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Aspects of Ammonia as Green Fuel for Propulsion Systems of Inland Water Vessels

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Ships are a crucial backbone of the transport system for goods and people. However, the currently utilized fossil fuels require a green replacement. Ammonia produced from green hydrogen is an interesting, carbon-free green fuel, which has been demonstrated to be promising for maritime applications. Its application under the specific boundary conditions of river ships and other inland water vessels still deserves a closer evaluation. In this work, ammonia as a green fuel for propulsion systems of inland water vessels is evaluated regarding several technological aspects. These include onboard decomposition for hydrogen release, combustion of ammonia–hydrogen mixtures in internal combustion engines and the thermal integration of the different components. To achieve favorable combustion properties of the fuel, a certain share of the ammonia has to be decomposed in an ammonia cracker to produce a mixture of hydrogen and ammonia. First single-cylinder engine tests show that the combined combustion of ammonia and hydrogen allow an efficient and reliable process for the investigated high-speed engine concept. Efficiency values of nearly 40% at part load already are achieved. With proper system integration, it is possible to reasonably operate small- and medium-sized ships with ammonia as a green fuel.

1. Introduction

Water transport is a major and irreplaceable mean of transporting people and particularly goods. Generally, ships provide the most efficient and therefore most climate-friendly method of transport. However, further improvement of the greenhouse gas emissions will be needed to cope with mankind's aims for a sustainable future even in this field. Potentially climate neutral mobility might be realized utilizing battery in road-based applications. Yet, for ships, the energy densities of batteries are too low for most application scenarios.[1] Hence, alternative ways of providing stored renewable energies for ships are needed. Green hydrogen is a promising option for this task, but the energy density of elemental hydrogen (both, compressed or liquefied) is still too low. Conversion of hydrogen into a liquid fuel is therefore highly interesting. Classical hydrocarbons, that could be produced via synthesis gas from hydrogen, seem attractive in this regard as conventional engines could be used. Yet, they require a concentrated carbon source, for example, from carbon capture and storage facilities, if no energy demanding and expensive direct air carbon capture is applied on a large scale. Consequently, the availability of CO_2 becomes a limiting factor for production capacities, which prohibits their widespread application.[2] In contrast, ammonia can be produced from hydrogen by conversion of hydrogen with abundantly available nitrogen.[3]

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Consequently ammonia has started drawing major attention by researchers, industry, and policymakers as a storage form for hydrogen and energy.[4,5]

Ammonia can be utilized directly in internal combustion engine (ICE) as a fuel. However, its combustion properties are not optimal for engine operations. Particularly its low ignitability and flame speed pose some challenges, especially for high-speed engines, as well as its potential corrosive attack.[6] Mixing with a certain amount of (easily ignitable) hydrogen as a pilot fuel can help to handle this issue.[7] The provision of this hydrogen could be facilitated by decomposition of a small share of the ammonia immediately before the ICE in a cracker unit. To realize such a process in a reasonable manner, proper system integration is required.

In future, there will be a high demand to transport ammonia as hydrogen carrier from the production sites to the consumers. The long distance transport is going to happen with large sea-going vessels, propelled by very large slow-speed two-stroke engines. These vessels will deliver to typical ports, in Europe, for example, Antwerp or Rotterdam. From there the further local distribution can happen most efficiently by inland water vessels, propelled by small high-speed four-stroke engines. Ideally, the transport ships themselves should be fueled with ammonia. In this way, the chemically bound imported energy is used directly to maintain the distribution chain without additional conversion losses beyond those in the combustion engine.

There is also a considerable efficiency advantage in the storage of cold liquefied ammonia compared to cold liquefied hydrogen due to the more favorable boil-off behavior and the higher energy density. This fact is relevant both for the transport of energy over long distances and for the use of seasonal storage facilities.[8]

The larger an engine is and the slower the engine speed is, the easier such an engine can be operated with ammonia. The operation of a small-sized high-speed engine with ammonia, however, is expected to lead to challenging conditions with the need to be solved enabling the local ammonia distribution chain with inland water vessels. Yet, inland water vessels fueled with ammonia show a large potential and deserve particular attention. So, in this study, the application of ammonia as a fuel for inland water vessels is discussed. It focuses on its energetic utilization in ICE considering major issues and opportunities in this context.

2. System Concept for Inland Water Vessels

Inland water shipping is using a big network of interconnected rivers, canals, and lakes, typically in Europe, Northern America, and the Far East. The quite unimpressive vessels transport mostly dry and wet bulk, but also containers. A further, extending application are inland water cruises with passengers. Beside self-propelled monohulls also push boats and tugs exist for moving unpowered barges. The ship sizes are often limited by the sizes of the lock basins, allowing the vessels to change altitude. These sizes are typically standardized in the respective regions. A typical size is the so-called Europe vessel for European class IV inland waters with a length of 85 m and a width of 9.5 m (https://de.wikipedia.org/wiki/Europaschiff). The maximum transport capacity of such vessel type is 1,350 t. In 2020 the average age of German inland water vessels is 46.7 years.[9]

The power demand of inland water vessels is specifically lower than for seagoing vessels due to the smaller sizes and less water resistance as the speeds are lower and nearly no waves and wind must be considered. The highest power demands are required for ascent trips on rivers against the current. The before mentioned so-called Europe vessel type has a typical power demand of 600 kW. In former times, this was handled by one medium-speed engine driving via a speed-reduction gearbox a single propeller with a quite large diameter. As river water levels are more often low because of less rain in Europe during the last decade, new vessels are designed with two or even three propellers with smaller diameter to reduce the ship's draught. These smaller propellers are driven by high-speed engines mechanically via Z-drive or electrically via generator. Of course, a reduced water level increases the power demand strongly for a Europe vessel type (see **Table 1**). With similar output, the ship speed is reduced to 50%, when the water level is reduced from 5 to 2.5 m and the draught is limited to 2 m although.

Till today most inland water vessels are using fossil diesel fuel or GTL. The future use of gaseous fuels like LNG or hydrogen is very limited due to space constraints on board to integrate the required tank infrastructure—pressurized or cryogenic. So only liquid alternative fuels like ammonia or methanol seem to be realistic for such applications, although the operations with such fuels increase complexity and require skilled staff on board for safe handling. As inland water vessels operate often in city areas or very close to large industrial locations, safe operation is a must under all circumstances.

3. Technological Aspects of the System Concept

Within the CAMPFIRE project, an ammonia-fueled propulsion plant concept has been developed for the later use of onboard inland water vessels as described above. Based on the given boundaries, the heart of the system will be an ammonia-fueled high-speed engine driving a generator and equipped with a cracker to decompose some of the ammonia to hydrogen and nitrogen, whereas the hydrogen is foreseen as pilot fuel for better ignition and efficient combustion of the ammonia. A more detailed concept will follow in the subsequent chapters. The generator will provide energy into a hybrid electrical drivetrain to reduce load variations from the cracker-engine unit and allow the distribution to several propeller drives. Further on, the hybrid setup provides redundancy as important requirement for a new technology implementation to ship propulsion. Of course, for higher power demands, the power generation and propeller drives are modular and can be multiplied according to the ship's requirements. During the concept planning and the basic engineering of a ship installation several challenges were found. 1) There are currently no regulations available from authorities and classification societies for such kinds of ammonia-fueled

Table 1. Influence of water level on ship speed at constant engine power.[70]

Engine power [kW]	Water level [m]	Ship's draught [m]	Ship speed [km h^{-1}]
600	5	2.5	17
600	2.5	2	8.5

ship propulsion systems, neither for sea-going nor for inland water vessels. 2) Safety data sheets usually warn that ammonia vapors form an explosive mixture with air. However, detailed investigations have shown that this is questionable, as pure ammonia decomposes into nitrogen and hydrogen before reaching the ignition temperature.[10] 3) Escaping ammonia is toxic to humans and, depending on concentration, harmful to health. 4) Escaping ammonia can also damage ecosystems (but is an important fertilizer worldwide, too).

So, it is essential to execute detailed safety investigations (HAZID and HAZOP) before or within the necessary discussions with the responsible authorities. Before realization on board of a ship, a full-scale testing and demonstration plant will be established ashore. This is foreseen at the CAMPFIRE Open Innovation Lab (COIL) close to Rostock/Germany. This test bed is foreseen to consider most relevant topics and requirements from maritime applications such as 1) constant and variable-speed engine operation; 2) safety concept including piping specifics and fire fighting; and 3) ventilation.

The whole testing facility will be used to optimize the ammonia-fueled combustion engine as well as the common operation of the cracker and the combustion engine. It will provide the possibility to simulate realistic ship engine operation and to optimize the system for high-dynamic operation requirements. Finally, it is foreseen to transfer the developed propulsion system concept into an existing inland water vessel including a respective ammonia storage tank system.

Three aspects of the technical development will be discussed in more detail. First, we will look at how the hydrogen required for ignition support can be obtained from ammonia via crackers. Then the development of the ICE combustion process is discussed. Finally, it is shown how the two systems, cracker and ICE, are integrated together.

3.1. Recovery of Hydrogen from Ammonia

In order to supply the required amount of hydrogen to the engine, a certain share of the ammonia feed has to be decomposed into hydrogen and nitrogen by the use of a suitable process.

