Special Report
**A Report from the
Advanced Motor Fuels Technology Collaboration Programme**

# Ammonia Application in IC Engines

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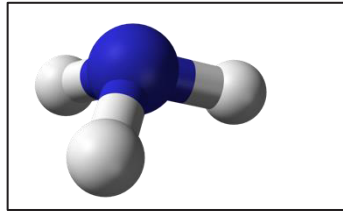# Ammonia Application in IC Engines

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May 2020

## *Summary*

Ammonia is right now investigated as a relevant fuel for combustion engines. It is considered to be interesting in the long term and particularly as a fuel for maritime transportation. Ammonia can be considered as a so called "electro fuel" since it can be produced through electrolysis of water followed by a catalytic conversion of hydrogen and nitrogen (from air) to ammonia. Unlike most other electro fuels, ammonia can be produced without use of a carbon source, only electricity, water and air is needed, which makes it advantageous in many respects. The electricity could be produced from wind- or hydropower, or from other sustainable sources, and the ammonia produced is thus a sustainable fuel. Ammonia burns without production of carbon dioxide during combustion.

However, there is almost no knowledge about the behavior of ammonia in a combustion engine. Ammonia has a relatively low calorific value, and on top of that, characteristics like low cetane number and low flame speed makes it difficult to apply in combustion engines. Therefore, it is necessary to carry out investigations on how to improve the applicability of ammonia for combustion engines.

The purpose of this report is to compile the investigations of ammonia as an engine fuel that have been carried out so far, and to conclude from the reported issues about the perspectives for the future application of ammonia.

The investigation indicates that passenger vehicles are a large implementation area, but need a large re-structuring of the present fuel supply system for the technology to be a success. Additional cons for this area is ammonia´s low energy density, not promoting it as a first choice for a small vehicle. Engine tests though showed good results for an ammonia fueled SI-engine with small amount of hydrogen. It seems as if ammonia is most suited for marine engines where low energy density is a less important issue. These engines are mostly base on diesel engines (or CI engines).

The vast majority of experiments found in the literature tested SI-engines. However, some have also managed to achieve satisfactory combustion using CI-engines. In terms of compression ratio, speed and load a general tendency from the literature is observed for both SI and CI. High compression ratios, low speeds and high loads are preferable for ammonia fueled engines. All those tendencies are primarily due to ammonia's low flame speed.

Marine engines fueled by ammonia with pilot fuel injection of diesel or other high-cetane fuels, could be a feasible application in the near future. Such engines have a large displacement volume and are operated at a constant low speed with high loads (supercharged), making them favorable for ammonia combustion.

Engine materials compatibility and storage of ammonia seem to be problems that can be overcome with proper choice of materials and technology. However, of particular concern with ammonia is the emissions of unburned ammonia, which is poisonous, and $N_2O$, which is a very strong greenhouse gas. The formation mechanisms behind these emissions are not well understood and need to be addressed in future investigations.

# Contents

# 1. Ammonia in internal combustion engines

Internal combustion engine fuels requires advanced properties and not exclusively the ability to be combusted. ICE's requires a fuel that can be used under various operating conditions (loads and speed) and it is therefore not a coincidence that gasoline and diesel are preferred today. These fuels meet the advanced properties within a wide range of operating areas. The properties include ignition and flame propagation. The use of ammonia in ICE has clear advantages as well as challenges.

A clear advantages of using ammonia is that the fuel is carbon-free and thus no CO2 is emitted when combusted. Furthermore, ammonia does not produce soot as it does not contain carbon. The low flame speed and low cetane rating of ammonia causes problems when combustion is attempted in existing ICE's, though if applied the right way an advantage can be obtained.

Obviously, challenges will arise when implementing ammonia in existing SI and CI engines, which are designed for the use of fuels such as gasoline and diesel. Several of these challenges may be predicted from Table 1, which illustrates some major differences of ammonias fuel properties compared to gasoline and diesel. Ammonia has a narrow flammability limit, high minimum ignition energy, a high self-ignition temperature [1] (650 ℃) and a low flame speed / flame propagation. These four properties in combination causes difficulties in obtaining proper combustion with varying loads and speeds. In addition, ammonia has a high heat of vaporization, which results in a significant temperature drop when ammonia is evaporated from liquid to gas, reducing the in-cylinder temperature. Also problems with freezing of injection nozzles can occur. On the other hand, when premixing fuel and air in gaseous form is applied, the large temperature drop during combustion is avoided, but by introducing the fuel through the intake manifold the ammonia vapor displaces a likewise amount of air and thus the volumetric efficiency decreases. The nitrogen content in ammonia also causes problems with NOx emissions, though this problem can be solved with a modified SCR catalyst.

## 1.1 Material considerations

A general consequence by combustion of ammonia is corrosion. This is due to water vapor formed during combustion. It is important that the materials in an engine is compatible with the fuel used. Several existing internal combustion engines contain cast iron, copper, nickel, aluminum and rubber. Possible compatibility issues with the above materials are key focus areas in this section.

Schmidt stated that when using ammonia, corrosion problems could be expected with copper, brass, aluminum, zinc and magnesium alloys [2].

A comprehensive compatibility study conducted by the army laboratory [3] has performed compatibility investigations using a high-pressure autoclave (bomb) and subsequently, to verify the results, a 120 hrs. run was conducted with a CLR spark ignition engine, using the poorest lubricant oil. During the experiment, the temperature and pressure of the bomb was equal to those found in engines. The bomb was pressurized with ammonia or ammonia combustion products and air. The studies were carried out by introducing a weighed amount of material into the bomb, the test was maintained for 5 hours. The

