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Nitrogen based propellants as substitute for carbon containing fuels

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1 Abstract

Nitrogen based fuels have several advantages over carbon-based fuels. No greenhouse gases (GHG) or health compromising compounds are emitted during the combustion and the subsequent waste gas treatment of most nitrogen based fuels. When nitrogen based fuels are produced with power from renewable sources, no GHG are emitted during the production process either. All nitrogen based fuels originate from ammonia (NH₃), which is produced via the Haber-Bosch-Process. Ammonia combustion engines have been developed and tested as prototypes for several decades. In recent years the interest mainly for use in naval propulsion systems has grown. Marketable fuel cells using ammonia are now commercially available, as well as fuel cells using hydrogen which was stripped from the ammonia. Hydrazine is a commonly used rocket propellant but is not used in civil environments due to its high toxicity. Ammonium nitrate and urea engines are fringe applications which were currently tested in laboratory environments. Production of nitrogen based fuels by using renewable power sources would be most economically feasible with energy produced in the global Sunbelt. Since the necessary Haber-Bosch technology is mature and plants are existing in all major

agricultural countries, the upscaling of ammonia production seems easily possible. The prime advantage of nitrogen based fuels are both, the intrinsic lack of carbon as well as the technological maturity of their production, transport and storage. As the various propulsion engines and the combustion technologies reach technical maturity, nitrogen based fuels will certainly become attractive for a decarbonizing world.

2 Introduction

Nitrogen based fuels are well known since several decades but rarely used for transportation purposes. Their inherent environmental advantage is the absence of any carbon dioxide (CO_2) emissions during combustion. Therefore, they may contribute significantly to the internationally demanded decarbonisation of the transport sector. However, easy access to fossil carbon-based gas (methane) and liquid fuels (derived from crude oil) during the past decades as well as their cheapness, low safety risks and established processing infrastructure made them the almost exclusive propulsion energy for transportation purposes. Crude oil is easily refined to e. g. kerosene, diesel, or gasoline. In the next decade the need to move away from fossil carbon-based energy may favour – at least in part - nitrogen as fuel in the transportation sector due to its ecologic advantages, the technological practicability and the relatively moderate changes needed to existing infrastructure for production and logistics.

As early as 1943, during the fossil fuel shortages in WW II, a retrofitted bus engine was propelled by ammonia (NH_3) in Belgium (Kroch 1945) (Figure 1). In the 1950ies an Austrian inventor redesigned a motor bike to run on hydrazine (N_2H_4) in a fuel cell (Figure 2). Hydrazine in combination with other fuels was used during WW II as a propellant for the German A4 rocket and the rocket engine driven German Me-163 interceptor airplane (Ziegler 1976). Hydrazine is still common in the Titan and Ariane rockets as well as in satellites and space ships (Haidn 2008). However hydrazine is not widely used because of its high toxicity (Table 1) (Bundesanstalt für Arbeitsschutz und Arbeitsmedizin 1991). Nitrous oxide (N_2O) injection in piston driven engines was used by high performance airplanes during WWII as an additional power booster.



Figure 1: Retrofitted bus with an ammonia driven internal combustion engine in 1943 during WWII in Belgium (Kroch 1945).

Non-fossil originated carbon-based fuels (often called “synthetic carbon fuels”) are very expensive in production and are currently used for niche applications only. Even after the global oil price shocks in 1973 and 1979/80, which were caused by geo-political disruptions (BP 2020), no serious actions were taken to reduce the dependency from fossil carbon fuels in the transportation or heating sectors on a global scale and only the nuclear power generation sector gained importance since the end of the 1970ies, mainly in technologically advanced countries (Roser 2020).

Even today most attempts to reduce or minimise the usage of carbon-based fossil fuels are not price driven. In fact, global oil prices have reached a relatively stable minimum caused by the increased application of fracking techniques in North America, political discord of the oil producing countries about production quantities and the current economic slow-down due to the SARS-CoV-2 pandemic (BP 2020; BBC 09.06.2020). Current attempts to reduce the usage of fossil fuels and to replace them with carbon free fuels are due to mounting concerns regarding the negative environmental consequences of rising global temperatures which are caused by the increasing atmospheric concentration of CO₂ and other greenhouse gases. The increasing global temperatures cause rising sea levels, more severe droughts, raging wildfires and the melting of permafrost areas. The resulting natural disasters, economic disruptions, social unrest and mass migrations will result in more refugee and rescue missions for the military forces (Reinhardt and Toffel 2017; Fourmeau and Zimmerman 2020).

The present article will provide an overview of the chemical production processes of nitrogen-based fuels using power from renewable energy sources as well as cover the safety issues of nitrogen fuels in comparison with carbon-based fuels. Also, propulsion technologies for nitrogen based fuels and possible global NH₃ production capacities will be discussed.

3 Nitrogen based fuels in Power-to-fuel processes

Power-to-fuel (PtF) is an umbrella term for processes using electricity from renewable sources for the production of gaseous or liquid fuels. Liquid fuels are the most attractive and cost-effective approach for storing and delivering energy for large scale applications. They are unmatched in terms of transportability and energy density (Andersson and Grönkvist 2019) compared with gaseous fuels (Table 1).

Liquid fuels come with higher production costs compared to gaseous fuels because more steps are required to produce them. Due to the second law of thermodynamics each energy conversion process – of which chemical synthesis is one - results in a loss of energy available to perform work (free energy). This fact leads with each additional step of synthesis to substantial losses in the useable fuel energy content (Atkins et al. 1990; Perner et al. 2018). Consequently, the number of production or energy conversion steps should always be kept as low as possible.

A selection of production pathways for nitrogen-based fuels is presented in Figure 2 . All processes start with the production of electricity from renewable sources (1). Electricity can be directly used in electric engines via battery storage. Electricity driven electrolyzers produce hydrogen (H₂), from water, which is the first possible chemical storage (Holleman et al. 1985). H₂ is a nontoxic gas under normal conditions, but handling is difficult due to its flammable and explosive properties (Table 1) (Bundesanstalt für Arbeitsschutz und Arbeitsmedizin 2020). The volumetric and gravimetric energy density of H₂ in compressed or liquefied form is high but it requires a significant amount of energy and safety precautions to reach these states (Table 1) (Andersson and Grönkvist 2019). H₂ is also a valuable base chemical, leading to further applications in fuel syntheses.