3.1.1. Ammonia Decomposition

The decomposition is often referred to as ammonia cracking and is an endothermic process with a reaction enthalpy of about 46 kJ mol^{-1}, as can be seen from Equation (1).

$$NH_3 \leftrightarrow \frac{1}{2}N_2 + \frac{3}{2}H_2 \qquad \Delta H = +45.9\,\text{kJ/mol} \tag{1}$$

Figure 1 shows the equilibrium ammonia mole fraction as a function of temperature at pressures of 1, 5, and 10 bar. In accordance with Le Chatelier's principle, the equilibrium shift can be achieved by increasing temperature, reducing pressure, or separating the product. While pressure reduction is a less relevant solution due to insufficient hydrogen output, the dissociation by shifting the product concentration is used in membrane crackers. The most common solution, however, is a temperature increase. In practice, the chemical equilibrium shown in Figure 1 is not achieved due to kinetic limitations, especially at low temperatures.

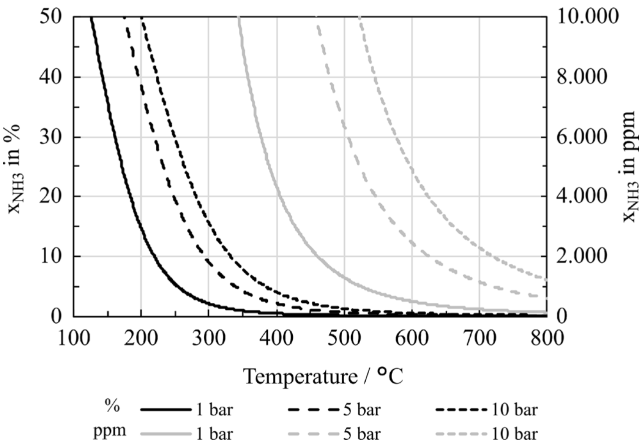

Figure 1. Simulated equilibrium ammonia mole fraction as a function of temperature at a pressure of 1, 5, and 10 bar, simulated with Aspen Plus.

To overcome the kinetic constraints, as in ammonia synthesis, solid catalysts are used in ammonia cracking technology (heterogenous catalysis). There are already numerous publications available on the development and characterization of ammonia cracking catalysts. A comprehensive review is given by refs. [11–13], for example. Active components investigated in the studies include Ru, Ir, Cu, Ni, Co, Mo, and different combinations of metals, such as, for example, Co–Mo, Ni–Mo, or bimetallic compositions with Ru.[11] Nickel and ruthenium are particularly interesting and currently the most widely used or mentioned candidates for ammonia cracking. Nickel shows technically relevant activity at temperatures above 600 °C and is also stable at high temperatures. Operating conditions are typically up to 900 °C; thus, equilibrium conditions can be reached and a residual ammonia content of about 100 ppm can be achieved.[11] According to the activity sequence of[14]

$$\begin{aligned} &Ru > Ni > Rh > Co > Ir > Fe >> Pt > Cr > Pd \\ &\quad > Cu >> Te, Se, Pb \end{aligned} \tag{2}$$

Ru exhibits the highest catalytic activity. Thus, the reaction temperature can be reduced compared to nickel. However, ruthenium is a precious and thus cost-intensive metal. Therefore, new low-cost catalytic compositions with a catalytic activity comparable to that of ruthenium are being actively researched.[11,13,15]

3.1.2. Ammonia Cracker

The decomposition of ammonia has been used for decades to produce a gaseous hydrogen–nitrogen mixture, also known as forming gas, which is used for applications such as soldering, welding, or brazing. The cracking process is usually carried out in electrically heated reactors with nickel catalysts at temperatures between 850 and 1000 °C to achieve a high conversion and thus a low residual ammonia content.[16] These systems, specially designed for the generation of forming gas, are unsuitable for the generation of hydrogen as a fuel source because the overall system efficiency is too low due to electrical heating. The systems are designed for stationary nominal operation and not for many start-up and shut-down procedures and high load dynamics; furthermore, the size and weight are not suitable for mobile applications.[17]

Ammonia crackers for use in the energy sector are the subject of research and development and—with a few exceptions—are not yet commercially available. The investigated concepts can be classified into four categories. 1) microreactors; 2) membrane reactors; 3) electrochemical reactors; and 4) packed bed reactors.

Microreactors (i) use characteristic lengths in the submillimeter range for intensified heat and mass transfer.[18] Membrane reactors (ii) combine cracking reaction and material separation in one system. With an integrated membrane, they allow continuous removal of the product and thus, according to Le Chatelier's principle, conditions beyond equilibrium. As a result, very low residual ammonia contents can be achieved.[17,19,20] Electrochemical reactors (iii) produce hydrogen from ammonia by means of electrolysis (ammonia electrolytic cell). Advantageous is the ability to produce pure hydrogen.[17,18] The reactor types (i)–(iii) mentioned above have in common that they are currently not suitable for hydrogen production in the kW range due to their stage of development, cost, durability, etc. The sole exception is a current development of a microreactor called *Ammonpaktor by Fraunhofer Institute for Microengeneering and Microsystems (IMM)*, which provides 70 kg of high-purity hydrogen per day for the operation of proton-exchange membrane fuel cells (PEM) for mobile and space-constrained applications.[21] In fixed bed reactors (iv), the catalyst is used in the form of a random bulk or as a structured and defined form, in particular as a metallic or ceramic honeycomb. The main advantages of honeycombs over bulk catalysts are low pressure loss, high mass transfer efficiency, and low diffusion resistance. In addition, monolithic catalysts are preferred when vibrations cause abrasion in classical bulk catalysts, for example, in exhaust gas treatment for cars, trucks, and more.[22,23] Most studies on reactor systems within the fourth category consider small-scale systems or refer to simulations.[17] Only a few studies consider the development and operation of reactors in a single-digit kW range as in Cha et al. Ryu et al. or Lamb et al.[24–26]

Ammonia crackers particularly designed for the propulsion system of inland waterway vessels are not state of the art and, to the authors' knowledge, have not yet been developed. The main challenges in designing these systems are the development and integration of a carbon-free heat supply, meeting the dynamic operation requirements of the engine, realizing optimized heat integration, and thus a high efficiency and long lifetime. The latter places very high demands on the materials used due to the harsh conditions characterized by temperatures of up to 900 °C and an ammonia-rich atmosphere. These conditions result in surface enrichment of nitrogen and induce material damage, also known as nitridation.[27] The nitriding resistance of various steels has been extensively investigated for conditions relevant to the Haber–Bosch process and thus for temperatures <550 °C. Within this temperature range, high-alloy austenitic steels and nickel-base alloys show high resistance against nitridation.[28] To the best of the authors' knowledge, the influence of conditions existing in ammonia cracking reactors on nitriding resistance has not yet been investigated and there are no certified materials for use in ammonia cracking reactors, at least none known to the public. According to the experiences gained at ZBT, IN600 shows good durability in cracker components investigated so far. Systematic studies have not yet been carried out and long-term experience is still lacking.

3.1.3. Development of an Ammonia Cracking Plant

The ammonia cracker is developed according to the requirements of the engine to the cracker product gas. The main requirements are summarized in **Table 2**. At full engine load, the cracker has to provide a hydrogen mass flow with an energy content corresponding to 10% of the total energy demand of the engine. With an engine output of 350 kW and typical efficiency values for engines of comparable size, this is equivalent to a hydrogen mass flow of 2.76 kg h^{-1} or a hydrogen output power of 92 kWH_2. The cracker product gas needs to be supplied at pressures between 6 and 8 bar, at temperatures below 60 °C and with a residual ammonia content below 5 mol%. According to the requirements imposed by mobile application, a monolithic catalyst system is to be used.

The heat required for the endothermic reaction is to be provided by a hot gas generated by a gas burner. The burner will be operated with ammonia and a certain amount of the cracker product gas. Experiments at ZBT have shown that the combustion of a fuel with a composition of $x_{NH_3} = 40$ mol%, $x_{N_2} = 15$ mol%, and $x_{H_2} = 45$ mol% has similar properties to the combustion of natural gas. Therefore, an ammonia content of 40 mol% is assumed. During process development, it must be taken into account that the load-bearing reactor wall temperature is limited due to the strength of the material used. On the example of IN600 and based on its strength values according to DIN EN 10 095, the temperature must not exceed 750 °C. Thus, the temperature of the hot gas passing through the reactor to provide heat for the reaction is also limited.

Process Development: The development of the process is carried out in Aspen Plus, Version 12. The main purposes of the simulations are 1) to develop a process design with optimized heat integration and thus high efficiency and 2) to determine energy and material flows, necessary for engineering ammonia cracking plant components such as reactor, burner, heat exchangers, compressors, etc. A simplified flow diagram of the developed process is depicted in **Figure 2**. Ammonia is fed to the process as a gas (10 bar, 20 °C) and is preheated in a first heat exchanger (1)

Table 2. Boundary conditions for the development of the ammonia cracking plant.