*Table 1. Comparison of fuel properties [1,23,41,42,43,44,45,46,47,48,49,50,51,52]*

| | Energy content (LHV) [MJ/Kg] | Energy content (LHV) [MJ/L] | Density [kg/m³] | Octane [RON] | Flame-velocity [m/s] | Flammability-limits [vol/%] | Minimum Ignition Energy [mJ] |
|---|---|---|---|---|---|---|---|
| **Cooled Ammonia (Liquefied)** | 18.6 | 12.69 (1 atm, -33℃) | 682 | >130 | 0.067 | 15-28 | 680 |
| **Compressed Ammonia (Liquefied)** | 18.6 | 11.65 (300 bar ,25℃) | 626. | >130 | 0.067 | 15-28 | 680 |
| **Cooled Hydrogen (Liquefied)** | 120 | 8.5 (1atm, -253℃) | 70.85 | >130 | 3.25 | 4.7-75 | ~0.016 |
| **Compressed Hydrogen (gaseous)** | 120 | 2.46 (300 bar, 25℃) | 20.54 | >130 | 3.25 | 4.7-75 | ~0.016 |
| **Diesel (n-dodecane)** | 44.11 | 32.89 (1 atm, 25℃) | 745.7[12] | <20 | ~0.80 | 0.43-0.6 | ~0.23 |
| **Gasoline (iso-octane)** | | (n-octane) | (n-octane) | | 0.41 | 0.95-6 | 1.35 |
| | 44.34 | 30.93 ( 1 atm,25℃) | 697.6 | 100 | ~0.58 (RON 90-98) | 0.6-8 (RON 90-98) | ~0.14 (RON 90-98) |
| **Methanol** | 19.90 | 15.65 (1 atm,25℃) | 786.3 | 108.7 | 0.56 | 6.7-36 | ~0.14 |
| **Ethanol** | 26.84 | 21.07 ( 1 atm,25℃) | 785.1 | 108.6 | 0.58 | 3.3-19 | 0.65 |

*-Note, this table is for comparison purposes only– not all values are obtained from experimental studies.*

materials were then examined for deleterious effects and analyzed by chromatography and infrared spectroscopy.

A weight gain of cast iron was observed. The weight change was expected to be due to some form of corrosion, which could also be observed visibly. Only a portion of aluminum surface was discolored, nevertheless the material underwent a greater weight change than cast iron, therefore aluminum is considered less suitable - however, the weight gain for both cast iron and aluminum was very small. The babbitt bearing materials underwent the highest weight change – however, once again this change was small. A heavy, tarnish-like oxidation and a pitted-type corrosion appeared on the surface of the sintered copper-lead bearing and the cast copper-lead bearing, respectively. By visual examination it was judged by the authors that the condition of these bearings would have been considerable worse if the test had been continued. Ammonia's effect on both rubber and neoprene was also noticeable, neoprene showed the greatest weight change, swelling and losing its shape.

Based on these studies, the authors conclude that even though all the materials experienced some deterioration, the effect was slight and the most commonly used materials in engine systems will be adequate for ammonia service, except copper which probably should be avoided.

The laboratory test results were verified by running ammonia in the CFR SI engine. The experiment showed that copper-lead bearings were the only material that underwent a significant weight loss, again indicating a reaction between ammonia and copper. It should be noted that using hydrocarbon fuel such as gasoline, high weight loss can also occur - yet it is concluded that it is likely to avoid using copper in an ammonia engine. The experiments did not show any other unusual detrimental effect on standard bearing materials and most engine components were clean after a test run of 120 hrs. However, the cylinder head and spark plug were covered by a rust film in areas without deposit buildup. Whether special protective lubricants are needed to avoid this is not concluded.

Also, Pearsall [4] observed that copper, brass and bronze was affected by ammonia and these materials should be avoided.  He mentioned that ammonia had no deleterious effects on various engine components, only parts made of brass, copper or bronze. At the experiments performed only one part were adversely affected which was the copper spark-plug gasket, these was completely dissolved after short time of operation. These gaskets were replaced by soft iron gaskets and no further trouble was encountered. From a run of 297 hours of operation with ammonia he noticed that the ammonia did not attack the copper in the copper-lead bearings or the aluminum piston alloy. Therefore, he concludes that only pure copper, bronze and brass are susceptible from attacks by ammonia. Graves [5] also thought that copper and brass was incompatible with ammonia.

It should be noticed that Gray's study was performed in 1967, the other studies are also from this period. Several studies dealing with the feasibility of ammonia refers with respect to compatibility to this study. However, several recent experimental studies (section 1.3,1.4) of ammonia in combustion engines are carried out and these do not mention any serious compatibility issues. Since ammonia is widely used in the industry e.g. refrigeration systems there must additionally be plenty of compatibility studies.


## 1.2   Safety concerns in engines

When considering using ammonia in vehicles new safety precautions are needed. However, this will always be the case when considering new fuels for use in vehicles. Normally associated safety concerns with engine fuels are the explosion hazards, this is however not that big of a concern for ammonia. The greatest concern is the toxicity, which can cause big consequences in case of leakage. However, it is thought by some that using ammonia in vehicles is as safe as gasoline [4,6].

For a further view into the safety concerns regarding ammonia a comprehensive report by Risoe national lab laboratory [7] asses the safety concerns regarding ammonia as a transport fuel.

The storage of gaseous ammonia in a metal ammine complex can overcome some of the safety aspects regarding liquid ammonia [12].

A possible concern when combustion of a hydrocarbon fuel and ammonia is the formation of hydrogen cyanide (HCN). Hydrogen cyanide is a highly toxic acid and can be lethal at a concentration of a few ppm in the air [8]. However, studies show that the concentration is below the allowable limit for HCN in SI

and CI-engines [9,10]. HCN can be formed from different combinations of carbon, ammonia and hydrogen [11]. Hydrogen cyanide is formed at oxygen deficit (when no catalyst is used) and should therefore not generally be a concern in internal combustion engines. Conditions for the formation of hydrocyanic acid may, however, occur locally in high temperature areas with oxygen deficiency where a reaction between the hydrocarbon fuel and ammonia could take place. If the possible formed hydrogen cyanide does not post oxidize later in the combustion process, in principle, hydrogen cyanic acid can be an emission product. Though, there have been no reports regarding emission of hydrogen cyanic when ammonia and hydrocarbon fuels are used in ICE.

## 1.3  Pure ammonia in IC engines

There are several studies [3,4,5,12,13,14,15,16,17], that have investigated the use of pure ammonia in both SI and CI engines. Experiments shows that satisfactory combustion is not achieved and in general a degree of engine modifications are needed to achieve combustion.

The stoichiometric air-fuel ratio of ammonia is 6.0466 compared to 14.322 for diesel, this means that more ammonia can be injected compared to diesel, based on the same amount of air. Which means ammonia can compensate for its lower energy density by injection of more fuel, and thereby achieving an energy density almost equal to that of diesel at stoichiometric air-fuel mixture [12].

