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AMMONIA IN RECIPROCATING INTERNAL COMBUSTION ENGINES

Past, present and the future

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Tässä opinnäytetyössä tutkin, millainen on tällä hetkellä ammoniakkia polttoaineenaan käyttävien polttomoottoreiden kehitys ja ovatko tähän mennessä suoritetut testit olleet onnistuneita. Tarkoituksena on löytää aikaisemmin suoritetut testit ja muodostaa niistä kattava yhteenveto.

Opinnäytetyön muotona on kirjallisuuskatsaus. Työn alussa tarkastelen merenkulkualaa yleisesti, sekä siihen liittyviä säädöksiä. Tämän jälkeen käsittelen ammoniakkia, sen valmistusta ja ominaisuuksia. Kolmannessa kappaleessa paneudun palamiskonsepteihin, sekä erilaisiin moottorityypeihin. Tämä kappale sisältää aiemmin suoritetut testit ammoniakilla. Viimeisessä kappaleessa tutkin ammoniakin tulevaisuuden näkymiä polttoainekäytössä.

Tässä työssä esiteltävät tutkimukset ovat käyttäneet ammoniakkia polttoaineena polttomoottoreissa, jotka ovat kaikki 4-tahtisia mäntämoottoreita. Useimmiten tarvittiin apupolttoainetta parantamaan ammoniakin palamista. Polttoaineen syttyminen ja poltto oli mahdollista monilla eri ammoniakkisuhteilla. Saadut tulokset kannustavat tutkimaan aihetta lisää ja kehittämään ammoniakilla toimivia moottoreita vielä pidemmälle.

Avainsanat ammoniakki, polttomoottori, palaminen, merenkulku

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ABSTRACT

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In this thesis the current situation with ammonia fuelled engines and the success of performed tests are investigated. Purpose of the work is to find out previously performed tests and compose a summary of those.

The thesis will be made as literature survey. At the beginning maritime industry and regulations are investigated. Production and properties of ammonia is presented in the second chapter. Different combustion concepts and engine types are being introduced in the third chapter. The future of ammonia as a fuel is consider in the last chapter.

Studies presented in this thesis have been trying to run engine with ammonia. This thesis focused only on reciprocating engines with a four-stroke cycle. Some pilot fuel was usually needed to improve combustion properties. Ignition and combustion were possible with different proportions of ammonia. The results are encouraging to further develop engines to be powered by ammonia.

Keywords Ammonia, combustion engine, combustion, and maritime

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LIST OF ABBREVIATIONS

CHP	Combined heat and power
CI	Compression ignition
CNG	Compressed natural gas
CR	Compression ratio
DI	Direct injection
EGR	Exhaust gas recirculation
GHG	Greenhouse gases
GWP	Global warming potential
HCCI	Homogeneous charge compression ignition
HFO	Heavy fuel oil
HP	Horsepower
IC	Internal combustion
ICE	Internal combustion engine
IEA	International Energy Agency
IMO	International Maritime Organization
LNG	Liquefied natural gas
MBT	Maximum brake torque
MDO	Marine diesel oil

NH_3	Ammonia
PM	Particulate Matter
RCCI	Reactivity controlled compression ignition
RON	Research octane rating
RPM	Revolutions per minute
SCR	Selective Catalytic Reactor
SI	Spark ignition
SMR	Steam methane reforming

1 MARINE INDUSTRY

Marine transportation is responsible for around 940 million tonnes of CO_2 emissions in a year, which is approximately 2.5% of the global greenhouse gases (GHG). According to the forecasts this amount will increase considerably in the future if no swift mitigation measures are issued. International maritime organization (IMO) has set up a target to reduce total greenhouse gas emissions from ships by at least 50% by 2050 compared to the year 2008. These goals are referring to the Paris Agreement.[1] According to the 3rd IMO GHG study the global greenhouse gases could increase between 50 and 250 percent by 2050 in case there are no changes in the current practices. Thus, the objectives stated in the Paris Agreement would be endangered.[2]

Shipping volumes have been increasing a lot during a couple of last decades and ships are getting bigger. Growing online shopping is also affecting the sea freight quantities. Shipping industry is changing together with e-commerce, and it needs to adopt a new, more digital way of working. The number of ships is going to increase all the time, which means that each new vessel needs to achieve even more strict emission criteria.

There are a lot of untapped potential to reduce shipping emissions cost-effectively. The efficiency of the modern engines has reached the point where big improvements tend to be rare. However, utilizing different fuel types could cut down the amount of emissions. With better route planning and speed optimization it could be possible to gain significant savings in fuel consumption, which also means lower emissions. Figure 1 below shows how much greenhouse gases could be reduced in different areas in vessels.[3]

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[1] International Maritime Organization, 2021
[2] European Commission, 2021
[3] European Commission, 2021

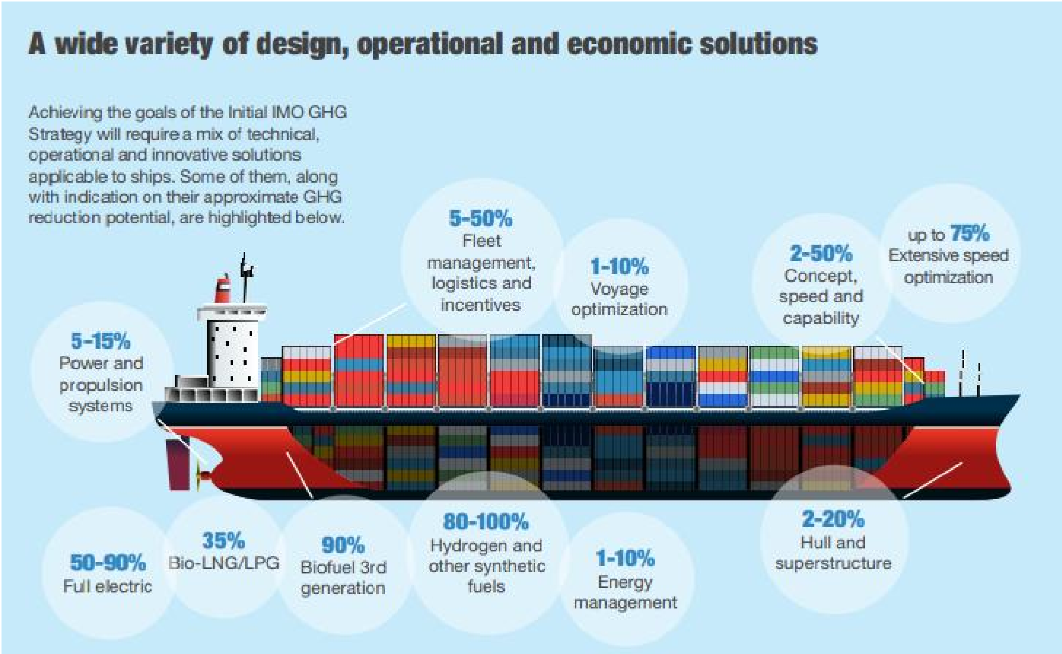

Figure 1. GHG reducing potential in ship design.[4]

1.1 International Maritime Organisation IMO

The International Maritime Organization (IMO) is a specialized agency of the United Nations. It is responsible of the safety and security in the shipping industry. IMO sets the standards for international shipping. Atmospheric and marine pollution from the ships are one of the organisation's main targets, together with sustainable development goals set by the United Nations. Strict rules are also promoting new innovations and security for maritime transportation to fulfil IMO's tightening regulations.

IMO consists of 174 member states and three associate members. These parties make the decisions and budgets published by IMO. The organization sets global guidelines so that legislation is concurring worldwide. This helps global shipping companies to perform according to the rules without overlapping, country specific

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[4] International Maritime Organization, 2018

instructions. Being aware of different laws would be much challenging if every country would have their own regulations.[5]

1.2 Marine fuels

> *"In 2016, IMO adopted mandatory requirements for ships of 5,000 gross tonnage and above will have to collect consumption data for each type of fuel oil they use, as well as other, additional, specified data including proxies for transport work. These ships account for approximately 85% of CO2 emissions from international shipping. The data collected will provide a firm basis on which future decisions on additional measures, over and above those already adopted by IMO, can be made."* [6]

The majority of the marine traffic is fuelled by heavy fuel oil (HFO) or marine diesel oil (MDO). Other fuels still represent quite small fraction. HFO and MDO have two main advantages, these are inexpensive and easy to get everywhere. To reduce GHG emissions in a way that was introduced in IMO's initial strategy, new alternative fuels for international shipping are needed globally. New greener fuels should be also easily available and reasonable priced. Electric and hybrid power should be also included into the consideration alongside with different fuels.

Continuous development and research are vital to meet the targets IMO has set. These objects will not be reached using fossil fuels. Zero-carbon ships need to be made more attractive and steer direct investments towards different fuels and new technologies. Infrastructure needs to be developed in a way that it supports supply of alterative low-carbon and zero-carbon fuels. [7]

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[5] International Maritime Organization, 2021
[6] International Maritime Organization, 2021
[7] International Maritime Organization, 2021

1.3 Greenhouse Gases

The main greenhouse gases are carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), ozone (O_3), water vapour (H_2O) and fluorinated gases. Water vapour is the most common greenhouse gas and it appears naturally in the atmosphere. Carbon dioxide is the most significant greenhouse gas produced by humankind. The majority of CO_2 produced are from using fossil fuels. Another major source for CO_2 emissions is deforesting of tropical forests.

Greenhouse gases absorb the thermal radiation in some specific wavelengths and then release part of that energy back to the atmosphere as a thermal radiation. This phenomenon is heating up temperature on the globe. The amount of greenhouse gases has been an increasing trend, which is then boosting global warming. In the past couple of centuries, the amount of greenhouse gases has been growing very intensely compared to time before.[8]

Global shipping produces a lot of GHG emissions. Figure 2 below shows where the most of CO_2 emissions from vessels are produced worldwide.

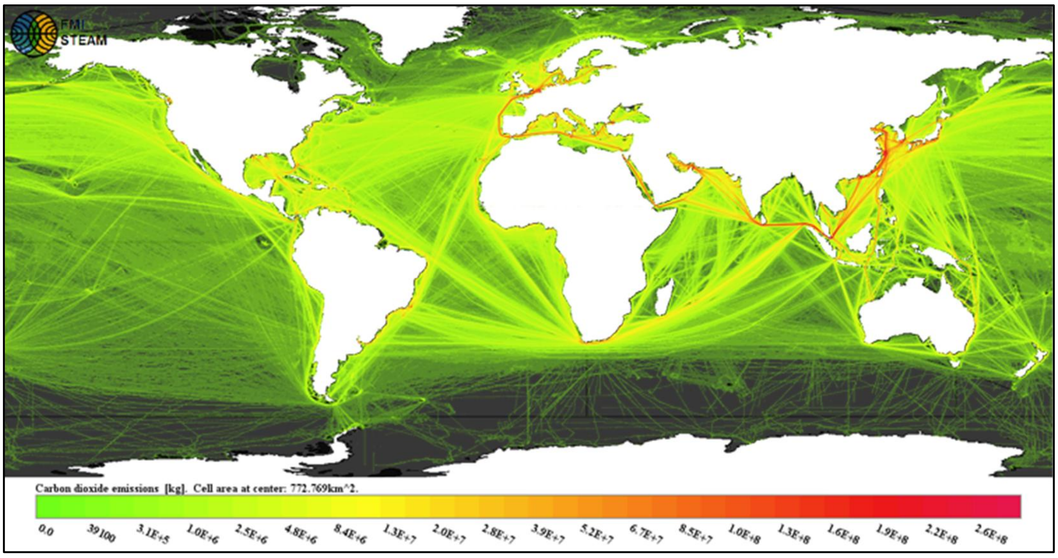

Figure 2. CO_2 emissions of ships globally.[9]

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[8] Ilmasto-opas, 2021
[9] Ilmatieteenlaitos, 2021

1.4 Other Emissions

Ships produce other emissions as well. Nitrogen oxides (NO_X) and sulphur oxides (SO_X) are two main emissions found from the exhaust gases. Burning fossil fuels are the main reason for NO_X forming. There is nitrogen in the air inserted to the engine and in the fuel itself. High temperature in combustion will produce more nitrogen oxides. NO_X scrubbers and NO_X burners cut down the amount of nitrogen oxides emissions. Selective catalytic and non-catalytic reactors (SCR and SNCR) are used to remove NO_X from exhaust gases.[10]

Sulphur oxides (SO_X) also comes from fossil fuels, such as oil, coal and diesel. When combusting fuel that contains sulphur, SO_X emissions will occur. The main form of sulphur from the ships is sulphur dioxide SO_2.

There are SECA-areas (Sulphur Emission Control Areas) around the world where the maximum amount of SO_X emissions is limited. IMO has set limits to these emissions. As vessels use fossil fuels with high sulphur content, scrubbers are used to clean exhaust gases and remove SO_X emissions. Otherwise ships cannot enter the SECA-areas.

Particulate matter (PM) emissions are a mixture of very small liquid and solid particles. PM emissions could form from many different sources. A combustion engine is one source as well. When combusting less processed fuels, such as HFO, which contains ash and a lot of sulphur, PM are formed from ash and SO_2 after they are cooled down and combined with water particles. A small part of the emissions can be soot emissions, which are small carbon particles coming out from the exhaust and produced when burning fossil fuels. Incomplete combustion causes soot emissions. [11]

[10] European Environment Agency, 2018
[11] U.S. Environmental Protection Agency, 2021

1.5 The Paris Agreement

The Paris Agreement was adopted in 2015 and it was taken into force in 2016. The main goal for the agreement is to battle against the climate change and limit the global warming to well below 2 or even 1,5 Celsius degrees compared to pre-industrial levels. Altogether 196 parties around the globe accepted this common target.