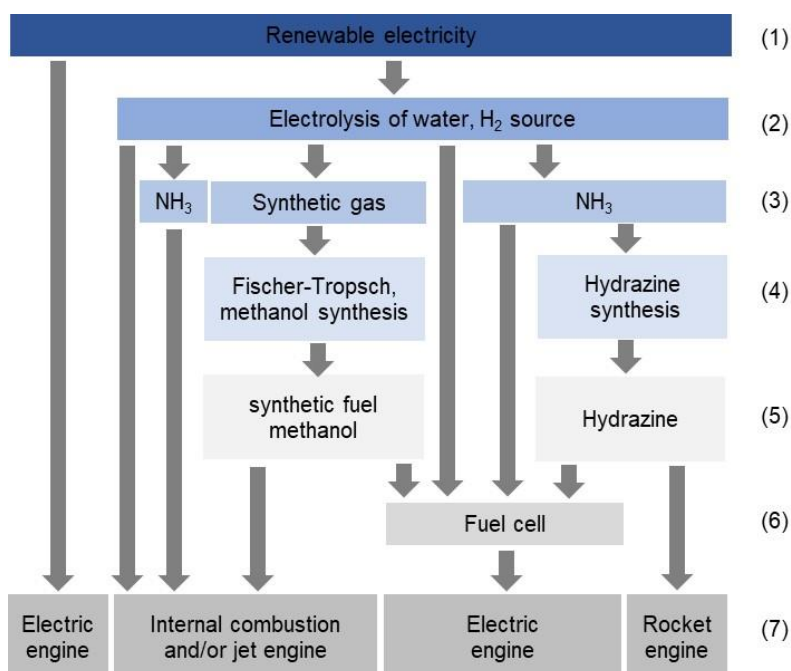


Figure 2: Schematic of power- to-X (PtX) production pathways and the usage of the products for mobility.

(1) Electricity production from renewable sources. Electricity can be used directly in electric engines. (2) Electrolysis of water and production of hydrogen (H_2). (3) Synthetic gas (syngas) or ammonia (NH_3) can be produced with H_2 . Syngas requires a CO_2 source from fossil or non-fossil sources. NH_3 requires nitrogen (N_2) from ambient air. (4) Reactors for the synthesis of organic compounds (synthetic fuels or methanol) or hydrazine. (6) Fuel cell for electricity production. (7) Engine technologies useable for different types of fuels. Electricity from the producing plants can be used directly in electric engines. H_2 , NH_3 and hydrazine can be either used in fuel cells, which power electric engines or in internal combustion and rocket engines. Modified after (Sterner 2019; Perner et al. 2018; Grinberg Dana et al. 2016).

NH_3 produced by the Haber-Bosch process (Holleman et al. 1985) is the first of several possible nitrogen based fuels (3). Nitrogen (N_2) is needed as a base component (Formula 1) and normally extracted from ambient air. NH_3 can be used as a base chemical for further synthesis (4), in fuel cells (6) or in internal combustion or jet engines (7). Hydrazine and its methyl derivatives are used as long term storable rocket fuels (Haidn 2008). Because hydrazine is extremely toxic (Bundesanstalt für Arbeitsschutz und Arbeitsmedizin 1991) (Table 1), its usage is only allowed in environments where no substitutes are possible, e.g. in military and space technologies. Fuels which are based on nitrates (NO_3^-) - including aqueous solutions of urea, ammonium nitrate and their mixtures - are currently tested in laboratory environments (Grinberg Dana et al. 2016).

Carbon based fuels (often simply called synthetic fuels) derived from the Fischer-Tropsch process or methanol from methanol synthesis can be obtained via the production of synthetic gas (syngas) (Holleman et al. 1985). These chemical processes require CO_2 as the carbon source. Non fossil CO_2 sources (secondary carbon sources) as well as their production costs were discussed in (Lauf 2020b). Methanol can be used in fuel cells and methanol or synthetic fuels can also be used in internal combustion and jet engines.

Ammonia and hydrazine are generally more toxic than conventional fossil or synthetic fuels (Table 1). Many countries define maximum workplace air concentrations for mean daily exposure to humans (e.g. for Germany: Bundesanstalt für Arbeitsschutz und Arbeitsmedizin 1991; Bundesanstalt für Arbeitsschutz und Arbeitsmedizin 2020). Hydrogen as the first fuel generated from electricity is not toxic but extremely inflammable and explosive. It is odourless and can only be detected by elaborate technical devices. NH_3 is also toxic but self-alarms

due its pungent smell. The limit of detection (LOD) by the human nose is about 4 times lower than the allowed workplace air concentration (Assumpção et al. 2014). The unpleasant smell of NH₃ normally forces humans to leave a contaminated area before health risks occur. However, if suddenly exposed to high concentrations, the human nose can no longer detect it. Hydrazine is the most toxic and inflammable of the fuels discussed. Ammonia is 200 times less toxic than hydrazine and not inflammable. The smell of hydrazine is similar to that of NH₃, but less intense. Ammonium nitrate is not toxic but explosive in solid state while urea is neither toxic nor inflammable.

The carbon-based methanol and diesel fuels are less toxic than NH₃ but inflammable. A maximum workplace air concentration for diesel is not given, as it is a mixture of many components. The most toxic component is benzene. Synthetic diesel may differ from its fossil counterpart, as the Fischer-Tropsch synthesis can be managed to result in less toxic by-products.

Table 1: Maximum workplace air concentrations in parts per million [ppm], flammability and energy density for selected alternative fuels as well as for ethanol and carbon dioxide. State of aggregation at ambient air temperature and pressure: g = gaseous, l = liquid, s = solid). Energy content expressed as the so called inferior heating value (net caloric value, H_i) Citations: (1) (Bundesanstalt für Arbeitsschutz und Arbeitsmedizin 2020); (2) (Bundesanstalt für Arbeitsschutz und Arbeitsmedizin 1991); (3) (Holleman et al. 1985); (4) (Beyer and Walter 1988); (5) (Grinberg Dana et al. 2016); (6) (Beilicke 2010); (7) (Reitmair 2013).

	Maximum workplace air concentration [ppm]	Inflammable and/or explosive	Energy content, H _i [kWh/kg]
Hydrogen (g) (H ₂)	- (1)	Yes (3)	33,3 (6)
Ammonia (g) (NH ₃)	20 (1)	No (3)	5,2 (6)
Hydrazine (l) (N ₂ H ₄)	0.1 (2)	Yes (3)	5,5 (6)
Urea (s) (H ₂ NCONH ₂)	- (1)	No (3, 4)	2,6 (6)
Ammonium nitrate (NH ₄ NO ₃)			
- Solid	- (1)	Yes (5)	-
- Aqueous solution	- (1)	No (5)	-
Methanol (l) (CH ₃ OH)	100 (1)	Yes (4)	6,3 (6)
Ethanol (l) (CH ₃ -CH ₂ OH)	200 (1)	Yes (4)	7,5 (6)
Diesel fuel (l) (analogue to F-34)	- (1)	Yes (1)	11,8 (7)
Carbon dioxide (g) (CO ₂)	5 000 (1)	No	-

The so-called inferior heating values or net caloric value H_i of a selection of fuels (referenced to weight) are shown in Table 1. H₂ shows the highest H_i value. The nitrogen-based fuels NH₃ and N₂H₄ as well as methanol and ethanol show inferior heating values within the same order of magnitude. H_i is rising with the increasing number of chemical bonds of the respective compound. The energy content of diesel fuel is highest, as it contains much more chemical bonds. From the perspective of H_i values, diesel appears to be the most promising fuel to produce. However, the H_i does not reflect the amount of energy needed – or, in other words, the amount of free energy lost - to produce these components from steps (3) to (5) in Figure 2. If the energy content of the product and the energy needed for its synthesis are accounted for, H₂ is the best fuel to use and NH₃ is the second best.

