Experimental HCCI engine using hydrogen and ammonia
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Next Generation Combined Heat And Power HCCI Engines Operated On Hydrogen And Ammonia From Power-To-Fuel Storage Systems

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Abstract
As the proportion of renewable electricity is rising, the need for mid- and long-term storage becomes unavoidable. To that end the production of hydrogen and ammonia from excess electricity shows great potential. An Homogeneous-Charge Compression-Ignition (HCCI) engine is studied to use both storage fuels for heat and power production. The experiments were performed on a 15.3:1 compression ratio HCCI engine that successfully operated from pure hydrogen up to 60 \%vol. in ammonia. The limited test bench intake conditions did not allow for higher ammonia concentrations. EGR effectively limited the fuel-NO\textsubscript{x} emissions.

Introduction
As the renewable energy production increases in lots of countries to meet the CO\textsubscript{2} emissions reduction goal, the need for electricity storage has never been so high. This storage has various purposes such as balancing the electricity network [1, 2], providing flexibility, hence decreasing the need for back-up fossil fuel energy sources [3, 4], increasing the utilisation factor of the installed renewable energies (reducing their payback time) and allowing for more renewable energies to be incorporated into the network [5, 6]. Even though these purposes are interconnected with each others, they require different storage time-scales. With an increasing share of renewable energy, more and more long-term storage is needed [2]. As more renewable energy is produced, short-term storage is not sufficient to balance the grid and absorb excess production. Therefore, daily, weekly and monthly storage are needed to match the overall production and consumption of electricity if we ever want to achieve 100\% renewable electricity.

Several technologies like hydro-pumping, compressed air storage and power-to-fuel can be used for long-term storage [2]. Power-to-fuel shows a tremendous opportunity giving its smaller CAPEX, smaller levelized cost of energy and greater installation sites potential than the other long-term storage technologies [7, 8, 9]. This study focuses on hydrogen and ammonia storage fuels given that their production and use can be fully decentralized and sustainable: they only require water and nitrogen to be produced from electricity and their combustion products in ideal conditions are water and nitrogen. Hydrogen is obtained from the electrolysis of water with an efficiency of about 70\% based on its Lower Heating Value (LHV) for commercialized alkaline electrolyzers. Yet hydrogen is not convenient for storage given its very low energetic density of about 10 kJ L\textsuperscript{-1} in normal conditions. To improve its storage density, many solutions exist and are recapitulated in Table 1. These storage technologies greatly impact the overall efficiency and the obtained properties are not always desirable: the energetic density of compression storage is rather low; the liquefaction storage has a low efficiency; organic liquid and metal hydrides are expensive and require a specific process to set hydrogen free. Therefore compressed hydrogen is still preferred, but only up to mid-term storage.

Table 1: Comparison of various hydrogen storage technologies

<table>
<thead>
<tr>
<th>Storage technology</th>
<th>State</th>
<th>Energy density (GJ/m\textsuperscript{3})</th>
<th>Overall efficiency (LHV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compressed [10, 11]</td>
<td>700 bar 293K</td>
<td>4.5</td>
<td>59%</td>
</tr>
<tr>
<td>Liquefied [12, 11]</td>
<td>1 bar 20K</td>
<td>8.5</td>
<td>49%</td>
</tr>
<tr>
<td>Metal Hydrides [13]</td>
<td>1-3 bar &gt;293K</td>
<td>15</td>
<td>-</td>
</tr>
<tr>
<td>Liquid Ammonia [40]</td>
<td>9 bar 293K</td>
<td>13</td>
<td>41-54%</td>
</tr>
</tbody>
</table>

