Ammonia as fuel for internal combustion engines?
An evaluation of the feasibility of using nitrogen-based fuels in ICE.

Master’s Thesis in Sustainable Energy Systems

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Department of Applied Mechanics
Division of Combustion
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Cover:
Buses in Belgium during World War II, fuelled by ammonia [Kroch E.].

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ABSTRACT

Although alternative fuels are being widely discussed for Internal Combustion Engines (ICE), little attention and knowledge is available on nitrogen based fuel. An interesting idea is if it’s possible get into the world’s natural nitrogen cycle, instead of the carbon cycle. That means capturing nitrogen in a similar, but easier fashion as capturing CO₂ from air. Therefore, the aim of the study is to investigate nitrogen based fuels to be used in existing ICE with as small modifications of the engine design as possible.

The criteria of nitrogen based, closed loop produced fuel compatible with the design of an existing ICE utilizing small design modifications would be a breakthrough in the global vehicle fleet.

A theoretical study was conducted in order to investigate the possibility of using nitrogen-based fuels in internal combustion engines. This idea prompted up since ammonia has been used as fuel for buses in Belgium during World War II [Kroch E].

Modern time issues such as climate change and depletion of fossil fuels could be solved by using a possible carbon-free nitrogen-based fuel. There are several nitrogen based fuel/fuel mixtures but not all are suitable for use in existing engine designs since many of these are aimed for use as rocket fuel. Our judgement is that ammonia, mainly used in dual fuel concepts, is the only convenient nitrogen based fuel for possible use in internal combustion engines in an reasonable future unless a major scientific breakthrough occurs.

Ammonia is today mainly produced from natural gas that emits a large amount of carbon dioxide when combusted. It is thus more convenient to use natural gas direct in a natural gas vehicle rather than producing ammonia of it.

Alternative production processes based on sustainable sources, i.e. solar and wind (electricity) can’t compete economically with hydrocarbons. A possible competitive carbon-neutral production method for future is to produce ammonia by biomass gasification that would enable almost zero carbon emission propulsion when considering Well-To-Tank. Using biomass for ammonia is better than using it for bio-fuel (hydrocarbon) production considering corn as feedstock. This is due to the larger amount of corn needed for bio-fuel production compared to ammonia production.

A future use of biomass for ammonia production opens a window of opportunity to realize a carbon-free Well-To-Wheel chain.

There are no engines currently that can run on ammonia, or ammonia as dual-fuel, at today’s standards and with the same operating conditions. The work performed are rather at research level, mainly as fuel research on Cooperative Fuel Research (CFR)
engines, and have some way to go before being possible for engine application in transport vehicles. There is no engine architecture at present that supports ammonia as fuel.

Ammonia as fuel for internal combustion engines is not possible in the near-term future if a carbon-free Well-To-Wheel chain is required. It might be possible, if further research is conducted in future. Nitrogen based fuels do not seem to be an alternative for low Green House Gas (GHG) emissions in automotive engines. Currently, only ammonia seems feasible as fuel in engines. Being locally “low-carbon”, meaning emitting no or low GHG emissions, it cannot compete on the total Well-to-Wheel chain. Additionally there is a large gap in the engine technology and application to meet todays and future requirements.

Key words: ammonia, nitrogen based fuel, internal combustion engine, well-to-wheel, well-to-tank, ammonia production, carbon-free, fuel, hydrogen, Haber-Bosch, electrolysis
APPENDIX I (Search methods to find possible nitrogen based fuels)

APPENDIX II (Ammonia’s compatibility with infrastructure)
Preface

In this study, the possibility of using nitrogen based fuels compatible with existing engine concepts/designs, i.e. with no major change of the industrial structure, was investigated. The work has been carried out from January 2014 to June 2014. This project is an initial study by Volvo Car Corporation to investigate if it is possible to find a fuel in the natural nitrogen cycle, i.e. based on nitrogen instead of carbon, in order to reduce CO$_2$ emissions (GHG) in transport vehicles. The study was carried out at Volvo Car Corporation in Sweden, with literature search conducted at Chalmers university’s library. This study was financed by Volvo Car Corporation.

The project has been carried out with the help of Mr Lars-Olof Carlsson as supervisor and with Dr Andreas Hinz as the champion of this topic. Examiner at Chalmers University of Technology is Professor Ingemar Denbratt. Their role in this study has been appreciated very much; this study could never have been conducted without their help and professionalism.

Gothenburg, Sweden June 2014

Emtiaz Ali Brohi
<table>
<thead>
<tr>
<th>Notations</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>ASU</td>
<td>Air Separation Unit</td>
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<tr>
<td>CCS</td>
<td>Carbon Capture and Storage</td>
</tr>
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<td>CI Engine</td>
<td>Compression-Ignition Engine</td>
</tr>
<tr>
<td>CNG</td>
<td>Compressed Natural gas</td>
</tr>
<tr>
<td>EHB</td>
<td>Electrolysis with Haber-Bosch process</td>
</tr>
<tr>
<td>GHG</td>
<td>Greenhouse gases</td>
</tr>
<tr>
<td>ICE</td>
<td>Internal Combustion Engine</td>
</tr>
<tr>
<td>MMH</td>
<td>Monomethylhydrazine</td>
</tr>
<tr>
<td>OTEC</td>
<td>Ocean Thermal Energy Conversion</td>
</tr>
<tr>
<td>SI Engine</td>
<td>Spark-Ignition Engine</td>
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<tr>
<td>SMR</td>
<td>Steam Methane Reforming</td>
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<td>SSAS</td>
<td>Solid State Ammonia Synthesis</td>
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<td>TTW</td>
<td>Tank-to-Wheel</td>
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<tr>
<td>UDMH</td>
<td>Unsymmetrical Dimethylhydrazine</td>
</tr>
<tr>
<td>WTT</td>
<td>Well-to-Tank</td>
</tr>
<tr>
<td>WTW</td>
<td>Well-to-Wheel</td>
</tr>
</tbody>
</table>
1 Introduction

Fossil fuel as an energy source is not a sustainable solution to future energy requirements. The reason of fossil fuels being the primary fuel is the cheap price of it, which has led to a technological lock-in.

It has the disadvantage of being a finite source and also issues with security of supply because of the continuously high level of demand for it.

Other issues contributing to the desire of replacing fossil fuels are such as the on-going climate change that has led to an increase in global temperature and its related environmental effects, where the main perpetrator is Green House Gases (GHG) that forms a vapour blanket in the atmosphere which traps the heat, leading to the global temperature increase. It is an important issue since increasing the amount of GHG in the atmosphere compromises the ability of future generations to have the same living standard as we do today.

The major GHG that is emitted mass basis is carbon dioxide, which is emitted by the use of fossil fuels. This has led to CO₂ taxes being implemented that increase the price of fossil fuels, which might result in earlier implementation of alternative fuels than expected.

The use of fossil fuels in the transport sector have increased the global CO₂ emissions from the transport sector with 45% from year 1970-2005 and analysts estimate that CO₂ emissions from year 2007-2030 will increase with approximately 40% [OECD (2010)]. This increase in carbon emission from the transport sector has prompted countries around the world to react, where the US President Barack Obama has set a CO₂ emission target of 70-80 g/km for year 2025. The CO₂ emission targets set for year 2030 may be as low as 60 g/km [Euractiv].

Replacing fossil fuels with alternative and renewable fuels will eradicate/decrease the issue of carbon emissions and support a sustainable future.