However, compressions ignition of pure ammonia in existing diesel engines is difficult to achieve, since the combustion properties of ammonia is much different than those of diesels, especially ammonias low cetane number [3,13].

A study by Gray et al. [3] tested liquid ammonia by direct injection in a CFR engine. To achieve combustion at 900 RPM they had to raise the compression ratio to 35:1, implement a heating jacket and raising intake air temperature to 150 ℃. The ignition timing were in the range of 90 to 70 BTDC, this combined with the high heat of vaporization, indicated an air-fuel mixture that were close to homogeneous, therefore it was not a classical diesel combustion, in the sense of a heterogeneous air-fuel mixture. Since the compression ratio was raised to 35:1 to achieve combustion, a new engine design is probably also needed when running on liquid ammonia in CI engines.

Starkman et al. [14] also proved that combustion of liquid ammonia in a CFR engine was possible at a compression ratio of 35:1 with heating of the cylinder and air of ~100 ℃ and ~50 ℃, respectively.

Another study by Pearsall et al. [13] showed that compression ignition of liquid ammonia at a compression ratio of 30:1 was not possible, hence a compression ratio of 35:1 seems to be the minimum required compression ratio for compression ignition of ammonia alone in CFR engines.

It has also been tried to achieve combustion of ammonia in a modified CI engine with the use of mechanical devices on the engine itself to lower the ignition requirements. High energy spark plug, glow plug and special high temperature glow coil in the development stage. All the ignition sources were installed at the top of the swirl chamber (the pressure pickup hole). It was not possible to obtain combustion with the use of spark plugs and glow plugs. This may be due to the location close to the swirl chamber, where high velocity of the gasses could quench the flame before it could propagate - it could also be due to the fact that a proper air/fuel ratio could not be obtained. However, with the glow coil at the same location it was possible to achieve combustion at a compression ratio of 23:1 with the

use of a heating jacket and air temperatures of 65 ℃. Though the combustion was still sensitive to the flow rate and location of the glow coil [3].

Another study [14] also tried to implement spark plugs in a compression ignition-engine fueled by liquid ammonia alone. They found that satisfactory combustion was achieved at compressions ratios of 16:1-24:1, though no clear gain was obtained at compressions ratios above 20:1. Best performance was achieved at injection timing of 150-180 BTDC of liquid ammonia. Compared to pure diesel operation, ammonia operations showed 10% less power at a comparable air-fuel ratio.

It is also a general perception that satisfactory combustion in existing SI engines is not possible to achieve when operated on ammonia alone. Starkman [15] found that in a standard spark ignition engine it is necessary to use some kind of combustion promoter to achieve satisfactory combustion.

Mørch et al. [12] studies showed the same - Mørch could achieve combustion but with a strong tendency to cut out when running on pure ammonia.

Mozafari - Varnuspadrani [16] also tried to run on pure ammonia without major engine modifications, the engine was running at a constant speed of 2000 rpm, and ammonia was injected in liquid phase. To achieve combustion, it was necessary to warm up the engine on methanol as fuel and the ammonia was then gradually injected. Finally complete transition from methanol to ammonia could be obtained. Combustion of ammonia could only be sustained at a compression ratio of 15: 1 and in a narrow range of equivalence ratio from 0.88 - 1.15, and still the combustion tended to be erratic. It was managed to run on pure ammonia for up to 90 minutes in one test. In other tests the engine stopped after only 10-15 min. However, it was expected to be related to the ignition system since, after some time, it was apparent that the spark plugs could have been damaged in the tests involving high compression ratio. It was not possible in every test to switch from methanol to pure ammonia, due to ammonia's narrow flammability limits. The highest BMEP and thermal efficiency were obtained at slightly rich mixture at an equivalence ratio of 1.05. But still, with a significantly lower BMEP and thermal efficiency compared to gasoline. At an equivalence ratio of 1.05, 11.8% unburned ammonia was measured in the exhaust and at an equivalence ratio of 0.885, 23.2% was measured. In terms of emissions, the concentrations of oxides of nitrogen were of the same orders as with gasoline operation.

Gray et.al. [3] managed to achieve combustion by making various mechanical changes, in which way it was possible to achieve combustion on pure ammonia at engine speeds up to 2200 RPM. During the experiments, very high compression ratios, two spark plugs, increased spark energy and a shrouded intake valve for added turbulence was used. However, at part throttle operation or lower compression ratios it was still necessary to add a combustion promoter in the form of hydrogen. Cornelius et al [17] also found that an engine runs poorly, fueled on ammonia alone, but that increased spark energy, increased compression ratio and engine supercharging could improve the performance to some extent. Pearsall [4] found that a four-cylinder SI-engine with no changes besides addition of an LPG carburetor, was able to run at speeds up towards 1045 RPM but with very erratic combustion and with low power output (0.895 hp). Small changes to the carburetor choke, venturi and main metering jet allowed the engine to run op to 1951 rpm and to produce maximum output of 9.2 hp at 1200 rpm. Additional modifications to the carburetor, and changes of the ignitions system, spark plug gap, spark plug reach, swirl, fuel supply system and the compression ratio – could make the engine perform remarkably better.

It is well known that ammonia is difficult to ignite (table 1). An improved ignitions system such as the Mallory Magneto which has a remarkably larger spark duration compared to the standard system, produced a substantial increase both in peak power obtainable and maximum permissible operating speed. It appears that ammonia fuel wants a "fat", "hot" spark with long duration. Pearsall also found out that increasing the spark plug gap from 0.030 to 0.100 inch made it possible to increase the maximum power and the maximum engine speed. The effect was much greater at 4000 rpm than at lower engine speeds and from 0.110 – 0.120 inch the improvement became close to asymptotic. If the gap was increased too much, it resulted in bad engine performance, which could be due to a multiplicity of small sparks instead of one rich spark at the gap.

Another important factor was the spark plug reach. A dramatic improvement in performance could be obtained with longer reach. Pearsall found that the optimum location was 0.875 inch into the combustion chamber – which is as low as the electrodes can go without being stuck by the pistons and the position was close to the center of mass relative to the combustion chamber at top dead center. The only plugs with this reach available, was not designed for engine operation and effect of overheating could be seen after 122 hours of operation. However, it should be possible to develop spark plugs for this purpose.