This agreement is a great milestone in climate change actions as now all nations involved aim towards a common goal and targets. Greenhouse gas emissions have now reached their top level and the future trend shall be downwards. Otherwise that long-term temperature goal will not be reached. By the mid-century the globe should be climate neutral.[12]

International shipping is not included in the Paris Agreement; however, IMO is committed to reduce greenhouse gas emissions in that area.[13]

1.6 Future

Ship building in the future is going to change as new vessels must meet the minimum criteria which will get progressively tougher over time. According to the regulations, the new ships built in 2025 will be 30% more energy efficient compared to ships built in 2014. Ship design has an important role in fuel savings.[14]

Speed optimization is one of the future topics in marine industry. It means that ships are not steaming full speed to the next port, where they must wait for their docking turn for a couple of days. Ships have specific time when they can enter the dock and optimise speed of the ship so that they can run straight to the pier. In this way fuel is saved as ships can run at lower speeds. Potential saving in fuel

[12] United Nations Climate Change, 2021
[13] International Maritime Organization, 2021
[14] International Maritime Organization, 2021

is quite massive with this method according to IMO and they calculated up to 75 % drop in greenhouse gases. This change means that also ports needs to be modernized. Ports should be communicating with ships and plan the entering order of arriving vessels. It will work such as air traffic control at airports.[15]

[15] European Commission, 2021

2 AMMONIA

Ammonia NH_3 is an inorganic compound in gas or compressed liquid form. It is composed of a single nitrogen atom covalently bonded to three hydrogen atoms. This toxic colourless gas with suffocating and pungent odour is highly corrosive.[16]

Table 1. Properties of ammonia

Molecular weight	17,031 g/mol[17]
Density	0,696 g/L (liquid) [15]
Melting point	- 77,7 ℃ (195,5 K) [15]
Boiling point	- 33,85 ℃ (239,3 K) [15]
Flash point	132,4 ℃ (405,6 K)[15]
Autoignition temperature	651 ℃ (924,2 K)[18]

It should be noted that ammonia is not suitable to use with all materials. It can be explosive with gold, silver, mercury and combinations of these materials. Fluorine, chlorine, bromine, iodine, hypochlorite and ethylene oxide may also explode when get mixed with ammonia. It has a highly corroding effect on materials such as copper, aluminium, silver, zinc and combinations of these. When using ammonia, these should be taken into consideration.[19]

16 International Maritime Organization, 2020,
17 O'Neil M.J, 2013
18 National Fire Protection Association, 2010
19 Työterveyslaitos, 2017

The majority of produced ammonia in the world is used for fertilizers, more than 80 % of it. Nitrogen released from ammonia is an essential nutrient for growing plants.[20] The rest of the usage is divided between mining, pharmaceutical, textiles, refrigeration and other end-user industries.[21]

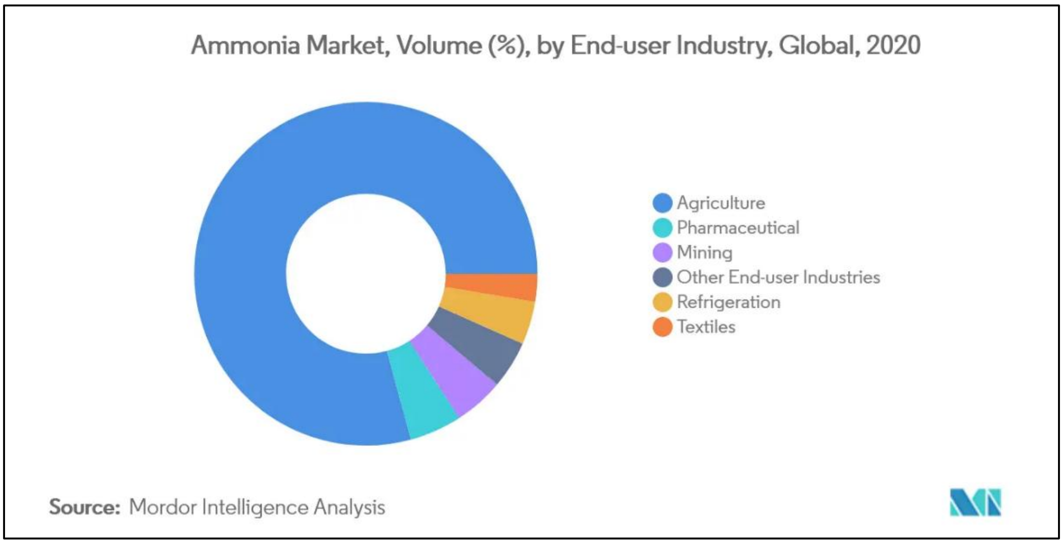

Figure 3. Ammonia market.[22]

In the future ammonia market will be more spread out to other fields as well. Agriculture might still be the biggest one, but fuel usage is going to grow massively according to forecasts. Using ammonia as fuel in marine industry might be the biggest sector of ammonia usage in 2050, while today ammonia usage for fuel is zero. In 2050 it might be approximately 125 million tons annually, according to International Energy Agency (IEA) calculations. The amount of total ammonia demand will be about 355 million tons yearly in 2050. The usage will increase in power plants as well in vessels. Figure 4 below demonstrates how ammonia demand may increase. The growth in existing usage will be quite modest, but because of the world's population increase, also a need for fertilizers are growing. The biggest increase will take place in energy- and transportation sectors. Container ships and tankers may be the first ones to implement ammonia into fuel, mainly because the fuel supply is easier to arrange, and costs could be divided

[20] The Fertilizer Institute, 2021
[21] Mordor Intelligence, 2020
[22] Mordor Intelligence, 2020

between many users. In power plants ammonia could be used as co-firing fuel besides coal. This will cut down CO_2 emissions. [23]

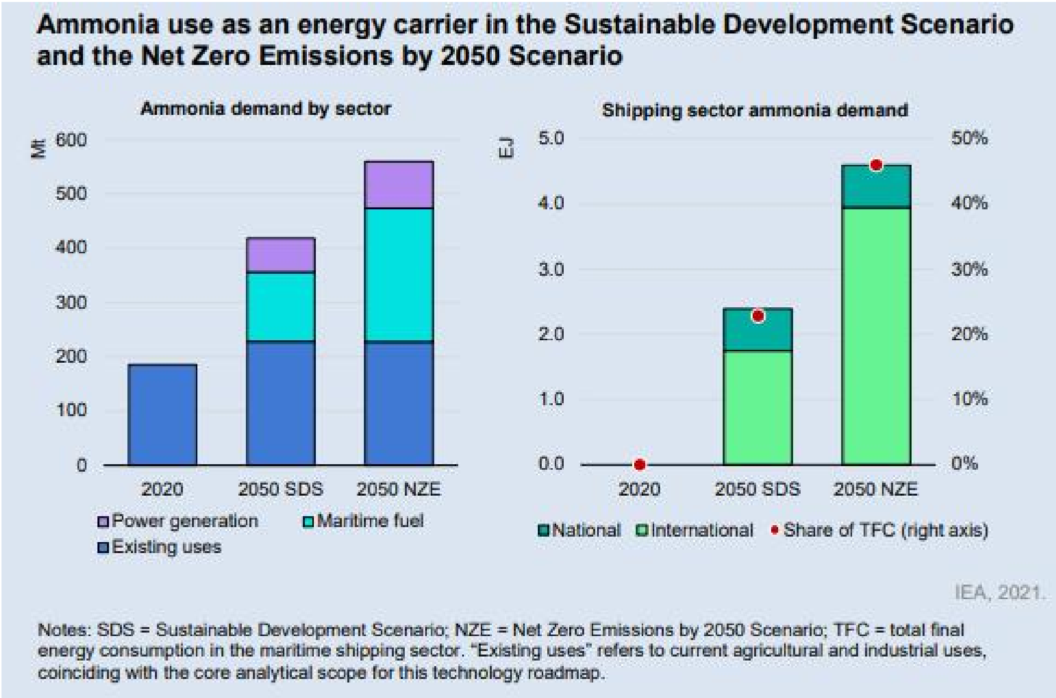

Figure 4. Future scenarios of ammonia usage. [24]

2.1 Ammonia Production

Ammonia (NH_3) is made from nitrogen (N) and hydrogen (H). There are a few different ways to produce ammonia. How green the alternative it is depends on how ammonia and its components have been generated. The Haber-Bosch process is used for the biggest amount of the 235 million metric tons of ammonia produced in 2019 globally. Ammonia is the second highest produced chemical in the world and China makes the major amount of it in the world.[25]

One of the main components in ammonia is nitrogen gas. There is 78 % of nitrogen in the atmosphere, so it is available anywhere with massive amounts. Th rest of

[23] International Energy Agency, 2021
[24] International Energy Agency, 2021
[25] Statista, 2020

the atmosphere consists mainly of oxygen (21%), leftover 1 % consists of other gases, such as hydrogen and carbon dioxide as well as other particles. [26]

Nitrogen can be taken out of the atmosphere mostly with the cryogenic air separation method. Nitrogen bonds are very stable and to break them requires a lot of energy. Hydrogen and nitrogen are then bonded together to generate ammonia. Producing ammonia causes huge amounts of greenhouse gas emissions, since the Haber-Bosch method is highly pollutant. Solely this ammonia production process is responsible for over 420 million tons of CO_2 annually and that represents 1 % of all CO_2 emissions globally.[27] The Haber-Bosch process needs a lot of energy for heat and pressure and because that energy is mainly produced with fossil fuels, it explains the huge emissions. The emissions of producing nitrogen and hydrogen comes on top of that. Hydrogen production from fossil fuels especially causes a lot of emissions. Making hydrogen will produce 830 million tons of CO_2.[28]

Today hydrogen is nearly completely produced from fossil fuels, mainly from natural gas and coal. Renewables currently represent a very small amount of all hydrogen production. If using renewable energy for electrolysis with water, produced hydrogen could be considered as green hydrogen. To achieve lower CO_2 emissions, the production of hydrogen needs to be transferred to clean electricity. There has been a significant reduction in production costs of renewable energy which has caused that hydrogen can be produced with lower costs too. Thus, in the future the production volumes of low carbon or carbon free hydrogen are expected to rise. All these factors have a great impact on lowering global CO_2 emissions. The price for green ammonia is still much higher than ammonia produced with fossil fuels. When the production of renewable energy is growing, also its price should go down. That would make a green ammonia more affordable.[29]

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[26] NASA, 2016
[27] Liu X, 2020
[28] International Energy Agency, 2021,
[29] Business Finland, 2020

There are two ways of producing hydrogen in Europe that dominate: steam methane reforming from natural gas (SMR) and partial oxidation of heavy oils (POX). Steam reforming from natural gas, is the most used and most suitable from the technical point of view. Outside Europe other sources such as coal and fuel oil are used. For example, China produces most of its ammonia by coal gasification. Thus, the world's gasification plants are mainly located in China. Making hydrogen from natural gas with steam reformation means that heated steam reacts with methane under high temperature and pressure in the occurrence of a nickel-based catalyst. That separates hydrogen from carbon monoxide. Partial oxidation is a non-catalytic exothermic process with coal or oils which requires high pressure and temperature. [30]

Figure 5 below shows how much more CO_2 emissions ammonia production causes compared to diesel and petrol production. Energy consumption is huge in ammonia production and how the used energy is produced is affecting the amount of emitted CO_2 emissions. Especially in the POX method emissions are a big issue. Producing ammonia with current industrial methods has a more negative impact on the environment than using a fossil fuel on an energy basis. Today the manufacture of ammonia causes so much emissions and uses so much energy and water that the benefit of using carbon free fuel is lower than using fossil fuels.[31]

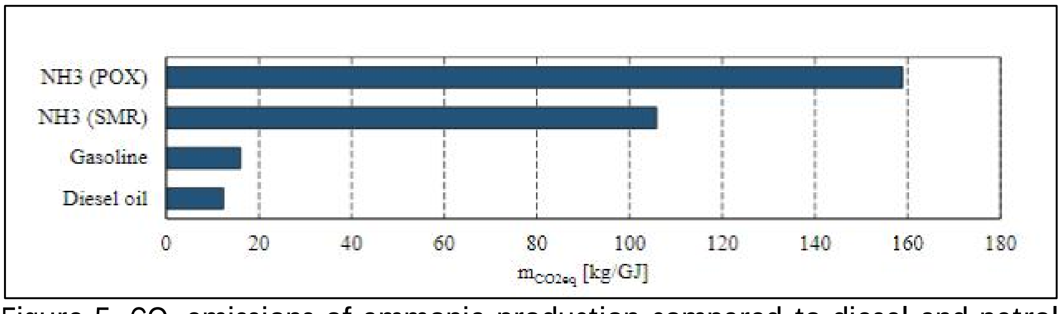

Figure 5. CO_2 emissions of ammonia production compared to diesel and petrol fuels.[32]

[30] Lasocki J, 2018
[31] Lasocki J, 2018
[32] Lasocki J, 2018

2.1.1 Haber-Bosch Process

Producing ammonia was invented in 1909 when Fritz Haber and Carl Bosch invented a new, modern and economical way to make it. This method is still in use today as almost unchanged. This new method made the world's population growth possible as synthetic fertilisers were needed for food production. About one-third of the whole food amount produced today, is because of this process and synthetic fertilisers. Without the Haber Bosch process world population and food production would be much less than it is today.[33]

In the catalyst process nitrogen reacts with hydrogen in high temperature and pressure with the presence of a metal catalyst. The diagram below visualises how this process takes place. Before this process, nitrogen and hydrogen have been produced and pure gases are inserted into the compressor in the correct ratio.

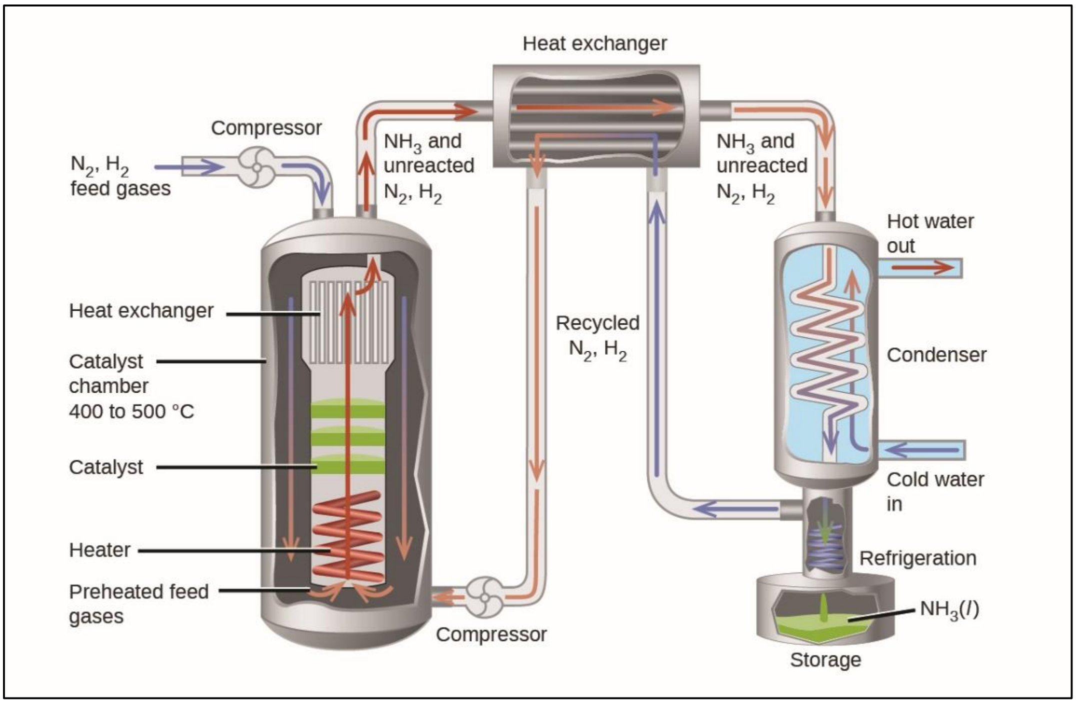

Figure 6. Haber-Bosch process.[34]

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[33] Flavell-While C, 2010
[34] Lumen Learning, 2021

Before this catalyst process, the raw materials such as natural gas and air have been processed. To have ammonia as a great future fuel with smaller carbon footprint, it could be seen that the Haber-Bosch process is the bottleneck in ammonia production as it produces harmful emissions.[35]

2.2 Ammonia as a Fuel

Hydrogen has many good properties; it is quite easy to produce and has great ignition properties, to mention a few. As a fuel it is very potential, but it is difficult to handle and storage onboard is challenging due to low energy density in volume. One solution would be combining it with nitrogen, and it becomes ammonia. That could be stored in a liquid form in a modest pressure and it is a great hydrogen carrier. Fuel tanks for ammonia are much simpler and cheaper to produce than tanks for hydrogen. If looking for a carbon free fuel, which is easier to handle, then ammonia is a one good option. Basically, nitrogen could be taken out of air and hydrogen out of water to produce ammonia. If only renewable energy is used to make electricity for its production, then it could be considered as a totally carbon free fuel. Excess energy from environmentally friendly sources could be stored into a non-electric form of energy such as ammonia.