Description	Value
Energy content of hydrogen on the engine fuel	10%
Hydrogen power of the cracker product gas	92 kW
Cracker product gas pressure	6–8 bar
Cracker product gas temperature	<60 °C
Residual ammonia content of cracker product gas	$x_{NH_3} < 5$ mol% (corresponds to conversion >90%)
Catalyst	Monolith

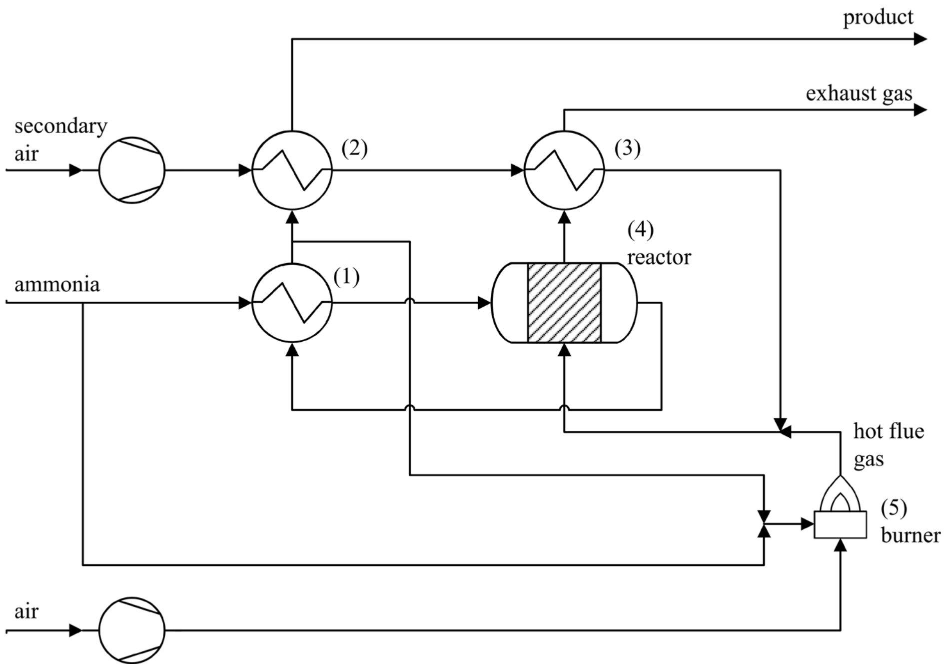

Figure 2. Simplified process flow diagram of the ammonia cracker.

before being decomposed in the reactor 4). The product gas is then used to preheat the educt. A partial flow of the product gas is taken downstream of the first heat exchanger 1) and is fed to the burner (5) along with a second ammonia educt stream. In a second heat exchanger 2), the product gas is cooled to the required temperature of 60 °C, thereby preheating a secondary air stream. The temperature of the secondary air stream is further increased by the flue gas emitting in the reactor in a third heat exchanger 3), thereby cooling down the exhaust gas. The preheated secondary air stream is used to control the flue gas temperature and, as the flue gas is used to heat the reactor, in the end to control the reactor temperature.

For the configuration shown, simulations were performed, varying the hot flue gas temperature between 750 and 1900 °C and the fuel gas composition between 10 mol% and 40 mol% NH_3. Within this range of parameters and for the condition shown in Table 2, the required hydrogen output power of the cracker product gas is between 100 and 120 kW. The amount of energy provided by the burner is between 22 and 24 kW and the total amount of ammonia required is between 18 and 24 kg h^{-1}. The efficiency of the process is calculated according to Equation (3) and is based on the lower heating value and considers the energy required for compressors but neglects heat losses.

$$\eta_{\text{Cr}} = \frac{\dot{m}_{\text{H}_2} \cdot H_{L_{\text{H}_2}} + \dot{m}_{\text{NH}_3} \cdot H_{L_{\text{NH}_3}}}{(\dot{m}_{\text{NH}_{3\text{Cr}}} + \dot{m}_{\text{NH}_{3\text{B}}}) \cdot H_{L_{\text{NH}_3}} + \frac{1}{\eta_C} \cdot P_C} \tag{3}$$

The efficiency strongly depends on the amount of secondary air required to control the hot gas temperature to the desired value and ranges from 83% to 92%. The influence of the fuel gas composition on efficiency is comparatively negligible.

Detailed Engineering, Construction, and Testing: Based on the results of the process simulation, the cracker concept is developed and the ammonia cracker, including reactor, burner, and heat exchangers, is designed. A crucial basis for reactor development is a suitable catalyst including a corresponding kinetic model. In order to identify the most appropriate catalyst, various monolithic catalyst systems (ceramic and metallic) are procured and extensively investigated with regard to their conversion as a function of temperature, gas hour space velocities, and pressure as well as long-term stability. Based on the evaluation of the results, a suitable catalyst is chosen and its kinetic model is determined.

For these studies, a test rig as shown in **Figure 3**a and an appropriate evaluation method[17,29] are already available at ZBT. The test rig mainly consists of an integral reactor, gas supply (NH_3, H_2, N_2), and gas analysis (Emerson x-Stream). A principal sketch of the integral reactor is shown in Figure 3b. The reactor tube with an inner diameter of 1" is surrounded by an electrical heating shell. The test rig allows the variation of gas hour space velocities up to 30 000 1/h and temperatures up to 900 °C. Currently, the operating pressure is being extended from 1 bar to 13 bar to carry out tests even under elevated pressure.

Based on the developed kinetic model and supported by multiphysics simulations in COMSOL Multiphysics, the ammonia cracker is designed in detail. This is followed by the engineering and construction of the ammonia cracking plant, comprising the cracker, balance of plant components, rack, enclosure, etc., including an appropriate programmable logic controller (PLC). The ammonia cracking plant is put into operation at the ZBT and is extensively tested and optimized. The plant will then be containerized, installed at the COIL in Poppendorf near Rostock (Germany), and finally coupled with the engine for extensive testing of the entire system.

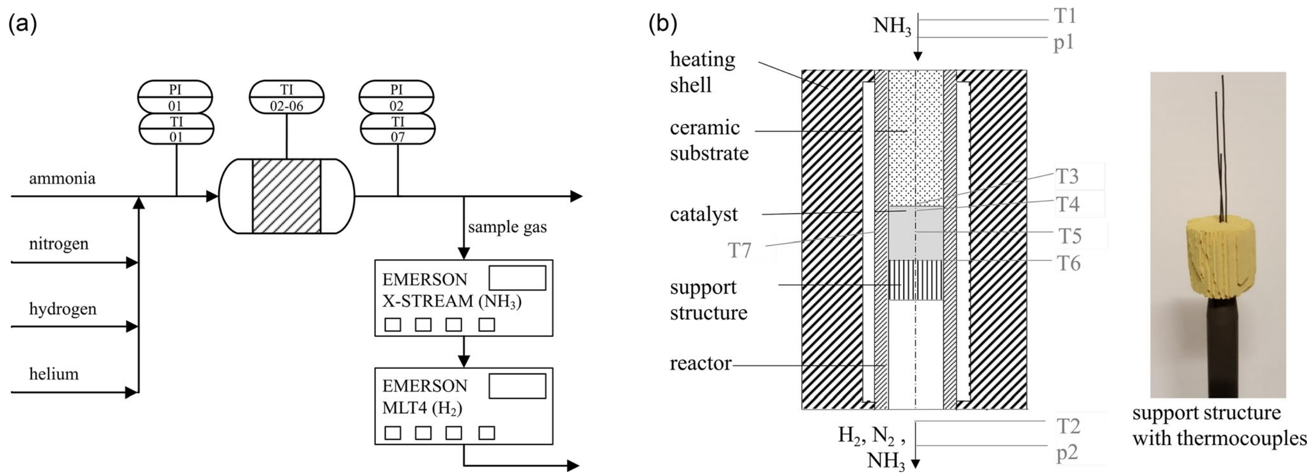

Figure 3. a) Simplified flow diagram of the test rig for catalyst characterization and b) cross section of the integral reactor.

3.2. Internal Combustion Engine

The ICE is the most relevant energy converter to produce propulsion and auxiliary power in shipping today. This is expected to continue for quite some time due to its potential to utilize different fuel types by respective adaptation. Due to the pressing demand for a replacement for fossil ship propulsion systems, more research projects have focused on the use of ammonia as a fuel in ICEs in recent years.[30] So this technology is considered as the heart piece for the current project as well. This section provides an overview of ammonia as fuel for ICEs, potentially related combustion concepts, and the utilized development methodologies.

3.2.1. Challenges of Ammonia as a Fuel

Ammonia as a fuel presents a number of challenges: on the one hand, with regard to combustion properties, and, on the other hand, with regard to material compatibility, which has not been an issue with conventional fuels to date. Both aspects are discussed in the following sections.

Some of the relevant chemical and physical properties of ammonia with regard to the conversion in ICE are shown in **Table 3**. For comparison purposes, other conventional fuels (diesel, gasoline) as well as methane and hydrogen were also added.

The lower heating value of ammonia is significantly reduced compared to other fuels. Using carbon-free fuels, however, ammonia has the advantage over hydrogen that ammonia is already present in liquid form at moderate pressures and temperatures ($p = 8.5737$ bar at $T = 20$ °C[31]). This results in higher volumetric energy density compared to highly compressed (600 bar) or liquid hydrogen (**Figure 4**).

The main challenges in using ammonia as a fuel are the high value of minimum autoignition temperature and the low laminar flame speed. In order to ensure safe ignition and low burning duration of ammonia–air mixtures, it is purposeful to use promoter fuels like hydrogen or diesel fuel. An overview of possible combustion processes for internal combustion engine using ammonia as a fuel is given in Section 3.2.2.

Another special feature of ammonia is its particularly large enthalpy of vaporization. A rapid drop in pressure, for example, at leakage points, is always associated with a sharp drop in temperature, which usually appears in icing.

In addition to the combustion challenges, material compatibility and lubrication issues must be considered when using ammonia as a fuel. The compatibility of ammonia with materials used in the field of design and sealing technology is relatively limited, as **Figure 5** indicates.

Although ammonia has been produced and used for over 100 years, only a few materials are suitable here. A wide range of materials used in engine design and apparatus engineering is not approved to be used with ammonia or is explicitly not suitable for this purpose. In terms of sealing materials, NBR or EPDM are not fully suitable for use with gaseous or liquid

Table 3. Properties of different fuels for internal combustion engine concepts.