One option that has been put forward to counter the increase of carbon emissions is the use of bio-fuels, but it may have its side effects when considering deforestation, emissions from pesticide use and also loss of carbon stock.

Another option is ammonia that is carbon-free and can be handled with the existing technology and infrastructure in same manner as propane is handled.

This lead to the idea if it is possible to find a fuel in the natural nitrogen cycle, instead of the carbon cycle, as a way to reduce the GHG emissions.
2 Background

Ammonia has been used as fuel in vehicles during World War II. Belgium’s then transport department was informed in 1942 that diesel fuel would not be available due to the on-going war [Kroch E]. The bus passengers had increased with 30% during the war time and engineers had to find a solution to substitute this shortage of diesel fuel. Best option was the use of coal gas but it was not feasible due to its low energy content and would require large storage volumes. This resulted in blending coal gas with ammonia as fuel for buses, where coal gas acts as a combustion promoter due to ammonia’s reluctance to combustion.

These buses were scrapped as soon as fossil fuels became readily available again.

Ammonia as an area for fuel research was a result of the US military realizing that 65% of the total tonnage required for combat and transport operations during war time consisted of fuels and lubricants [Garabedian, Charles G., Johnsson J (1965)]. The military conducted research for alternative fuels. Their research idea was to build mobile nuclear reactors and thereby produce ammonia locally to fuel their vehicles. A locally produced fuel would decrease their transport costs and increase their independence towards third parties. These mobile reactors were meant to be applicable in 1980:s, but were never realized for unknown reasons.

Alternative fuels have been desired previously to decrease the dependency from fossil oil and the reduction of transport costs, but today’s main concerns are the carbon emissions being emitted and to it related climate changes. The search for alternative fuels (ammonia in this case) paused for a while after 1960:s, but is becoming an interesting area of research again.

Above information prompted the idea of investigating if it is possible to leave the carbon based fuels and find a fuel from a “natural” nitrogen cycle that could propel our vehicles without any larger modifications of the internal combustion engine design.
3 Nitrogen based fuels

A literature search was conducted in order to find possible nitrogen based fuels. See appendix I for search strategies and results.

Generally, the literature search for fuels based on Nitrogen didn’t result in many references. There were fuels from highly specialized applications like space and aero devices/engines for power generation and others that were researched at very basic level as shown in Table 3.1.

Fuels aimed for use in highly specialized applications are in solid state and don’t have the capability of working under a wide operational range, but work more like a gas turbine that can operate at few specific loads. An ICE is able to operate at any load depending on how much load is applied by using the gas pedal while gas turbines have fewer fixed load points that it can operate at, it is thus less adjustable. These solid state fuels are suitable for use in such as gas turbines/rocket engines where the fuel input is almost at its maximum the whole time and is not easily variable as an ICE where fuel input is easily adjusted with driving patterns. Other fuels are at very basic research levels where obtaining just a reaction has been the goal.

Table 3.1 Highly specialized application fuels and basic research level fuels

<table>
<thead>
<tr>
<th>Fuel mixture</th>
<th>Chemical formula</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonium Perchlorate + Trimethylammonium perchlorate</td>
<td>NH₄ClO₄+C₁₇H₂₆ClN₃O₆S</td>
<td>Basic research level; Combustion</td>
</tr>
<tr>
<td>Ammonium nitrate + Ammonia</td>
<td>NH₄NO₃+NH₃</td>
<td>IC-engines, research at very basic level; Gas turbines</td>
</tr>
<tr>
<td>Hydrazine+ MMH/UDMH+ hydrazine hydrate+urea/ammonia+ metal hydride</td>
<td>2N₂H₄+CH₃(NH)NH₂/C₂H₈N₂+H₆N₂O₆+CO(NH₂)₂ / N H₃ +metal hydride</td>
<td>Basic research level; Engines (water-, land, air based)</td>
</tr>
<tr>
<td>Hydrazine/UDMH/ MMH+NO₂</td>
<td>N₂H₄/C₂H₈N₂ / CH₃(NH)NH₂+NO</td>
<td>Missile Propellant</td>
</tr>
</tbody>
</table>
A number of “reasonable” fuels were selected from the literature search to propel vehicles. These fuels are presented in Table 3.2 and discussed thereafter.

Table 3.2  List of "reasonable" Nitrogen based fuels from literature survey.

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Chemical formula</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonia</td>
<td>NH₃</td>
<td>SI-engine</td>
</tr>
<tr>
<td>Ammonia in dual-fuel applications</td>
<td>NH₃+additional fuels</td>
<td>SI &amp; CI engine</td>
</tr>
<tr>
<td>Hydrazine(monopropellant)</td>
<td>N₂H₄</td>
<td>Fuel-cell, Rocket propellant</td>
</tr>
<tr>
<td>Liquid Nitrogen</td>
<td>N₂</td>
<td>Expansion Engine</td>
</tr>
</tbody>
</table>

3.1 Ammonia

Ammonia as a fuel has the benefit of being carbon-free and can be handled in the existing infrastructure (see Appendix II).

Internal combustion engines, both Spark Ignition and Compression Ignition, have been tested with ammonia as fuel, but ammonia has it’s disadvantages as a fuel.

Presently the disadvantages related to ammonia as fuel for an internal combustion engine are [Kong S.C, Gross C.W., (2012)]:

- Very high auto-ignition temperature (651 °C)
- Low flame speed
- High heat of vaporization
- Narrow flammability limits (16-25% by volume in air)
- Toxic
3.2 Ammonia in Dual-fuel applications

Ammonia can be mixed with other substances to overcome its disadvantages as a fuel, both for Compression-Ignition (CI) and Spark-Ignition (SI) engines.

Possible fuels to be used in SI-engines in addition to ammonia are hydrogen and gasoline while additional fuels for use in CI-engines are Dimethyl Ether (DME) and (bio)diesel.

Gaseous fuels are more preferred for use in SI-engines since it can be introduced into the engine with gaseous ammonia [Garabedian, Charles G., Johnsson J (1965)], while fuels with higher Cetane number are better for use in CI-engines due to the better ignition characteristics [Kong S., Reiter A.J (2010)].

3.3 Hydrazine

Hydrazine is mainly used as a foaming-agent, in pharmaceuticals and as rocket fuel [Wikipedia_hydrazine]. It has an ammonia-like odour and burns with a colourless flame.

In military application, the jet fighter F-16 uses hydrazine to power its emergency unit. Furthermore, it is used as a propellant for space vehicles. However, it is extremely unstable and highly toxic. An extremely unstable fuel is not suitable for direct use in IC engines and toxicity is another disadvantage that creates problems to handle this fuel.

3.4 Liquid nitrogen

Another nitrogen based fuel is liquid nitrogen that can be used as “fuel” that generates work by expansion. Storage temperature for liquid nitrogen at ambient pressure is 77 Kelvin, enabling the capability of generating work by expanding at temperature differences from storage temperature (77 K) to ambient (300 K) [Knowlen C., Williams J., Mattick A.T, Deparis H., Hertzberg A. (1997)].

It works by having liquid nitrogen stored in vessel that is pumped into economizer and a heat-exchanger thereafter. The nitrogen expands in the heat-exchanger that utilizes the ambient air as heat source. Gaseous nitrogen expands further in the turbine shaped engine to generate work and runs thereafter through the economizer before being released as exhaust.

This type of engines utilizes the temperature difference where work is generated by expansion of nitrogen from liquid to gaseous phase.