The ignite properties of ammonia are not so good as with hydrogen. Ammonia has a high resistance to autoignition, which causes delays for combustion. Adding some other fuel to improve ammonia’s ignition properties would be a good idea. In the majority of the studies mentioned in this thesis, some pilot fuel was used to upgrade combustion characteristics. Pure ammonia can be used as a fuel in internal combustion engines, but power output and running behaviour is not ideal. The guideline could be that some combustion promoter is needed. Hydrogen is one of the best promoters and it was used in many different tests.

[35] Lasocki J, 2018

Ammonia needs three times more storage space in a ship than HFO to have the same amount of energy. Ammonia is also two times heavier than HFO. These factors need to be taken into consideration when designing ships powered by ammonia. Ships have more storage space for fuel options than other commercial vehicles. Larger tanks and new pipelines could be fitted with minor difficulties.[36]

Marine vessels have large engines that are running at a low speed. A large displacement volume suits well with ammonia combustion. With the help of pilot fuel, marine applications may be the most suitable starting point for ammonia fuel.

Because ammonia is used widely around the world, the whole supply chain already exists. Many ports have storage and transportation options for ammonia which could be used to refuel the ships. Ammonia could be taken into common use with modest investments. It is easily scalable fuel for bigger amounts.

Ammonia has a high octane number, which means that there might not be any knocking issues. The octane number measures ability of a fuel to resist knocking when used in Otto SI ICE. [37] Compared to hydro-carbon fuels, ammonia needs less air for complete combustion. A half atom of oxygen is needed for ammonia combustion, when carbon needs two atoms of oxygen.[38]

[36] C-Job, 2021
[37] Britannica, 1998
[38] Kroch E, 1943

Table 2. Pros and cons of ammonia as a fuel

+	-
+ No carbon, green fuel	- High autoignition temperature
+ High hydrogen density	- Low flame speed
+ Easy to store and don't need high pressure to be liquefied	- Highly corrosive
+ Reasonable manufacturing costs	- Very high latent heat of vaporization (high cooling effect)
	- NO_X emissions
	- Toxic
	- N_2O (GWP effect 298 x CO_2)

Ammonia has a cooling effect during the combustion, and it could be noted when designing the engine. The cooling system could be smaller than in an engine running with a conventional fuel. The efficiency of the ammonia powered system is better if the cooling factor is considered in the calculations.[39]

2.3 Ammonia vs Other Fuels

As mentioned before, ammonia does not have so good combustion properties as hydrocarbon fuels. Being a carbon free fuel, ammonia has become interesting in the current situation when the amount of greenhouse gases needs to be reduced. Handling and storage are also an advantage of ammonia fuel as it does not need very low temperatures such as LNG or hydrogen, for example. To keep ammonia in a liquid form, the needed storage pressure is quite modest, too.

[39] Zamfirescu C, 2009

Ammonia has a high octane number, which means that the engines could be run with higher compression ratios without knocking issues. Low flame speed, narrow flammability limit and high needed ignition energy are disadvantages of ammonia. During the combustion, ammonia will drop pressure and temperature due to high latent heat of vaporization. A booster fuel would improve combustion properties of ammonia. A natural choice could be hydrogen, which was used in many studies presented in this thesis.[40]

The energy density of ammonia is 11,2 MJ/L, which is much lower if compared to diesel, for example. Compared to hydrogen, ammonia has a higher energy density, therefore, it is a good hydrogen carrier. The energy density of ammonia is considered high, even if it is lower than some hydrocarbon fuels. When comparing the ammonia-air mixture and the gasoline-air mixture with equal volumes of stoichiometric air-fuel mixtures, heat content of ammonia-air mixture is about 20 % lower. [41]

Table 3. Fuel comparison table. [42]

	Ammonia	Hydrogen	Ethanol	DME	Gasoline	Diesel
Formula	NH_3	H_2	C_2H_6O	CH_3OCH_3	$C_nH_{1.87n}$	$C_nH_{1.8n}$
Phase	Liquid	Liquid	Liquid	Liquid	Liquid	Liquid
Density (g/cm3)	0.60[a]	0.071[b]	0.79	0.67	0.75	0.86
Boiling point (°C)	−33	−253	78	−25	33–190	> 200
Latent heat of vaporization (kJ/kg)	1370	445.6	840	467	305	270
Stoichiometric air/fuel mass ratio	6.06	34.3	9.0	9.0	14.6	14.5
LHV (MJ/kg-fuel)	18.5	120.0	26.9	27.6	44.0	42.5
LHV_{st} (MJ/kg-stoichiometric)	2.62	2.71	2.69	2.65	2.82	2.74
HHV (MJ/kg-fuel)	22.5	141.9	29.7	31.7	47.3	44.8
HHV_{st} (MJ/kg-stoichiometric)	3.19	4.02	2.97	3.17	3.03	2.89
Volumetric energy density (MJ/L)	11.2	8.4	21.3	18.5	33.0	36.6
Flammability limit in air (vol %)	15.0–28.0	4.1–74.8	3.3–19	3.4–18.6	1.3–7.1	0.6–6.5
Autoignition temperature (°C)	651	585	363	235	248–412[c]	226–233[d]
Maximum flame speed (ms^{-1})	0.07	2.9	0.39	—	0.37–0.43	—
Minimum ignition energy (mJ)	8	0.02	0.65	0.2	0.2–0.3	—
Octane number (RON)	> 111	≥ 120	107	—	92–98	—
Cetane number	—	—	—	>55	—	40–50

[a] density at 25 °C and 10 bar.
[b] density at −253 °C and 1 atm.
[c] octane number of 68–87.
[d] cetane number of 41–68.

[40] Lesmana H, 2019
[41] Cornelius W, 1965
[42] Lesmana H, 2019

2.4 Emissions from Ammonia Combustion

Using ammonia as a fuel in combustion engines generates emissions, too. A great benefit of ammonia is that it is a carbon free compound, so no carbon dioxide emissions are being produced. With ideal combustion conditions, water and nitrogen are the only combustion products produced, but that is difficult to reach. NO_X emissions are the ones that are harmful and needs to be reduced. A catalyst system should be used to remove harmful emissions from the exhaust gases. With lower combustion temperatures NO_X emissions are not formed. N_2O emissions are very harmful greenhouse gas, which also are a result of burning ammonia.

Unburnt ammonia is a poisonous emission and occurs from the combustion of ammonia. To keep engine efficiency on a good level, the air excess ratio for ammonia should be under 2. Even with these settings there are unburnt ammonia found from the exhaust. It is difficult to avoid ammonia slips into exhaust side.[43]

If leaner mixtures are used with ammonia, also the amount of emissions increase because of combustion is not efficient. The amount of ammonia in exhaust gases grows due to poor combustion efficiency. With richer mixtures and higher ammonia content the amount of emissions is lower. When using more hydrogen in fuel, emission amount increases. This is because of the combustion temperature rises and NOx emissions start to form.[44]

[43] Bro K, 1977
[44] Lhuillier C, 2020

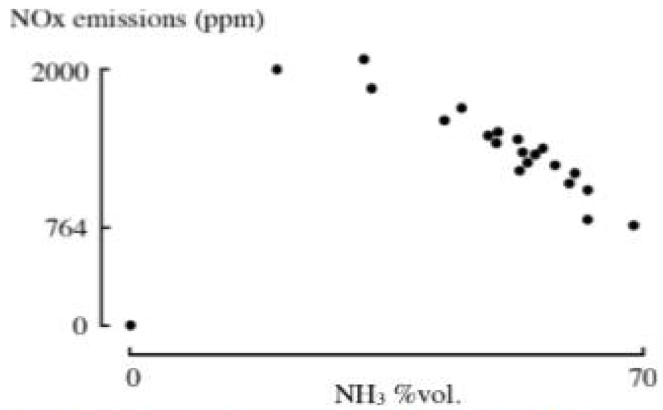

Figure 10. Measured NO_x emissions as a function of the ammonia mixture content for operating conditions # 2,3,4,5. NO_x emissions are smaller than 6 ppm for pure hydrogen combustion and are in the order of 750 to 2000 ppm as soon as some ammonia is added in the mixture.

Figure 7. NOx emissions with different ammonia proportions in HCCI engine.[45]

The combustion of ammonia is usually performed together with some other supporting fuel, which includes carbon and that generates carbon emissions. To avoid those emissions combustion promoter should be also carbon free, such as hydrogen for example.

The EGR and SCR systems help to reduce harmful emissions from exhaust gases. It was noted that the EGR system cuts down NO_X emissions significantly, but N_2O emissions still occurred despite the EGR system and with the combustion temperature lower than 1400 K.[46]

In 2010 there was an experimental test done with a dual fuel diesel engine and a great amount of data was collected about exhaust emissions the engine produced during the test with different diesel and ammonia proportions. Figure 8 below, shows NO and CO_2 emissions from a diesel engine with different ammonia proportions, at steady state conditions at different engine loads. These figures indicate that increasing the share of ammonia has a great impact on CO_2 emission reduction. Another intresting finding was that with even a small amount of

[45] Pochet M, 2017
[46] Pochet M, 2017

ammonia NO emissions drop to a very low level. Increasing ammonia to 40 % or more, the amount of NO emissions start to rise above pure diesel emissions.[47]

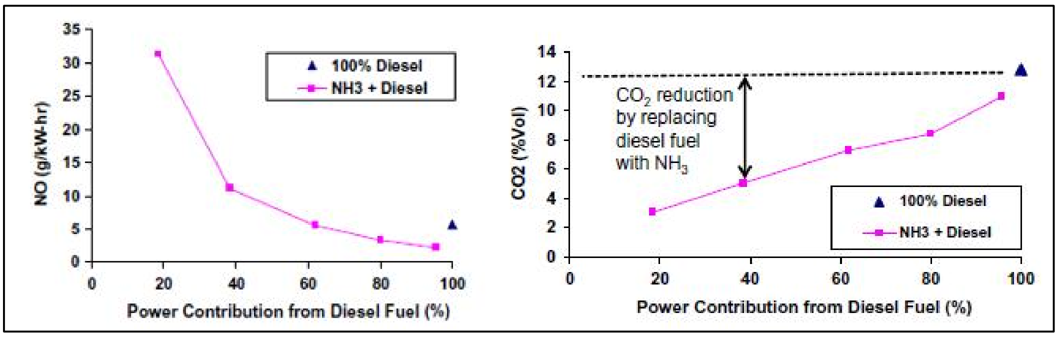

Figure 8. NO and CO_2 emissions with different ammonia proportions in diesel engine.[48]

Some emissions become lower when increasing the ammonia proportion in the engine and some emissions increase. If only pure ammonia is burned, then there are only nitrogen-based emissions forming, such as NO and N_2O. An exhaust gas treatment system is needed in any case to reduce harmful exhaust-emissions despite the used fuel.

2.5 Safety

As known, ammonia is a toxic substance and it needs to be handled with certain procedures. As ammonia is an old and well-known substance, which has been used in fertilizing industry more than 100 years, there are comprehensive regulations already in place. That is helpful when taking it into a more extensive use as a fuel. What comes to storing ammonia, there are already huge tanks that can store 60 000 tonnes of ammonia and tankers that can take up to 80 000 tonnes of ammonia out to the sea.[49]

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[47] Reiter A.J, 2010
[48] Reiter A.J, 2010
[49] C-Job, 2021

"Although ammonia is designated as a non-flammable gas for shipping purposes by the United Nations and the U.S. Department of Transportation, it is flammable in air within a certain range of concentrations. Because these concentrations are quite high, it would be extremely difficult to reach those conditions in an outdoor shipping situation. The fact that ammonia gas is lighter than air and that it diffuses readily in air makes it difficult to create a flammable situation outdoors. In confined spaces, vessels, or in controlled process conditions, it is possible to ignite gaseous ammonia." [50]

As even small amounts of ammonia can be smelled, it is easily detected if there are leakages. Human can smell proportions as low as 5-50 ppm. Gas detectors are used with ammonia to detect even small amounts. Exhaust gases should be also monitored if there is an ammonia slip taking place during the combustion. Bigger proportion of over 5000 ppm of ammonia can be fatal if inhaled. To work with ammonia, proper protective equipment is needed, such as gloves, gas mask and protective clothing. For example, butyl rubber is suitable material for clothing and gloves. [51]

Anhydrous ammonia has following hazard pictograms according to the CLP regulation ((EC) No 1272/2008) with a signal word danger:

H221 - Flammable gas

H331- Toxic if inhaled

[50] Liar, 2008
[51] Työterveyslaitos, 2017

H314 - Causes severe skin burns and eye damage

H400 - Very toxic to aquatic life

Ammonia should be stored in tanks with a moderate pressure in liquid or gaseous form. Leakage detectors should be added into the storage area. If leakage is detected, the area should be isolated and ventilation started. The reason for leakage should be identified and stopped. The storage area should be cool and dry, away from any heat and ignition sources.[52]

Engines using gaseous fuel are usually equipped with double walled pipes to prevent fuel leakages. As ammonia is a toxic compound, it should also be operated with double wall pipes and leakage detectors.

[52] Työterveyslaitos, 2017

3 COMBUSTION CONCEPTS

3.1 Basics of Internal Combustion Engine

There are two different main types of reciprocating internal combustion engines, spark ignited (SI) and compression ignited (CI). In the SI engine, also known as Otto engine, fuel is premixed with air before entering the cylinder and normally ignited by a spark. This injection type is called Port fuel injection (PFI). In the CI engine, also known as diesel engine, only air is inserted into the cylinder and fuel will be injected directly into the combustion chamber and autoignited by the high in-cylinder temperatures after compression. This injection type is called Direct Injected (DI). [53]

In a combustion engine are two or four stokes. This thesis only focuses on four stroke engines. The four-stroke cycle in direct injected engine and in Otto combustion engine is generic. Differences between these two combustion types are in ignition and how fuel is inserted into the combustion chamber.

In the CI engine the first of the four strokes is intake. During the intake stroke the inlet valves open and air is sucked into the cylinder when the piston is going down. In the second stroke called compression stroke, the valves are closed, and the piston moves up compressing the air. When the air is compressed, its temperature rises significantly. Fuel is directly injected into the cylinder in the third stroke called power stroke. Hot air ignites the fuel at the same time as the piston reaches its top level. Combustion increases the temperature and pressure in the cylinder and forces the piston downwards creating the power to rotate the crankshaft. In the last stroke called exhaust stroke, the piston starts to move back up again and the exhaust valves are opened. The piston pushes exhaust gases out of the cylinder. After these four strokes, the whole cycle starts again.