	Unit	NH_3	H_2	CH_4	Diesel	Gasoline
Lower heating value	$MJ\,kg^{-1}$	18.6[67]	120[67]	50[67]	42.5[71]	44.5[71]
Stoichiometric air-fuel ratio	$kg\,kg^{-1}$	6.1[72]	34.3[71]	17.2[71]	14.5[71]	14.6[71]
Minimum autoignition temperature	°C	650[67]	520[67]	630[67]	180–320[71]	260–460[71]
Maximum laminar flame speed for $T = 298$K, $p = 0.1$Mpa	$m\,s^{-1}$	0.07[67]	2.91[67]	0.37[67]	≈0.4[73]	≈0.4[73]
Flammability limit (Equivalence ratio)	–	0.63–1.4[67]	0.1–7.7[73]	0.5–1.7[67]	0.75–2[73]	0.7–2.5[73]
Adiabatic Flame Temperature	°C	1800[67]	2110[67]	1950[67]	2327[71]	2307[71]

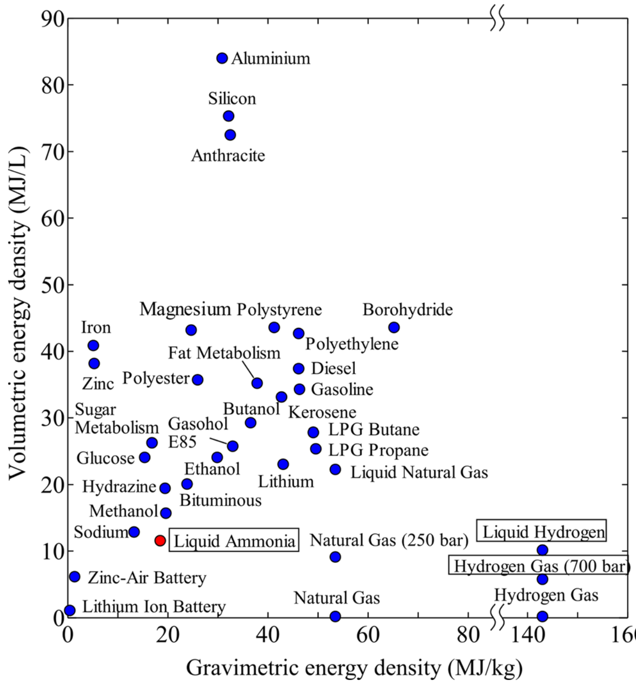

Figure 4. Gravimetric and volumetric energy density of combustible materials and batteries according to ref. [67].

ammonia. In addition to the limited choice of sealing materials, the significant interaction of ammonia with copper-containing engine components must also be considered. These include oil heat exchangers, rocker arm bearings, connecting rod bearings, and piston pin bearings.

According to the given boundary conditions within this project and the potential for injection of both gaseous and liquid fuel, a gas injector was chosen as baseline for the project. The Liebherr injector family LDI for gaseous direct injection with a pressure range of 20–60 bar provides the best basis for further adaptions because of its modular design.

For operation with liquid ammonia, it was necessary to adapt the needle design. However the overall sealing concept could still be maintained. Furthermore all static sealings were substituted by ammonia resistant versions. Also lift and spring pretension had to be adapted for the particular applications. The establishment of the best spray pattern needs further development work. It is therefore planned to use interchangeable blow caps. Depending on the specific application, such as the position of the injector, there is a need for appropriate solutions, which are being prepared together with the Karlsruhe Institute of Technology (KIT).

In contrast to injection systems for conventional liquid fuels, the design for ammonia does not require particularly high system pressures. However, the extreme cooling, in case of leakage or pressure drop as a result of evaporation, must be taken into account in the constructive design. This can have an impact on the dimensioning of components.

Challenges for the lubrication system of engines with the use of ammonia as a fuel are currently insufficiently known. At the state of research, the effect of ammonia enrichment in lube oils is not clear for example. From the refrigerant industry it is known that the solubility of ammonia is good in mineral oils.[32] The effect on the lubricity is unknown. The lubricity of lube oil strongly depends as well on the capability of lube oils to bind water as a main component of the exhaust gas from ammonia combustion. Other important issues that need to be addressed in future research on lubricating oils are outlined in **Figure 6**.

3.2.2. Combustion Concepts for Ammonia

There are various approaches for the use of ammonia in ICE. A general classification of different combustion processes is shown in **Figure 7**.

Essentially, a distinction can be made between spark-ignited (SI) and compression-ignited (CI) combustion processes. In both groups, an ignition promoter is added in addition to the

CHEMICALS	METALS					PLASTICS, ELASTOMERS & LEATHER																			
A: Excellent, B: Good, C: Fair to Poor, D: Not recommended - No Data	Aluminum	Carbon Steel	Cast/Ductile Iron	304 Stainless Steel	316 Stainless Steel	Acetal	Buna	CSM (Hypalon)	EPR, EPDM	Fluorocarbon	Fluoroelastomer (FKM)	Geolast (Buna & Polypropylene)	Hastelloy C	TPE	Leather	Nitrile (TS)	Nitrile (TPE)	Nylon	Polychloroprene	Polypropylene	PTFE	PVDF	Santoprene (EPDM & Polypropylene)	UHMWPE	Urethane
Ammonia 10%	A	A	A	A	A	D	A	D	A	-	D	A	A	-	-	-	-	A	A	A	A	A	-	-	-
Ammonia Anhydrous	A	A	A	A	A	D	B	-	A	D	D	-	A	D	D	-	-	B	B	A	A	A	A	A	-
Ammonia Aqueous	-	-	-	-	-	B	-	-	-	-	-	-	-	-	-	-	-	B	-	A	A	A	-	A	-
Ammonia Gas — Cold	-	-	-	-	-	-	A	-	-	A	-	-	-	-	-	-	-	-	A	-	A	-	A	A	-
Ammonia Gas — Hot	-	-	-	-	-	-	C	-	-	D	-	-	-	-	-	-	-	-	B	-	A	-	A	A	-
Ammonia Liquids	D	-	A	A	-	D	-	-	A	-	D	-	B	-	-	B	B	-	A	A	A	A	A	D	B
Ammonia Liquors	A	-	A	A	-	-	-	-	-	D	-	-	-	-	-	-	-	-	A	-	A	-	A	-	-
Ammonia Nitrate	C	A	A	A	A	C	C	D	A	-	D	D	B	-	-	A	A	D	C	A	A	A	A	-	B
Ammonia, anhydrous	B	A	D	B	A	D	C	D	A	-	D	D	B	D	-	B	B	B	A	A	A	D	A	A	-
Ammonia, Gas (Cold)	-	-	-	-	-	A	A	-	A	-	D	-	-	D	-	A	B	-	A	B	A	D	A	-	B
Ammonia, Gas (Hot)	-	-	-	-	-	-	C	-	-	-	D	-	-	-	-	-	-	-	B	-	A	-	-	-	-
Ammonia, Liquids	D	-	A	-	A	-	B	-	-	-	D	-	B	-	-	-	-	B	A	A	A	A	-	-	-
Ammonia, Water	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Figure 5. Ammonia material compatibility according to ref. [68].

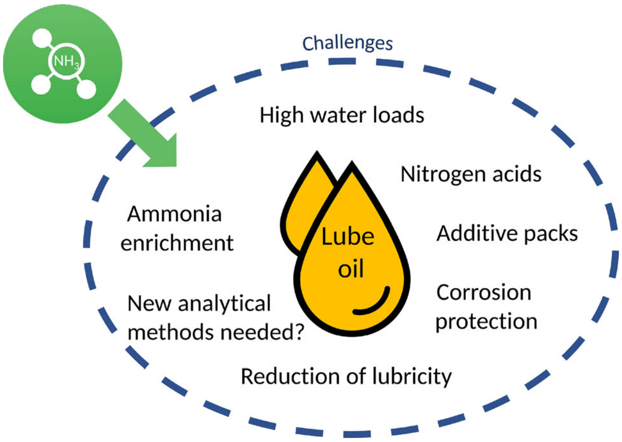

Figure 6. Challenges for lube oil with ammonia as a fuel.

ammonia to improve the ignition phase of the ammonia and the burning rate of the air-fuel mixture. Compression ignition with diffusive energy conversion and without a promoter is another option for the conversion of ammonia in combustion engines. Because of the high autoignition temperature (cf. Table 3), the aspired air must be compressed to a very high degree. This necessitates geometric compression ratios of the engines of at least 35:1.[33] Technically, such high compressions pose high challenges to the mechanical and thermal load capacity of the engine as well as its lubrication.

Therefore, in the past, priority has been given to the study of various combustion processes with promoter fuels corresponding to Figure 7. Theoretical and practical investigations using a laboratory burner to increase the combustion speed of ammonia–air mixtures were carried out as early as 1945 by Tanner.[34]

For premixed conversion of ammonia by spark plug, the influence of ignition energy on spark ignition engines was investigated in 1966 by Cornelius et al.[35] The fuel was injected in gaseous form into the air intake of a V8-engine with 3.5 L displacement. Here, the effect of increased ignition voltage as well as dual ignition were analyzed.

In 1988, Mozafari-Varnusfadrani[36] carried out experiments on a single-cylinder engine (bore: 76.2 mm, stroke: 111.1 mm) with variable compression ratio. A compression ratio of 15:1 was set for ammonia. Among other things, the evaporation of the ammonia and the resulting cooling of the air–ammonia mixture made it difficult to ignite the mixture in the combustion chamber.

