia can contribute to the green transition in maritime transport.

2. AMMONIA AS AN ALTERNATIVE FUEL

Studies focusing on ammonia as a fuel reveal an increasing interest and a growing research community in recent years compared to earlier periods (Herbinet et al., 2022b). Ammonia can be converted into energy either through fuel cells or internal combustion engines. Table 1 presents the physical and chemical properties of ammonia alongside those of other fuels (Hu et al., 2023).

Ammonia is a versatile compound offering numerous industrial and environmental advantages. As a colorless gas lighter than air, it has the capacity to disperse rapidly in the environment. Since it is less dense than air, ammonia rises and spreads out rapidly, reducing the likelihood of concentrated pockets of the gas lingering in one area. This quick dispersion can minimize the risk of harmful exposure or accumulation, making it safer in certain situations compared to heavier gases that tend to settle. However, while this characteristic helps with dispersion, it also means that ammonia can spread over a wide area, requiring careful management to prevent environmental or health hazards (Asman et al., 1998). Its relatively low cost makes it a preferred compound across various industries and sectors (Chehade & Dincer, 2021). Additionally, its sharp and characteristic odor allows it to be easily detected even at low concentrations, which is a significant safety advantage. While ammonia is widely recognized globally as a fertilizer, its versatility has positioned it among the most produced chemicals in the world. Over 80% of global ammonia production is used as fertilizer, but it also finds applications in controlling

nitrogen oxide (NO_x) emissions in exhaust gases (Jiang et al., 2020), as a component in cleaning products (Maxwell, 2004), as a refrigerant gas (Pearson, 2008), as a solvent (Gilberg & Seeley, 1982), as a bleaching agent in the paper industry (Tornatore et al., 2022), and as a reducing agent in metallurgy (Iwamoto et al., 2022). This widespread usage and global production network make ammonia a resource that is readily available in almost every part of the world. For the maritime sector, this global accessibility of ammonia is a significant advantage.

Furthermore, ammonia's low reactivity poses less risk of accidental fires or explosions compared to other fuels, making it a safer option for storage and transport. This characteristic makes ammonia particularly advantageous in industries such as maritime shipping, where high safety standards are critical.

However, ammonia is also a toxic compound and poses serious risks to human health, especially when inhaled in large quantities. Its irritant nature necessitates careful handling (Swotinsky & Chase, 1990). Due to its alkaline properties, it is corrosive and can cause damage to metal surfaces upon prolonged contact. Special precautions must therefore be taken during its storage and transportation (Khaksar et al., 2024). Ammonia's high latent heat of vaporization requires more energy for evaporation, which limits its usability as a liquid fuel. This characteristic can lower in-cylinder temperatures, impacting combustion properties and reducing efficiency (Ryu et al., 2014).

Table 1. Physical and chemical properties of ammonia alongside those of other fuels (Hu et al., 2023)

Property	Units	Ammonia	Hydrogen	Methane	Gasoline	Diesel
Density at 1 bar, 25°C	kg/m ³	0.718	0.0837	0.667	736	849
Lower heating value	MJ/kg	18.8	120	50	44.5	45
Latent heat of vaporization	kJ/kg	1370	455	511	348.7	232.4
Boiling point	°C	-33.34	-252.7	-161.5	35-200	282-338
Specific heat capacity Cp	kJ/(kg K)	2.19	14.30	2.483	2.22	1.75
Volumetric energy density at 1 bar, 25°C	GJ/m ³	11.3	4.7	9.35	33	36.4
Octane number (RON)		130	>100	120	90-98	8-15
Autoignition temperature	°C	657	500-577	586	230	254-285
Laminar flame speed	cm/s	7	351	38	58	86
Flammability limit (φ)		0.63-1.4	0.1-7.1	0.5-1.7	0.55-4.24	0.8-6.5
Stoichiometric air-fuel ratio by mass		6.05	34.6	17.3	15	14.5
Adiabatic flame temperature	°C	1800	2110	1950	2138	2300