Fluctuating power supply from renewable plants and storage of electric energy

Electricity is difficult to store on a large scale. It has to be provided “on time” to enable efficient and effective processes in all sectors of society. Most providers ensure this flexibility by providing excess production capacity in plants with inherent ultralow response times (e.g. gas powered plants). Power from renewable sources usually can't be managed in this way as it has to be produced when e.g. the wind blows or the sun shines. Therefore, the key enablers for the shift to renewable energy sources are efficient means of storing renewable electricity

for times when it is not generated and distributing the stored energy effectively over large distances. Hydro powered dams and biogas plants are the only renewable energy producing technologies which are adjustable to fluctuating electricity demands. However, they are not available on a scale needed for many industrial processes.

Three forms of storage are considered in this article: a) batteries, b) physical storage and c) chemical storage. This scheme is not the conventional classification of physics and chemistry. Energy in batteries is stored due to electrochemical processes. Physical storage in this article means gravitational, kinetic and thermal energy. Chemical storage means the synthesis of new compounds where the energy is stored in chemical bonds.

Large scale electrochemical storage in batteries is not yet economic and affordable, although a pilot project in Australia shows promising results in levelling fluctuations and peaks in the electricity demand during the summer months for a community of 30 000 households (DER SPIEGEL 2017). Physical storage using pumped hydro power stations is a mature technology but limited by topographic conditions. Environmental and social problems invoked in building them are paramount and have led to an almost complete construction freeze during the past decades in the western world (Sinn 2017; Bundesministerium der Justiz und für Verbraucherschutz 2020). Chemical storage of electricity is currently intensely studied. It is the preferred storage solution because the energy carrier can be directly retransformed into electricity by fuel cells, internal combustion engines, jet engines etc or used as fuel for mobility.

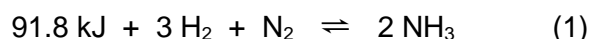
The focus of the following sections is on the production steps of nitrogen based fuels from renewable electric power, in comparison with carbon bases fuels.

4 Industrial scale production of nitrogen-based fuels

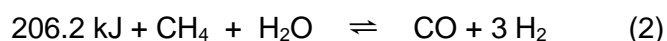
Ammonia

Ammonia is a poisonous (Table 1), colourless and lighter-than-air gas with a characteristic pungent smell. Its synthesis (artificial nitrogen fixation) from atmospheric nitrogen (N₂) and hydrogen (H₂) was invented before WWI by the German scientists Fritz Haber and Carl Bosch. The so called Haber-Bosch process was implemented at an industrial scale during WWI (Holleman et al. 1985) and provided the German Empire with nitrate (NO₃⁻) which could not be obtained from the mines in Chile as they were controlled by the Allied forces. Nitrate was needed for the production of explosives like nitroglycerine and dynamite. Since more than 100 years the Haber-Bosch process remains virtually unchanged and this mature technology provides NH₃ at low costs. Nowadays about 70 % of the global ammonia production of about 11,3 * 10⁹ t in 2014 is used for fertilizer production (Ritchie and Roser 2020).

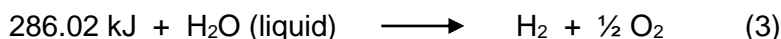
The chemical reaction is performed using catalysators at >10 MPa pressure and temperatures between 400 – 500 °C (Holleman et al. 1985).



Currently about 90% of the hydrogen needed for the process is obtained via synthetic gas by steam gas reformation of fossil resources (typically gas or coal) which releases huge amounts of CO₂ (Holleman et al. 1985).



Hydrogen can also be obtained by the expensive process of electrolysis of water (Holleman et al. 1985) which requires large amounts of electric energy (Lauf 2020a).



Industrial sized Haber-Bosch plants have their own on-site N_2 supply, which is obtained from ambient air (78% N_2 , 21% O_2 and other gases). In steam gas reforming plants, the ambient air is used in the clean-up of the synthetic gas (Formula 1) resulting in a pure N_2 gas. In electrolyser plants, pure N_2 gas can be generated either by cryogenic distillation of liquified air or by membrane filtered compressed ambient air. The latter is less expensive and delivers lower, but sufficient, N_2 purity grades. (Holleman et al. 1985; thyssenkrupp Industrial Solutions AG 2020)

Hydrazine

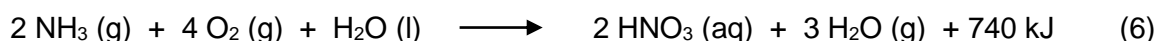
Hydrazine is a toxic and carcinogenic oily liquid. Its smell resembles that of NH_3 . For safety reasons it is mostly used in the form of hydrazine hydrate which is unstable and even as in aqueous solution dangerous to handle. At industrial scale three pathways for hydrazine (N_2H_4) are in common use which all use NH_3 as base chemical. The most common pathway is the two step Raschig synthesis in which the sodium salt of hypochloric acid (NaClO) is used as oxidant for NH_3 (Holleman et al. 1985).



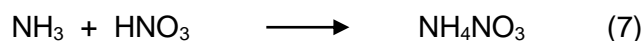
Ammonium nitrate

Ammonium nitrate (NH_4NO_3) is globally produced in large quantities as a raw material for most common nitrogen fertilizers. It is produced in two steps: Nitric acid (HNO_3) production from NH_3 and subsequently NH_4NO_3 production from nitric acid. Both steps are often performed at the same industrial site. The production and handling of NH_4NO_3 involves mature technologies.

Ammonia as a gas (g) from the Haber-Bosch process is oxidised with oxygen (g) in the presence of platinum/rhodium catalysts in solid state (s) to nitric acid (HNO_3) which is dissolved in the water formed during the reaction and which results in an aqueous solution (aq). This process is called Ostwald process.



Ammonium nitrate is produced by the acid-base reaction of NH_3 in aqueous solution and HNO_3 in aqueous solution. The dissolved salt is then dried and handled in solid state.



Ammonium nitrate is explosive and therefore widely used in mining and quarrying. As fertilizer it is mixed with lime (calcium carbonate, CaCO_3) and oil to prevent its explosive properties (Holleman et al. 1985). However, several catastrophic accidents have occurred ever since the Haber-Bosch- and Ostwald processes were first established in Germany on an industrial scale. In 1921 at the BASF Oppenau/Ludwigshafen manufacturing plant in Germany approx. 400 tonnes of stored ammonium sulphate nitrate exploded and killed 559 persons, mostly workers of the plant (Figure 3) (Abelshausen 2003). The most recent explosion occurred in 2020 in Beirut (Lebanon), when approx. 2750 tonnes of stored ammonium nitrate exploded in a warehouse at the harbour (BBC 05.08.2020).