Several modifications were made to the fuel system through testing, and based on the engine performance, Pearsall et al. developed an ammonia carburetor, which had a good match between desired and achieved fuel flow. Furthermore, engine performance and the maximum speed when running on pure ammonia was increased by implementing swirl deflectors.

Large improvement in performance of an ammonia fueled engine can be obtained by increasing the compression ratio. This is believed to be due to the great increase in flame propagation rates as compression ratio is increased. The optimal compression ratio relative to the performance could not be utilized in this test and a compression ratio of 10.26:1 was used. Otherwise peak cylinder pressures were too high and the peak firing pressures was beyond the safe limit for operation of the SI-engine with the cast iron crankshaft.

All these improvements made the engine perform remarkably better. The engine could start, run and accelerate. The engine had a maximum output of over 40 hp at 3000 rpm when fueled by ammonia alone. Low rate of flame propagation caused engine performance to decrease rapidly at higher speeds (above 3000 RPM) and at 4000 rpm with a power output at only 20 hp. At higher speeds it was therefore necessary to add hydrogen, however, the hydrogen requirements for this engine have been reduced from 5 to 1.5 mass% at high speeds. At high speeds with small amounts of hydrogen the engine could produce about 53 hp at 4000 rpm. Gasoline produced about 68 hp at 4000 rpm, this could partly be due to the fact, that they could not use the optimal compression ratio.

Graves [5] was also able to ignite ammonia at a compression ratio of 10.2:1 in a four-cylinder spark ignition engine with an additional spark plug for each cylinder. The ammonia was heated and completely evaporated before it was passed to the carburetor. In this manner Graves could run the engine at 2000 rpm. The main problem in this experiment was ammonia slip from the exhaust.

Pearsall [4] demonstrated that it could be preferable to convert a CI-engine into a spark ignition engine, because of the CI-engines high compression ratio and good air flow. With the converted diesel engine, it was likewise possible to run on ammonia alone and experiments could be performed at higher

compression ratios. 16:1 was found as the optimum. The converted CI-engine had a lower BSFC compared to the previously described SI-engine which the author says indicates that a large bore is preferable - the four-cylinder SI engine had a bore of 3-7/8-inch and the converted two-cylinder CI-engine had a bore of 5-3/4-inch. Additionally, the more concentrated combustion chamber and a more centrally placed spark plug could contribute to lower BSFC.

With the modified CI-engine, Pearsall showed that it was possible to have a higher power output compared to a CI-engine with diesel alone or ammonia with diesel pilot injection. He even managed to obtain supercharged diesel output with un-supercharged spark-ignition operation (CI modified to SI-engine). He mentioned that as well as the CI-engine has inherent advantages over the SI-engine, the SI-engine has advantages over a pilot fuel CI-engine such as the ability to run at part-load and a more reliable ignition source. He mentioned that the development of a more advanced fuel injection system could overcome some of the CI-engine's issues.

## 1.4 Dual-fuel

Since combustion in existing ICE's without major modifications is difficult to achieve using pure ammonia, alternatives are needed. The combustibility of ammonia can be improved with the use of combustion promoters. Combustion promoters are more reactive fuels, which are used with the ammonia to improve the ignitability and flame speed. Combustion promoters could be common ICE fuels such as diesel and gasoline, also alternative fuels such as biodiesel, hydrogen, ethanol, DME etc. Dual-fuel solutions is an area with little experience, hence there is a lot of development needed in terms of control of injection and ignition of the fuels and optimal design of the systems. However, different types of preliminary experiments are already carried out with dual-fuel solutions on existing CI and SI engines.

### 1.4.1 Ammonia in spark-ignition engines

#### 1.4.1.1 Gasoline and ammonia

It is of interest to investigate the use of ammonia with gasoline as the combustion promoter for several reasons. First, gasoline is almost accessible worldwide and a dual fueled engine running on ammonia and gasoline enables the engine to run on gasoline alone, which is preferable as studies shows that idle operation on ammonia is inconvenient [19,20]. Furthermore, the presence of ammonia greatly increases the octane rating of the fuel mixture hence, operation on ammonia/gasoline is not limited by knock. In addition, the use of gasoline as a combustion promoter also avoids the problem of storing high pressure gas or advanced cracking equipment on board, as necessary when using hydrogen [26,19].

Several studies investigating the use of gasoline and ammonia in an SI-engine were gasoline is used as the combustion promoter have been carried out. Two recent experimental studies [20, 21] investigates the performance of gasoline and ammonia with direct gaseous injection [21] and with port injection of ammonia [20]. The use of direct injection of liquid ammonia is known to give better volumetric efficiency, when at liquid phase, ammonia does not displace a large amount of air, and cools the intake mixture resulting in higher density. However, the gain in efficiency is still small [15]. Additionally, there is a significant temperature reduction in the compression temperature and increase in mixture nonuniformity. It is of great interest to improve the combustibility of ammonia, and direct injection of ammonia is counterproductive to this [16]. Therefore, port injection is widely used, however K. Ryu et al.

[21] has carried out an experimental study to make use of a custom gaseous ammonia injector to accommodate these issues.

K. Ryu et al. carried out experiments on a CFR engine using a constant compression ratio of 10:1 at a constant speed of 1800 RPM. To increase the volumetric efficiency, gaseous ammonia was injected with a custom direct injection module at 370, 320 and 270 CAD BTDC. At each injection timing different injection durations were investigated with different amounts of gasoline being port injected as a base power to facilitate combustion. In terms of best power output, the injection timing and duration varied at different operating conditions. In general, best power output was achieved with injection timing of 320 CAD BTDC at low loads and 370 CAD BTDC at high loads.

Results indicates that ammonia/gasoline operation can provide the equivalent energy to gasoline operation alone at the range of loads tested. Pressure and heat release study shows gasoline/ammonia combustion exhibits characteristics of a conventional SI-engine. However, a lower peak pressure is achieved compared to pure gasoline combustion because of ammonias lower flame temperature and flame speed [21]. Though, ammonias high knock resistance allows higher compression ratio and thereby higher peak pressures [20]. As the load of ammonia increased (longer injection duration) the combustion duration decreased, which indicates that addition of ammonia to a certain extent increases the combustion rate. It should be noted that ammonia does not increase the combustion rate to the extent that gasoline did, however the combustion duration of ammonia and gasoline is comparable to that of gasoline. The author also thought that this could be due to the enhanced combustion intensity caused by the strong turbulence in the gasoline-air mixture prior to ignition, as a result of the direct injection of ammonia [21].