[53] Heywood J.B, 1988

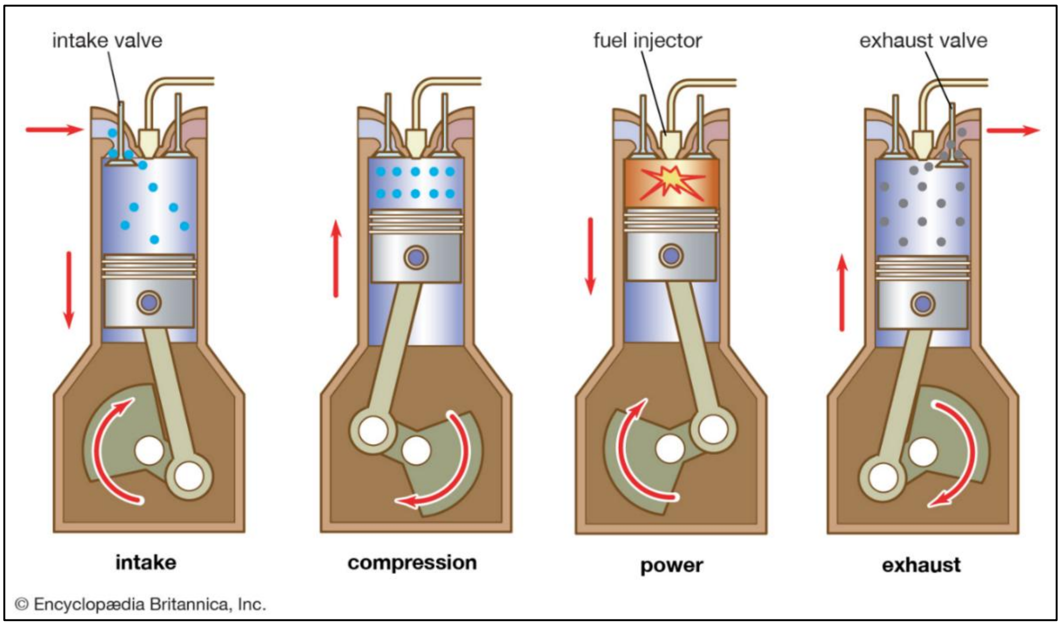

Figure 9. Diesel combustion.[54]

In the SI engine fuel is inserted already in the intake stroke as when the piston is going down, it causes the air-fuel mixture to be sucked into the cylinder. Air and fuel have been mixed before entering the cylinder in the inlet manifold. In the second stroke called compression stroke, the valves are closed, and the piston starts to move up compressing the air-fuel mixture. As the piston reaches its top level and the air-fuel mixture is compressed, the spark plug ignites the mixture. This will start the combustion and forces the piston downwards creating the power to rotate the crankshaft. This stroke is called power stroke. In the last stroke called exhaust stroke, the piston starts to move back up again and the exhaust valves are opened. The piston pushes exhaust gases out of the cylinder. The whole cycle will be repeated after these four strokes.

[54] Britannica, 1999

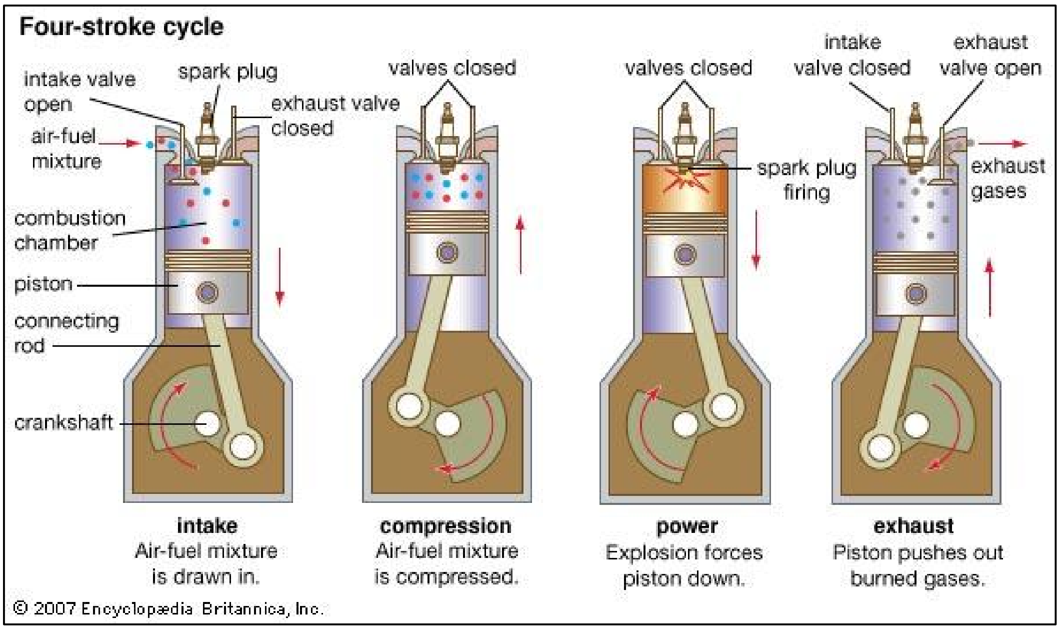

Figure 10. Four stroke cycle in SI engine.[55]

Homogeneous Charge Compression Ignition (HCCI) is a combination of diesel and Otto engines. In the HCCI engine, air and fuel is premixed as in the SI engine and then compressed such as in the CI engine. The air-fuel mixture is compressed so much that temperature reaches autoignition temperature and the combustion process starts.[56]

HCCI combustion produces almost no NOx emissions compared to an ordinary petrol engine because the combustion takes place at a lower temperature. The combustion is also slower than in petrol engines, which means that chemical reactions also take more time. Comparing ICE systems, HCCI offers the highest potential heat efficiency and this means lower CO_2 emissions. The HCCI engine works better with higher compression ratios. Intake temperature needs to be higher at lower compression ratios. The weakness of this system is that stable combustion takes place only in a very limited range. Knocking may happen because of premixed fuel, which is another weakness of HCCI combustion

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55 Britannica, 2007
56 Charalambides A, 2012

especially with leaner air-fuel ratios. These are issues that need to be develop more. [57]

Reactivity Controlled Compression Ignition (RCCI) is a dual fuel system with two or more fuels with different reactivity. Low reactivity fuel is inserted into cylinder together with air, as in the Otto engine. That mixture is heating up when compressed as the piston moves up. Temperature rises, but it will not ignite. During the compression stroke fuel with high reactivity is injected into the cylinder and it ignites the combustion. Diesel acts as a high reactivity fuel and ammonia as a low reactivity fuel due to their cetane numbers. The combustion is controlled by different fuels and their reactivity. [58]

The Dual fuel (DF) engine is a combination of two different combustions types in the same engine, Otto and diesel. The DF engine can use different types of fuels and switch between fuels seamlessly. Gaseous and liquid fuels can both be used, and the system detects which fuel is inserted and changes the combustion type. Unlike the HCCI engine, an DF engine can be ignited either with a spark such as an Otto engine or use a compression ignition such as in a diesel engine. [59]

3.2 First Engines Using Ammonia as a Fuel

The first small motor powered by ammonia was developed and patented in Italy by Ammonia Casale Ltd. in 1935 and 1936. Their process was called the Gazamo process. There was a shortage of diesel fuel during World War 2 and some compression ignited diesel buses were converted to run with ammonia with the help of coal gas and this Gazamo process. An ammonia tank was attached on the front and coal gas tanks on the roof of the bus. Ammonia was stored in a liquid form and coal gas in a gaseous form. Ammonia vaporized when going through a

[57] Nissan motor corporation, 2021
[58] Wisconsin Engine Research Consultants, 2021
[59] Wärtsilä, 2021

heater and inserted in a gaseous form into the mixer. There were two inlets in the mixer unit, one for ammonia and one for coal gas which then was mixed before entering the cylinder. Only coal gas was used when the engine was started. After the engine had warmed up, inserting ammonia as a fuel could be started. The bus driver could gradually increase the proportion of ammonia and decrease proportion of coal gas from the cockpit. About 100 buses in Belgium were fuelled with anhydrous ammonia in 1943. The buses covered several tens of thousands of miles with ammonia. [60]

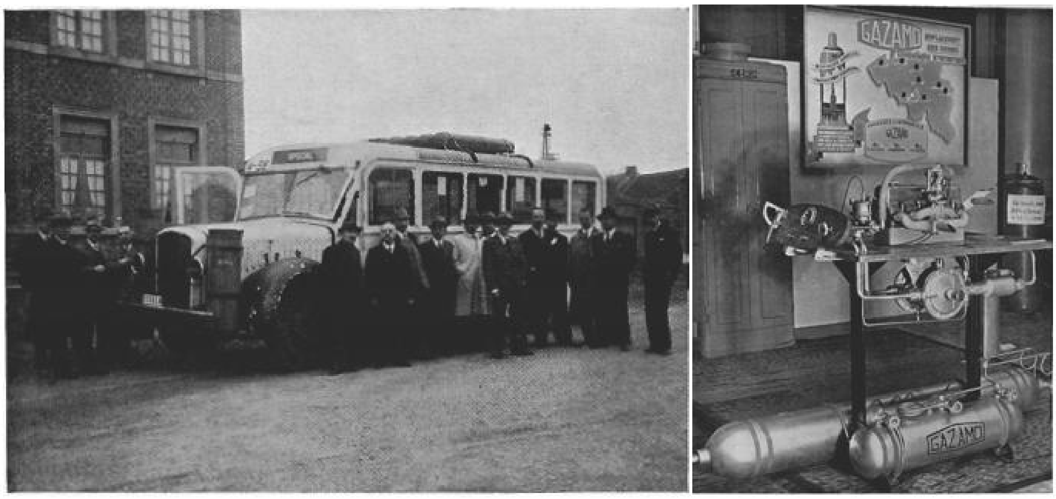

Figure 11. Ammonia powered bus and Gazamo's ammonia engine at fuel exhibition.[61]

In the 1960s research continued using ammonia as a fuel. General Motors Corporation investigated anhydrous ammonia as a fuel in the reciprocating SI engine. The US army was looking for alternative fuel for military vehicles and to be less dependent on hydrocarbon fuels. They found out that pure ammonia is not working well with conventional engines. Tuning the engine with supercharging and higher compression ratio and adding hydrogen into the fuel, they were able to get better performance figures out the engine. [62]

[60] Kroch E, 1943
[61] Kroch E, 1943
[62] Cornelius W, 1965

The testing of ammonia decreased when entering the 70s. Interest towards ammonia increased again in the 2010s, where both SI and CI engines where investigated. Many research efforts in ammonia combustion are focused on SI engines. Newer studies start to investigate CI engines as well. The main principle and observations were quite similar. Burning ammonia directly in the internal combustion engine (ICE) requires certain number of additives or catalysts, which is because ammonia has low flame temperature, low laminar burning velocity and high ignition energy. Hydrogen is one of the best options to support the ammonia combustion. Hydrogen will speed up the combustion, resulting in even a better combustion behaviour than in gasoline engines. Petrol, diesel, natural gas or other reactive fuels can be used as well, to improve the combustion of ammonia. These add-ons contain carbon, which will consequently emit CO_2 emissions. In many studies hydrogen or diesel was added to improve the combustion of ammonia. The amount of needed booster fuel depends on the engine specifications and speed. Considering from emissions' point of view, the hydrogen suits best. Needed hydrogen could be obtained from ammonia by catalytic reforming even on board. [63]

3.3 Ammonia Concepts Tested in Diesel Engines

Pure ammonia as a fuel was tested in 1966 in a diesel engine using compression ignition. Ammonia was inserted in two different ways, injected directly into the combustion chamber or into the intake manifold and heated so that it vaporized by the heat provided from heating elements. In the first direct injected ammonia compression ignition test, the combustion was possible with high compression ratio of 35:1 and with intake temperature of 422 K. In this study they were able to reach needed conditions to have a combustion of ammonia, since the injection timing was 70 to 90 degrees Before Top Dead Center the ammonia mixture was

[63] Pozzana G, 2012

evaporated and almost homogeneous. The combustion type has then been HCCI type. The engine was equipped with two different fuel pumps for different fuels. When they added diesel as pilot fuel, compression ratio and intake temperature could be lowered down to 30:1 and 339 K. The engine behaviour was better when diesel fuel was added. The pilot injection needs to begin approximately 40 to 50 degrees Before Top-Dead-Center and main ammonia injection at 12 degrees Before Top-Dead-Center to have the best results. If ammonia was inserted later than that, then the combustion did not happen. Ignition delay increased when amount of ammonia was higher. The lowest possible compression ratio where the combustion happened by using pilot fuel was 15,2:1, which is much smaller than what was needed with pure ammonia. Other pilot fluids than diesel was tested too. Dimethyl hydrazine and amyl nitrite were used. Compression ratio could be even lower with these two fluids to have a combustion. Tested amount of both pilot fuels was 10 % by weight. Compression ratio with these mixtures could be lowered to 24,4:1 with amyl nitrite and to 23,2:1 with dimethyl hydrazine. In the third test when ammonia was premixed with air, the combustion type changed to pilot ignited premixed Otto. This method worked, but the combustion was fast with high cylinder pressure rates. After these tests, hydrogen was considered. 10 % hydrogen by weight of ammonia was mixed with air at the intake side and ammonia injected directly into the combustion chamber. Air temperature lowered to 339 K and compression ratio set to 21:1. The combustion properties improved with hydrogen, but energy needed for ignition remains almost the same. This study finds out that correctly positioned ignition source would help the combustion of ammonia too. The combustion of ammonia in a diesel engine was possible, but the engine did not give satisfactory performance figures. More research and the engine modifications were needed. [64]

In 1967 ammonia was used to fuel a diesel engine with diesel as a pilot fuel. The engine was air-cooled two-cylinder version from the Continental AVDS-1790 tank

[64] Gray J.T, 1966

engine. There were two different methods that were used to test the combustion of anhydrous ammonia. In first attempt ammonia was premixed with air and then inserted into the cylinder of an CI engine. Diesel fuel was used as a pilot fuel to help ignite the combustion. In second attempt the engine was updated into spark ignited and acting such as an Otto engine. The combustion was successful with both ways with different engine modifications. Using only liquid ammonia as a fuel in the CI mode and with compression ratio 30:1, the combustion was not possible. The combustion occurred by using vaporous ammonia and diesel as pilot fuel in the CI engine, but the engine behaviour was rough and unstable. Ammonia was tested in both liquid and vapour forms. The combustion was possible only with vaporous ammonia. Comparing power output of these two different ignition types was not easy as they act so differently, but the SI engines seems to have higher performance figures and better running behaviour. In the SI engine compression ratio could be lower. Tested compression ratios in SI mode was 12:1, 16:1 and 18,6:1. With lower compression ratio fuel consumption increased. Higher compression ratio seems to be better with ammonia. Ignition happens approximately 10 degrees earlier with spark ignition than in compressed ignition. In this study they managed to get the engine running with ammonia, but with those specifications, power output isn’t very good. With an engine designed to run with ammonia, results might have been way different.[65]