3. AMMONIA PRODUCTION

Ammonia production is carried out globally in large-scale facilities, with an annual production volume of 240.38 million metric tons as of 2023. It is projected that production will reach 276.14 million metric tons by 2026 and 289.89 million metric tons by 2030 (Global Ammonia Annual Production Capacity, n.d.). Fig.1 shows the annual growth in global ammonia capacity (Hatfield, 2020). According to the figure, net 58 million tonnes of net capacity change had been observed during this period. This production predominantly serves the fertilizer industry but also plays a significant role in industrial and energy sectors. Among the leading

ammonia-producing countries, China ranks first with a share of 31.9%, followed by Russia (8.7%), India (7.5%), and the United States (7.1%) (Ammonia's Potential Role in a Low-Carbon Economy, n.d.). These countries collectively meet a substantial portion of the global ammonia demand, showcasing their critical role in the supply chain.

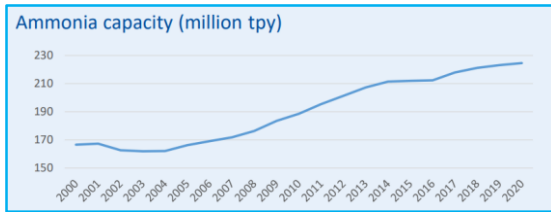


Fig. 1. Annual growth in Ammonia capacity, 2000-2020 (Hatfield, 2020)

Ammonia is produced through a catalytic reaction of nitrogen and hydrogen under high pressure and temperature. This process, commonly known as the Haber-Bosch method, accounts for the majority of global ammonia production. Nitrogen is sourced from the atmosphere, while hydrogen is typically derived from fossil fuel feedstocks, particularly natural gas. Using an iron-based catalyst, nitrogen and hydrogen combine under high-temperature (400–500°C) and high-pressure (150–250 bar) conditions to form ammonia (NH₃) (Pawar et al., 2021). However, this production process is highly energy-intensive and creates environmental impacts due to the reliance on fossil fuels. Alternative electrochemical methods show promise for ammonia synthesis, offering the potential for lower energy and water consumption compared to the electrolysis-based Haber-Bosch process. Yet, these methods have not achieved the technological maturity required for commercial-scale implementation.

To mitigate the environmental impact of ammonia production and transition toward a more sustainable process, the integration of renewable energy sources has become increasingly important. Renewable resources such as wind and solar energy can be utilized to produce green hydrogen via electrolysis. This green hydrogen can replace fossil fuel-based hydrogen, significantly reducing the carbon footprint of ammonia production. Additionally, emerging electrochemical methods powered by renewable energy could provide a sustainable alternative to the energy-intensive Haber-Bosch process, enhancing both economic and environmental efficiency (Zhang et al., 2020).

Solar energy holds significant potential as a renewable energy source for ammonia production. Electricity generated from solar energy can be used to produce green hydrogen via water electrolysis, which can then be combined with nitrogen to produce ammonia sustainably. Research indicates that the cost of producing green ammonia currently ranges between \$580 and \$641 per metric ton of NH₃ (Kakavand et al., 2023). Projections suggest that the global cost of green ammonia production could decrease to \$370–\$450 per metric ton of NH₃ by 2030 and to \$285–\$350 per metric ton of NH₃ in optimal regions by 2050 (Fasihi et al., 2021).

In addition to solar energy, wind energy also holds great potential in the field of ammonia production and is considered a complementary resource for sustainable energy transitions. Both offshore and onshore wind farms offer significant opportunities for ammonia production systems, providing strategic solutions for energy storage and balancing needs. Studies have demonstrated that wind energy-supported ammonia production enhances

energy efficiency, economic feasibility, and reduces carbon emissions. For example, Morgan et al. highlighted that ammonia production powered by wind turbines in isolated regions reduces reliance on diesel fuel and lowers costs (Morgan et al., 2014). Similarly, Motta et al. identified solid oxide electrolysis as the most promising technology for ammonia production supported by offshore wind energy, emphasizing its long-term competitiveness (Díaz-Motta et al., 2023).