A more comprehensive study carried out by Assanis et al. [20] focused on the highest possible amount of ammonia that could substitute gasoline within the rough limit, COV(IMEP$_n$) ≤ 3, for different loads, compression ratios and speeds in a CFR engine with possibility of supercharging. The experiments showed that the majority of gasoline used in a spark ignition engine could be replaced with ammonia when IMEP$_n$ >400 kPa. However, it is also concluded that a spark ignition engine does not generally give tolerable performance when fueled on ammonia alone and at idle close to 100 % gasoline was required. The authors found that no specific ratio of ammonia/gasoline exist for every combination of load and speed but that a fuel mix map, which specifies the proportion of ammonia that can replace gasoline yielding acceptable operation as a function of speed, compression ratio and load exist. Too much ammonia resulted in the engine fired with an excessive roughness, vice versa if too much gasoline was used knock free combustion at maximum brake torque (MBT) timing could not be obtained.

Experiments also showed that ammonias knock resistance allowed operating at higher IMEP$_n$ compared with the use of gasoline alone. In addition, the efficiencies at higher load were better, due to the fact that MBT spark timing could be used at high IMEP$_n$ . When fueled with gasoline alone it was required for all the gasoline operating points to retard the spark timing from MBT when IMEP$_n$ >400 kPa, otherwise knock occurred.

The effect of the necessary retarded combustion timing for 100 % gasoline is reflected by the thermal efficiency. At a compression ratio of 9:1, speed of 1000 RPM, and WOT (IMEP$_n$ =700 kPa) the net indicated thermal efficiency was 28.4% for 100% gasoline, the indicated thermal efficiency was 33% at the rough limit for ammonia/gasoline. The thermal efficiency was almost constant from the rough limit fuel mix at 82% NH3/18% gasoline to a fuel mix at 25% NH3/75% gasoline.

From the experiments some general trends could be derived. The higher the IMEP (load) the greater proportion of ammonia could replace gasoline - and the higher the speed between 1000-1600 RPM, the smaller amount of ammonia could replace gasoline. Another tendency is that the higher the compression ratio, the higher was the proportion of gasoline that could be replaced by ammonia. Fuel mix at the rough limits, however, had a surprisingly weak dependence on the compression ratio compared to the strong dependence on load. The author explains this based on the fact that ammonia's long ignition delay places the spark (at MBT) in a crank angle region where the compression ratio has little influence. At the rough limit, the spark timing at MBT, was for all points more than 50 degrees. The instantaneous compressed charge density in this crank angle region is proportional to the load. The fuel mix appears to be weaker determined at the charge density at TDC and stronger determined by the compressed charge density at the spark.

Because of the compression ratios weak effect at reducing the required amount of gasoline and also a diminished effect on the thermal efficiency, if the compression ratio was too high, it is recommended by the authors to use a compression ratio of 10:1 in a SI-engine. There is however, a significant efficiency gain when the compression ratio is raised from 8:1 to 10:1. No real difference in efficiency was shown in the compression ratio interval of 10:1 to 12:1, however, at compression ratio 12:1 exist a small margin of error between MBT knock and rough limit, therefore, a compression ratio of 12:1 is not preferred. At a compression ratio of 14:1 and 16:1 it was not possible to add enough gasoline to provide adequate flammability, without knocking at TDC. Though, it is estimated that improved combustion chamber geometry could give a higher optimal compression ratio near 12:1 with respect to the higher thermal efficiency, and knock and rough limits. It is thought by the authors that the pancake geometry of the CFR engine resulted in the maximum efficiency being achieved at a lower compression ratio[20].

With regards to the influence of speed, experiments show at 1000 and 1300 RPM that it is possible to operate with up to 100% ammonia at some high $IMEP_n$ values (in the supercharge regime) at the rough limit - whereas it is not possible at any points at 1600 RPM regardless of the load. Increased speed results in longer ignition delay and burn duration, resulting in an increase in the MBT spark advance - which in turn results in a reduction in compressed charge density at the spark. A general requirement for increased flame speed could also contribute to this trend. One way to shorten the burn duration and ignition delay is to implement plasma jet ignition [22] or dual ignition [17,23].

Running the CFR engine at a speed of 1600 RPM, compression ratio of 8:1 and IMEPn of 550 kPa resulted in a rough limit at 63 % ammonia / 37 % gasoline and the fuel mix at MBT spark timing was at 13% ammonia / 87% gasoline. Whereas running the engine at higher load (WOT = 700 kPa) and lower speed (1000 RPM) and a compression ratio of 9:1 the rough limit was at 82 % ammonia / 18 % gasoline and at the MBT knock limit 43% ammonia / 57% gasoline. This illustrate the effect of speed and load on the combustion of ammonia and gasoline [21].

Experiments by K. Ryu et al. [21] with a compression ratio of 10:1 at a constant speed of 1800 RPM found that a combustion efficiency of approximately 98% is achieved at all loads of ammonia/gasoline combustion, hence ammonia slip increased with the increase in load. $NO_x$ emission also increased together with the increase in load, however the brake specific $NO_x$ emission decreased with increasing load. Though the $BSNO_x$ emissions were much greater compared to pure gasoline combustion, which is expected to be a result of fuel bound NOx from ammonia, since thermal $NO_x$ is very unlikely to be

formed, because of the low flame temperature of ammonia. The increased $NO_x$ emissions can be removed with an SCR catalyst. With ammonia being easily available, implementation of such a system would be desirable. The BSCO emissions at all loads are only slightly lower compared to pure gasoline combustion, the BSHC for all loads are slightly higher compared to pure gasoline combustion, even though significantly less carbon-based fuel was present. This indicates that incomplete combustion of gasoline occurred caused by the lower flame temperature and flame speed of ammonia, which would explain the increase in BSHC and the only slight decrease in BSCO.