Ten years later in 1977 Klaus Bro and Peter Sunn Pedersen from Technical University of Denmark tested four different fuels in a diesel engine. An ammonia was one of these fuels. Other three was methane, ethanol and methanol. After testing all these alternatives, ammonia was found out to be least suitable to be used in a diesel combustion, but all fuels can be used in a direct injection diesel engine with the help of a pilot fuel. Main issue with ammonia was a slow combustion and unburnt ammonia emissions. The motor used in this test was a small water-cooled single cylinder DI engine with variable compression ratio from

[65] Pearsall T, 1967

4,5:1 to 17,7:1. Gaseous ammonia was premixed with the air before entering the cylinder. Diesel was used as a pilot fuel also in this study. Pilot fuel was needed at least 30 % from the energy basis view. Smaller proportion of the pilot fuel affected to the combustion negatively. Replacing the diesel pilot fuel with hydrogen was studied also and it was found out that maximum 10 % of the diesel amount could be replaced with hydrogen. When exceeding 10 % of the hydrogen proportion, pilot fuel ignition was detected to get unstable causing failures in ignition and finally causing the engine to stop. With leaner air-fuel ratios, more unburnt ammonia could be found from exhaust gases and the combustion happens only partly. The combustion is also slow. It was noted that the intake air temperature could be as low as 333 K to perform the combustion of ammonia. When the intake air was heated up to 573 K, the combustion was improved, and the engine runs more smoothly.[66]

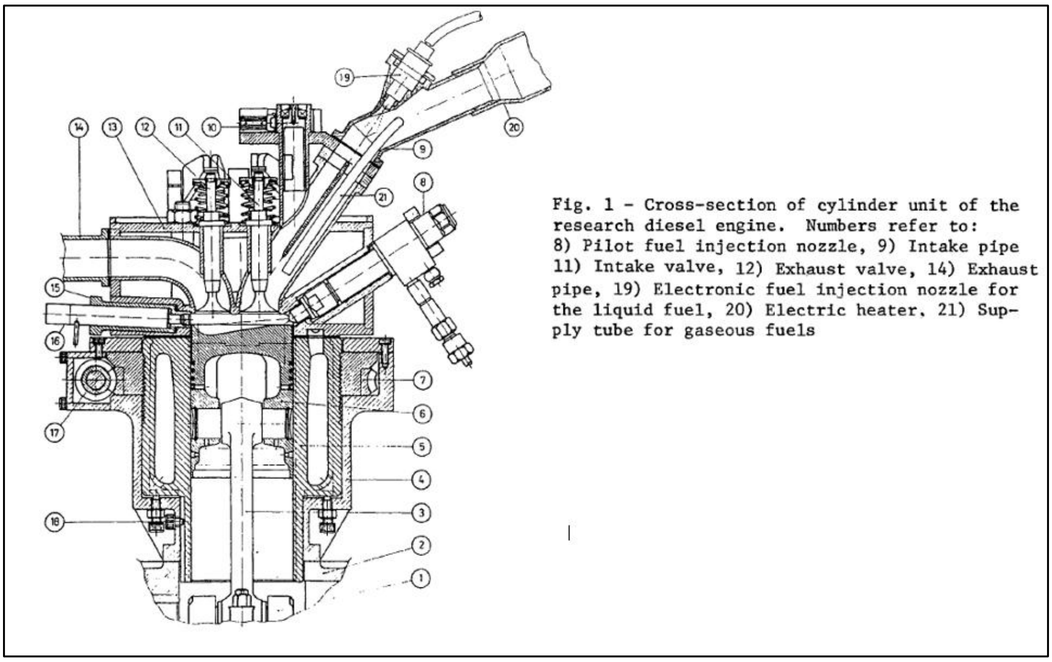

Figure 12. A cross-section of cylinder unit in the test engine. [67]

[66] Bro K, 1977
[67] Bro K, 1977

In 2010 a dual fuel diesel engine was tested with adding vaporous ammonia into the intake manifold and then starting the combustion with diesel. When the amount of ammonia replaced diesel, there was more unburnt ammonia found from the exhaust. The test was performed in two different ways. In the first part of the study engine was tested with constant power. Different amounts of ammonia and diesel tried. The required amount of diesel was between 40 – 60 % of the fuel energy and the rest was ammonia. If using more than 60 % of the diesel fuel energy, the combustion might not be occurred as ammonia-air mixture can be too lean. The combustion did improve with the higher proportion of ammonia. The amount of diesel should not be too low either as it won't be enough to initiate ammonia for the combustion. Using greater amount of ammonia, fuel efficiency started to be getting low. In another testing mode amount of diesel was lowered to fixed proportion which was equal to 5 % of the maximum torque of the engine at same speed of 1000 rpm. Ammonia acted as a primary fuel and the power output was adjusted with the amount of ammonia.[68]

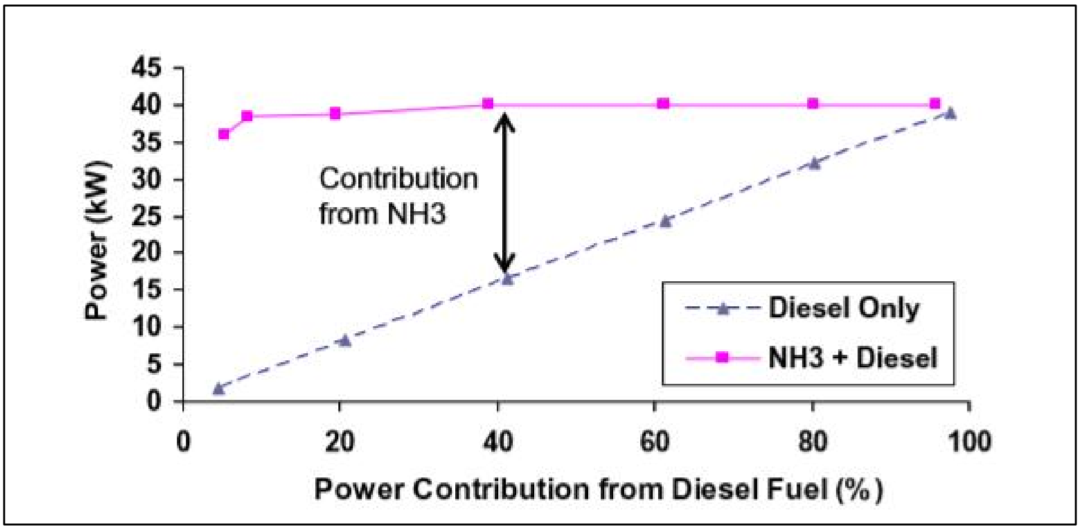

Figure 13. Test engine power output with different diesel-ammonia proportions. [69]

[68] Reiter A.J, 2010
[69] Reiter A.J, 2010

The engine was multi-cylinder, diesel powered and turbocharged. Compression ratio was 17:1. The test engine delivered the same power with ammonia and diesel what it would be delivered with pure diesel. The tests were performed at constant speed of 1000 rpm, which represent the normal running speed. Contribution from ammonia was enough to reach the same power output from the diesel engine. The combustion efficiency of ammonia in this study was nearly in the same level than in SI and CI engines when these are running with almost stoichiometric conditions. The bottom line of this study was that with the current setup of the test engine, ammonia as a fuel is not applicable for use. Modifications such as after-treatment for the exhaust and the tuning of injection strategies would be needed to test. An ammonia found from the exhaust is higher than what is allowed in regulations, even though the majority of the ammonia was consumed during the combustion. With some updates to the engine, ammonia is suitable fuel for the CI engines with the help of pilot fuel. From the power point of view ammonia with diesel pilot fuel matches the power output of the same engine running with only diesel. Results of the ammonia combustion are encouraging and when the emissions are reduced it would be suitable to use as a fuel in the CI engines. [70]

3.4 Pre-mixed Combustion

Fuel and oxidizer are mixed homogeneously before inserted into the cylinder chamber for the combustion. The premixed combustion is usually performed with the spark ignition. The fuel-air ratio in stoichiometric mixtures is l =1 in theory. The lambda value may vary in practise as it depends from the circumstances of the process [71]. This method was widely used in the different tests of ammonia combustion. Using ammonia blends in the SI engine, compression ratio could be

[70] Reiter A.J, 2010
[71] Heywood J.B, 1988

quite high. As ammonia has high octane number, it will resist the engine from knocking.

Direct injection or port injection could be used to feed ammonia into the SI engines. Difference between direct injection and port injection is that in direct injection ammonia is injected directly into the cylinder and in port injection ammonia is injected into the intake manifold. The air manifold pressure cannot be higher than ammonias vapor pressure. In room temperature at 25 °C the vapor pressure is about 9 bar and at 50 °C about 20 bar. If exceeding vapor pressures, ammonia will not gasify and remains liquid when entering the cylinder. Because latent heat of vaporization of ammonia is quite high, there will be a noteworthy temperature drop during the combustion process. Compared to gasoline, latent heat of vaporization is four times higher. Fuel pressure can be about 2 to 5 bar when using port injection in automotive applications. That could be reached with the standard port injectors easily. [72]

3.4.1 Ammonia Concepts Tested in Spark Ignited Otto Engines

In 1965 a single cylinder SI engine was used to test ammonia as a fuel. The research was conducted by General Motors Corporation. Ammonia was stored in a liquid form in the tanks and then in a heat exchanger it vaporized into gas. A gaseous ammonia and air were premixed before the combustion. Some tests in this study was performed by adding hydrogen into the ammonia-air mixing chamber. The engine was working with ammonia-air mixture, but performance figures was not as good as with petrol. Power output was only 17,5 % of the peak power made with petrol. A lot of ammonia was found from the exhaust gases, which indicates that the combustion process needs some tuning. Updating ignition system into dual ignition, power output was doubled from approximately 4 horsepower to over 8 horsepower. Higher compression ratio enabled also higher load.

[72] Xiang, H. W., 2004

Compression ratio in engine was first 9,4:1, the higher it gets the more power the engine was creating. The highest tested compression ratio was 18:1, which resulted to almost 14 hp. An ammonia fuelled engine could still not reach as high engine speeds as with petrol. Adding a supercharger engine could run with higher rpm, but the compression ratio needed to be lowered. Best results were found out with the compression ratio of 15:1. With the help of these modifications motor was performing partly better than with the petrol, gaining over 24 hp. Adding a small amount of hydrogen (0-3 % by weight) had a positive impact. Difference was greater at higher speeds. The best amount of hydrogen was depending if the engine was equipped with supercharger or not. Without supercharger the amount of hydrogen needs to be bigger and 3 % of H_2 was showing the greatest results. After 3 % results start to decrease. In supercharged configuration the best results were achieved with the amount of 1,2 % of H_2.[73]

Another study was performed in 1964-65 also with the single cylinder SI engine. Anhydrous ammonia was inserted in a vapor form and it then partly decomposed into nitrogen and hydrogen. In this study the spark timing was advanced slightly. The temperature of the cylinder was raised to have better operating behaviour. Fuel consumption was much greater compared to hydrocarbon fuels. Increase in the consumption was from 2 to 2,5 times more due to the lower heating value of ammonia. The output power with anhydrous ammonia was in between 70 and 77 % of the total power that hydrocarbon fuels could produce. In this study, it was usually little over 70 % at compression ratio of 10:1. Minimum proportion of hydrogen was 4 – 5 % by weight, when the engine was running in middle speed. When the engine was tested with lower proportion of hydrogen, the performance decreased rapidly. Too high hydrogen proportion causes also problems with too fast ignition. The amount of needed proportion depends of the engine speed. Higher rpms need more hydrogen. Liquid ammonia with hydrogen gives higher power output than vapor ammonia and hydrocarbon fuel. Spark power needs to

[73] Cornelius W, 1965

be higher than in the petrol fuelled engine to get the same kind of performance figures. Used compression ratios during this study was between 8:1 and 10:1. Higher compression ratio and added hydrogen both improves the combustion process.[74]

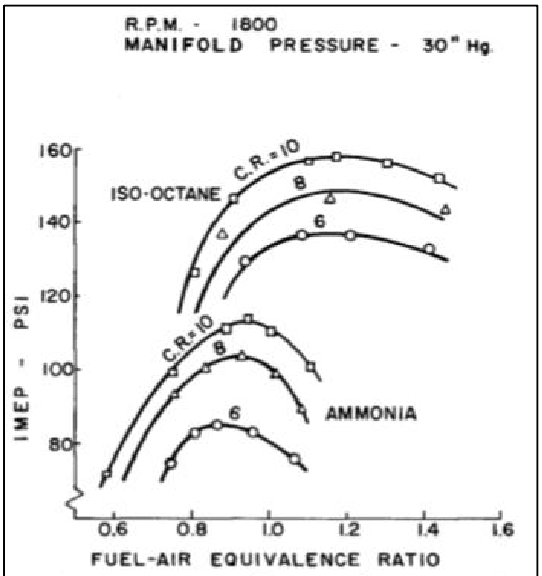

Fig. 20 - Comparative performance of ammonia and isooctane

Figure 14. Performance curve comparison with ammonia and iso-octane fuels. [75]

In 2012 a twin-cylinder SI engine was tested with ammonia and hydrogen as a combustion promoter. Both fuels were injected into the intake manifold in a gaseous form. Ammonia was stored in a liquid form and heated up so that it vaporized before injected into manifold. Fuel-air ratio was kept in stoichiometric l =1 and when proportion of hydrogen increased the engine running stability improved. With minimum needed amount of hydrogen, the power of the engine was slightly less than what it would be with petrol fuel. Figure 15 below, shows that in higher RPMs difference is greater than at lower RPMs. Power shortage is between 10 – 25 % compared to petrol. Adding more hydrogen, this gap will be smaller. In this study a minimum amount of the hydrogen was between 7 to 11 % of the hydrogen to ammonia energy ratio. Running the engine on full load, needed

[74] Starkman E.S, 1965
[75] Starkman E.S, 1965

amount of hydrogen could be lower (7 %) than at half load (11 %). The test was successful, and ammonia could be used as a fuel with the help of hydrogen. The power output of the engine was lower compared to petrol fuelled version, but finding better mixing ratio of ammonia and hydrogen, power difference will be reduced.[76]

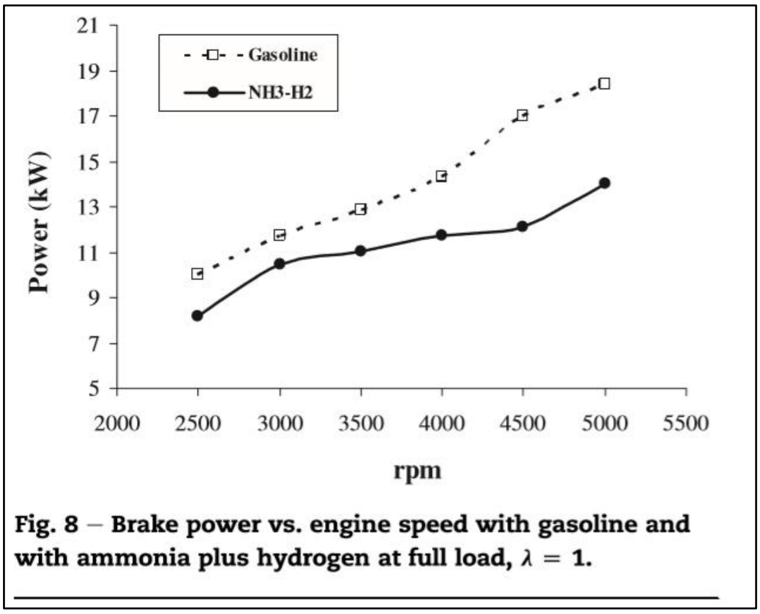

Figure 15. Power output with petrol fuel and with ammonia/hydrogen blend.[77]

In 2020 an SI engine was tested with the ammonia-hydrogen mixed fuel. The tested amount of ammonia varied a lot during the test. Investigated proportion of the hydrogen differs from 0 % to 60 % by weight. Best results were achieved with 20 % amount of hydrogen. The test engine was a modern four-cylinder petrol engine from PSA group. It had a compression ratio of 10,5:1, intake side temperature was set to 323 K and the intake pressure between 1,0 – 1,2 bar. In this experiment they run it with only one cylinder. Supercharging the engine and increasing the intake pressure, would be beneficial for better power output of the ammonia fuel.