Energy density of compressed air is lower than liquid nitrogen and these two alternatives have the disadvantage of requiring a large volume container [Knowlen C. Mattick A.T, Bruckner A.P, Hertzberg A. (1998)]. Lower energy density and high storage pressure of compressed air results in liquid nitrogen being more favoured.

A liquid nitrogen vehicle with an onboard vessel containing 350 litres liquid nitrogen can provide a driving range as an ICE vehicle [Knowlen C. Mattick A.T, Bruckner A.P, Hertzberg A. (1998)]. Liquid nitrogen as fuel can be useful for those interested in expansion engines, but it would even then be more suited for use in a hybrid solution due to lower energy density compared to gasoline.
3.5 Basic research fuels and specialized application fuels

The fuels aimed for highly specialized applications and those at very basic research level are based on mixing different substances in order to obtain a nitrogen based fuel mixture. A large amount of chemical reactions can be obtained just by using a fuel and an oxidizer.

Some of these are more aimed for use as a rocket fuel and others have just been researched at basic level in order to acquire a fuel that achieves combustion. These fuels are not applicable in an ICE or have a long way to go before becoming potential fuels for use in an ICE. Fuel for an ICE requires advanced properties rather than just combustion as in the case of some of these fuel mixtures. Some of the fuels/fuel mixtures are discarded due to fuel mixtures being more aimed as a rocket fuel or researched at very basic level. The discarded fuels are briefly described in the following parts.

3.5.1 Highly specialized application fuels and basic research level fuels

The Ammonium perchlorate/Trimethylammonium perchlorate (TMAP) flame was only stable to some extent at very low concentrations of TMAP in a nitrogen atmosphere [Jain S.R, Adiga K.C (1982)]. This mixture is unstable especially at stoichiometry where burning becomes erratic and even small explosions occur. Melting point of the mixture changes with different concentrations and a decrease in the melting point produce a decrease in the sensitivity of an explosive. This mixture is not suitable for use in internal combustion engines due to its instability and that the present research has been done at a very basic level only containing a combustion chamber.

The Hydrazine/UDMH/ MMH+NO₂ mixture is an intended fuel for missile propulsion [Perlee H., Imhof A., Zabatekia M]. The mixture ignited when in contact with nitrogen tetroxide producing a white cloud of fine particles, but an ignition did not take place at every test. An ignition occurred at ambient temperature (25 °C) when the mixture came in contact with nitrogen tetroxide. It is more suitable for use as missile propellant and is not suitable for use in an ICE due to the spontaneous ignition at ambient temperature. This present research is at very basic level and a successful ignition is not observed at every test.

3.5.2 Basic research level fuels

From a patent publication [Adelman Barnet R (2008)] the Nitrogen based fuel (Hydrazine⁺ MMH/UDMH+ hydrazine hydrate⁺ urea/ammonia + metal hydride) is known. It has only a simple drawing where it only shows a fuel that reaches the input of the engine. This patent is about introducing a mixture of fuel to an engine and no specific engines have been suggested. It only names possible fuels that can be mixed in order to obtain one complete fuel and not specifically which ones. Also, it seems that none of the suggested fuels has been tested at any level.

Further, an ammonia nitrate (which is a salt) mixture has been tested in order to overcome difficulties with having ammonia as a fuel [Ganley C. G, Bowery M.S (2011)]. This fuel utilizes a dual-fuel approach to facilitate the combustion of
ammonia. Tests were conducted on a free-burning propane flame and combustion without the help of a propane flame has not been tested. This fuel is not considered as a complete fuel and therefore not suitable for use in an ICE. Another disadvantage is that this mixture is presently at a very basic level. It has yet not been tested in any engine model.

The fuel mixtures above will not be investigated any further as they are not applicable in existing engines. However, some might become interesting in the long-term future, but that is out of the scope of the present study.

3.6 Summary of nitrogen based fuel

Some of the reviewed fuels are more intended as fuels for rocket propulsion and others have been researched at a very basic level where achieving a combustion reaction in general has been the goal.

A modern fuel for a state-of-the-art combustion engine has to be able to operate within the conditions of the existing engine design. It should not be a too fast reaction and not a slow, but fulfil the operation characteristics for defined by the existing engine design.

These fuel mixtures are not capable for use in existing engine designs:

- Liquid nitrogen engines are at laboratory stage and the concept of liquid nitrogen as fuel is not suitable for use in existing engine designs.
- Hydrazine is extremely unstable which makes it unsuitable for direct use in ICE and highly toxic that requires cautious handling.

There is presently no nitrogen based fuel that is suitable for the possible use in an ICE except ammonia. Thus, for nitrogen based fuels, the core is ammonia that can be blended with other fuels in order to facilitate combustion under controlled conditions.
4 Well-To-Tank Considerations (Ammonia)

Ammonia combustion emits only water and nitrogen, which makes it a carbon-free fuel when considering Tank-To-Wheel (TTW). Production method(s) of ammonia will determine if it is carbon-free when considering Well-To-Tank (WTW). A carbon-free production method would enable a carbon-free fuel since the TTW process itself does not emit any carbon.

4.1 Production of ammonia

Ammonia production method(s) have to be considered in order to find an optimal way of producing ammonia. Production of ammonia is a vital part for use of it as a carbon-free fuel.

4.1.1 Current, main stream, production method

Approximately 70% of the ammonia globally produced is currently using natural gas as starting point, while the remaining 30% use mostly coal [Bartels J.R. (2008)]. The price of ammonia depends therefore on the natural gas price. In turn, the ammonia price affects the food prices because of its major use as a fertilizer in the farming industry.

Today, most of the globally available ammonia is produced by the Haber-Bosch process where hydrogen and nitrogen are combined over an iron oxide catalyst. The catalytic converter in the Haber-Bosch process operates at 380-500 °C and is temperature controlled by the fed gas being heated in addition to the emerging reaction heat from the exothermic synthesis of ammonia (46.22 kJ/mol). An overview of the Haber-Bosch process is shown in the Figure 4.1 where natural gas and water is mixed in order to form water vapour and thereby hydrogen. In this process, natural gas functions as both, a fuel and hydrogen source.

![Figure 4.1 Schematic picture of Haber-Bosch process.](Fertilizer)

An approximate energy of 30 GJ of natural gas is needed to produce one ton of ammonia [Zamfirescu C., Dincer I. (2010)] using the Haber-Bosch process. In addition, ammonia produced by utilizing natural gas emits approximately 1.87 tonnes of CO₂ per ton ammonia produced. This is a rather large amount of carbon emissions and therefore the Haber-Bosch process is not a sustainable method for the production of ammonia with the target of using ammonia as a fuel. Other measures have to be found in order to achieve a sustainable, carbon emission free ammonia production.
4.1.2 Alternative ammonia production methods

Alternative ammonia production methods have to be found in order to obtain a carbon free Well-To-Wheel process chain.

Fossil fuels are presently dominating the ammonia production due to the low production cost level related to it. However, ammonia can be produced from renewable sources. Ammonia produced by using water as the solely hydrogen source can be feasible when utilizing electrolysis [Holbrook J.H., Leighty W (2009)].

Electrolytic plants have been operated previously to produce ammonia, but suffered from the price of electricity consumed and the cost for the process equipment.

Ammonia production via electrolysis has been used in several countries where the electricity was obtained from hydropower. These plants were built in the 1940’s and dismantled in 1980’s [Holbrook J.H., Leighty W (2009)]. The cost of production, maintenance of ageing facilities and low efficiency of electrolysers made them unattractive. Ten hydro plants where operated globally whereby three in Zimbabwe, Peru and Egypt may still be in operation.