In the case of long-term storage (months to seasons) or in the case of high quantity of electricity storage, a higher density storage solution is preferable. In that regard, ammonia shows very interesting features (see Table 1). Obtained from hydrogen and air through the Haber-Bosch process, which requires high temperature and pressures (~150 bar, ~400°C)
ammonia is a fuel convenient for storage since it is liquid under 9 bar of pressure and at ambient temperature. Commercially available small units can produce liquid ammonia from electricity, air and water with an efficiency of 42% (LHV) [15, 16]. Even though such processes are not optimized energetically. Conventionally, ammonia is industrially produced from natural gas or coal with an efficiency of about 72% (LHV) [14]. In this process, the hydrogen necessary for the Haber-Bosch process is obtained from the steam reforming of natural gas or coal, which is 90% efficient (HHV) [17]. Therefore, the industrial efficiency of the Haber-Bosch process is about 80%. Fuehrmann et al. have estimated an efficiency for a non-optimized Haber-Bosch of 76% (LHV) [18]. Therefore we will consider a mean efficiency of 78% (LHV) for the Haber-Bosch process for further calculation. To compute an overall efficiency for industrial ammonia production we finally need to take into account the energetic cost for the air separation unit (production of the nitrogen stream: 0,04-0,07 GJ/GJ N₂ [18, 19]). Therefore, the industrial production of liquid ammonia from electricity, air and water can reach an efficiency of 54% (LHV) if we combine the cost of water electrolysis, the Haber-Bosch process and the nitrogen extraction. We see that, by looking at the storage efficiencies, ammonia is energetically competitive to other hydrogen storage technologies. Moreover, taking into account the liquid state, non-leaking, energetic density and clean properties of ammonia we must acknowledge its high potential as a long-term storage fuel and future energy vector [20].

Having a dual-fuel storage system (i.e. ammonia and hydrogen), we would need a technology able to use both of them to produce back electricity when needed. The fuels could be mixed under various concentrations depending on their respective availabilities. For this purpose, piston engines have the huge advantage of being multifuel to some extent and low cost, a parameter of primary importance when dealing with renewable energy storage. Moreover, piston engines are suited to Combined Heat and Power (CHP) applications hence a higher overall efficiency. Several spark- and compression-ignition engines have been experimented in the past decades to burn ammonia. Still, ammonia having a low flame speed and high auto-ignition resistance, combustion promoters like gasoline, diesel or hydrogen were used [21, 22, 23, 24]. In our hydrogen-ammonia case and to meet the efficiency constraints and pollution regulations, we decided to experimentally investigate the use of an Homogeneous-Charge Compression-Ignition (HCCI) engine. HCCI engines allow high compression ratios together with low in-cylinder temperatures (no thermal-NOx) while being multifuel suited. The multifuel capability of HCCI engines has been demonstrated in several studies [25, 26, 27] and we have numerically assessed the specific case of both hydrogen and ammonia in a previous study [28].

Ammonia and hydrogen do not contain any carbon atom hence they do not emit CO₂, CO or unburned hydrocarbons. Therefore the biggest pollution concern is related to NOx emissions, especially since ammonia contains nitrogen. Indeed, the Zeldovich pathway relevant at 1800 K is not the only source of nitrogen oxide. Fuel-NOx can arise from the nitrogen contained in ammonia. Even though ammonia complete combustion leads to the production of N₂, some NOx might be produced through the incomplete combustion route. Still, these are two competing pathways. If we look at a general level, the incomplete combustion of ammonia is less exothermic that the complete one and requires a higher concentration in oxygen. Therefore, to avoid the production of fuel-NOx we need to shift the equilibrium of the incomplete combustion reaction towards the reactants by either deceasing the temperature or decreasing the oxygen availability [29, 30].

As the temperature of the combustion cannot be decreased due to ammonia auto-ignition resistance, one might think of running at stoechiometric levels (thanks to massive Exhaust Gas Recirculation (EGR)) to suppress any excess oxygen. Indeed, when ammonia was first experimented in SI engines, no increase in NOx emissions was observed as SI engines are conventionally operated at stoichiometry.