Figure 3: Aerial photo of the BASF Oppenau/Ludwigshafen (Germany) production plant after the devastating explosion of 400 tonnes of ammonium sulphate nitrate in 1921 causing 559 fatalities (Abelshauer 2003). The crater in the foreground indicates the location of the storage area where the explosion happened.

Urea

Pure urea is a non-toxic and non-explosive crystalline solid which easily dissolves in water or alcohols. It is used as fertilizer in agriculture and for the reduction of NO_x in power plants and combustion engines. Sold under the trademark “AdBlue” it contains one third of urea mixed with water. Other applications are as a pharmaceutical for the treatment of skin diseases. The production of urea at an industrial scale became possible after the Haber-Bosch process was established. Carl Bosch and Wilhelm Meiser established an urea production site in 1922 (Holleman et al. 1985).

For urea production NH₃ and CO₂ are mixed at temperatures of 170 – 220 °C and at pressures between 12.5 – 25.0 * 10⁶ Pa (125 – 220 bar). The reaction is in equilibrium and can be pushed towards the desired urea product by adding NH₃ in excess (Holleman et al. 1985).



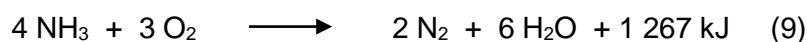
5 Waste gas properties and applications of nitrogen-based fuels

The composition of waste gases are defined by the energy conversion technology used. Waste gases from fuel cells contain only the products of a complete combustion with no side products. In the case of carbon-based fuels these are carbon dioxide (CO₂) and water (H₂O) in the case of ammonia- and nitrate-based fuels these are N₂ and H₂O. The waste gases of urea contain CO₂, N₂ and H₂O.

Fossil fuels do contain varying amounts of sulphur. The maximum sulphur concentration of fuels is often regulated by local laws. Sulphur burns into a mixture of sulphur oxides (SO_x). In carbon-based fuels volatile organic compounds (VOC's) and particulate matter (PM) are formed during incomplete combustion. Depending on the combustion temperature, the nitrogen (N₂) and oxygen (O₂) from the air form a mixture of nitrogen oxides (NO_x). This process occurs for both, carbon- and nitrogen-based fuels and sparked an intense environmental debate over the future use of diesel engines. In nitrogen based fuels nitrous oxide (N₂O) and NO_x may form as products of an incomplete fuel combustion. (Baird 1995; Holleman et al. 1985; Pavlos and Rahat 2020)

Ammonia

The complete combustion of ammonia under laboratory conditions is shown in Formula 9. No greenhouse gases (CO₂, N₂O, NO_x) and no toxic components (NO_x, SO_x, VOC's and PM) are released to the atmosphere (Holleman et al. 1985).



A selection of ready to use solutions as well as development projects in early and advanced stages with emphasis on NATO members and partners is given below. Intensive research and development work in this field is also done by the Peoples Republic of China, the Republic of Korea and Japan.

Ammonia in NH₃-fuel cells

Fuel cells provide optimal combustion conditions with no secondary reactions. However, NH₃-fuel cells are not yet a mature technology and research and development efforts are being undertaken on a global scale (Assumpção et al. 2014; Cinti et al. 2016; Holleman et al. 1985). Currently a pilot project which is partly financed by the EU Horizon 2020 SHIPFC program is upscaling a 100 kW NH₃-fuel cell to a 2 000 kW version. It will be installed the long haul vessel "Viking Energy", allowing emission free sailing for 3 000 hours annually. The system should be operative on the vessel by the end of 2023. The NH₃ needed will be produced by electrolysis. (SHIPFC 2020)

Ammonia in H₂-fuel cells

Ammonia is also useable in H₂-fuel cells. The NH₃ is catalytically split into N₂ and H₂. The N₂ is released directly into the air while the H₂ is fed into the fuel cell. No secondary products are formed. Such H₂-fuel cells systems powered by NH₃ can be purchased for private sector applications (GENCELL, Israel). They provide uninterruptable power supply (UPS) for critical infrastructure i. e. hospitals or main power supply for remote communities or remote telecommunications infrastructure (GENCELL WORLDWILD 2020).

Ammonia in internal combustion engines

A Canadian inventor showed the feasibility of diesel engines retrofitted in commercially available cars and trucks to run on pure NH₃, as well as standard carbon-based fuels mixed with NH₃. Prototype cars and trucks are operating (Vezina 2020). Ammonia is also tested under laboratory conditions as sole fuel in internal combustion engines in the shipping sector by the Finnish shipping company Wärtsilä. Results are not available yet, but first tests seem promising (Figure 4 a) (Wärtsilä Helsinki Campus 2020). The German engineering company MAN has already developed a NH₃ driven internal combustion engine and is currently building cooperations with shipyard companies for its implementation (Figure 4 b). (MAN Energy Solutions 2019)

While NH₃ as fuel shows no CO₂, PM, VOC's or SO_x emissions, other emissions from unburnt NH₃, N₂O and NO_x are significant. Therefore post treatment technologies for cleaning these exhaust gases are needed. Mature technologies like selective catalytic reduction, SCR are available (MAN Energy Solutions 2019; Pavlos and Rahat 2020).

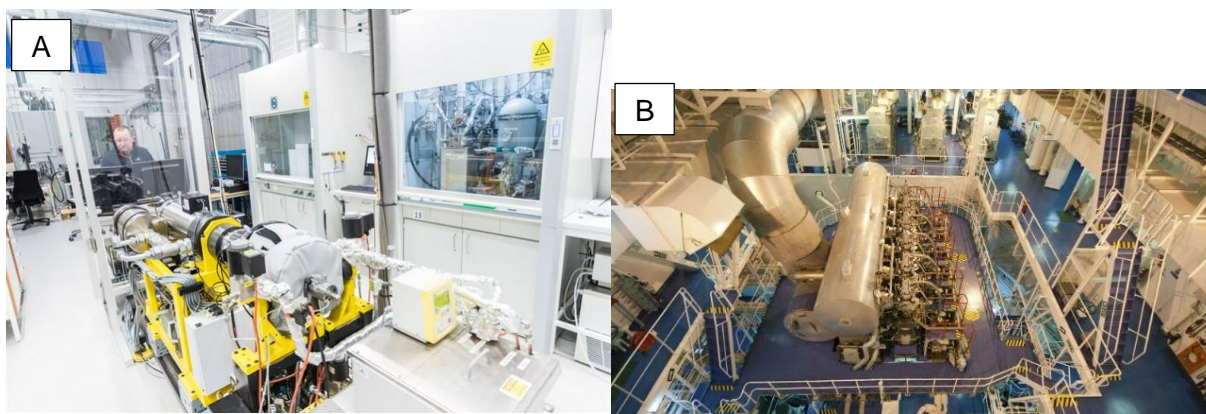


Figure 4: A) Test engine for using NH_3 as fuel in an internal combustion engine in a laboratory at the Wärtsilä Helsinki Campus of the Wärtsilä Corporation (Finland) (Wärtsilä Helsinki Campus 2020). B) Engine test room at MAN Energy Solutions (The Maritime Executive 2020)