Another approach is the thermo-chemical ammonia synthesis where a two-stage thermo-chemical process is used to decrease the energy requirement and production cost. Al₂O₃ is reduced in an endothermic process to Aluminium Nitride (AlN) and CO₂ with nitrogen and a carbon sources. [Bartels J.R. (2008)] AlN is thereafter combined, through an exothermic process, with water to produce ammonia and Al₂O₃.

This Al₂O₃ can be re-used in the first process and the CO produced can be used for methanol production. A carbon-free source is necessary when reducing Al₂O₃ to AlN and CO₂ in order to obtain a carbon-free methanol production.

A second approach is Solid State Ammonia Synthesis (SSAS) where a solid state electrochemical process is used to produce ammonia from water, nitrogen and electricity. SSAS is suitable for use with renewable sources.

It uses between 7000-8000 kWh per produced ton of NH₃ compared to EHB (Electrolysis plus Haber-Bosch) process that uses 12000 kWh per produced ton of NH₃ [Bartels J.R. (2008)]. Electrolysis including the subsequent Haber-Bosch process obtains hydrogen from electrolysis using water and electricity as an energy source.

Different sources for producing ammonia are shown in the Figure 4.2. Steam methane reforming (SMR) uses methane for obtaining hydrogen from hydrocarbon chain while gasification is used for coal and biomass.

Electricity sources can be used for electrolysis in combination with an Air Separation Unit (ASU) that supplies hydrogen and nitrogen to the Haber-Bosch synthesis loop (synloop).

Nuclear and solar based ammonia production processes include a high-temperature heat source and can therefore use a thermo-chemical process step to obtain hydrogen. The thermo-chemical process step is more efficient and economically beneficial compared to electrolysis, but some electricity would still be needed to power the ASU. End products are pure oxygen and ammonia.
Coal gasification contributes to an accumulation of carbon emissions, but almost no carbon will be emitted if coal gasification with sequestration is used. This option with sequestration transfers the carbon issue into the future rather than solving it and is judged to be not a sustainable production method. In general, producing ammonia by processes using fossil fuels such as natural gas and coal as a starting point are judged to be not a sustainable method due to the large amount of carbon being emitted.

4.2 Discussion on ammonia feasibility

Different methods of ammonia production are compared to other energy carriers such as natural gas, synthetic gasoline produced via electricity and biomass. This is done in order to find an optimal way of ammonia production.

Most of the ammonia produced today uses natural gas as starting point and it might be a better option to use the natural gas direct in the vehicle instead. A comparison is conducted in chapter 4.2.1 in order to compare an average vehicle fuelled by either ammonia or natural gas. The comparison is based on respective level of CO$_2$ emissions for each fuel considering the same driving range for both vehicles.

As previously discussed, see chapter 4.1.2, ammonia can also be produced using electricity as energy source. In chapter 4.2.2 it will be considered if the electricity is better utilized to produce synthetic gasoline rather than ammonia.

A third option to produce ammonia is by biomass gasification and a comparison, see chapter 4.2.3, is conducted for this option to determine if biomass is better utilized as a source for bio-fuel production or ammonia production.
4.2.1 Comparison of natural gas for ammonia production or direct use in a vehicle

A comparison of using natural gas direct in a vehicle or using the natural gas to produce ammonia via the Haber-Bosch process must be conducted in order to determine which of these emits less carbon. It is assumed that the natural gas from well to the Haber-Bosch process or to the vehicle tank emits equal amount of possible carbon emissions and this part is therefore not taken into consideration. Carbon emissions emitted from the Haber-Bosch process and the vehicles Tank-To-Wheel will be considered.

Data known:
Carbon emissions from producing one ton ammonia from natural gas are 1.87 ton.
Ammonia energy content is: 18.8 MJ/kg
Compressed natural gas (CNG) energy content is: 50 MJ/kg [Supple D.]

An average natural gas vehicle is considered to have a fuel consumption of 1.87 MJ/km and carbon emissions of 105.3 g CO₂/km [European Commission (2011)]. These both values for fuel consumption and carbon emissions are an average and do not represent all driving styles and driving patterns. The real carbon emission will certainly be higher due to cold starts, start & stops etc.

A possible ammonia fuelled vehicle is also considered for comparison, where it consumes same amount of energy per km as the average natural gas vehicle. Ammonia fuelled vehicle might not have the same efficiency/fuel consumption as a natural gas vehicle and this number is quite positive for an ammonia fuelled vehicle. Values obtained for ammonia will be the best possible conditions which might not be so in real case.

This will make one ton of ammonia (18800 MJ) to be sufficient for a driving range of:
18800/1.87 = 10053 km
One ton of ammonia using natural gas as starting point emits 1.87 ton CO₂ and is sufficient for a driving range of 10053 km, but using natural gas direct in the vehicle to drive the same distance will emit:
105.3* 10053= 1058 kg CO₂ ← which is 800 kg less than from the production of
1 ton NH₃
This shows that assuming an ammonia vehicle with same energy consumption as an average natural gas vehicle will emit approximately 800 kg more CO₂. Using natural gas to produce one ton ammonia emits approximately 1.87 ton CO₂ and would have a driving range of 10053 km while driving the same range with natural gas saves approximately 800 kg CO₂. Using natural gas in the vehicle is a better option than producing ammonia of it.

Producing ammonia by using natural gas as starting point is not a competitive method and other alternatives have to be found.
4.2.2 Electricity for ammonia production compared to gasoline production

Using electricity for ammonia production or synthetic gasoline will be compared in order to determine if using electricity for ammonia production is competitive.

A proposed system is shown in the Figure 4.3 based on proven technologies that are optimized to work with other sub-systems and for low cost operation [Lackner K.: Closing the carbon cycle]. Only air capture technology is at laboratory stage, but another option is to capture carbon from exhaust emitted from power plants.

Advanced automation and control strategies were the biggest challenge and a negative aspect is that mass production can only be feasible if the operator can be able to control thousands of units.

Figure 4.3  Hydrocarbon production through electricity obtained from solar power.

Calculations are based on Figure 4.3.

The input energy is 9.2 GJ that produces 34 gallons (128.7 L) of synthetic gasoline, which has an energy content of approximately 4.4 GJ.

One ton of ammonia is chosen for comparison because of simplicity.

Energy content in one ton ammonia is 18.8 GJ and producing synthetic gasoline with the same energy content requires that:

\[
18.8 / 4.4 = 4.27 \text{ times more energy needs to be fed in}
\]

Energy input to deliver the same amount of energy as one ton ammonia is:

\[
9.2 \text{ GJ} \times 4.27 = 39.3 \text{ GJ}
\]

Energy amount needed to produce synthetic gasoline with an energy content of 18.8 GJ (same as one ton ammonia) is converted in kWh in order to compare it with the electricity needed to produce one ton ammonia with Electrolysis plus Haber-Bosch process:
This amount of energy (39.3 GJ) equals to 10,912 kWh.

Energy consumption for this process is almost the same as with Electrolysis plus Haber-Bosch process (12,000 kWh).

The result shows that the amount of energy needed to produce synthetic gasoline having energy content of 18.8 GJ (which is the energy content of one ton ammonia) is less than energy needed for production of one ton of ammonia. Approximately 800 kWh is saved by producing synthetic gasoline than producing ammonia via Electrolysis plus Haber-Bosch process that consumes 12,000 kWh per produced ton of NH₃.