Hydropower is another renewable energy source offering sustainable and environmentally friendly solutions for ammonia production. Hydropower generates electricity through the kinetic energy of water flowing from dams, which can be used for hydrogen production and ammonia synthesis. Studies indicate that hydropower-supported ammonia production costs approximately \$400 per ton in facilities with a capacity of 200 tons/day (Rivarolo et al., 2019). Since this process is entirely renewable, it is environmentally friendly and can be enhanced with various technologies to improve efficiency.

Geothermal energy, derived from underground heat, can also be utilized for electricity generation and subsequently applied to ammonia production (Shamsi et al., 2024). Economic analyses of green ammonia production systems using geothermal resources show unit costs of \$74.57/GJ and an annual total cost of \$123 million per year. Geothermal-based systems provide high energy efficiency and environmental benefits, though costs can vary depending on system size and efficiency levels. Both geothermal and hydropower have significant potential to enhance the sustainability of ammonia production.

The integration of renewable energy sources into ammonia production is critical for both environmental sustainability and economic feasibility. Resources such as solar, wind, hydropower, and geothermal energy can reduce dependence on fossil fuels in ammonia production, significantly lowering carbon emissions. These methods, supported by green hydrogen production, not only improve environmental outcomes but also have the potential to enhance energy efficiency and reduce long-term costs. Research suggests that innovative systems incorporating these resources can offer competitive solutions for ammonia production. However, factors such as technological maturity, infrastructure requirements, and regional resource potential must be carefully considered in this transition. Renewable energy-based ammonia production represents a crucial step toward achieving clean energy goals.

4. ENGINE AND COMBUSTION CHALLENGES

Although alternative methods such as fuel cells are available for energy recovery, the combustion of ammonia in internal combustion engines emerges as a significant approach for energy production. The combustion of ammonia, either in its pure form or as a blend with other fuels, holds particular importance due to its energy production potential and the complexity of the chemical and thermodynamic processes involved in internal combustion engines. However, the use of

ammonia in internal combustion engines presents technical challenges due to its low combustion rate and weak reactivity. Additionally, the formation of nitrogen oxides (NO_x) as by-products during the combustion process poses a significant environmental concern. Therefore, a comprehensive examination of the scientific principles and technical phenomena associated with the use of ammonia in internal combustion engines is crucial. This understanding will be essential for evaluating the potential of this innovative fuel and optimizing its application.

4.1. Ignition Delay

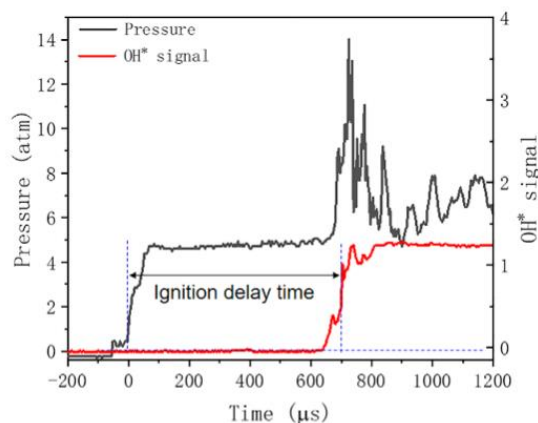


Fig. 2. Ignition delay definition for ammonia-methane/air mixture (Xiao et al., 2020)

Ammonia presents challenges in its use within internal combustion engines due to its low combustion rate and high ignition temperature. In high-pressure compression ignition systems, such as diesel engines, the low reactivity of ammonia prolongs the ignition delay period, which directly impacts engine performance (Reiter & Kong, 2008). Ignition delay refers to the time interval between fuel injection into the cylinder and the onset of combustion, a process that significantly influences the thermodynamic efficiency of the engine and exhaust gas emissions. Fig. 2 indicates the definition of ignition delay time (Xiao et al., 2020). The figure shows the typical pressure curve and ignition time, which illustrates the definition of the ignition delay period.