Ammonia and diesel in dual fuel internal combustion engines

In recent years the diesel engine has received a great deal of scrutiny with respect to NO_x and PM emissions. Emission treatment systems (i. e. AdBlue injection) are now widely available to minimise these emissions and became standard in many truck engines. With respect to the decarbonisation of the economy, dual fuels of NH_3 and lower auto-ignition temperature fuels like diesel fuels are in early testing phases. Preliminary results show that conventional diesel engines can use NH_3 /diesel mixtures but produce high amounts of NH_3 and NO_x emissions. Adjustments on the injection system may reduce the emissions, but the implementation of an after-treatment system is required to meet emission standards. (Pavlos and Rahat 2020)

Ammonia in new settings

Ammonia as carrier for H_2 is a versatile agent for innovative energy solutions. The decomposition of NH_3 into N_2 and H_2 is a well-known process (see above, NH_3 in H_2 fuel cells). The H_2 gained may be used either in pure H_2 combustion engines or in dual fuel (H_2 /diesel) combustion engines (Wang et al. 2013).

Hydrazine

As early as in May of 1944 the German Luftwaffe put a rocket engine powered interceptor aircraft into active service. The Messerschmitt Me-163 "Komet" used a volatile fuel mixture of T-Stoff (80% hydrogen peroxide and 20% water) and C-Stoff (hydrazine hydrate, methyl alcohol and water), which provided a maximum thrust of 1 500 kp (3 300 lb.). The airplane set the speed record for its time at 1 170 km/h or 700 mph. A surviving airplane is on display in at the Smithsonian's Boeing Aviation Hangar at the Steven F. Udvar-Hazy Center in Chantilly, VA (USA) (National Air and Space Museum 2021). The first operational military use of hydrazine as rocket propellant was in the German A4 ballistic long range artillery rockets (also known as V-2) which were launched in late 1944. The same A4 type rocket started successfully from the deck of a US aircraft carrier in 1947 initiating the era of seaborne rocket launches. (Zaloga 2003).

Hydrazine (pure or in mixture with e. g. dimethyl hydrazine) is a very commonly used liquid rocket fuel. It ignites as a hypergolic fuel (self-igniting fuel mixture) if brought in contact with an oxidizer like dinitrogen tetroxide ($\text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4$) thus requiring no external ignition devices or chemicals. Hydrazine based liquid fuels are e. g. Aerozin 50 used in the USA built Titan rockets and UH 25 used in the European Ariane rocket. It is estimated that currently about 500 satellites in orbit use hydrazine based small control rockets for position and orbit control. In the NASA Space Shuttles missions, the high toxicity of hydrazine required careful pre-launch and post-touchdown checks for N_2H_4 leaks by teams wearing protective gear and self-contained breathing equipment (Jenkins 2016).

Many naval forces currently use hydrazine in their submarine rescue systems for emergency surfacing by rapid displacement of the ballast tank water upon injection. The RESUS (REscue system for SUBmarineS) uses hydrazine which catalytically decomposes in the ballast tanks and creates buoyance. (ArianeGroup 2020)

Nitrate and urea-based fuels

Nitrate-based fuels burn under optimal laboratory conditions without releasing CO₂, VOC, PM or NO_x. Urea-based fuels do not release NO_x under optimal laboratory conditions but always release CO₂. (Grinberg Dana et al. 2014; Grinberg Dana et al. 2016). Whether this can be also achieved in service engines has not been tested yet. A fuel infrastructure is not existing but ammonium nitrate could be transported as non-toxic substance in solid state or in aqueous solutions. The solid state – when handled properly – is also non-explosive. However, accidents occur on a regular basis (c.f. Fig 3).

6 Ammonia combustion in internal combustion engines from an engineering point of view

If the question is the feasibility of using ammonia in internal combustion engines there is only one simple answer: yes, an internal combustion engine can be driven with either ammonia or its mixtures. This answer remains valid for Compression-Ignition Engines (CIE) and Spark-Ignition Engines (SIE) likewise. A gas turbine can be “fired” with ammonia blends as well. This has been proven several times through basic research, feasibility studies, experiments and prototypes. Nevertheless, the challenge is not to offer a new propulsion technology to the public or markets, it rather is to suggest a new propulsion technology which can replace the existing technology.

In the following, the focus is more on feasibility and less on economic competition, which is discussed separately. While it is not very difficult to replace passenger cars after a couple of years of service it is more difficult to modify a fleet of hundreds of container freighters where the life cycle of the asset is 25 years and more. The logical solution is a dual use technology that provides a sufficient transition period for the new technology with a minimum of drawbacks on the overall performance. A dual use technology in this context means that either one or the other fuel is used for combustion. No mixtures of fuels are used.

Compression-Ignition Engines (CIE)

Ammonia is flammable, but the ignition temperature is higher than for petroleum-based fuels. Thus, it is not possible to use ammonia as a sole fuel in a CI-engine due to the high compression ratios needed for ignition/combustion (Pearsall and Garabedian 1967; Brohi 2014). Very high compression ratios as much as 35:1 are needed for ammonia as fuel in CI-engines (Kong and Reiter 2011). Therefore, the use of a pilot fuel is required in order to achieve and maintain a certain ignition temperature and compression ratio. Very common and useful pilot fuels are diesel or Dimethyl Ether (DME) – a synthetic substitute for diesel fuel. Fuels with higher cetane numbers show generally better ignition characteristics with ammonia (Pearsall and Garabedian 1967). An ammonia content up to 95% was feasible with only 5% diesel fuel when used in a John Deere engine. However, the optimal mixture is 40% diesel with 60% ammonia since a diesel amount larger than that would limit the ammonia’s flammability (Reiter and S.-C. Kong 2008). Due to the DME chemical characteristics it can be mixed directly with liquid ammonia and injected into a CI engine. Researchers at the Iowa State University (USA) demonstrated this in 2013 when they successfully used it in an off-the-shelf diesel engine.

The original setup used for the exploration of highly advanced liquid ammonia direct injection was designed very similar to a diesel direct injection system. A fuel combination of ammonia and DME was directly injected into the engine, using conventional to slightly early diesel injection timings. However, it was observed that conventional injection timing or even earlier injection timing was insufficient to achieve more than 40% ammonia content in fuel. Thus, in an attempt to increase the operating range and maximum percent of ammonia in the fuel,

highly advanced injection timing was used. Such highly advanced injection timing transforms conventional diesel combustion into a homogeneous charge compression ignition (HCCI) combustion. The highly advanced injection allows the heat loss due to the vaporization of the ammonia to be mitigated over a longer time period thus reducing its negative effects (Zacharakis-Jutz 2013).