Also on a small SI engine, experiments with ammonia and hydrogen were carried out by Mørch et al.[37] For a stable combustion process, a hydrogen content of at least 5% (volumetric) must be supplied. With the same fuels, basic experiments were performed on a single-cylinder engine with 0.5 L displacement by Frigo et al.[38] The energetic admixture of hydrogen had to be increased to 7% in full load operation to limit the coefficient of variation for indicated mean pressure (IMEP) to 4.5%. For part-load operation, the hydrogen percentage had to be increased to 10–12% for stable engine operation.

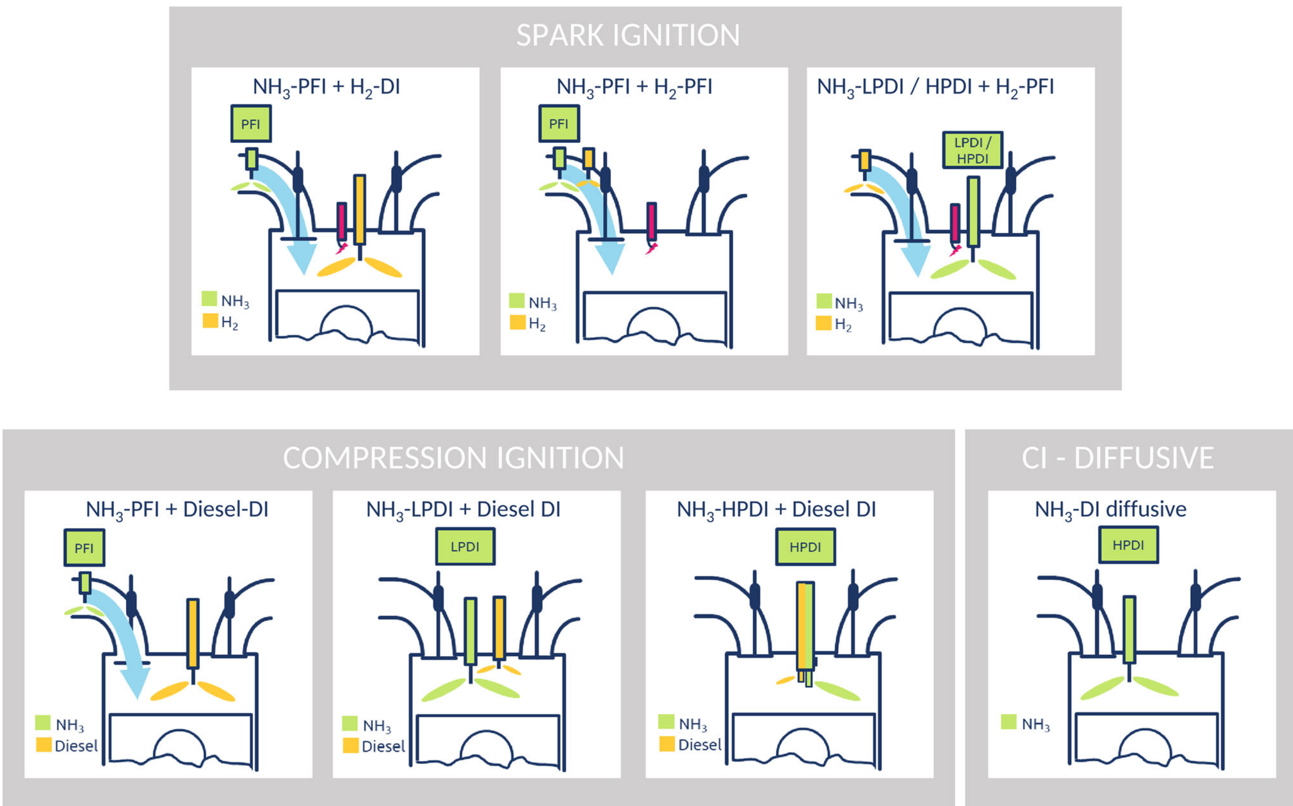

Figure 7. Combustion concepts for ammonia as a fuel in ICE.

Other experiments were conducted by Youngmin on a three-cylinder passenger car engine.[39] In the experimental setup, ammonia and gasoline were injected into the engine's intake manifold via separate injectors. On the test bench, an energetic proportion of ammonia of up to 80% was achieved at 1440 rpm at full-load.

Ryu et al. studied the influence of direct injection of gaseous ammonia into the combustion chamber of a single-cylinder research engine with spark ignition.[25] Gasoline was used as the ignition promoter, which was injected into the intake manifold of the engine. As a result, slightly lower specific fuel consumption was achieved when operating with ammonia and gasoline in combination. Nitrogen oxides (NO_x) as well as unburned ammonia (NH_3) emissions were increased compared with gasoline-only operation. With regard to carbon monoxide (CO) emissions, a reduction was achieved compared to gasoline operation.

The investigations on the operating limits of a modern gasoline direct injection (GDI) spark ignition engine fueled with ammonia and hydrogen at very low engine load of up to 275 bar IMEP were studied in ref. [40]. An ammonia fuel share of 90% could be achieved in the range between 650–2000 rpm.

Wermuth et al. investigated SCE for stationary power supply with a bore of 145 mm and a speed of 1,500 rpm.[41] While the NH_3/H_2/air mixture is added upstream by cylinder intake, a fraction of H_2 is used in a prechamber to ignite the mixture. A load range of 3–25 bar IMEP could be achieved while reaching ammonia shares of 100% at high load.

Youngmin et al. carried out experiments on a common rail (CR) diesel passenger car engine in addition to the experiments on the SI engine with ammonia–gasoline mixtures.[42] In this work, the ammonia was injected into the intake manifold. The diesel fuel promoter was injected directly into the combustion chamber via the CR system installed on the engine. The amount of ammonia was up to 38% energy content.

In the experiments of Nadimi et al. substitution rates of diesel fuel of up to 84% were achieved on an 86 mm bore diesel engine.[43] In this case, the coefficient of variation (COV) of the IMEP was over 6%. With increasing ammonia content the NH_3 emissions increased significantly. The concentration of nitrous dioxide (N_2O) was below 100 ppm over the diesel fuel substitution rate.

Dual-fuel operation with dimethyl ether (DME) and ammonia was studied by Zacharakis et al. on a GDI engine with 0.3 L displacement.[44] For the experiments, ammonia and DME were mixed in a tank and injected directly into the combustion chamber of the engine via a high-pressure pump and injector. At a fuel mixture of 40%/60% (DME/NH_3), high cyclic fluctuations were observed in part-load operation, which became smaller with increasing load. Operation with higher ammonia contents was limited by the high enthalpy of vaporization and thus the strong cooling in the combustion chamber.

The influence of NH_3–DME mixtures on the combustion process of a CI engine with 0.3 L displacement was also studied by Gross.[45] In this work, the focus was on single-fuel injection compared to multiple-fuel injection. To reduce the long ignition delay of ammonia, a preinjection of DME was injected before the main injection. For a fixed ratio of the two fuels (20% NH_3/80% DME), the influence of the distance between preinjection and main injection was investigated. It was found that the preinjection should not be introduced further than 35° BTDC, so that the distance between the energy conversion of the pilot amount and the main injection amount of the fuel is not strongly separated.

The focus of the studies from Cai et al. has been on the emission behavior of a ammonia-diesel fueled compression ignition engine with a variation of injection strategies.[46] In addition to standard measurements of emissions such as NH_3, NO_x, THC, CO, etc., hydrogen cyanide (HCN) was also measured which is known for its strong toxicity.[47] It could be observed that implementing an early pilot injection improved the ammonia combustion efficiency from 74% to 89% but worsened the emission performance. This could be compensated by advancing the start of the main injection but with the disadvantage of increased NO_x emissions.

Niki et al. also investigated the influence of early preinjection of diesel fuel[48] and a split diesel fuel injection.[49] Here, a positive effect on the amount of unburnt NH_3 in the exhaust gas was demonstrated. A further reduction of ammonia in the exhaust gas could be achieved by postinjection of diesel fuel.

The influence of a very early pilot injection with second injection of diesel fuel into a premixed ammonia–air mixture was also investigated by Mante.[50,51] It was shown on a single-cylinder research engine with 1.29 L displacement that very early preinjection achieves a significant improvement in the energy conversion of the ammonia–air mixture, thus offering the potential to increase the energy content of ammonia in the fuel mixture.

Investigations on ammonia direct injection in combination with diesel fuel pilot injection were carried out by Stenzel et al. on a single-cylinder research engine with 5.17 L displacement.[52] Here, ammonia is injected into the combustion chamber at up to 500 bar as well as diesel fuel using a multineedle injector. The same injection system is used for analyses by Frankl et al. on an optically accessible engine (derivative of an MTU 4000 diesel engine).[53]

Coppo et al. performed combustion process analysis on a single-cylinder research engine with 15.7 L displacement.[54] In this experimental setup, two high-pressure injectors were used for ammonia and diesel fuel. At a break effective mean pressure of 20 bar at 750 rpm, engine operation was shown with a fuel share of 40% ammonia to 60% diesel.

Another method to use ammonia in a diesel engine is with the use of a high-pressure dual-fuel combustion process. Here, both ammonia and diesel are injected directly into the combustion chamber under high pressure. Scharl et al.[55] investigated this setup in a rapid compression–expansion–machine to show detailed influences of key combustion parameters like spray interaction angle and relative injection timing. Despite observed effects such as the diesel flame being extinguished by ammonia if the time between injections was too short, an energetic ammonia content of up to 96.8% was measured at the set operating points.