### 1.4.1.2 Ammonia dissolved in gasoline

Another approach to use ammonia with gasoline is through the use of thermostated vapor liquid equilibrium (VLE) in high pressure cells, which can dissolve ammonia in gasoline. Experiments shows that 4.5%v ammonia can be dissolved in pure gasoline, at a pressure of 345 kPa and a temperature of 13.5 ℃ [24]. The use of ethanol or methanol as an emulsifier can enhance the solubility of ammonia and gasoline [25]. Experiments show that gasoline with 20%v ethanol and 12.9%v ammonia is a preferable mixture for use in SI-engines in terms of ECU control. This mixture leads to improved power at high speeds and similar power at lower speeds compared to pure gasoline in a conventional SI-engine [25]. The use of ammonia/ethanol/gasoline blends achieve higher octane rating; therefore, it is thought that higher compression ratios in new SI-engines is possible with this blend [24]. Emissions from these blends are however not available and are needed in order for this concept to be considered [24,25].

### 1.4.1.3 Hydrogen and ammonia

Many studies recommend the use of hydrogen as combustion promoter in an SI engine fueled by ammonia [4,12,19,26,27,28]. Hydrogen's combustion characteristics are preferable when combined with ammonia, at the right ratio hydrogen can make up for ammonias slow flame speed and ignition requirements. Hydrogen has a minimum ignition energy of 0.016 (table 1) and Verkamp et al. showed that small amounts of hydrogen were able to reduce the required amount of energy significantly [29]. A replot of the data was shown in Pearsall's report and this plot showed that the addition of 5 mass% hydrogen could reduce the required amount of energy to that of hydrocarbons (~0.3 mJ) [4].

Ammonias content of hydrogen can be utilized by dissociation of ammonia in a catalyst driven by exhaust gas heat [4,12,19,27,28]. Hence, only ammonia is needed as fuel input and only an infrastructure of ammonia is needed. Furthermore, the absence of carbon in both hydrogen and ammonia eliminates carbon-based emissions. The only concern in terms of emissions are oxides of nitrogen and ammonia slip which studies most likely can be removed with a modified SCR catalyst according to [12,19,27,28].

A commercially ruthenium-based catalyst has been demonstrated to dissociate ammonia into hydrogen and nitrogen in order to use together with ammonia in an SI engine. The catalyst is able to fully convert ammonia to hydrogen at a temperature of 450℃ and above. To obtain proper hydrogen fuel flow the catalyst bed in the ammonia decomposition system is divided into four parts inside a heat exchanger. Therefore, the system in principle consist of four ammonia decomposition reactors. Two heating elements with capability of reaching the desired temperature is also implemented in the heat

exchanger, so the system can be driven by both electricity and exhaust gas heat. Additionally, two heating elements is implemented in the ammonia delivery system to keep the ammonia at gaseous state. The system has been verified by testing in order to produce adequate hydrogen flow when powered by electricity alone. Experiments shows that at an air-fuel ratio of 1 and speeds between 2500-3500 RPM, the exhaust gas temperature is sufficient to run the system without electricity as aid. Whereas with an air-fuel ratio of 1.2 the exhaust gas temperature was insufficient to run the system alone, hence help from heating elements was needed. However, the experiments used a hydrogen content that was higher than the required content for adequate combustion of ammonia/hydrogen [19,26,28].

A strategy of storing ammonia is by using a metal amine complex, as mentioned earlier. When storing ammonia in a metal amine complex, heat is needed to release ammonia from the complex and to dissociate ammonia to hydrogen. Experiments indicates that it is possible to cover the majority of the heat required to extract a mixture of ammonia and hydrogen from a metal amine complex (Mg $(NH_3)_6Cl_2$), through the use of exhaust gas heat. However, it is expected that only 2/3 of the ammonia content can be extracted at ideal conditions [12]. A possible reload process of the amine complex is proposed to compensate for this [30]. Furthermore, at low speeds and cold start the use of exhaust gas heat may not be sufficient to achieve 2/3 conservation of the ammonia content. The conversion ratio also greatly depends on the ratio of hydrogen/ammonia needed. Since hydrogen is obtained from decomposition of ammonia, more heat is required at higher hydrogen concentrations [12].

Studies shows issues with SI engines when fueled alone by either ammonia or hydrogen [section 1.3]. The fuel characteristics makes it preferable to operate at high compression ratios. It is thought that a suited compromise by mixing hydrogen and ammonia can be achieved [12].

Experiments examined in this section are performed by port injection of ammonia and hydrogen in a gaseous state, which has shown no problems. The gaseous ammonia and hydrogen do however, displace a great amount of air, and the charge density is therefore reduced. Other studies have used different approaches to accommodate this [17,21].

In terms of excess air ratio, the highest efficiency is achieved at slightly higher ratios than 1, and the highest mean effective pressure are achieved at slightly lower ratios than 1 [12].

By increasing the compression ratio, mixtures of ammonia/hydrogen can achieve similar mean effective pressure compared to gasoline run at the CR knock limit. The increase in compression ratio yields a significantly higher indicated efficiency of ammonia/hydrogen compared to gasoline. Since the same power output can be achieved with hydrogen/ammonia mixtures with a higher efficiency, the increase in CR compensates, with respect to engine power, for the air dilution from port injection of ammonia and hydrogen. When CR are raised from 11.64 to 13.58 almost no increase in efficiency is observed, whereas it is observed that the indicated mean effective pressure is raised [12].

The lowest indicated thermal efficiencies and pressures are found with high amounts of hydrogen. This is due to an increase in the intake air dilution caused by hydrogens lower density. 5 vol-% hydrogen resulted in smooth engine operation and 10 vol-% at stoichiometric is optimal in terms of highest efficiency and mean effective pressure [12]. Other found that 8 vol-% (1% mass) hydrogen was sufficient [15,31,3].

Measurements of emissions reveal most favorable operation at stoichiometric conditions and MBT timing, in terms of NO, $NO_2$ and $N_2O$. However, at these conditions, ammonia slip is high. The NO content is in fact lower than in the gasoline exhaust, at this condition, though leaner conditions will increase the formation of NO. The $NO_2$ share of the total $NO_x$ emission is higher than for gasoline, 3-4% for $NH_3$ and less than 2% for gasoline [27].