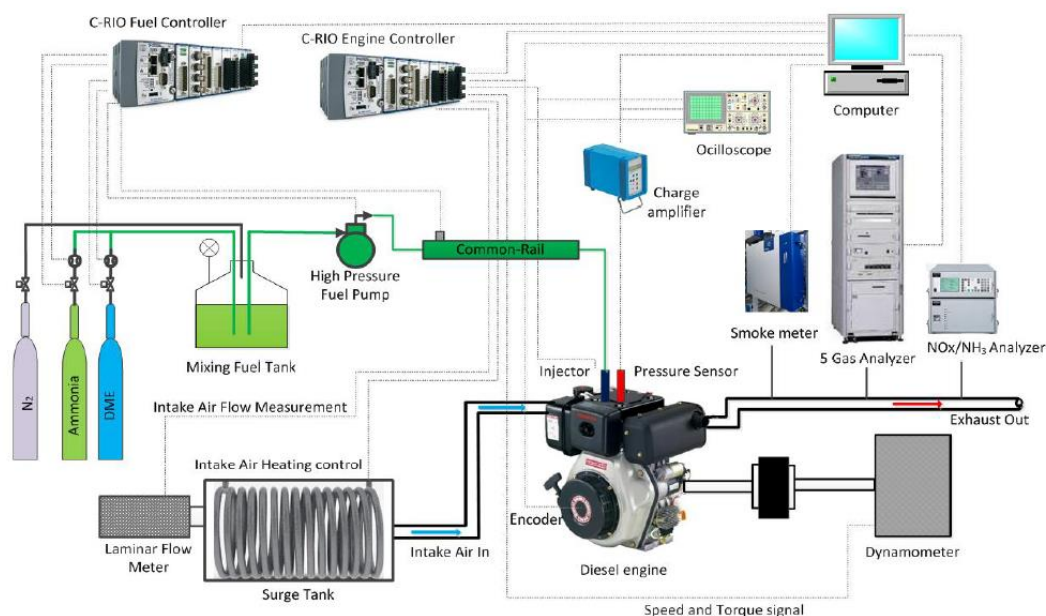


Figure 5: Schematic of an experimental apparatus for highly advanced liquid ammonia direct injection testing (Zacharakis-Jutz 2013).

The technical retrofitting efforts will have to include additional fuel installations (tank, mixing tank, pumps, and valves), inject assembly upgrade, engine management software (compression ignition timings) and extensive exhaust treatment system. The implementation of CI engine technology is feasible and requires moderate retrofitting only. A significant drawback, however, is the unstable performance at alternating loads. The use of pilot fuels for NH₃ engines is a double fuel technology. Therefore, these engines do not avoid CO₂ emissions completely but rather reduce them substantially.

Spark-Ignition Engines (SIE)

The use of ammonia as sole fuel for SE-engines is possible but requires significant changes to the ignition hardware. For instance, ammonia as sole fuel has been patented by Toyota where they suggest that several plasma jet igniters arranged inside the combustion chamber or plural spark plugs that ignite the ammonia at several points will facilitate ammonia combustion (EP 2378105 A; EP 2 378 094 A1). Those changes are not trivial and would probably require the redesign of the entire cylinder head. As of now, there is no single fuel asset on the market which would be at the serial production level or even close to that. More promising are double-fuel applications. Hydrogen dissociates at 400 °C and can be used as a combustion promoter for ammonia as fuel. A hydrogen content of 3-5% weight basis is the minimum amount of hydrogen required as combustion promoter (Starkman and Samuelsen 1967). For comparison: Using gasoline as a combustion promoter requires a compression ratio of 10:1 for optimal operation with a gasoline content of 30% (Grannell et al. 2008).

Researchers from Iowa State University (USA) conducted a trial with a Cooperative Fuel research (CFR) Engine and had to overcome significant upgrade challenges while adjusting the injection assembly for the gaseous ammonia usage.

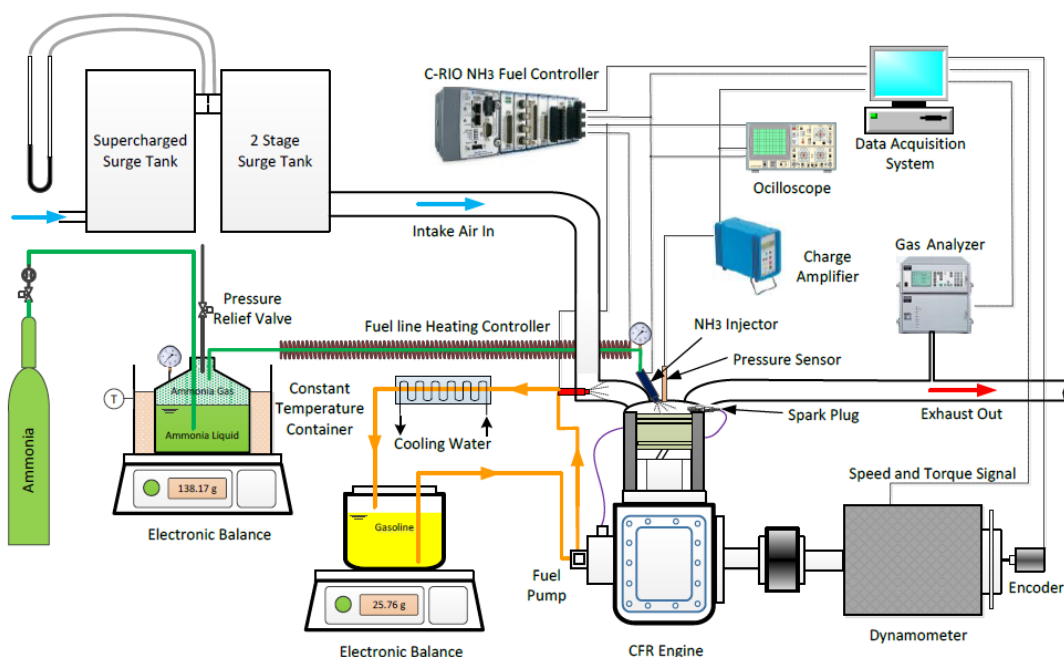


Figure 6: Schematic of an experimental setup for testing gaseous ammonia direct injection (Zacharakis-Jutz 2013).

Furthermore, they (Zacharakis-Jutz 2013) assessed that the required changes and add-ons for the ammonia injection such as an ammonia vaporizing unit, an ammonia gas preheating and ammonia direct injection system, are not suitable for small-scale engines. With respect to retrofitting efforts, the statements made about CI engines apply as well: The subsystems to be modified are injection assembly, engine management and exhaust after treatment. In the case of SI engines the injection assemblies are more complex and voluminous.

NH₃ as a fuel of the future

As of today, it is not easy to say how the future for ammonia as a fuel for combustion engines may look like. From an engineering perspective, the answer is positive. All the challenges and setbacks described above are manageable issues and all these issues can be solved with state-of-the-art technologies. All required technologies are available and the only thing to do is to find applications where the advantages of ammonia combustion dominate over the existing disadvantages.

Based on the research discussed above, it is obvious that when using ammonia a volumetric enlargement of equipment is unavoidable: larger tanks with additional equipment, the usage of pilot fuels and comprehensive exhaust after-treatment subsystems. This automatically reduces the number of possible applications. The large space demand paired with a limited response time to fast changing load demands indicates that two common applications are likely: In stationary power generation facilities and as naval propulsion systems. Both applications could provide a significant contribution towards global GHG emission reduction if implemented at a large scale.