Ammonia may cause higher ignition delays because it requires high-energy bonds and lower ignition temperatures. This can affect the efficiency and performance of the engine, necessitating specific adjustments for engines operating on ammonia (Kurien & Mittal, 2022; Huo et al., 2024).

The combustion processes of ammonia are highly temperature-dependent. At sufficient temperatures, increased heat reduces ignition delay and facilitates combustion. However, ammonia's requirement for a high ignition temperature can hinder ignition under low-temperature conditions. B. Wang (2023) and Wang, et al. (2023) reported that gradually increasing the ammonia proportion in a fuel blend significantly extends ignition delay. In contrast, X. Wang et al. (2024) demonstrated that factors such as ammonia vaporization, increased premixed ammonia equivalence ratio, and reduced ambient oxygen concentration can further prolong

ignition delay during the combustion of n-heptane fuel. To address these challenges, Zeng et al. (2024) investigated various injection strategies, aiming to optimize the combustion process through methods such as staged injection and adjusted injection timing. Additionally, Okumuş et al. (2024), in a parametric study, suggested that increasing the compression ratio of diesel engines helps reduce ignition delay, presenting this finding as a potential solution to improve combustion performance.

4.2. Laminar Burning Velocity

The laminar burning velocity is a fundamental parameter that describes how a planar flame propagates through a stationary, unburned mixture under specific pressure and temperature conditions. Thus, while a fuel with a higher laminar burning velocity is expected to facilitate faster combustion in an engine, fuels like ammonia with low laminar burning velocities may result in slower combustion processes. In ammonia-diesel blends, the laminar flame speed is influenced by several factors, including the fuel-oxygen mixture ratio, in-cylinder temperature and pressure conditions, mixture homogeneity, the presence of additives, oxidizer type and concentration, and turbulence levels within the engine.

Wei et al. (2024) explored the use of methanol to improve the low laminar burning velocity of ammonia. Methanol, due to its high reactivity, enhances ammonia's combustion performance by producing H, OH, and O radicals during combustion. Their study demonstrated that the addition of methanol significantly increased the laminar burning velocity of the ammonia/methanol blend and improved combustion efficiency while limiting carbon emissions. Similarly, (Xiao & Li, 2022) investigated dimethyl ether (DME) and found that mixing DME with ammonia positively affected the laminar burning velocity. The addition of DME improved ammonia's burning rate through its chemical kinetics and thermal effects, enabling more efficient and lower-emission combustion.

Among the most extensively studied methods in the literature to enhance ammonia's combustion properties is blending it with hydrogen. Hydrogen's high reactivity significantly contributes to increasing ammonia's laminar burning velocity. Ammonia-hydrogen blends allow for more efficient combustion by accelerating the burning process, as evidenced by several studies (Jamrozik & Tutak, 2024; B. Wang, Yang, et al., 2023; N. Wang et al., 2024; Y. Wang et al., 2021).

5. CONCLUSION

Ammonia is emerging as a promising alternative fuel in the maritime industry, aligned with global sustainability goals and regulations aimed at reducing greenhouse gas emissions. Its unique chemical properties and the potential for integration with renewable energy-based production methods make it a significant component in reducing the carbon footprint of maritime transport. However, technical and safety challenges such as low laminar burning velocity, ignition delay, and toxicity highlight the need for targeted technological innovations to optimize ammonia use. The incorporation of hydrogen and other additives offers an important solution for enhancing combustion performance and

reducing emissions. Furthermore, integrating renewable energy sources into ammonia production is critical for improving environmental sustainability while lowering costs. In the transition to low-carbon fuels, ammonia provides a viable path to achieving zero-emission targets in the maritime sector. However, the success of this transformation depends on continued research, investment, and infrastructure development.

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