3.2.3. Combustion Process Development

The main challenges in developing an ammonia-based combustion process are primarily due to the chemical properties of ammonia. In particular, the rather poor combustion properties are described in the previous sections and the possible incompatibility of materials. Apart from that, there are a lack of validated simulation tools that would enable rapid evaluation and refinement of new concepts. Aspects such as atomization, evaporation, and mixing behavior, combustion behavior, and heat release of ammonia are far less well understood than for conventional fuels, for which there is a wealth of experience with corresponding modeling.

To achieve the ultimate goal of developing a combustion process for a multicylinder engine, the following strategy is used. A single-cylinder engine is used to test the basic concepts. The extensive instrumentation of this research engine allows the determination of the calibration quantities required for the essential 0D/1D simulations. The models validated on the single-cylinder engine are then used for the process development of the multicylinder engine. Certain quantities that cannot be measured directly are determined using detailed 3D flow simulations. These quantities are then fed into the 0D/1D tools. The final step is to apply the knowledge gained from the single-cylinder test bench and the validated 0D/1D models to the complete engine.

The experimental work on combustion process development is carried out in Karlsruhe on a single-cylinder engine (**Figure 8**) derived from the Liebherr multicylinder hydrogen engine. The multicylinder engine tests will be carried out in Rostock.

Simulation: Concerning the development process of engines, the use of numerical simulation methods is widely used since many years. Proven phenomenological and physical models are established with a variety of fuels. A lot of experience is gathered in the field of conventional fuels like diesel, gasoline, or methane and implemented in common software tools for 0D/1D and 3D computational fluid dynamics (CFD) simulations. Nevertheless, the upcoming renewable fuels like hydrogen, ammonia, methanol and especially blends of them still need more research in terms of the use in simulation because they aren't deeply implemented in the available software tools. This accounts for example the implementation of laminar burning velocities, detailed reaction mechanisms or even physical fuel properties.

To address these challenges, the methodology in this research project uses both simulation and experimental results to achieve the project goals of gaining knowledge for the optimized design of an ammonia-fueled marine engine. In this project, a 0D/1D and a 3D CFD model of the investigated engines will be developed to show the potential of H_2/NH_3 combustion beyond the experimental capabilities. This includes, for example, variation of the ammonia fuel fraction, variation of injection and ignition timing, fuel and air conditioning, or valve timing on the combustion process side, and in terms of geometric purposes, for example, variation of piston geometry, spark plug location, or cylinder head and valve geometry.

In order to achieve a satisfactory accuracy of the simulation results, initial engine data such as cylinder pressure and rate of heat release and other boundary conditions are used to calibrate the developed models.

The predictive 0D/1D model is created using the GT-Power software tool from Gamma Technologies, which is well established in the industry.[56] This model aims to simulate the behavior of the later installed full cylinder engine, but first a model of the 1-cylinder research engine is developed at the KIT laboratory to gain experience and calibration data as soon as possible. The combustion model used will be the SITurb model, which is a widely used two-zone model. While many submodels from the GT-Suite library are used, the implementation of the H_2/NH_3 fuel mixture requires some adaptations of the models. In particular, the necessary calculation of the laminar flame velocity, the ignition delay times, and the pollutant formation are taken into account. In this study, the detailed reaction mechanism of[57] is used to calculate the mentioned quantities.

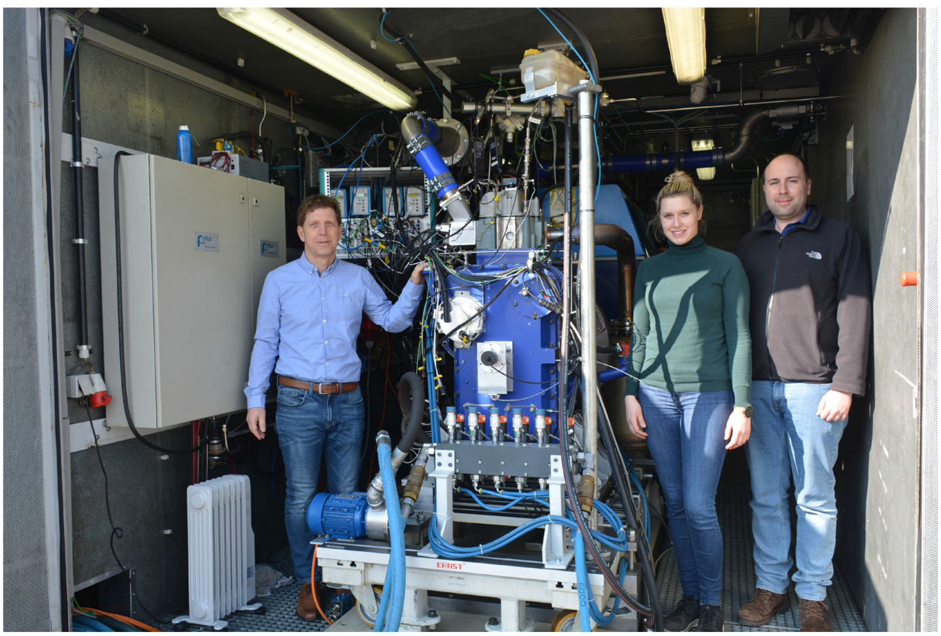

Figure 8. Single-cylinder engine at KIT in Karlsruhe.

The results of the 0D/1D simulation can either be used to simulate other engine operation points than those investigated in the experimental studies or they can be integrated in the dynamic simulation of the cracker–engine–ship system.

The 3D CFD simulations are carried out using the commercial software CONVERGE CFD.[58] It is used in order to determine quantities that are not accessible by measurement, but which are necessary for the 0D/1D modeling. Particularly with regard to the atomization behavior of the initial liquid fuel ammonia, a simulation based on first principles would be desirable, since the suitability of common models for use with ammonia is largely unknown. However, due to the significant computational requirements of a level set or volume of fluid simulation, an Euler–Lagrange method is used. We therefore follow the dispersed particle modeling approach as described by Zhang et al.[59] Combustion simulation is performed using a direct chemistry approach (SAGE) in combination with an appropriate flamelet model. However, the main focus of the 3D simulations in the context of this work is to increase the reliability of the 0D/1D models, which are essential for the design of the full-engine operating strategy.

Single-Cylinder Experiments: The single-cylinder research engine for the development of the new combustion process was built on a test bench at the Institute of Internal Combustion Engines at KIT. Originally designed for hydrogen operation only, the engine has to be extended by some components for dual fuel operation with hydrogen and ammonia. The engine data is shown in **Table 4**.

An obvious necessary extension of the engine is an additional injector for ammonia injection. Therefore, two separate fuel infrastructures for hydrogen and ammonia are required. Both fuels are provided in gas cylinders. While hydrogen is already available at a pressure of 300 bar, the ammonia pressure must be increased to the desired injection pressure by means of a compressor. As this is a spark ignition engine combustion process, a spark plug is required for ignition. Hydrogen is always injected in gaseous form into this engine. For ammonia, both gaseous and liquid injection are provided. Since ammonia has a very low calorific value of only 18.8 MJ kg^{-1} compared to diesel fuel, the injection system must be designed for comparatively large mass flows in order to achieve diesel-like mean effective pressures. Due to the high enthalpy of vaporization of 1.371 MJ kg^{-1}, the cylinder charge is very strongly cooled during the injection of ammonia. This results in advantages with regard to knocking behavior and nitrogen oxide emissions.

Ammonia is difficult to ignite and has low burning rates. Conventional spark ignition is therefore not sufficient to initiate combustion with pure ammonia. For this reason, hydrogen is added to the cylinder charge. Hydrogen requires a very low minimum ignition energy. If the hydrogen starts to burn first, the ammonia can also be ignited by the energy released. The hydrogen also ensures a faster burn-through, which is important for high efficiency. One of the aims of this study is to investigate how far the hydrogen content can be reduced in order to still ensure reliable ignition at all operating points and how this affects the efficiency.

Table 4. Single-Cylinder engine data.

Cylinder	1
Stroke	157 mm
Bore	135 mm
Compression ratio	14
Max. speed	1900 rpm
Operating principle	4-stroke
Displacement	2.24 L
Type	modified Liebherr hydrogen engine

The engine is equipped with a cylinder pressure sensor, an exhaust pressure sensor, an intake pressure sensor, and an ammonia fuel pressure sensor. This allows detailed analysis of the gas exchange and combustion process. The ignition currents are also recorded to ensure reliable misfire detection by the ignition system. The engine is supplied with air via an external compressor. The maximum charge pressure is 4 bar. Heating of the charge air up to 60 °C is possible. In order to adjust the intake-to-exhaust pressure ratio as in standard turbocharger operation, the engine has exhaust throttle valves.

In addition to optimizing the combustion process, this project also focuses on exhaust emissions. Special attention is paid to hydrogen slip and nitrogen oxides. Carbonaceous emissions can only come from the engine oil in this combustion process. Therefore, the formulation of the lubricating oil, which must be adapted to the special conditions of ammonia operation, is of great importance. Particular attention must be paid to high water ingress. Up to six different oil pressures can be applied at different points on the test engine.

In addition to the combustion process itself, the safety aspects of test bench operation also pose a great challenge. Unlike hydrogen, ammonia is not highly flammable, but it is highly toxic. Even very low concentrations can cause lung burns when inhaled. Contact with skin or eyes can lead to chemical burns and blindness. In addition to sensory monitoring of the test stand by a warning system, it is therefore necessary to wear ammonia-proof face and breathing masks as well as protective clothing when working in the test stand.