While the usage of ammonia for power generation may sound like fiction for the European audience, it does play an essential role in Asian (Japan, Korea, China) future energy strategies (Figure 7) (Harding 2020). Japan for instance is strongly heading towards ammonia usage in the near future. Green ammonia is supposed to be generated by renewables (though imports are needed) and used in gas turbines for power generation. Japanese industries conducted successful tests and are now able to engage 100% ammonia driven turbines (without any pilot

fuels). Within the near future, ammonia will cover at least 1% of the country's electricity demand.



Figure 7: Ammonia storage facility in Japan (Harding 2020).

In general, NH_3 represents a very economic storage option for renewable power. It is also much easier to handle than storing electric power in secondary cells or hydrogen. Another promising application is in the maritime sector. The future of naval propulsion systems is on the brink of undergoing significant changes. Political and public demands result in national and international environmental regulations and expect the industry to provide solutions. Ammonia is one of several mature solutions to address these challenges and will compete with LNG, LPG, hydrogen, biofuels and syngas. From many points of view ammonia is a strong competitor and makes especially sense if being implemented with a strategic approach and not in a case-by-case scenario. Several research activities provided prove of concept for ammonia technologies but did not go beyond laboratory and test environments yet. The next step could be the presentation of a fully functioning device as a minimum viable product being able to serve the market requirements.

The project performed by Wärtsilä Corporation with the support of the Norwegian Government (see chapter 5) might deliver such a device. The project successfully passed the laboratory trials in Finland in 2020 and was then moved to Norway for further development. A maritime vessel with ammonia propulsion is expected to sail in 2023. If successful, that vessel would be much more than just a working prototype. It will be able to provide information on the necessary depth and the volume of retrofitting naval engines for use of ammonia. Besides that, the vessel will allow both, to formulate the ammonia supply infrastructure requirements and to evaluate the economic framework conditions of using ammonia as fuel.

Today, it is difficult to predict whether ammonia will win the competition for the fuel of the future or will end up in scientific libraries as a “missed chance”. What is sure, however, is that if ammonia propulsion will reach the market, it is going to be first in the maritime sector.

7 Conclusions and outlook

Electricity production from renewable sources is well established. From 2018 on it became cheaper on the international energy market than electricity produced by fossil power plants (Kost et al. 2018; The International Renewable Energy Agency 2019). Decarbonising the economy demands both, energy storage options for time periods when renewable energy sources are not available and production of carbon neutral or no-carbon fuels for mobility and e.g. heating. Large scale storage of electricity in batteries is currently not economic. Physical storage in pumped hydropower stations is possible if certain geological and topographic conditions are met, but public acceptance is low. Flywheel storage technology is not yet widely established but appears promising. Chemical energy storage in newly synthesised compounds seems an interesting pathway.

According to the second law of thermodynamics, each conversion is ultimately coupled with losses in free energy (Atkins et al. 1990). Therefore, the number of production steps for fuels should always be kept to a minimum. Hydrogen is the first fuel product of the electrolysis of water and shows the least loss of free energy (Holleman et al. 1985). Hydrogen can be used as a fuel in (a) fuel cells – as currently tested in pilot projects in public transportation buses (Waterstofnet 2020) and trains (VDI 2018), (b) blended into natural gas pipelines for heating purposes (Atlantic Council 2020; Sadler 2016) or (c) used as pure H₂ as an chemical basic material (Gasunie Waterstof Services B.V. 2020). In The Netherlands, a consortium of the Gasunie pipeline operator, Groningen harbour and Shell Netherland built a wind farm to power electrolyzers for H₂ production. The project was started at the beginning of 2020 (N.V. Nederlandse Gasunie 27.02.2020). In all those technologies mentioned, the final product of the incineration process is H₂O. The disadvantages of using H₂ are its highly inflammable and explosive properties as well as its low energy density as gas. Thus, before transport and storage, a liquefaction or pressurisation is necessary which is expensive and energy consuming (Table 1).

Hydrogen can be further on processed to ammonia which is mostly known as a precursor for nitrogen fertiliser production (nitrates and urea), but is also used as fuel since many decades. NH₃ may also serve as a chemical storage substance for H₂. Catalytic dissociation of ammonia produces N₂ and H₂. The hydrogen can then be used in all applications mentioned in the paragraph above. NH₃ is easier and safer to handle and to transport than H₂. Applications supplying power in remote areas are already established (GENCELL WORLDWILD 2020). Since additional transformation steps cause further energy losses, direct uses of ammonia should be preferred. The most promising short term NH₃ applications are in marine vessels. Both, ammonia driven fuel cells (SHIPFC 2020) and internal combustion engines (Wärtsilä Helsinki Campus 2020) are on the brink of their first real life tests. Both technologies will provide CO₂- and SO_x- emission free mobility. However, such internal combustion engines need selective catalytic reduction (SCR) treatment systems) because the NH₃, N₂O and NO_x emissions are high. These treatment systems are mature and well established technologies in ships, as they are already used with carbon based fuels for reducing NO_x emissions (MAN Energy Solutions 2019). These combined technologies would have a huge positive impact on decreasing the pollution with SO_x, PM and heavy metals in harbours and coastal regions since the fuels currently used in most large ships are waste products from the crude oil refining processes and are highly enriched in substances hazardous to health. The concentrations permitted for these hazardous substances in shipping fuels are currently much higher than for land based mobility fuels (Umweltbundesamt - UBA) - but this may change soon.

Zhao et.al. (2019) estimated the costs for different non-fossil fuels from source-to tank in cars. He compared several hydrogen-, nitrogen and carbon-based fuels produced from renewable electricity, H₂ from electrolysis, methanol and Fischer-Tropsch syntheses. On the source to tank basis, NH₃ as a fuel is superior to H₂ and methanol. The efficiency of the NH₃ fuel cells, however, has to be improved to sustain the cost advantage of NH₃.(Zhao et al. 2019)

Ammonia is toxic but self-alarmed to humans due to its pungent smell and it is neither inflammable nor explosive. Ammonia is widely used as a cooling agent in the food industry, in sporting arenas and in emission treatment systems in ships. NH₃ production, transportation and distribution by ships and trucks is common practise. Safety routines are well established during maintenance and repair works (Bundesministerium für Umwelt, Naturschutz und nukleare Sicherheit 2018; MAN Energy Solutions 2019). The practical obstacles for large scale NH₃ usage seem smaller than for H₂ usage.

Ammonia is one of the most commonly produced commodities on a global scale. In 2014 approx. 113 x 10⁶ tonnes of NH₃ were produced globally. Production, transportation and distribution capacities are available on all continents (Figure 8) (Ritchie and Roser 2020). Countries with large agricultural and industrial sectors show high levels of production.