At an ignition timing of 15 degrees BTDC (optimal ignition) and at TDC with an air-fuel ratio of 1.1 a peak in NO emission is visible, which corresponds well to other emissions studies with gasoline. At these conditions the peak in NO emission is dominated by thermal $NO_x$. Another mechanism seems to take over at leaner conditions, with another peak in the NO emission, which is thought to be fuel bound $NO_x$ from the ammonia at low temperatures [27]. The reason for the $NO_2$ share of the total $NO_x$ being slightly higher than for gasoline is thought to be higher concentrations of $NO_2$ in the flame zone, when nitrogen is present in the fuel, and the subsequently quenching of its transformation to NO in the post flame area [27]. Mørch et al. [12] and Comotti et al. [28] verifies these findings, that the NOx emissions are greatest with an excess air-fuel ratio between 1.1 and 1.4.

$N_2O$ emissions are thought to be a product of $NH_3$ reacting with NO. The elementary reaction where $NO_2$ is reacting with $NH_2$ radicals at low temperature (temperatures found at the expansion and exhaust stroke), is thought to be the dominating contributor to the formation of $N_2O$. The excess air-ratio and spark timing has a large influence on the $N_2O$ content in the exhaust gas. Late ignition increases the "low temperature" in the expansion and exhaust stroke, which promotes the formation of $N_2O$. A higher excess air ratio raises the formation of $NH_2$ and $NO_2$, also promoting the formation of $N_2O$. Experiments confirms that at leaner mixtures with late ignition timing the $N_2O$ content are highest. $N_2O$ is below detection limit (<10ppm) at MBT timing - despite the fact that $N_2O$ compared to $CO_2$ is 300 times more competent relative to the greenhouse effect[27], the effect of $N_2O$ will be negligible in the small quantities measured relative to $CO_2$, which is normally represented in percent of parts in the exhaust [32].

One study found [27] for an ammonia/hydrogen fueled engine that ammonia slip is dependent of compression ratio and increases as the compression ratio is raised. Experiments showed that at excess air ratios above 1, ammonia slip was not affected by excess air ratio. The slip was also independent of ignition timing and this could be due to a stepwise combustion of hydrogen and homogeneous ammonia. This is in contradiction to HC emission from an SI engine fueled by gasoline, which is highly dependent of ignition timing. The ammonia slip was in the range of 1000 ppm which is higher than the allowable 10-25 ppm according to EURO IV [33]. This calls for exhaust after treatment

It is expected that a modified SCR catalyst can reduce the $NO_x$ emission from hydrogen/ammonia combustion through the use of the ammonia from the ammonia slip [12,27]. Experiments showed that the exhaust gas temperature was within the required range for the SCR system to work successfully. For complete reduction of $NO_x$, a ratio of 1, between $NO_x$ and ammonia in the catalyst is required. Experiments indicates a ratio above one. To accommodate this an ammonia bypass can be implemented. Issues with insufficient exhaust gas temperature under cold start can presumably be solved with a pre-oxidizing catalyst, to achieve a fast SCR reaction. An ammonia trap is also a necessity

to capture ammonia slip after cold start [27].

In terms of cold-start operation, a larger hydrogen flow is required in order to facilitate combustion at low speeds [16,19,20,26]. To accommodate these, different approaches are suggested. One suggests that the use of a hydrogen storage tank can deliver the required hydrogen flow, which then can be recharged under normal engine operation [19]. Another method suggest that the use of electricity and a larger heat exchanger could be sufficient to produce the larger amount of hydrogen [26].

## 1.4.2 Ammonia in compression-ignition engines

### 1.4.2.1 Diesel and ammonia

Diesel as well as gasoline is accessible worldwide, which make diesel and ammonia combustion a topic of interest for the same reasons as gasoline.

Gray et al. [3] proved successfully combustion by direct injection of both liquid ammonia and diesel at compression ratios between 30:1 and 15.2:1, with the use of a CFR engine with heating of intake air to 65℃ and injectors to 100℃ at speeds of 900 RPM and 1800 RPM. The heating was done to prevent freezing of the injectors since ammonias high heat of vaporization and boiling point of -33℃. Experience from testing shows that ammonia needs to be injected at least 40 CAD before the end of the diesel injection, if later no ignition can be obtained, and ignition delay increased with the amount of ammonia introduced to the engine. However, in this study a different method for introducing ammonia into the engine was tested. Gray injected ammonia into the air-intake in the form of vapor and directly injected diesel. This method showed a better pressure output compared to direct injection of ammonia, though the volumetric efficiency was decreased.

Pearsall [4] used this strategy successfully in a V2 supercharged diesel engine with compression ratio of 18.6:1. Compared to pure diesel operation they achieved an indicated power and an indicated thermal efficiency for the ammonia/diesel operation that was 32% and 13% higher, respectively. The fact that ammonia/diesel operation could achieve a higher power output and thermal efficiency than pure diesel operation was described by Newhall [34] in a theoretical study of ammonia in CI engines. In the study [4] they further found that a raise in the cylinder head temperature had a positive effect on the performance and that the fuel consumption was best at lower speeds, presumable caused by ammonias low flame propagation rate. In addition, they found that throttle operation of ammonia/diesel was not possible.

Later in the study they converted the same CI-engine to an SI-engine running on only ammonia by substituting the fuel injectors with a high-performance ignition system. They achieved even higher power output compared to ammonia/diesel operation and was able to run throttled at part-load conditions.

Two recent experimental studies [18,35] investigated ammonia and diesel combustion in a commercial turbocharged four-cylinder diesel engine. Test were performed at a compression ratio of 17:1. Ammonia was injected in the air intake and diesel was directly injected.

The following results are from a test strategy that consisted of varying the ratio of diesel and ammonia to achieve the same power output as diesel operation, at 1000 RPM:

The brake specific fuel consumption (BSFC) for ammonia and diesel had opposite tendencies. When the diesel content is low (less than 15% energy based) the diesels BSFC are too high and when the diesel content is high (more than 60% energy based) the ammonia BSFC is too high. The more ammonia present, the lower the in-cylinder flame temperature - this combined with light-load diesel operation results in a low diesel fuel efficiency. When a lot of ammonia are substituted with diesel the ammonia-air ratio may be close to the flammability limit of ammonia, resulting in a mixture that are too lean to combust efficient, hence high BSFC.