[76] Frigo S, 2012
[77] Frigo S, 2012

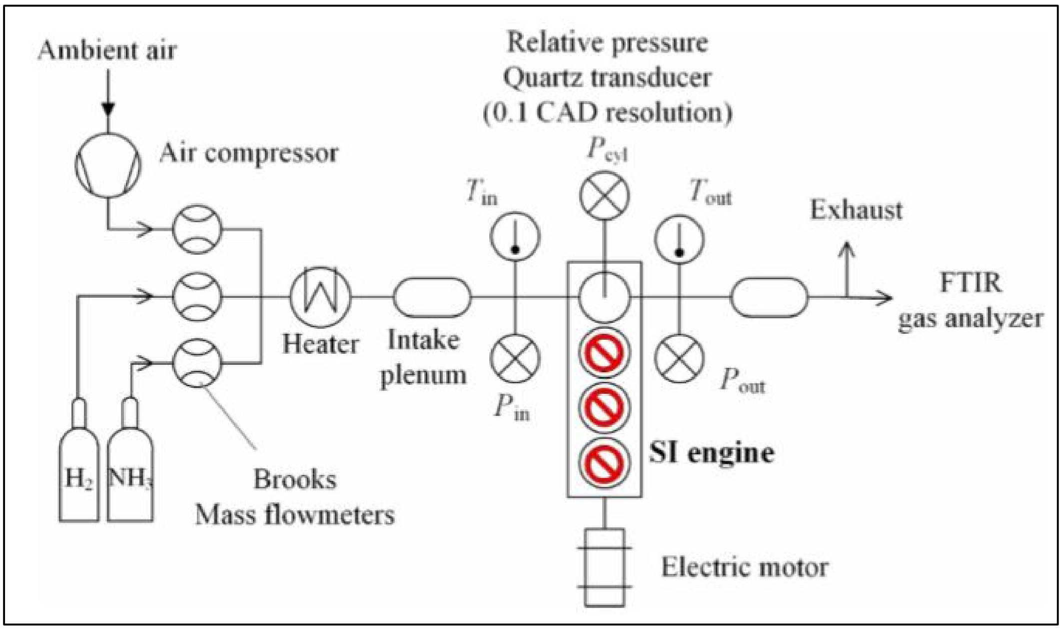

Figure 16. Setup of the test engine. [78]

The combustion was successful with wide range of hydrogen proportions and stability of the engine was great. Ignition timing must be advanced with all the different hydrogen proportions. Ignition needs to be advanced more when used lower amount of hydrogen. The combustion was possible with pure ammonia, but small amount of hydrogen would help to have a better behaviour from the engine. Ammonia-air mixture without hydrogen was stoichiometric Φ = 1,0 (equivalence ratio Φ = 1/lambda). Increasing the amount of hydrogen, fuel-air ratio could be leaner. Ignition timing should be advanced also with rich fuel-air ratios. There was no larger benefit to increase the equivalence ratio overly high as it will only result to excess fuel found from the exhaust side, without any advantages. The conclusion from this study is that ammonia suits well for a fuel in the SI engine with none or just minor updates into the engine. Hydrogen improves the combustion and best results are achieved with modest proportions.[79]

[78] Lhuillier C, 2020
[79] Lhuillier C, 2020

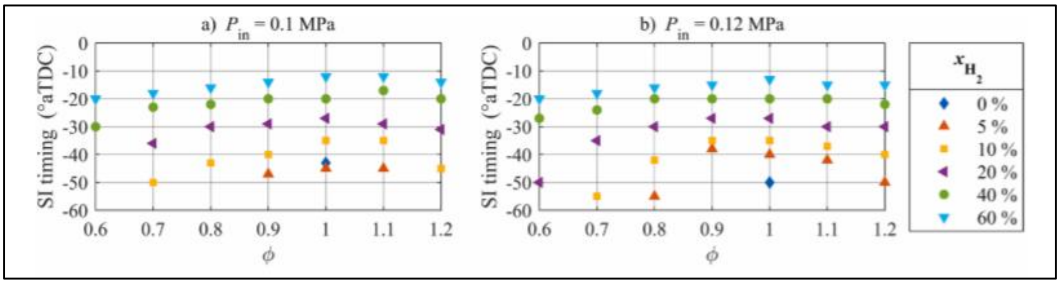

Figure 17. Optimized Ignition timing with different hydrogen amounts and equivalence ratios. [80]

In 2020 natural gas and ammonia was tested in a turbocharged SI engine. The engine was a medium speed engine and the test was performed at low-load speed of 840 rpm. Natural gas was the main fuel in this study and ammonia act as the secondary fuel. Natural gas was compressed in fuel tanks, into the pressure of 200 bar. Temperature was set to 313 K with the help of heat exchanger. Before injectors, the pressure of natural gas dropped to 8 bar. Ammonia was supplied in a gaseous form too. Needed pressure depends of the temperature. Pressure of the ammonia in supply line was set to 4,5 bar. The amount of ammonia tested was from 0 % to 50 % by volume and in intervals of 10 %. Equivalence ratio was between 0,67 and 0,83 (λ 1,2 - 1,5) it was increased with 0,1 intervals. The maximum brake torque (MBT) of the engine was the target when timing was adjusted. Timing of an ignition was advanced in this setup, but MBT operation was not reached because of lower efficiency of the combustion due to the needed high level of ignition energy of ammonia. When larger proportion of ammonia was used, ignition timing was also more advanced. In this study they found out that if equivalence ratio is 0,83 (λ 1,5) the combustion efficiency drops rapidly after NH_3 split ratio goes above 10 % as figure 18 below indicates. [81]

[80] Lhuillier C, 2020
[81] Oh S, 2021

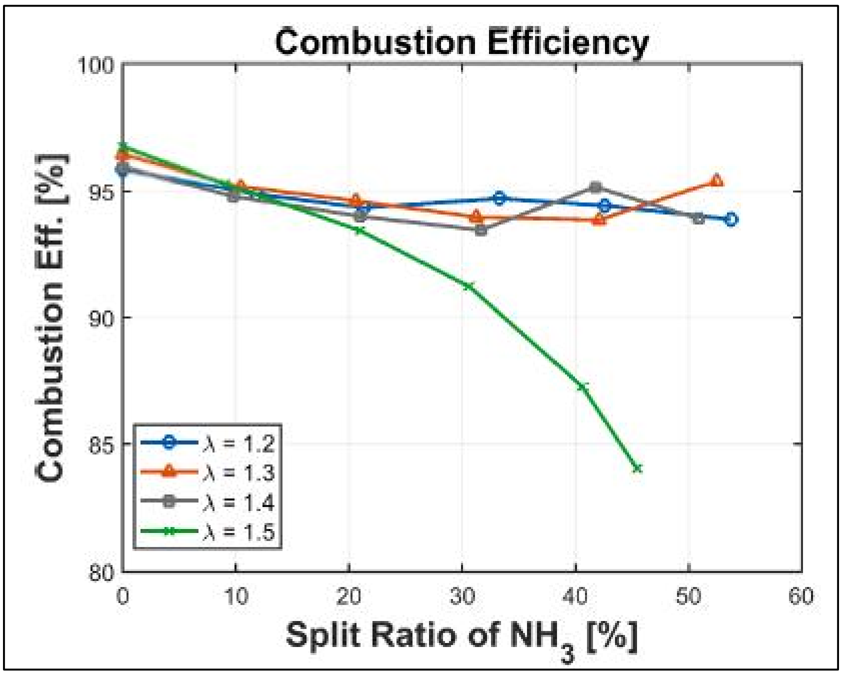

Figure 18. The combustion efficiency with different ammonia split ratios and air-fuel ratios.[82]

It indicates that air-fuel ratio should not be too high or otherwise the combustion efficiency will drop. With higher proportions of ammonia CO_2 emissions decreases, which is a wanted effect. The fuel amount needs to be increased when ammonia proportion increases to have the same power output of the engine. This study finds out that the ideal air-fuel ratios with ammonia and natural gas was 6.06 [kg-air/kg-NH_3] and 17.19 [kg-air/kg-natural gas] respectively. Figure 19 below, shows that different proportions of ammonia have effect to cylinder pressure and heat release rate. Ignition timing was kept same in all these different values, so the differences could be noted more clearly. At later point heat release curve started to increase with equivalence ratio 0,83 (λ 1,5) and with 50 % split ratio. The conclusion is that air-fuel ratio needs to be controlled all the time to have the engine performing well and to avoid increasing of emissions. Results of this test was got by combining experimental and calculated data. [83]

[82] Oh S, 2021
[83] Oh S, 2021

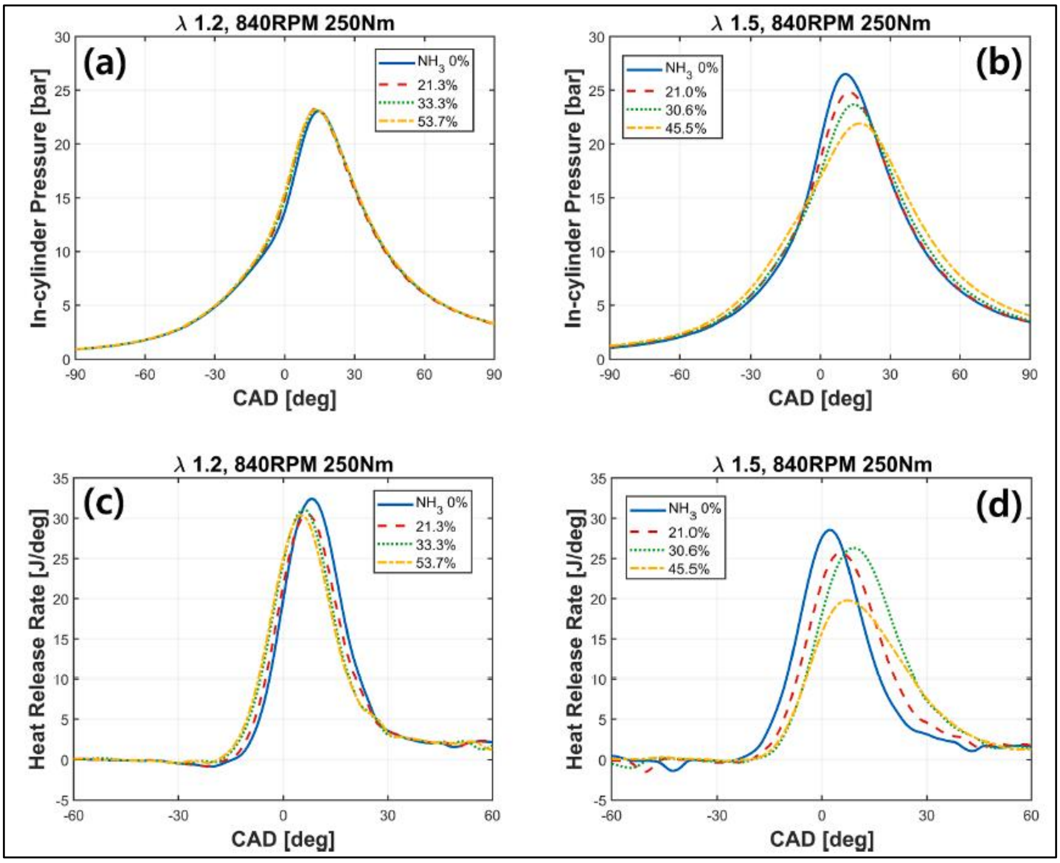

Figure 19. In-cylinder pressure and heat release with various ammonia split ratios. [84]

3.4.2 Homogeneous Charge Compression Ignition Engines

An HCCI engine with ammonia was investigated in 2016 by group of researchers from Belgium. They performed simulated combustion tests with four different fuels in the HCCI engine and ammonia was one of these fuels. Other three was methane, methanol and hydrogen. The combustion of ammonia in the test engine required over 500 K temperatures at intake side. There was a slight drop of 40 K in the needed temperature when intake pressure was raised from 1 bar to 2 bar, which shows that the intake pressure has some effect to the charge reactivity since a lower inlet air temperature was needed. The needed intake temperature is quite high and that kind of values are difficult to provide in real life engine applications.

[84] Oh S, 2021

High temperatures have also an impact for the amount of the fuel inserted as higher temperature is lowering the density of the air-fuel ratio at intake side. On the right side of the figure 20 below, there is visible that equivalence ratio is also affecting to the needed temperature and the charge reactivity. Change is not so high as it is with the intake pressure and as ammonia has greater heat capacity than air, temperature rises together with the ratio. Increasing compression ratio has same effect than increasing intake pressure, i.e. intake temperature could be lower. Despite of these kind of changes in engine properties, needed intake temperature still needs to be high and that needs plenty of energy and a practical solution in the real engine applications.