4.2.3 Biomass for ammonia production compared to bio-fuel production

Using biomass for ammonia production will be compared to using biomass for ethanol production.

The world’s first biomass to ammonia plant has been introduced in the United States (Iowa State) [Schill S.R].

The amount of corn cob to produce one ton ammonia is 3 ton [Schill S.R]

Energy content of corn is 18.5 MJ/kg  [Zych D., (2008)]

Energy content of ethanol is 20 MJ/L [Wikipedia biofuel]

The amount of corn needed to produce one litre ethanol is 2.15 kg [Wikipedia ethanol]

Energy needed to produce one ton ammonia that needs 3000 kg corn with an energy content of 18.5 MJ/kg result in a total energy of:

\[
3000 \text{ kg} \times 18.5 \text{ MJ/kg} = 55,500 \text{ MJ}
\]

This amount of energy is converted into litres of ethanol, where one litre of ethanol contains 20 MJ:

\[
\frac{55,500 \text{ MJ}}{20 \text{ MJ/L}} = 2775 \text{ L}
\]

The amount of corn needed to produce 2775 litres of ethanol is:

\[
2775 \text{ L} \times 2.15 \text{ kg/L} = 5962 \text{ kg corn}
\]

The comparison shows that using biomass (corn cob in this case) for ammonia production requires only half of the mass compared to bio-fuel. Almost 3 ton more corn cob is needed to produce bio-fuel instead of ammonia. Producing ammonia from biomass is a better option than producing bio-fuels and would use less area.

Using biomass in a sustainable way to produce bio-fuels has the limit to substitute 15-30% of the fossil fuels [ERTRAC (2014)], which shows that biomass can be used to a certain limit in a sustainable way.

Producing ammonia by biomass gasification and using it as a possible fuel might not be able to replace all fossil fuels being used in the transport sector today, but it does open a window of opportunity to replace fossil fuels to a certain extent.
4.3 Summary

The comparison conducted in chapter 4.2.1 resulted in less carbon emissions being emitted when natural gas is directly used in the vehicle rather than using natural gas for ammonia production that is used as fuel in the vehicle.

Using electricity for synthetic gasoline production proved to be a better option than producing ammonia according to the comparison conducted in chapter 4.2.2. The electricity needed for options, producing synthetic gasoline or ammonia, does not differ much, but it is more convenient to produce synthetic gasoline instead of ammonia due to simplicity regarding infrastructure and existing combustion engine designs. Electricity producing sources that are intended for ammonia production such as Ocean Thermal Energy Conversion (OTEC), nuclear power, solar power and wind power is therefore not interesting for ammonia production.

A comparison between using biomass for bio-fuel production or ammonia production was conducted in chapter 4.2.3 and resulted in ammonia being a better option than bio-fuels. This is due to the larger content (almost double) of biomass needed to produce bio-fuels than the amount needed for ammonia production in order to obtain same amount of energy.

These comparisons resulted in natural gas and electricity for ammonia production being not competitive. Natural gas is better utilized when used directly in a natural gas vehicle and electricity is better utilized when producing synthetic gasoline instead of ammonia. Biomass is the only carbon-free option that is better utilized when used for ammonia production than producing bio-fuels of it. Nor does biomass transfer the carbon emission issue into the future, but his technology is not commercially available yet. Biomass does create the possibility of a carbon-free ammonia production method in near future.
5 Automotive propulsion on nitrogen-based fuels

5.1 Possible ammonia based propulsion

Ammonia was the core fuel for automotive propulsion of the nitrogen based fuel studied. Only ammonia as a fuel or ammonia dual fuel solutions for both SI-engines and CI-engines have been researched.

Different fuels can be blended with ammonia for SI-engines and CI-engines in order to facilitate the combustion.

Categorizing of the possible fuel mixtures for use in different propulsion technologies such as fuel cells, SI-engines and CI-engines is seen in Figure 5.1.

Figure 5.1 The figure shows different technologies paths to be used for vehicular propulsion using nitrogen based fuels.
5.2 Ammonia in ICE

Ammonia affects the CI-engine and SI-engine operation differently where a high auto-ignition temperature, narrow flammability limits creates problem for ammonia use as fuel in a CI-engine and high latent heat of vaporization causes large drops in gas temperature at the time of injection which complicates it even further.

The use of ammonia in SI-engines is limited by narrow flammability limits and low flame speed causing incomplete combustion [Garabedian, Charles G., Johnsson J (1965)].

The fuel can be introduced into the cylinder in two different ways, i.e. port-injection or direct-injection. Port-injection displaces the air supplied to the combustion chamber and reduces thereby the volumetric efficiency of the engine. Direct-injection reduces the in-cylinder temperature significantly due to ammonia’s high latent of heat [Kong S., Zacharakis-Jutz G., Ryu K. (2013)].

Injecting liquid ammonia gives better volumetric efficiency since it does not displace the air and cools the intake mixture.

One possible way to enhance mixing and thereby facilitate combustion of ammonia is to create turbulence in the combustion chamber. However, too small swirl has no effect on the combustion whereas too high swirl affects the combustion negatively by blowing the flame out due to slow propagating ammonia flame [Pearsall, T.J. and Garabedian, C.G., (1967)].

It should also be noted that ammonia is more suitable for lower engine speeds due to its low flame speed [Cooper J.R., Crookes R.J., Mozafari A., Rose J.W. (1991)].

Different researches being conducted are presented below, some done with ICE and others on Cooperative Fuel Research (CFR) engines. CFR-engines are also called Cetane motors that are used to determine cetane number of different diesel fuels [Wikipedia Cetane].

Ammonia is corrosive to copper, copper alloys, nickel and plastics and these materials have to be avoided in an ammonia fuelled engine [Kong S.C, Gross C.W., (2012)].

5.2.1 Compression-ignition engine

5.2.1.1 Ammonia as mono-fuel

Very high compression ratios as much as 35:1 are needed for ammonia as fuel in CI-engines [Kong S. Reiter A.J (2010)]. Liquid ammonia that is used in CI-engines does not result in combustion with compression ratios high as 30:1 [Pearsall, T.J. and Garabedian, C.G., (1967)].

Only ammonia as fuel in a CI-engine is not possible due to the high compression ratios needed for ignition/combustion.
5.2.1.2 Ammonia dual-fuel

Fuels with higher cetane number are better for use with ammonia due to better ignition characteristics [Pearsall T.J., Garabedian C.G. (1967)]. Ammonia content up to 95% was feasible with only 5% diesel fuel energy basis with a John Deere engine. But optimal mixture is 40% diesel – 60% ammonia since a diesel amount large than that would limit ammonia’s flammability [Kong S.C., Reiter A.J. (2008)]. Other tests have suggested an optimal diesel content of 20-40% mass basis [Cooper J.R., Crookes R.J., Mozafari A., Rose J.W. (1991), Pearsall, T.J. and Garabedian, C.G. (1967)].

An engine tested with biodiesel and ammonia as fuel performed in same way as a diesel & ammonia with same performance characteristics [Kong S.C., (2007)]. But the operation characteristics differed when Dimethyl Ether (DME) was used with ammonia as fuel, where ammonia content up to 80% was feasible [Kong S.C, Gross C.W., (2012), Kong SC., Zacharakis-Jutz G., Ryu K. (2012)].