Optical Intake Manifold Test Bench: Since only little is known about spray formation during ammonia injection by means of a high-pressure injector (cf.[60]), optical investigations for spray analysis are being carried out at KIT. It should be noted that these optical studies are only a secondary aspect of combustion process development. However, they are extremely valuable, especially for the calibration of numerical atomization models, and are therefore worth mentioning.

An optically accessible intake pipe was designed and attached to the engine (see **Figure 9**). The optical accessibility is achieved by two opposing planar glass windows. While one side is illuminated by means of an LED (light-emmiting diode), the scattered light on the opposite side can be detected with a high-speed camera. This makes it possible to visualize the liquid phase of the fuel spray. From this, the penetration depth, penetration speed, and spray angle are determined. The evaporation behavior of the spray is characterized. Injection pressures of up to 60 bar can be investigated here. Due to the toxicity and corrosiveness of ammonia, these tests cannot be carried out as usual in a conventional injection chamber.

Multicylinder Engine Testing: To test the multicylinder engine in the COIL, it will be coupled with a generator. This unit will be installed in a container with all the necessary auxiliary systems as

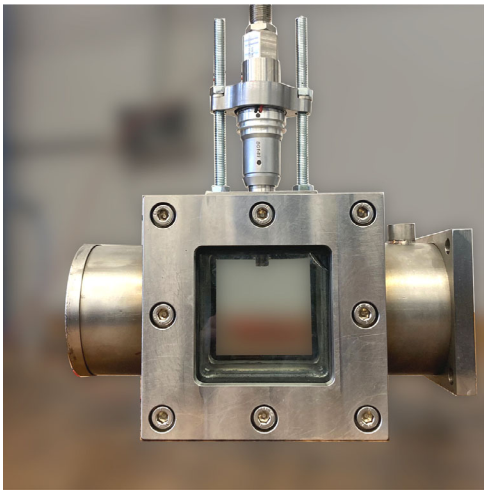

Figure 9. Optical intake manifold.

well as automation and monitoring equipment (**Figure 10**). The cracker system will be housed in a separate container for close proximity to the genset container. The complete setup is planned to allow and demonstrate operation according to maritime requirements, especially with regard to transient operation scenarios. Both containers will be equipped with a full set of scientific instrumentation to allow detailed study and optimization of the ammonia combustion.

The multicylinder engine is based on a hydrogen-fueled version of the Liebherr D966 engine type (**Figure 11**). The characteristics of this six-cylinder engine, called A966, are given in **Table 5**. The output will be up to 350 kW in accordance with the typical needs of European inland water vessels.

3.3. System Integration

As shown in Section 3.1, the recovery of hydrogen from ammonia can be achieved after reaching a certain temperature in a

Figure 11. Hydrogen-fueled Liebherr base engine (Liebherr Machines Bulle SA).

catalytic cracker unit. For a system consisting of an ICE and cracker unit, the heat supply needed for the hydrogen recovery means losses in efficiency. Therefore, the amount of energy needed for the decomposition should be minimized. In order to maximize the efficiency of the system, thermal coupling between the engine and cracker unit should be considered.

The engine provides a certain amount of waste heat which could theoretically be used to recover hydrogen from ammonia. Some studies have discussed the potential of this approach. Ryu et al.[61] analyzed a spark ignition engine powered by gasoline and ammonia. Here, the gasoline was injected into the air intake and the gaseous ammonia directly injected into the cylinder after running through a decomposition catalyst. The catalyst was located in the hot exhaust stream of the engine. Energy from the exhaust gas is transferred to the catalyst without any species transfer taking place. This system allowed a share of the ammonia to be decomposed into hydrogen and nitrogen before entering the engine. The experimental work carried out by Ryu et al. shows that the hydrogen generated by ammonia decomposition resulted in improved engine performance and reduced exhaust emissions. Moreover, the used catalyst was very effective for

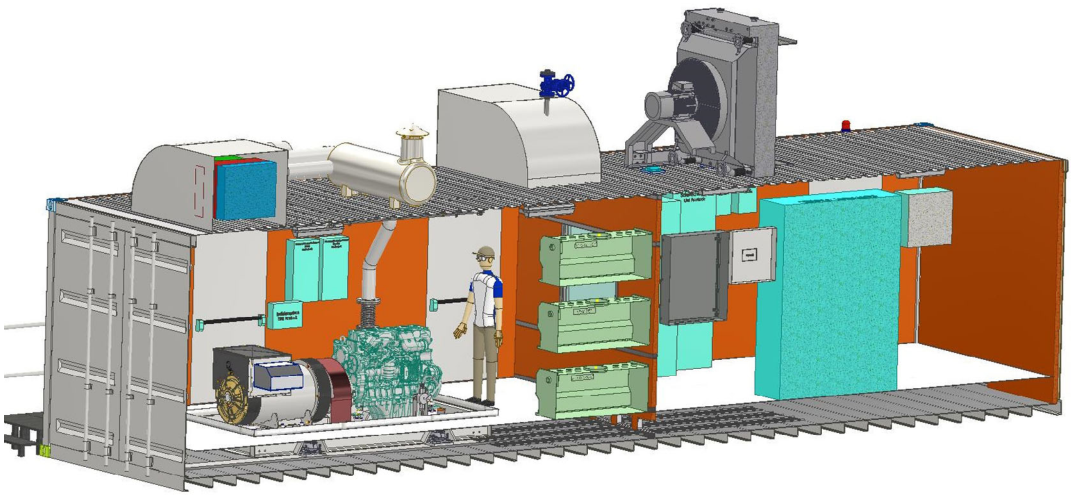

Figure 10. Ammonia-fueled genset container concept.[69]

Table 5. Main technical data of Liebherr base engine A966 (Liebherr machines Bulle SA).

Rated load with ammonia	up to 350 kW
Rated speed	1500 rpm
Engine configuration	in-line engine
Cycle	4-stroke
Number of cylinders	6
Bore	135 mm
Stroke	157 mm
Displacement	13.484 L

low-to-medium flow rates of ammonia, resulting in significantly increased engine power and decreased fuel consumption.

Comotti and Frigo[62,63] carried out research on an ICE powered by ammonia and small amount of hydrogen. The hydrogen was provided by a catalytic cracker reactor which was integrated in the exhaust system. Pure ammonia and a mixture of ammonia, hydrogen, and nitrogen was then injected into the air intake. As a conclusion, Comotti and Frigo confirmed the cracker reactor performance and verified the feasibility of thermal coupling between engine waste heat and a cracker unit. Nevertheless, an additional electric heater was integrated in the system to ensure a good cold start performance and to improve steady-state operation.

Sittichompoo et al.[64] examined the partial replacement of gasoline fuel with hydrogen which was produced on board, implemented on a direct ignition engine. The results show a significant potential for improving the fuel economy and reducing the CO_2 emissions of the engine. In this present study, the system integration of the ICE and the cracking unit is considered on a theoretical basis. As a first approach, a static 0D model was created. The model uses literature data for the ammonia conversion rate of the cracking unit. In addition, a data map-based submodel of the engine has been implemented. This provides a tool to analyze the potential of the system integration and thermal coupling of the components. **Figure 12** illustrates the model of the system integration schematically.

The engine submodel contains a data map which specifies the load-dependent fuel consumption, meaning the amount of pure ammonia (Path 1) and cracker product gas (Path 2) needed for a certain engine load point. The majority of the chemical energy fed into the engine is provided by pure ammonia. In addition to this, the energy share of hydrogen is variable in this model and can be set to a certain value in the engine submodel. Furthermore, in the controller submodel, data from the engine and cracker is collected and the fuel mass flows are regulated accordingly.

The cracker product gas (Path 2) contains hydrogen, nitrogen, and ammonia. The chemical composition is calculated in the cracker submodel and depends on the conversion rate of the cracker, which is read from a data map. The data map shows the dependency of the conversion rate on the temperature of the reactant gas fed into the cracker. The chemical composition of the cracker product gas is directly related to the conversion rate. If the temperature of the reactant gas (pure ammonia) is low, a smaller amount of hydrogen is provided to the engine. In this case, the controller would increase the mass flow through the cracker to ensure the needed energy share of hydrogen is provided. In consequence, the mass flow of ammonia in Path 1 would be lowered to maintain the required load.

Ammonia is liquid at the system pressure. Before it is fed into the cracker it is vaporized and preheated. As shown in Figure 12 the evaporation of ammonia is supported utilizing the warm cooling water of the engine. For preheating, two heat exchangers come into use. One uses the hot exhaust stream of the engine and the other one recovers heat from the cracker product gas. Furthermore, an internal heat source is considered inside the cracker submodel. This extra heat source ensures a minimal catalyst temperature to ensure conversion rates above the required value. The model shown was used to calculate the needed