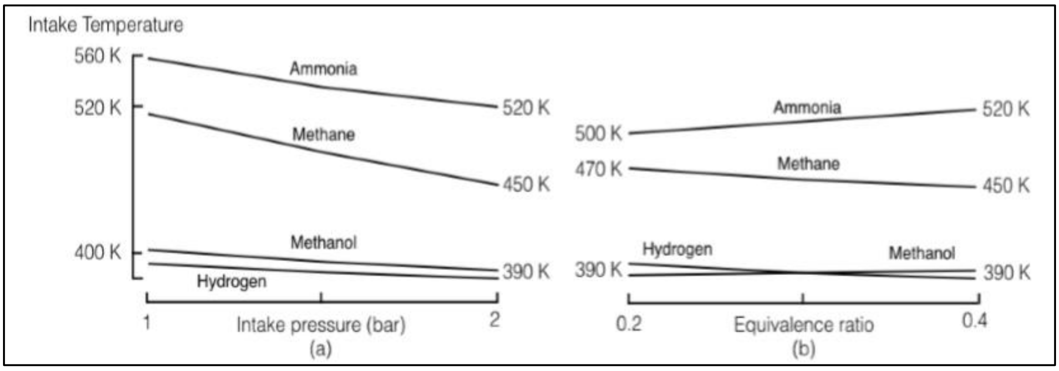

Figure 20. Required intake temperature for onset of the HCCI combustion with different intake pressure and equivalence ratio. [85]

Different compression ratios were tested during simulation, ratios were between 16:1 and 20:1. The test engine was equipped with the heat exchanger and turbo-compressor to provide needed heat and pressure. As ammonia needs so high temperatures, these were not able to create temperature high enough. Observations in this study states that equivalence ratio needs to be over 0,41 so that exhaust gases could provide adequate energy to meet these criteria. This study shows that when the intake pressure or equivalence ratio is two times higher, the density of power double also. Because of the high auto-ignition temperature of ammonia, they will not use it alone, but mix it with methanol or

[85] Pochet M, 2016

hydrogen. Having a high, over 0,3 equivalence ratio with the hydrogen or methanol fuels, it may cause ringing, i.e. knocking combustion. Mixing these fuels with ammonia seems to be the best solution to have, but best proportions was not studied. Conclusion is that pure ammonia is not reactive enough to be used alone as fuel in an HCCI engine. [86]

Another HCCI engine was tested with simulation in 2017 with ammonia hydrogen mixture. Steady combustion properties were achieved with 30 % of added hydrogen by weight and with compression ratio of 16:1. The equivalence ratio was set to 0,28. Also in this study the intake temperature needs to be so warm that it was hard to achieve. Pressure in the intake was raised and fuel heater added to reach higher temperatures at the intake side. The combustion was possible with temperature of 473 K and with 1,5 bar pressure. A compressor was used to increase the intake pressure. The engine in this study did not run with pure ammonia. Using only hydrogen as a fuel it may cause engine ringing, i.e. knocking, with higher compression ratios. Adding ammonia into fuel mix will prevent ringing, since both fuels share the same radicals. With the help of hydrogen, the combustion was possible with ammonia up to proportion of 70 % by weight. The intake pressure and compression ratio need to be high with ammonia. This study states that the engine with adjustable compression ratio would be ideal to be used for variable ammonia-hydrogen blends.[87]

In 2021 published a study from China, where an HCCI medium speed marine engine was tested with ammonia together with hydrogen. The test was performed with wide range of different engine conditions and hydrogen amounts. Tested hydrogen proportion was from zero to 40 % by weight and equivalence ratio between 0.4 – 1,0. Compression ratio of the engine was 15,5:1. Both ammonia and hydrogen were premixed with air at intake side before entering the cylinder. The intake air temperature tested between 280 to 520 K and the intake pressure

[86] Pochet M, 2016
[87] Pochet M, 2017

between 1 to 3 bar. The engine speed was steady 800 RPM. In figure 21, there are results of ignition properties with different pressure and temperature values. Lines with different colours are presenting the fire line which means that in all values on the right side of the line an ignition will happen. It shows that needed temperature and pressure are lower if the proportion of hydrogen is higher. [88]

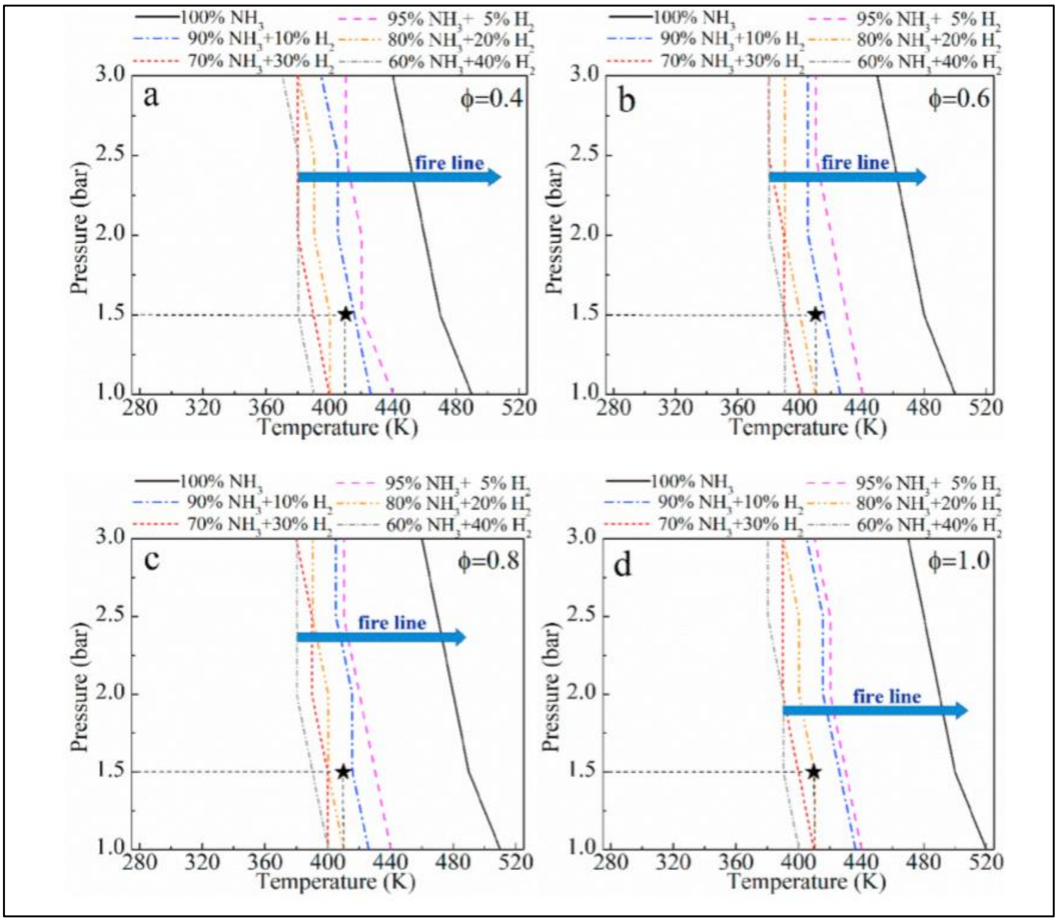

Figure 21. Ignition boundaries with different ammonia/hydrogen mixtures and equivalence ratios in the HCCI engine. [89]

With higher intake pressures, temperature could be lower. There is quite significant difference between pure ammonia and hydrogen boosted ammonia. Even quite small amount of hydrogen has a big impact in improving ignition of the ammonia. Results shows that with higher equivalence ratios, intake pressure and

[88] Wang Y, 2021
[89] Wang Y, 2021

temperature need to be higher too. Typical operation conditions are marked with the star in figure 21. These conditions at intake side was 1,5 bar pressure and temperature of 410 K. Only 30 % and 40 % of hydrogen proportion was on the right side in all tested equivalence ratios. In study they continued testing with the amount 30 % of hydrogen. [90]

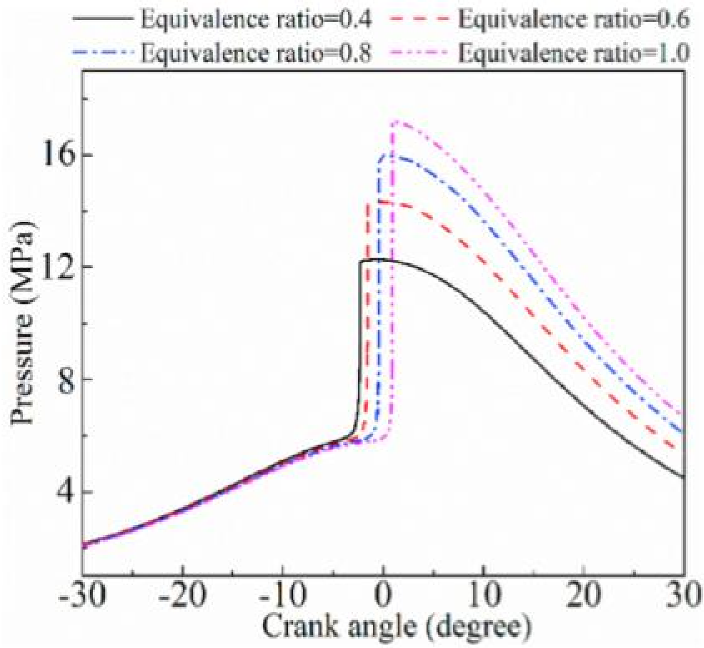

Fig. 3 – In-cylinder pressure curve of engine at HCCI combustion mode under different equivalence ratio (70% NH_3 + 30% H_2).

Figure 22. Cylinder pressure with different equivalence ratios.[91]

Pressure in the cylinder started to rise, when equivalence ratio increased. It also affected to ignition timing, which was slightly delayed with higher equivalence ratios. As ammonia has a low flame speed, it increased as amount of hydrogen increases. Peak in flame speed was found in equivalence ratio about 1,1 in all different mixing ratios. [92]

[90] Wang Y, 2021
[91] Wang Y, 2021
[92] Wang Y, 2021

3.5 Patents

Patents around ammonia fuelled engines was also investigated to see if there are some ongoing development around this topic. There are lot of patents where ammonia was involved, but not so many related to the engines running on ammonia. In below graphs there are patents of similar topic than this thesis. The first graph is showing years when these patents have been done. Some of the newest ones are not yet granted. Another graph is showing where these patents are coming from. Japan and United States have the most of these patents. Toyota corporation seems to be the most active around ammonia with over half of all these patents.

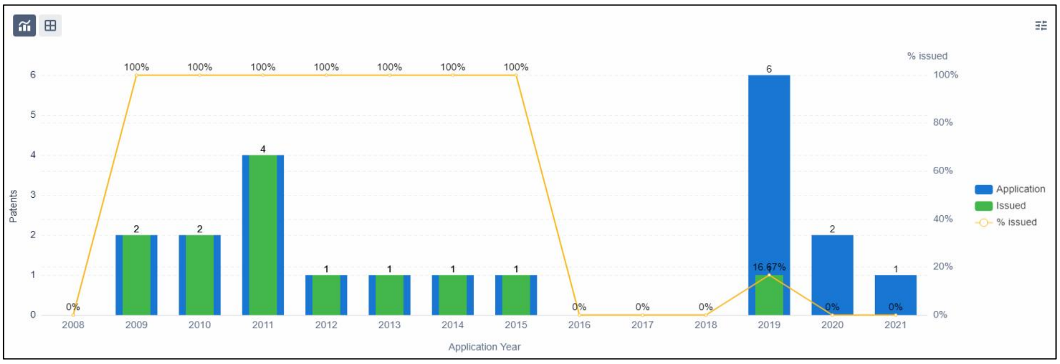

Figure 23. When the different patents are created.[93]

[93] Patsnap, 2021

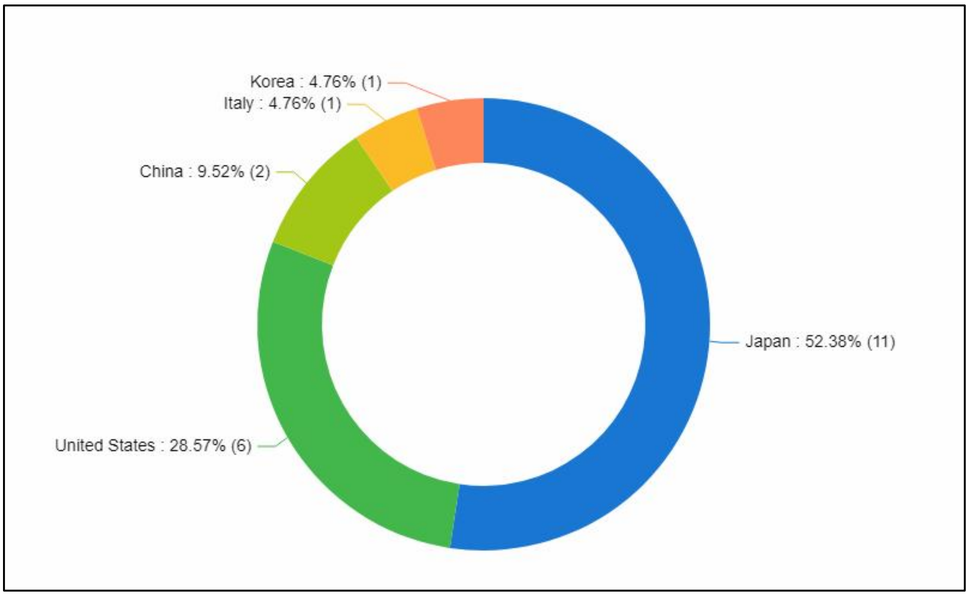

Figure 24. Countries where the patents are made.[94]

3.5.1 Examples of Granted Patents

Here is a couple of summaries of these patents to show what kind of inventions are patented around this topic.

Patent JP2020183337A is one of the newest ones from 2019. Hydrogen generator needs a certain temperature to work properly and it takes some time to gain that after starting up the engine. This patent is for generating the hydrogen right after the start. Oxidation reaction is heating the system so that hydrogen could be made right from the beginning. Air and ammonia are mixed by controlling the amount of air. Temperature drops when air is inserted, air is suppressed, and residence time becomes longer. This creates heat from the reaction and system could be used to generate hydrogen from the beginning.

[94] Patsnap, 2021

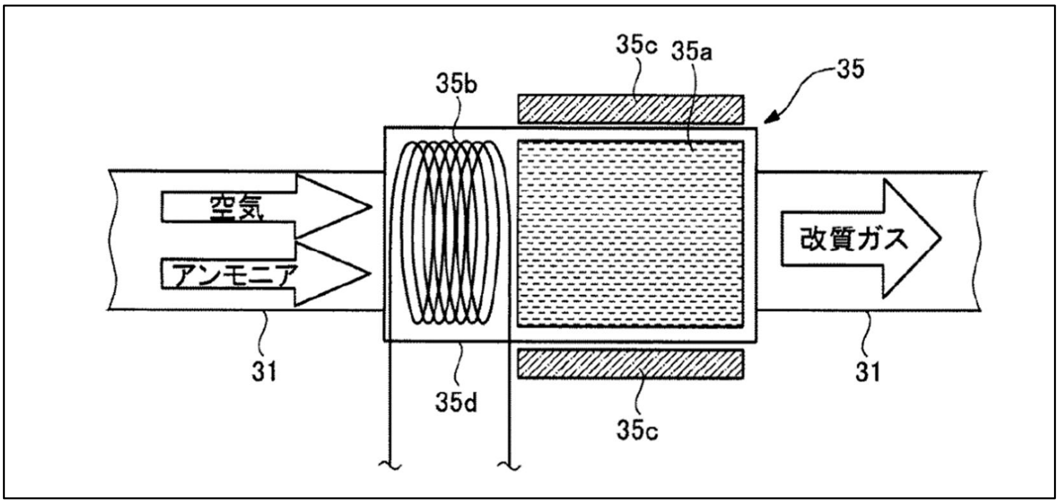

Figure 25. Schematic structure of the reformer in patent JP2020183337A.[95]

Patent US8904994B2 is about a dual fuel engine and reformer system. Heat from the exhaust is used to reform ammonia into hydrogen and nitrogen. Hydrogen could be used as a second fuel. The system detects the amount of ammonia and add another fuel in the same proportion to improve the combustion. Operating parameters are changing according to the ratio of ammonia in the fuel. More ammonia means increased intake air temperature and more air. The engine is equipped also with the compression ratio changing mechanism and EGR system. The highly combustible fuel is inserted first before ammonia and ammonia is then injected right after self-ignition point. In the SI engine there would be 2 injections, first before the first half of a compression stroke and a second injection of smaller amount of ammonia in a latter half of the compression stroke, just before the ignition. Ammonia is in liquid form when inserted and it atomizes during injection.