Engines tested with ammonia and (bio) diesel/DME as fuel are at research level and have a long way to go before becoming feasible for use in vehicles.

5.2.2 Spark-ignition engine

5.2.2.1 Ammonia as mono-fuel

Combustion of ammonia in SI-engine can be facilitated by having stronger igniters, compacted combustion chamber and longer spark plugs in order to overcome ammonia’s reluctance to combustion [Pearsall, T.J. and Garabedian, C.G., (1967)]. An improved combustion can also be achieved by supercharging [Cooper J.R., Crookes R.J., Mozafari A., Rose J.W. (1991)]. Ammonia only as fuel has also been patented by Toyota where they suggest that several plasma jet igniters arranged inside the combustion chamber or plural spark plugs that ignite the ammonia at several points will facilitate ammonia combustion [Toyota, Asian Industries, (2010)].

5.2.2.1.1 Computerized models

Catherine Duynslaegher and Rui Liu performed computerized models to study ammonia’s performance in an ICE [Duynslaegher C., Jeanmart H. Vandooren J. (2009)]. Rui Liu used the Lindstedt’s mechanism and it has been proved in previous work that large disagreement between experimental and simulated results exist when using the Lindstedt’s mechanism.

Two different computerized models were studied by Catherine Duynslaegher using Konnov’s mechanism, where ignition of ammonia was achieved by an electric arc of about 2 kV in one of the tests [Duynslaegher C. (2011)].

She observed the other model that laminar burning velocity increased with CR where a burning velocity up to 45 cm/s could be obtained with right compression ratio and equivalence ratio [Duynslaegher C., Jeanmart H. Vandooren J. (2009)].

Ammonia as the only fuel in a SI-engine has not been realized at a serious level. Suggestions have been made without any further steps to make this technology feasible in existing vehicles.
5.2.2.2 Ammonia dual-fuel

Hydrogen is able to disassociate at 400 °C and can be used as a combustion promoter with ammonia as fuel [Starkman E.S, Samuelsen G.S, (1967)]. A hydrogen content of 3-5% weight basis is the minimum amount of hydrogen to be used as combustion promoter.

An electric vehicle prototype with a 15 kW engine uses hydrogen and ammonia in order to recharge the battery in Italy, where the optimal hydrogen content at full load and half load is 7% respective 11% [Frigo S., (2012)]. Long time performance of the engine/vehicle has to be determined though. The amount of NOx is high at hydrogen content 10% and would require after-treatment [Sorensson S.C, Mørch C.S, Bjerre A. Gøttrup M.P, Schramm J. (2009)].

Having gasoline as a combustion promoter requires a compression ratio of 10:1 for optimal operation with a gasoline content of 30% [Granell S.M].

Liquid ammonia would reduce the in-cylinder temperature and thereby hinder subsequent turbulence causing deteriorated combustion and misfire. Gaseous ammonia is therefore direct-injected, where gasoline is port-injected to enhance the combustion. Idle operation requires 100% gasoline but can be reduced to as much as 20% energy basis [Kong S., Zacharakis-Jutz G., Ryu K. (2013)].

Most of the engines are Cooperative Fuel Research (CFR) engines which are used to determine the cetane rate of diesel fuels. These engines can’t be compared to existing engine designs, nor are these tested engines suitable for use in existing vehicles.

The only engine of the reviewed ones that has been implemented to a certain level is the ammonia and hydrogen engine in Italy, even if it only was used to produce electricity to re-charge the battery of the electric vehicle.

5.3 Fuel cells

Fuel cells (FC) are mentioned in order to determine if a change of technology (ICE to FC) in future can enable the use of any possible nitrogen based/ammonia based fuel.

5.3.1 Ammonia fuel cell

Ammonia harms PEM fuel cells and can just be used cracked in an Alkaline fuel cell. It is therefore used directly only in Solid Oxide Fuel Cell (SOFC) [Brown T, (2013)].

Direct ammonia high temperature solid oxide fuel cells (SOFC) are in general not suitable for transport application due to the slow start-up and brittleness of their ceramic components [Rong L., Tao S., (2010)].

This option of using ammonia fuel cell in vehicle is not possible at present, but might be feasible in future. Fuel cells would require a whole new industrial concept and require more investment in addition to sufficient time to develop a proper vehicle. Ammonia fuel cell is not suitable for use in transport and is not in the interest of this study.
5.3.2 Hydrazine fuel cell

A hydrazine fuel cell vehicle has been made by Daihatsu where hydrazine is pumped into a fuel tank and stored in a fixing member. Water from another tank is pumped into the fuel tank and dissolves the hydrazine which is then used in a fuel cell. However, hydrazine is toxic and the fuel cell has low voltage at high current density and problems with fuel permeating through the membrane [Daihatsu motor, (2009)].

Only a prototype has been developed that is used for different shows and the aim of the study is to find an engine for use in existing vehicles. The option of a fuel cell is not interesting for this study and also the maturity of the technology is questionable with certain issues such as fuel permeating and low voltage.

5.4 Summary

The literature search to find possible automotive propulsion on nitrogen based fuels resulted in several different technologies with CI-engine having ammonia only as fuel and dual fuel options where ammonia was mixed with either (bio)diesel or DME. Ammonia only as fuel and dual fuel option was also found for SI-engines where ammonia was mixed with hydrogen or gasoline. Other technologies such as direct ammonia fuel cells and hydrazine fuel cells were found, but these were not suitable for use in existing vehicles due to ammonia fuel cell not being possible for use in transport and the hydrazine fuel cell technology was questionable due to fuel permeation and low voltage. Ordinary ICE will possibly be replaced with fuel cells to a certain extent if it shows to works significantly better. A shift from ICE to fuel cell would require a whole new industrial concept and large investment. Fuel cells have not reached the technological maturity level in order to becoming commercially available and would require more time to reach that maturity level.

Only ammonia as fuel is not possible for use in CI-engines due to high compression ratios. Dual fuel options tested in CI-engines were performed at research level that has long way to go before becoming possible for use in existing engine designs. These tests were more aimed to obtain combustion rather than compatibility with existing engine designs.

Ammonia as fuel in SI-engine has not been tested at serious level to make it feasible for use in existing vehicle. Patents and computerized models have been made but no serious approach has been made lately. Previous tests have been performed using ammonia and gasoline where a diesel engine was converted into a SI-engines and the aim was to obtain combustion only.

Many of conducted tests for dual for option for SI-engines have been performed on Cooperative Fuel Research (CFR) engine, which is used to determine cetane rate of diesel fuels and is not at existing engine design level. Only engine to have been implemented to a certain level is the hydrogen and ammonia engine in Italy where it was used in a prototype. The small 15 kW engine generated electricity to re-charge the battery of the electric vehicle.

The ammonia-hydrogen engine is the only engine that has been researched at a level higher than the other options. This engine might be a better option to research further in future rather than engines that have not been researched at any “serious” level yet.


6 Discussion and conclusion

The literature search conducted to find possible nitrogen based fuels for possible use in engines resulted in only ammonia being suitable for this task. In such application ammonia is the core fuel that can be mixed with other fuels in order to facilitate combustion. Most of ammonia produced today uses natural gas as starting point and emits thus a large amount of carbon. Other methods have to be considered to obtain a sustainable way of producing ammonia. Natural gas is better utilized when used direct in the vehicle rather than producing ammonia and using it as fuel. It is better to produce synthetic gasoline than ammonia when the source of energy is electricity. Using biomass as a feedstock is the only sustainable way to produce ammonia. In this case it is to recognize that our analysis shows that using biomass (corn cob in this case) for ammonia production requires only half of the mass compared to bio-fuel production.