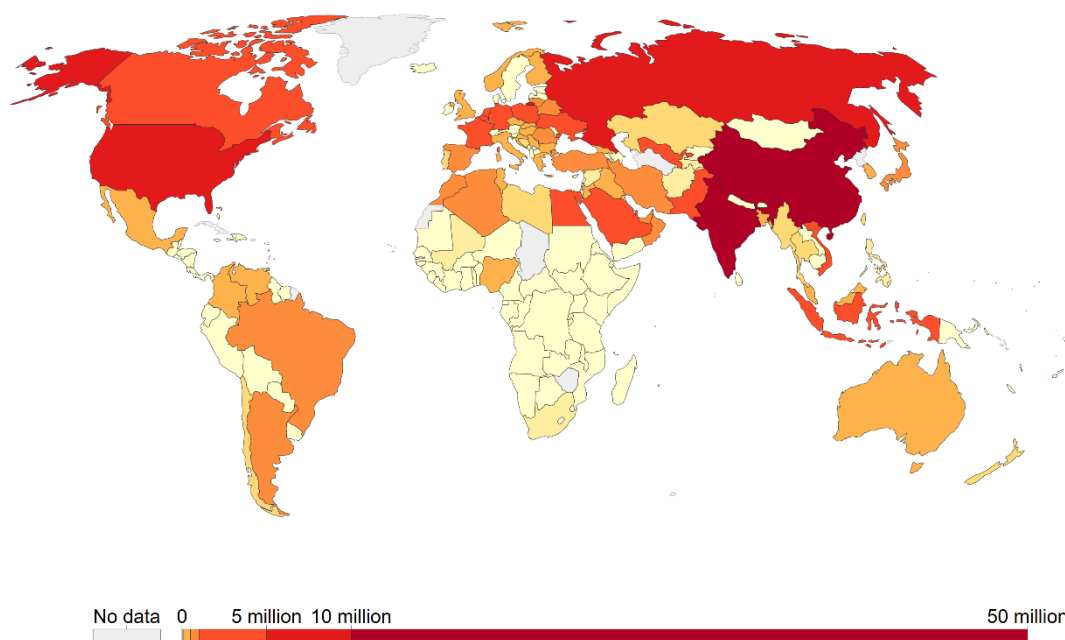


Figure 8: Global nitrogen fertilizer production in 2014. Global production in 2014 was 113.31×10^6 tonnes (Ritchie and Roser 2020).

Using NH_3 as fuel would require a significant upscaling of the production capacities. Under the given conditions this seems a manageable task and various CO_2 -free or low CO_2 - routes are thinkable. On a larger scale, additional plants for ammonia production would be needed. If powered with renewable electricity for the electrolysis of water, the overall CO_2 emission could be substantially reduced. Many of the countries with a large NH_3 production output are located in the global Sunbelt (Figure 9) between 35th degrees of northern and southern latitude, where global yearly irradiation is the highest. These regions are very well suited for solar electricity production. The German plant manufacturer Thyssen-Krupp already offers small scale Ammonia production plants with H_2 obtained by electrolysis of water with electricity gained from renewable sources (thyssenkrupp Industrial Solutions AG 2020). Upscaling of these plants is surely possible. MAN Energy Solutions (Denmark), the producer of two-stroke NH_3 internal combustion engines for ships, proposes the production of NH_3 fuel in plants in the Australian deserts, powered by electricity from solar parks (MAN Energy Solutions 2019).

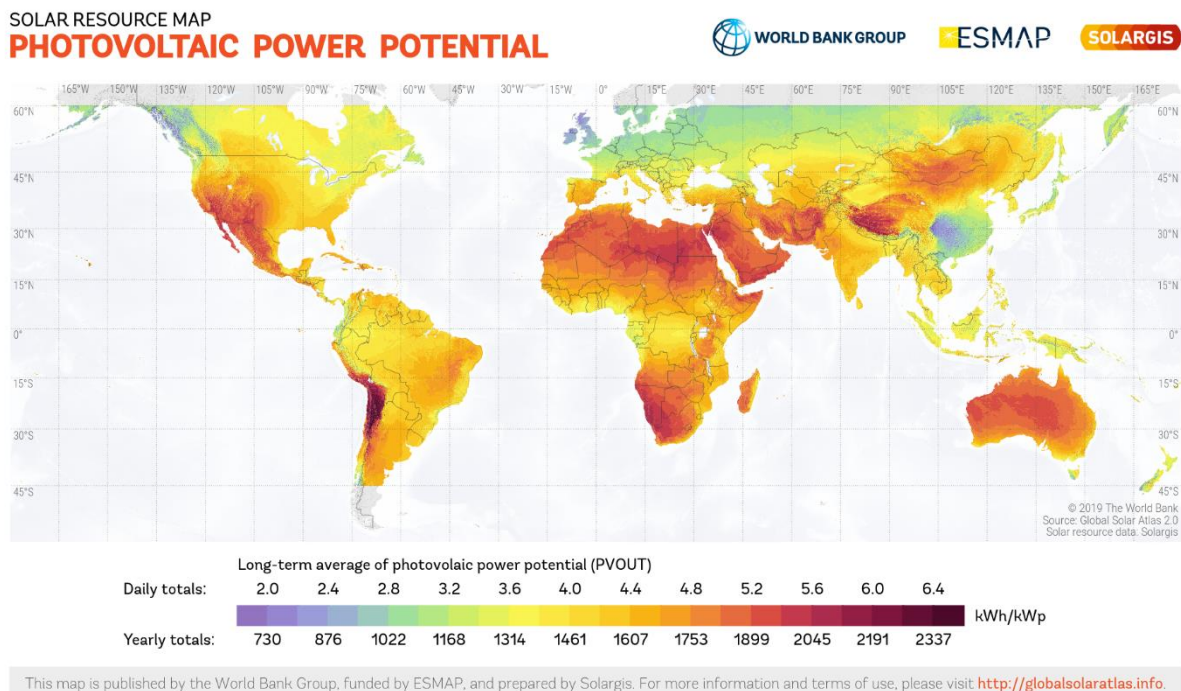


Figure 9: Global map of photovoltaic power potential (THE WORLD BANK, 1818 H Street, NW Washington, DC 20433 USA 2020).

Hydrazine is highly toxic and applications for the general public are unlikely. It is currently used as a fuel in space travel and military applications only. Nitrate and urea based fuels are in early laboratory testing phases. Whether these fuel-technologies will reach marketability is not yet conceivable.

In the future we will surely experience intensified research and development for using fuels on a nitrogen basis. The prime advantages of nitrogen based fuels are both, the intrinsic lack of carbon – with exception of urea - as well as the technological maturity of their production, transport and storage. As the various propulsion engine and combustion technologies reach technical maturity, nitrogen based fuels will certainly become attractive fuels for a decarbonizing world.

For the next years it appears to be a prudent diversification strategy for NATO nations and partners to establish a balanced strategy of investments in Power to Liquid technologies at home and in politically stable regions and to include nitrogen fuel research in their portfolio. This will ensure own technological competence and leadership for promising technologies. -

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