[95] Patsnap, 2019

Another option is to inject ammonia into intake port in liquid and gaseous form. If the engine is cold, a heating system is needed to warm up fuels.

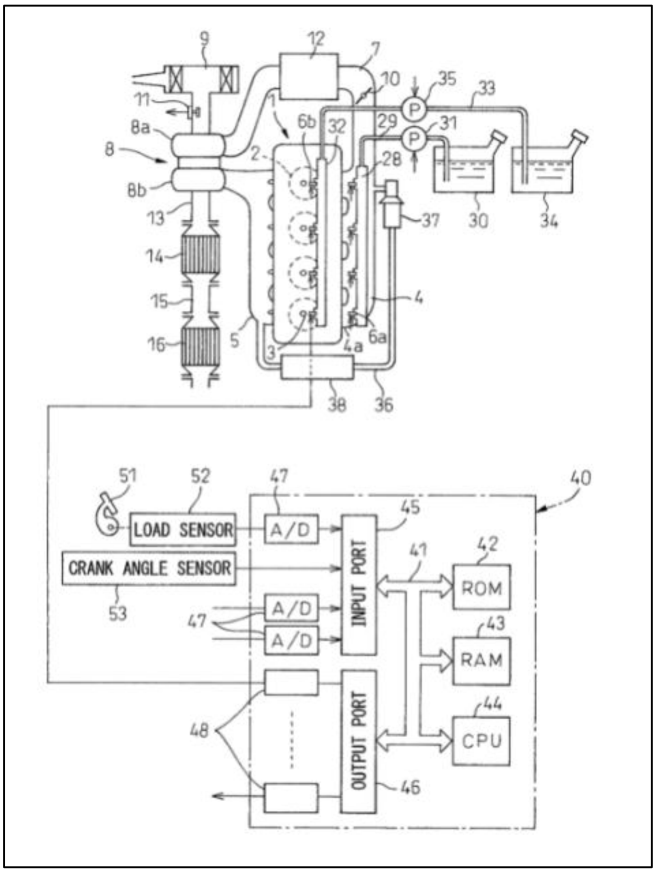

Figure 26. System layout in patent US8904994B2.[96]

3.6 Test Results

All the tests and studies mentioned in this thesis are summarized into the tables below. In the table 4 and 5 there are SI engines with the Otto combustion. The sixth table consist of the diesel engines and CI ignition with some exceptions. The seventh table presents the CI engines, but with HCCI combustion type. All studies in the tables four, five and six are experimental, but engine parameters in the table seven are mainly used in simulated tests. Even though these studies are from

[96] Patsnap, 2010

different decades, there are quite a lot of similarities. Same engine types are tested with similar setups.

The tested engine loads were not presented in majority of tests presented in this thesis. It could see as a result of insufficient tests and the engines are not running yet on full potential.

Table 4. Comparison of the engines with Otto combustion type

Year	1965	1965	2012
Combustion type	Otto	Otto	Otto
Ignition type	SI	SI	SI
Spark timing / combustion phasing	Advanced and higher spark power	Advanced and higher spark power	Advanced
Compression ratio	8:1 and 10:1	15:1	10,7:1
Equivalence ratio	0,8 - 1,0	-	1,0
Intake temperature	390 K	405 K	773 K
Intake pressure	1 bar	0,6 bar	0,5 bar
Form of ammonia fuel	Liquid and gas	Gas	Gas
Added fuel and proportion	Hydrogen 4-5 % by weight	Hydrogen 0-3 % by weight	Hydrogen to ammonia energy ratio between 7-11 %
Simulation/Experimental	Experimental	Experimental	Experimental
Conclusion of the test	The combustion was successful, but fuel consumption was much greater compared to hydrocarbon fuels.	With pure ammonia performance was poor compared to petrol fuelled version. Tuning the engine and adding hydrogen, they managed to get even better power output than with petrol.	The combustion was possible only with hydrogen. Power output of the engine was lower compared to petrol fuelled version. With better mixing ratio, power difference will be reduced
Source	[97]	[98]	[99]

[97] Starkman E.S, 1965
[98] Cornelius W, 1965
[99] Frigo S, 2012

Table 5. Comparison of the engines with Otto combustion type

Year	2020	2020
Combustion type	Otto	Otto
Ignition type	SI	SI
Spark timing / combustion phasing	Advanced	Advanced
Compression ratio	10,5:1	10,5:1
Equivalence ratio	0,6 - 1,2	0,67 - 0,83 (λ 1,2 - 1,5)
Intake temperature	323 K	-
Intake pressure	1,0 - 1,2 bar	0,5 - 0,65 bar
Form of ammonia fuel	Gas	Gas
Added fuel and proportion	0-60 % of hydrogen by weight (best results with 20 %)	50 – 100 % of CNG by volume
Simulation/Experimental	Experimental	Experimental
Conclusion of the test	The combustion was possible with pure ammonia. Adding hydrogen improved the combustion.	The combustion was possible. Target was to operate the engines at maximum brake torque (MBT) level, but they didn't reach it.
Source	[100]	[101]

[100] Lhuillier C, 2020
[101] Oh S, 2021

Table 6. Comparison of the engines with diesel combustion type

Year	1966	1967	1977	2010
Combustion type	Diesel	Diesel	Diesel	Dual fuel (NH3 PFI, diesel DI)
Ignition type	CI / HCCI	CI + SI	CI	CI + Otto
Spark timing / combustion phasing		Standard timing	Advanced slightly	Adjusted with fuelling rate
Compression ratio	35:1 (21:1 with H2, 30:1 with diesel)	30:1 in CI mode and 18,6:1 with SI mode	4,5:1 - 17,7:1	17:1
Equivalence ratio		0,64 - 0,9	0,63 - 2,0 (λ 0,5 - 1,6)	-
Intake temperature	422 K (339K with diesel and H2)	361 - 374 K	393 K (tested 333 K - 575 K)	-
Intake pressure	-	1,1 bar	-	-
Form of ammonia fuel	Gas	Gas and liquid	Gas	Gas
Added fuel and proportion	Diesel as a pilot fuel, 10 % by weight H2	Diesel as a pilot fuel	Diesel as a pilot fuel at least 30 % by energy + maximum 10 % of hydrogen replacing diesel as pilot fuel	Diesel 40-60 % by energy (5 % of the maximum torque by diesel in another mode)
Simulation/Experimental	Experimental	Experimental	Experimental	Experimental
Conclusion of the test	The combustion was successful, but performance figures was poor	The combustion was possible only with vaporous ammonia. In SI mode engine behaved better.	The combustion was successful, but the engine could not provide its full potential.	The combustion did improve with higher proportion of ammonia. Output performance of the engine was similar when using pure diesel as a fuel.
Source	[102]	[103]	[104]	[105]

[102] Gray J.T, 1966
[103] Pearsall T, 1967
[104] Bro K, 1977
[105] Reiter A.J, 2010

Table 7. Comparison of the engines with HCCI combustion type

Year	2016	2017	2021
Combustion type	HCCI	HCCI	HCCI
Ignition type	CI	CI	CI
Spark timing / combustion phasing	Adjusted with the fuel	Higher temperature helps to have better timing at the combustion	Slightly delayed with higher equivalence ratios
Compression ratio	16:1 - 20:1	16:1	15,5:1
Equivalence ratio	0,2 - 0,4	0,28	0,4 - 1,0
Intake temperature	520 - 560 K	473 K	380 - 520 K
Intake pressure	1-2 bar	1,5 bar	1,0 - 3,0 bar
Form of ammonia fuel	Gas	Gas	Gas
Added fuel and proportion	None	Hydrogen 30 % by weight	5-40 % of hydrogen by weight
Simulation/Experimental	Simulation	Simulation + experimental	Simulation
Detailed chemical kinetic mechanism simulation	Mathieu and Petersen	Mathieu and Petersen	Otomo
Conclusion of the test	The combustion of pure ammonia in HCCI engine was difficult. Intake temperature needs to be very high. With the help of methanol or hydrogen the combustion will be improved.	The combustion was possible, but not with pure ammonia. With the help of hydrogen, the combustion happened. Intake temperature needs to be very high in this test also.	The combustion was possible and even a small amount of hydrogen improved the combustion a lot.
Source	[106]	[107]	[108]

[106] Pochet M, 2016
[107] Pochet M, 2017
[108] Wang Y, 2021

4 FUTURE

There are many uncertainties and open questions with the future of ammonia. According to the forecasts, usage of ammonia in commercial vehicles as a fuel will increase. The safety and the use in other type of vessel than tankers require considering. Ammonia needs more space than current fuels, which needs to be noted when considering taking it into use. The total global shipping fuel consumption is much higher than ammonia production today, thus ammonia production needs to be increased a lot.

Another issue is the production of ammonia, how to produce it in a green way and with renewable energy. Currently producing green ammonia is more expensive than ammonia produced with fossil fuels. When the production of renewable energy is growing, also its price should go down. This would make a green ammonia more affordable. How much the price of ammonia will be changing, is still unknown. If ammonia is not made with renewable energy, there is no benefit in having a non-carbon fuel, as its production causes equal or even a larger amount of CO_2 emissions compared to the usage of fossil fuels we have today. Since the efficiency of manufacturing hydrogen by utilizing electrolysis is low, the process consumes more energy than what could be generated from the produced hydrogen, but with renewable energy the manufacturing process is less harmful to the environment. Thus, excess electricity could be used to produce ammonia. As when the number of renewable power plants grows, more regulation is needed for produced excess energy. When the production is higher than the consumption, excess energy could be used into ammonia production. In the future ammonia, nitrogen and hydrogen production will be much less polluting when electrolysis will be taken into a wider use.

Hydrogen is a great alternative to be used to improve the combustion of ammonia. Ideally, it could be made by on-board reforming of hydrogen from ammonia which is stored as a fuel. When burning ammonia, NO_X emissions are an issue, but ammonia could be also used to reduce the emissions with the SCR system. As ammonia needs to be heated before inserted into the cylinder, it could be possible to circulate ammonia in the SCR system in a way one part of it is used to reduce emissions and the other part of it is just heated up and used as a fuel. Hydrogen is the most advisable combustion promoter for ammonia. These could be bound together more closely in the future because it is more sensible to storage hydrogen in form of ammonia.

If ammonia demand increases, it may affect the food prices as well because of fertilizer prices. When more ammonia is produced it should lower the prices. New technologies for green ammonia production might increase prices at the beginning, as well. During this year the price for ammonia in Europe has increased enormously which is illustrated in Figure 27. The main reason for the price increase is the lack of natural gas in markets. A big increase such as this in the ammonia price might affect food prices as well. [109]

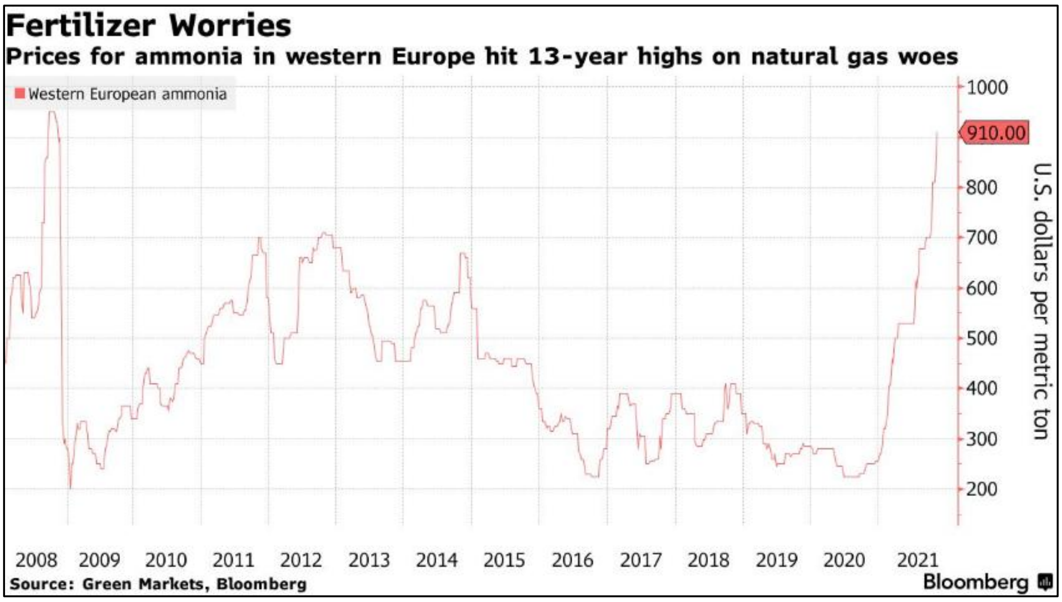

Figure 27. Ammonia price in Western Europe.[110]

If there is a new tax on fossil fuels guiding consumption and development towards carbon free fuels, then ammonia might be taking a bigger share of the global fuel market. Without bigger actions from governments, it can be presumed that no fast

[109] Bloomberg, 2021
[110] Bloomberg, 2021

changes from fossil fuels to ammonia will take place. Money is a good incentive, but for bigger fuel transformation, more actions are required.

Nowadays marine diesel oil (MDO) and heavy fuel oil (HFO) are the most used fuels in marine industry, because of the convenient costs. Ammonia needs to have a competitive price compared to these two in order to be attractive to the marine industry. It might be that some economical support is needed to even the price gap. A carbon tax was discussed during the United Nations Climate Change Conference at the beginning of November 2021 in the UK. Reducing usage of coal universally was one of the hot topics and it might increase the need of carbon free fuels.[111] Zero-emissions maritime routes were also presented as an invention.[112] It means that fuels which contain carbon cannot be used on those routes. These kinds of regulations are increasing interest towards carbon free fuels such as ammonia and accelerating the change out of fossil fuels.

It is fair to assume that research and development with ammonia as a fuel will continue and its usage will rise. It can be expected that the market share of ammonia as a fuel will be modest in coming years. It will start to increase slowly depending on how the development of ammonia engines emerges. Despite the drawbacks of ammonia, as low flame speed, it is still a potential alternative for hydrocarbon fuels. An ammonia powered engine should arrive into the markets in the coming years. It will be interesting to see how these will manage with the competition.

[111] United Nations, 2021
[112] United Nations, 2021

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