A literature search was conducted in order to find possible ammonia fuelled engines having preferably the same design as existing engines. It resulted in only ammonia as fuel-only and dual fuel for CI-engines and SI-engines. Only ammonia as a fuel is not possible in CI-engines due to the high compression ratios needed, but dual fuel options used by mixing ammonia with diesel, biodiesel or DME are at research level. The research conducted is primary aimed at obtaining and studying combustion of such fuel systems.

Ammonia only as fuel for SI-engines has not been used in engines having the same design as existing state-of-the-art engines. Only tests with Cooperative Fuel Research (CFR) engines or computerized models have been conducted lately. The dual fuel approach where gasoline or hydrogen is mixed with ammonia has been tested at research level with the aim of studying combustion of such fuel systems, i.e. similar to the CI-engine research. None of the engines tested has been implemented into a vehicle, except a hydrogen and ammonia engine in Italy that was installed on a prototype vehicle. The hydrogen and ammonia engine generates electricity to recharge the battery of the electric vehicle.

A recommendation for future studies would be to focus on the hydrogen and ammonia engine. Other engines tested have a long way to go before being feasible for use in existing vehicle applications. The hydrogen and ammonia engine has been implemented, even if at small scale where generating electricity has been the aim. A catalyst was used to decompose ammonia to hydrogen, which used energy from the exhaust gases. Start-up might be problematic due to that the engine has to reach certain speed and exhaust hot enough to decompose ammonia. This can be solved by having a small tank that stores extra hydrogen when the engine is running and use it at start-up. Ammonia does not contain carbon, but having ammonia and hydrogen will result in higher NOx emissions. An after-treatment must be used in order to reduce NOx being emitted into the atmosphere. Using an after-treatment such as a Selective Catalytic Reactor (SCR) is facilitated since ammonia is already onboard.

The literature search to find an ammonia fuelled engine with the same operation conditions as existing engines resulted in finding only engines being used at research level. These engines are no feasible for use in existing vehicle today. There is a long way for these engines to become compatible with existing vehicles. These engines
might become feasible in future and this study finds the ammonia and hydrogen engine capable of further research.
7 References


Daihatsu motor, (2009): Hydrazine supply device, fuel cell system utilizing the same, vehicle carrying the fuel cell system, and method of supplying hydrazine, patent EP 2043185 B1, Otsuko chemical company


Euractiv: http://www.euractiv.com/transport/eu-gears-co2-car-targets-2025-20-news-513192


Fertilizer: http://www.fertilizer101.org/sources/?storyid=15


Lackner K.: Closing the carbon cycle: Liquid fuels from air, water and sunshine, The Earth Institute, Columbia University, USA 2010


Supple D.: Units & Conversions Fact Sheet, Massachusetts Institute of technology, USA


William L. Ahlgren: The Dual-Fuel Strategy: An Energy Transition Plan, Electrical Engineering Department, California Polytechnic State Univeristy, USA 2011


Zych D., (2008): The viability of corn cobs as a bioenergy feedstock, University of Minnesota, USA 2008
Appendix I

The search methods to find nitrogen based fuels are listed below. These methods can facilitate any further research in future in order to determine if anything has changed. Searches conducted in order to find possible nitrogen based fuels.

"Nitrogen based" "fuels"; Scopus
Hits: 22
William L. Ahlgren: The Dual-Fuel Strategy: An Energy Transition Plan, Electrical Engineering Department, California Polytechnic State University, USA 2011

"Nitrogen based fuels" "engines"; Google.com

Hits: 98500
Nitrogen based fuels systems, WO 2008124034 A1

"nitrogen based" OR (carbon free) AND "fuel" AND "engine"; Scopus
Hits: 281
Ammonia/hydrogen mixtures in an SI-engine: Engine performance and analysis of a proposed fuel system, Sörrenson
Experimental results using ammonia plus hydrogen in a S.I. engine (Conference Paper), Frigo, S., Gentili, R., Ricci, G., Pozzana, G., Comotti, M.
Performance characteristics of a compression-ignition engine using direct-injection ammonia-DME mixtures (Conference Paper), Gross, C.W., Kong, S.-C.
Combustion and emissions characteristics of compression-ignition engine using dual ammonia-diesel fuel (Article), Reiter, A.J., Kong, S.-C

"nitrogen based" AND "propulsion"; Google.com
Hits: 64600
An evaluation for green propellants for an ICBM Post-Boost Propulsion System, Brian J. German, E. Caleb Branscome, School of aerospace engineering, Georgia
Institute of Technology, USA;

This article gave hint on nitrogen based fuels such as:

AMMONIUM PERCHLORATE
HYDRAZINE
MONOMETHYL HYDRAZINE
ROCKET ENGINE
TRIMETHYLAMMONIUM PERCHLORATE

trimethylammonium perchlorate fuel; Sciencedirect ** this due to trimethylammonium perchlorate found in book above
hits: 104

Combustion studies on ammonium perchlorate/trimethylammonium perchlorate mixtures, Jain

"nitrogen based" AND "propulsion" "vehicle application"; Google.com
Hits: 272
Daihatsu motor, (2009): Hydrazine supply device, fuel cell system utilizing the same, vehicle carrying the fuel cell system, and method of supplying hydrazine, patent EP 2043185 B1, Otsuko chemical company

"ammonium nitrate" "combustion" "fuel"; Google patent
Hits: 50 000

Searched "rocket propulsion fuel" and wikipedia afterwards, "external links" that directed to http://www.braeunig.us/space/propel.htm that resulted in a hint “nitrogen tetroxide” that was searched on google.com.
The search on Google with words " nitrogen tetroxide fuel"
Resulted in : FLAMMABILITY CHARACTERISTICS OF HYDRAZINE FUELS IN NITROGEN TETROXIDE ATMOSPHERES

"carbon free" OR(nitrogen based) "automotive" "propulsion"; Google.com
Hits: 12800

Appendix II

General information about ammonia and its compatibility with the infrastructure.

Ammonia

Even though hydrogen often is mentioned as the "future fuel" it does lack infrastructure, requires a very low storage temperature of -235 °C, has a low flash point endangering explosion with air and an invisible flame [Duynslaegher C., Jeanmart H. Vandooren J. (2010)].

Ammonia has been suggested as a hydrogen carrier for vehicles because it can be stored as liquid at ambient temperature at approximately 9 bars and can be handled in the same manner as propane. Ammonia might be more suitable as fuel than hydrogen due to the existing infrastructure for ammonia transport and handling, higher energy density than hydrogen, narrow flammability resulting in a non-flammable fuel during transport and that humans can smell it at concentrations as low as 5 ppm giving a pre-emptive warning in case of leakage [Zamfirescu C., Dincer I (2008)]. Handling and experience regarding ammonia is mature since it is used in large quantities as fertilizer in the farming industry [Kong S. Reiter A.J (2010)].

Products of ammonia combustion are water and nitrogen resulting in a low emission fuel that can reduce carbon emissions from vehicles. Properties of ammonia compared to other fuels can be seen in Table 1.2.