Heat release and pressure studies found that as more diesel was replaced by ammonia the longer the ignition delay and lower the peak pressure became. This is believed to be caused by ammonias higher resistance to auto-ignition and the reduction of diesel fuel spray, which decreases the fuel momentum for effective atomization and mixing leading to ignition. In terms of overall fuel efficiency, the optimal range was 40-60% diesel fuel energy.

One of the studies [18] found that at diesel fuel energy above 30%, the $NO_x$ emission was less than at 100% diesel energy. The other study [35] found that at a diesel fuel energy above 60% the NO emissions were significantly lower compared to 100% diesel operation. These tendencies were caused by ammonia's lower flame temperature compared to diesel's, which resulted in an overall lower flame temperature than with 100% diesel. Since NO formation was highly dependent of high temperatures in the cylinder, the NO emissions were lowered when diesel fuel energy were above 60%. However, below 60% diesel fuel energy, the bounded nitrogen in the ammonia had a significant effect on the NO emissions that were much higher than on pure diesel energy.

The generally lower in-cylinder flame temperature at all ratios of diesel and ammonia had a significantly effect on the HC and CO emissions, which were considerably higher compared to 100% diesel energy. In terms of soot emission, the more diesel fuel injected the more soot was produced, at an 80% ammonia fuel energy the soot emissions were almost negligible. As expected the CO2 emissions were reduced when more ammonia fuel was present. In the studies they found that the ammonia slip was at all times well above the limit of 50 ppm (approximately 1000-3000 ppm). This was believed to be caused by flame quenching on the cylinder walls and ammonia-air mixture trapped in the piston ring crevices - a consequence of using premixed ammonia-air. The overall combustion efficiency was found to be between 91% and 97% [18,35].

Bio-diesel showed the same tendencies as regular diesel, though with slightly more NOx but significantly lower HC in the exhaust [18].

Another strategy discussed consisted of keeping the diesel injection constant (5% energy basis) and varying the ammonia/air concentration, so ammonia was the primary fuel. The test showed that it is feasible to ignite large amounts of ammonia with a little amount of diesel spray. They achieved the same power compared to straight diesel operation, however, at different conditions. In terms of fuel efficiency (NH3 slip) and emissions the results were very poor. The leaner the ammonia-air mixture the more incomplete combustion was present because the mixture was to lean to facilitate successful combustion and flame propagation [18,35].

### 1.4.2.2 *Alternative fuels and ammonia*

[3] applied fuels of higher cetane rating (amyl nitrate 100 +), and CI combustion with ammonia was achievable at compression ratios as low as 12:1. A mixture of 10% dimethyl hydrazine and ammonia was also tried which could facilitate combustion at a compression ratio of 23.2:1, other mixtures resulted in unwanted reaction or deposit build ups. By direct injection of ammonia (66℃ air intake, 100℃ injectors) they introduced hydrogen (6-10%), acetylene (20%) or ether (15-20%) in the air intake and managed to achieved combustion at compression ratios of 21:1, 21:1 and 16:1, respectively[3].

A study with direct injection of DME/ammonia mixtures in a small CI engine demonstrated that successful combustion could be obtained. Thus, the more ammonia in the mixture the more retardation of the injection was needed. With a mixture of 60% ammonia it should be injected at 340 to 90 BTDC. The more ammonia that was present in the mixture the more HCCI like combustion characteristics was seen. Also less power and increased cycle to cycle variation were obtained, compared to 100% DME. Furthermore, HC, CO and $NO_x$ emissions increased as a result of higher ammonia content in the mixture, due to lower combustion temperatures and more fuel $NO_x$ [36].

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## 2. Discussion and perspectivation

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Ammonias fuel properties are causing difficulties when used in ICE's. These properties, are summarized in Table 1. Some of the property related issues have, in some investigations, been solved by mechanical means. Minimum ignition energy has been proved to be possible to overcome by implementing of a new ignition system and/or adding of a second fuel. Properties like flame velocity has only been possible to change to a proper degree with the addition of a combustion promoter. Thereby not making an engine fueled by ammonia alone favorable. Hydrogen has showed excellent characteristics in improving combustion of ammonia. Other combustion promoters like diesel and gasoline have also showed promising results, though at higher quantities, and not in full operating ranges. It is also seen that engine modification to a certain degree is a necessity, when using fuel-blends.

The vast majority of experiments found in the literature tested SI-engines. However, some have also managed to achieve satisfactory combustion using CI-engines. In terms of compression ratio, speed and load a general tendency from the literature is observed for both SI and CI. High compression ratios, low speeds and high loads are preferable for ammonia fueled engines. All those tendencies are primarily due to ammonia's low flame speed.

Successful implementation of ammonia is not a question of engine technology alone. The implementation must be seen in relation to the size of the change in the infrastructure, technology and expenses.

Passenger vehicles is a large implementation area, which need a large re-structuring of the present fuel supply system for the technology to be a success. Additional cons for this area is ammonias low energy density, not promoting it as a first choice for a small vehicle. Engine tests though showed good results

for an ammonia fueled SI-engine with small amount of hydrogen. However, also big variation in speeds and loads are present in a passenger vehicle. At idle, very low speeds and at high speeds, hydrogen or another power resource would be needed. Thereby making the addition of a hydrogen tank and/or advanced cracker equipment necessary onboard. Safety issues of onboard ammonia might be avoided with the use of metal amine complexes, but still very strict emission standards for the emission of ammonia exist. Ammonia slip can, however, be removed with the use of SCR after treatment when present in small amounts. At larger quantities it could be problematic and requires the implementation of an ammonia trap.

Marine engines fueled by ammonia with pilot fuel injection of diesel or other high-cetane fuels, could be a feasible application in the near future. Such engines have a large displacement volume and are operated at a constant low speed with high loads (supercharged), making them favorable for ammonia combustion. Additionally, dual-fuel marine-engines fueled by alternatives fuels like LPG already exist [39], and since ammonias physical properties are somewhat similar with LPG, experience from these engines could help accelerate the implementation of ammonia in marine engines. Ammonia carriers already have experience with handling and storage of ammonia, and could thereby benefit in terms of lower $CO_2$ emissions and economic savings from using already on-board fuel by implementation of ammonia fueled engines. As described in section 2 in case of an ammonia slip, ammonia will quickly evaporate and ascend into the atmosphere and the toxicity may therefore not be that large of a concern in this sector and safety could be easier to obtain.

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