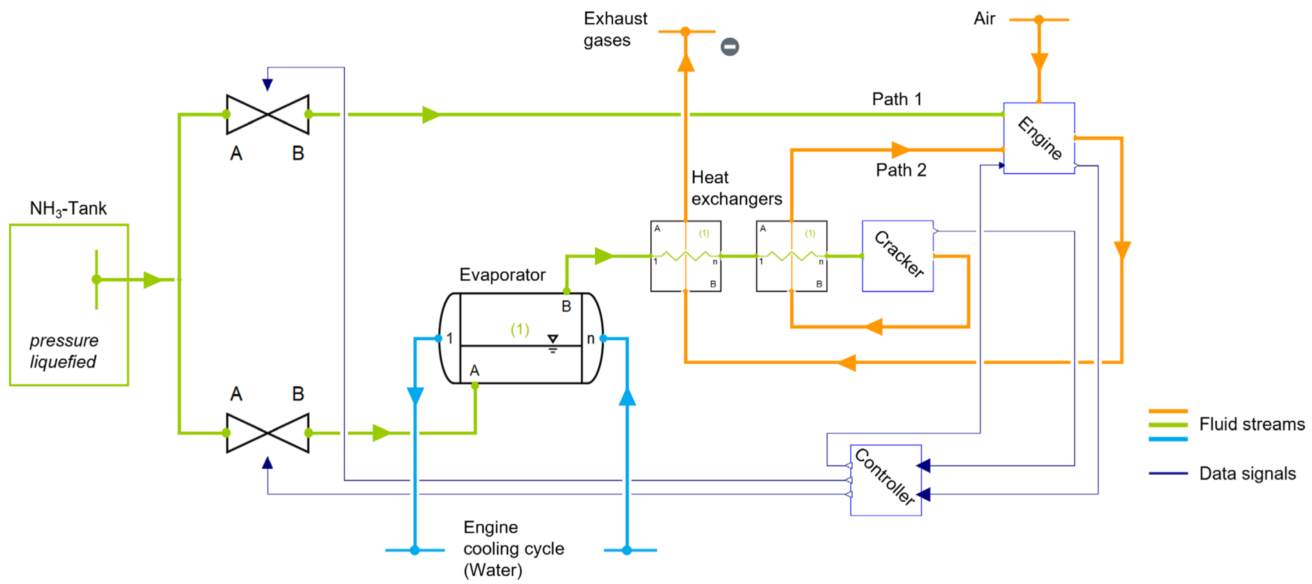

Figure 12. Model of the system integration (simulation software: Dymola).

amount of energy for the cracking of ammonia for the given six-cylinder engine in dependency of the engine load. Moreover, the energy saving by heat recovery from exhaust gas and product gas could be simulated for different cases. This was carried out by comparing two cases, both with the same required minimum catalyst temperature. The first case was simulated without any heat recovery and the second case with all heat recovery options. Afterward, the cases were compared in terms of the additional energy amount (from outside the system) needed to ensure the minimum catalyst temperature. This energy amount differs for different cracker reactant gas temperatures, meaning that when more energy is recovered from the cooling water, exhaust gas, and product gas, less energy is required for the internal heater. The difference in energy required by the system for internal heating is a measure for the efficiency of the overall system.

A simulation with the model running at different static points and a hydrogen energy share of 6–18% show a possible increase of the system efficiency of around 4% points. This value corresponds to a comparison between a case without any heat recovery and a case with maximum heat recovery. It has to be mentioned that this value is highly dependent on the exhaust gas temperature and the performance of the cracker unit in a real application. For further insight, experimental data from the six-cylinder engine and the cracker unit will be integrated into the model. Following this, after validation with experimental data and a realistic design of the heat exchangers, the static model can be transformed into a dynamic one. With this step the problematic cold start behavior and the dynamic operation of the engine can be simulated.

4. Safety Aspects

In addition to the purely technical details mentioned above, the issue of safety must also be addressed when it comes to ammonia, as this will have an impact on future legislation. Some safety aspects have already been mentioned in the section on test bench work, but here we will look at some general issues regarding the hazards of ammonia in relation to its regular use as a fuel[65]

Ammonia is toxic to humans and animals and has a negative impact on our environment when released into the atmosphere. It is flammable under special conditions only. The main focus of all safety measures must therefore be on toxicity, with fire and explosion protection being secondary.

The influence of ammonia on the human organism results from damage to the eyes, the respiratory tract, and the skin. The sensitivity results in this order. **Table 6** shows the effects of different NH_3 concentrations on humans. A clear advantage of ammonia is the early smelling of it at low concentrations.

Irritation of the eyes already occurs at relatively low concentrations and quickly leads to massive and permanent damage at higher concentrations. The eyes are the most important organ for people to find orientation and escape from the danger zone. Protection of the eyes must therefore be the highest priority of all measures and can easily be achieved with completely closed safety goggles (basket goggles). If ammonia does get into the eye, damage can be reduced by immediately washing it out with water (eye shower).

Table 6. Toxicity levels of ammonia according to.[74]

NH_3 concentration [ppm]	Effects on humans
0.5–50	Odor threshold
50–72	Does not disturb respiration significantly
100	Irritates the nose and throat and causes a burning sensation in the eyes and tachypnoe
200	Headache and nausea, in addition to the above symptoms
250–500	Tachypnea and tachycardia
700	Immediate onset of burning sensations in the eyes
1000	Immediate cough

The respiratory tract is also very sensitive to ammonia concentrations above 100 ppm, danger to life exists above 1700 ppm. Outdoor, filter masks are an effective means of protection because the danger arises only from the concentration of ammonia, not from the lack of oxygen. In indoor areas, on the other hand, a large leakage of ammonia may clearly reduce the oxygen concentration to such an extent that filtering of the breathing air is no longer sufficient. If the hazard assessment shows this situation, persons must be equipped with self-contained breathing apparatus.

Ammonia causes irritation on contact with the skin. In the case of liquid ammonia, this is accompanied by strong cooling (burns). Special protective clothing effectively prevents this. Immediate washing with water in case of contact is a simple but effective remedy (emergency showers).

A side aspect of using ammonia as a fuel is the reaction product of ammonia combustion. Especially deposits in the engine components and condensate of the exhaust gas can be toxic. Separate from the presence of ammonia, this poses a danger to maintenance staff especially. Detailed experiments on this are currently in progress.

Gaseous ammonia is lighter than air and rises into the atmosphere. In addition, ammonia, together with atmospheric humidity and solar radiation, forms several secondary products that return to the Earth's surface with the rain. Liquid ammonia is heavier than air and can be mixed with water. When dissolved in water, ammonia poses a significant hazard to all aquatic life. The escape of larger quantities of ammonia into the environment must therefore be avoided always. This also applies to wastewater during a fire-fighting operation.

In the following sections, the resulting technical measures are discussed. Special focus is put on marine usage, but also test bed application is considered. Important safety measures for handling ammonia as a fuel start with continuous monitoring: gas sensors and pressure monitors help to detect leaks at an early stage. Especially in closed rooms, a forced ventilation system with a sufficiently dimensioned air exchange volume must be installed and its function monitored. Permanent technical tightness can be achieved using specially tested or double-walled piping. All other areas where leakage cannot be fundamentally ruled out or where the escape of ammonia is even to be expected may only be entered by persons wearing protective equipment, see the sections earlier. In order to keep these areas with special requirements as small as possible in shipbuilding, it is recommended to divide them into zones. For this purpose, living areas or permanent workplaces are separated from the hazardous areas with at least two gas-tight walls and separated from each other as far as possible. If the sensor system detects a leakage of ammonia, the first step is to separate the system into sections using tightly closing shut-off valves. This helps to keep the amount of NH_3 escaping from a leaking part small. Since a leak at the tank cannot be controlled with this measure, a double-walled tank is inevitable.

Analogous to the procedure in refrigeration plant construction, it is suggested that the room air of the damaged plant section should be fed to a torch for neutralization. This minimizes the environmental impact and avoids the lavish disposal of ammonia-contaminated water. In the event of a fire at a plant operated with ammonia, all ventilation systems must be stopped and closed. For fire extinguishing, a gas-based suppression system, for example, using Halocarbons, is recommended. The use of water will lead to a large amount of ammonia-contaminated water to be collected for disposal. Foam extinguishing is expected to lead to a potential damage of the installed equipment. In literature, no events are known in which escaping ammonia caused an explosion. Explosions are only described in combination with other media, explicitly hydrogen or oil. The reason for that could be that the ammonia decomposition to H_2 and N_2 occurs at ≈600 °C[66] before the ignition temperature at 650 °C (Table 3). All explosion protection measures should therefore concentrate on the accompanying or emerging media.

5. Conclusion and Outlook

Due to the urgent need to reduce CO_2 footprints in all industries, also solutions for the shipping branch must be developed with high priority. Among others, green ammonia appears to be a promising fuel for ships. Worldwide trading and handling of ammonia are already in place and ease the establishment of a respective fuel supply chain. Ammonia can act as a hydrogen carrier as much less effort in transport and distribution is needed compared to pure hydrogen. Production can take place at locations where sufficient renewable energies such as wind or solar energy are reliably available. In the current project, a maritime propulsion system concept is developed based on a cracker-engine unit. The targeted applications for this setup are inland water vessels. Within this article, the technological aspects for establishing the system concept were discussed. The partly ammonia cracking toward hydrogen as an integral part of the combustion process as well as the impacts of ammonia on the engine setup and operation are evaluated. Further important topics are the system integration for future simple handling and the safety aspects to be considered on board. In the next development steps, the simulation tasks will be deepened and fed by the results from further systematic investigations on the single-cylinder engine. In parallel, the multicylinder engine is prepared to receive the latest setup based on the final simulation and single-cylinder engine results. As soon as the containerization of the multicylinder engine is finalized, the engine container will be tested at the COIL near Rostock/Germany. Later, this will be pooled with the ammonia cracker as a completed system for initial and later endurance testing.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

ammonia, ammonia crackers, ammonia engines, ammonia safety, cracker-engine power units, hydrogen, inland water vessels

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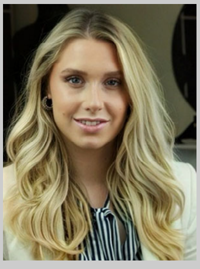

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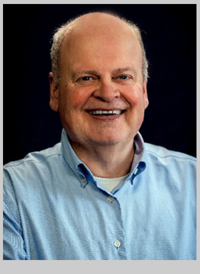

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