### Table 1.2 Ammonia comparisons with other fuels.

<table>
<thead>
<tr>
<th>Unit</th>
<th>Ammonia</th>
<th>Methanol</th>
<th>Ethanol</th>
<th>DME</th>
<th>Hydrogen</th>
<th>Methane</th>
<th>Ethane</th>
<th>Propane</th>
<th>Toluene</th>
<th>i-Octane</th>
<th>n-DCC*</th>
<th>n-HCC*</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAS RN</td>
<td>7664-41-7</td>
<td>67-68-6</td>
<td>64-17-5</td>
<td>115-10-4</td>
<td>1331-75-0</td>
<td>74-88-4</td>
<td>74-98-4</td>
<td>110-37-8</td>
<td>110-88-1</td>
<td>122-49-9</td>
<td>544-76-5</td>
<td></td>
</tr>
<tr>
<td>Mol. Mass</td>
<td>17.056</td>
<td>32.0419</td>
<td>46.064</td>
<td>46.064</td>
<td>2.0159</td>
<td>16.0425</td>
<td>30.0695</td>
<td>44.0956</td>
<td>92.1384</td>
<td>114.2385</td>
<td>179.3348</td>
<td>226.4412</td>
</tr>
<tr>
<td>Sp. Cgh. C</td>
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<td>0.3748</td>
<td>0.5214</td>
<td>0.5214</td>
<td>0.0000</td>
<td>0.7487</td>
<td>0.7989</td>
<td>0.8171</td>
<td>0.9125</td>
<td>0.8512</td>
<td>0.8451</td>
<td>0.8467</td>
</tr>
<tr>
<td>BOE</td>
<td>-33.34</td>
<td>46.65</td>
<td>77.85</td>
<td>-18.55</td>
<td>-252.07</td>
<td>-162.15</td>
<td>-80.55</td>
<td>-42.05</td>
<td>-110.65</td>
<td>99.25</td>
<td>215.85</td>
<td>286.05</td>
</tr>
<tr>
<td>BSST</td>
<td>bar</td>
<td>10.00</td>
<td>0.17</td>
<td>0.88</td>
<td>0.88</td>
<td>apparent apparent</td>
<td>0.88</td>
<td>0.88</td>
<td>0.88</td>
<td>0.88</td>
<td>0.88</td>
<td>0.88</td>
</tr>
<tr>
<td>Dens. Gas</td>
<td>0.6607</td>
<td>1.2926</td>
<td>1.8594</td>
<td>1.8594</td>
<td>0.0014</td>
<td>0.6471</td>
<td>1.2130</td>
<td>1.7788</td>
<td>3.7168</td>
<td>4.0679</td>
<td>6.8712</td>
<td>9.1345</td>
</tr>
<tr>
<td>Sp. Gr./Air</td>
<td>0.9977</td>
<td>1.0857</td>
<td>1.5997</td>
<td>1.5997</td>
<td>0.0699</td>
<td>0.5536</td>
<td>1.0376</td>
<td>1.5216</td>
<td>3.1794</td>
<td>3.9416</td>
<td>5.6777</td>
<td>7.8137</td>
</tr>
<tr>
<td>Dens. Lq.</td>
<td>Kg/m³</td>
<td>681.90</td>
<td>791.80</td>
<td>799.80</td>
<td>689.00</td>
<td>70.00</td>
<td>415.00</td>
<td>564.99</td>
<td>587.70</td>
<td>886.90</td>
<td>688.00</td>
<td>750.00</td>
</tr>
<tr>
<td>Sp. Gr./Wp</td>
<td>Kg/m³</td>
<td>0.0798</td>
<td>0.7990</td>
<td>0.6600</td>
<td>0.0700</td>
<td>0.8150</td>
<td>0.5465</td>
<td>0.6577</td>
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<td>0.6080</td>
<td>0.7590</td>
<td>0.7792</td>
</tr>
<tr>
<td>Sp. Hvy</td>
<td>Kg/m³</td>
<td>22.48</td>
<td>22.65</td>
<td>29.71</td>
<td>31.70</td>
<td>141.79</td>
<td>55.50</td>
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<td>50.33</td>
<td>42.44</td>
<td>47.47</td>
<td>47.25</td>
</tr>
<tr>
<td>Sp. L/h</td>
<td>Kg/m³</td>
<td>18.60</td>
<td>19.90</td>
<td>26.48</td>
<td>28.04</td>
<td>119.96</td>
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<td>46.34</td>
<td>46.53</td>
<td>44.34</td>
<td>44.11</td>
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<tr>
<td>Sp. Hvy</td>
<td>Kg/m³</td>
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<td>0.17</td>
<td>0.17</td>
<td>0.17</td>
<td>0.17</td>
<td>0.17</td>
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<td>0.17</td>
<td>0.17</td>
<td>0.17</td>
<td>0.17</td>
</tr>
<tr>
<td>Ave. P. Kg</td>
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<td>17.15</td>
<td>17.55</td>
<td>16.45</td>
<td>0.00</td>
<td>13.50</td>
<td>15.00</td>
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* DCC is Dodecane; HCC is Hexadecane

[William L. Ahlgren]
Storage

Ammonia can be stored two different ways, pressurized or at low-temperature [Bartels J.R. (2008)]

Pressurized storage keeps ammonia in liquid phase having a pressure above 8.6 bars at ambient temperature (20 °C), but ammonia is commonly stored at 17 bar to keeping ammonia in liquid phase if ambient temperature increases. Energy density of the liquid ammonia stored pressurized is 13.77 MJ/L. A rule of thumb is that 2.8 ton of ammonia can be stored per ton steel. This storage does not require energy to maintain the pressurized state.

Low-temperature storage is usually used for large-scale storage. This type of storage requires energy to maintain its low temperature and thereby avoid boil-off due to ambient temperature. Up to 41-45 ton of ammonia can be stored per ton steel. Less steel is needed compared to pressurized storage resulting in a lower capital cost. Lower capital cost is the reason why low-temperature is preferred for large-scale storage.

Energy density of the liquid ammonia stored in this way is 15.37 MJ/L compared to 13.77 for pressurized storage.

If storage time is assumed 182 days representing a period between winter and summer, will give a storage cost of 4.03 $/GJ for ammonia. It can be mentioned that this cost is much lower compared to hydrogen storage that costs 98.74 $/GJ.

Transport

Ammonia can be transported with truck, rails, ships and pipelines. As mentioned, ammonia can be stored pressurized or at low-temperature. Benefits with low-temperature and pressurized storage is that low-temperature storage is light-weight while pressurized storage doesn’t require energy to maintain its state.

Land-based transport such as road and rail are weight limited and heavier vessel decreases the amount of fuel that can be transported.

Road and rail transport ammonia pressurized for simplicity while ships can use either pressurized or low-temperature storage.

Highway-trailers can have a capacity of 43 530 L ammonia at a pressure of 20.7 bar or in 26.6 ton having a Higher Heating Value (HHV) of 600 GJ.

Rails can transport ammonia in pressurized vessels with a capacity of 126 810 L at 15.5 bar. Total amount that can be transported is 77.5 ton with a HHV of 1746 GJ.

Ships are capable of transporting up to 50 000 ton of ammonia stored at low-temperature.

Pipeline has the ability of transporting large amount of fuel over a large distance. It consists of pipes and compressor to boost pressure in the pipeline. Ammonia is quite often transported by pipeline due reduced costs. A carbon steel pipeline of 4830 km already exists to transport ammonia, but it should also be noted that ammonia in presence with oxygen corrode carbon steel. This can be avoided by having a small amount of water included with a recommended amount of at least 0.1% weight basis [Bartels J.R. (2008), EFMA, European Fertilizer Manufacturers Association (2007)].