For a naturally aspirated engine with a compression ratio of 16:1 we showed in [28] that the required intake temperatures for hydrogen and ammonia are 440 K and 610 K, respectively. For ammonia, the required intake temperature for the auto-ignition to occur is so high that it causes two issues: (1) it is not easy to provide such intake condition and (2) it is not efficient as it will increase the heat losses and reduce the mixture density, and consequently the volumetric efficiency. Therefore, to tackle the high resistance to auto-ignition of ammonia one might want to go for higher compression ratios and intake pressures instead of high intake temperatures. To the best of our knowledge, ammonia has never been experimented in a classical HCCI engine except for one unique experiment: Van Blarigan experimented pure ammonia combustion in a +40:1 free piston HCCI engine without preheating. The success of this pure ammonia HCCI engine ought solely to the very high compression ratio. Still, such compression ratio cannot be used in our case for two reasons: (1) the heat losses and friction losses due to higher pressures would ruin the overall efficiency and (2) the engine has to be able to run with pure hydrogen without ringing (equivalent of knocking for HCCI engines). Indeed, Ibrahim et al. observed a 16:1 compression ratio, naturally aspirated, hydrogen HCCI engine experiencing ringing with equivalence ratios higher than 0.3 [31]. This equivalence ratio limit was shown to decrease linearly.
with increasing compression ratio [32]. Therefore, to have an engine able to use both fuels efficiently, we need a trade-off between a high compression ratio to promote ammonia combustion and a limited compression ratio to prevent hydrogen from ringing.

This paper aims to demonstrate the feasibility of a HCCI engine operated under wide ammonia-hydrogen blending range. From the literature it appears that there is a knowledge gap in ammonia combustion under HCCI conditions as well as regarding fuel-NOx formation. In our dual-fuel storage context, an engine able to operate under a variable ratio of the fuels would be very desirable. Therefore a single HCCI engine will be experimented to assess ammonia resistance to auto-ignition and hydrogen promotion effect on ammonia. Then the performances will be analyzed and finally high EGR rates will be performed to evaluate the oxygen availability impact on fuel-NOx formation.

Specific Objectives and Methodology

Table 2 gives the specifications of the engine used for the experiments. It is a PSA DW10 engine retrofitted to a single-cylinder engine and operated under HCCI conditions. It is coupled to an electric motor fixing the rotational speed at 1500 RPM. For an efficient operation, the combustion (start and peak-point) must happen at an optimal timing. Still, HCCI engines have no direct control on the combustion onset. Therefore the intake temperature, intake pressure and mixture composition are tuned such that the combustion occurs when desired.

Table 2: Engine specifications

<table>
<thead>
<tr>
<th>Engine model</th>
<th>PSA DW10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Displacement volume, ( V_c )</td>
<td>499 cc/cyl.</td>
</tr>
<tr>
<td>Stroke/Bore/Conrod length</td>
<td>88/85/145 mm</td>
</tr>
<tr>
<td>Geometric/effective comp. ratio</td>
<td>16:1 / 15.3:1</td>
</tr>
<tr>
<td>Intake Valve Closing (CAD)</td>
<td>157 BTDC</td>
</tr>
<tr>
<td>Exhaust Valve Opening (CAD)</td>
<td>140 ATDC</td>
</tr>
<tr>
<td>Coolant temperature</td>
<td>95°C</td>
</tr>
</tbody>
</table>

We plot in Figure 1 the required intake temperature for every NH3:H2 ratio such that the auto-ignition occurs at Top Dead Center (TDC). The auto-ignition is taken here as the CA10, crank angle where 10% of the combustion heat has been released. These estimations are obtained with a in-house 0-Dimensional (0-D) model using a calibrated heat loss correlation for this engine in order to correctly estimate the auto-ignition onset. This model is further described in [28]. With an effective compression ratio of 15.3:1 and an intake pressure of 1.5 bar, the 0-D model estimates a required intake temperature of 625 K for ammonia to auto-ignite at TDC in the above-described engine. Still the maximal intake temperature that the test rig allows being 473 K, one will need to promote the combustion of ammonia. This can be done through addition of hydrogen: as shown on Figure 1, a 10%vol. content in hydrogen reduces the required intake temperature by 95 K. According to Figure 1, the test bench could operate up to 60%vol. in ammonia.

![Figure 1: Iso-CA10 curve (CA10 at TDC) for NH3:H2 blends. The 0D simulations are done for the above described engine, with an intake pressure of 1.5 bar and an equivalence ratio of 0.2. Hydrogen has a strong promotion effect on ammonia auto-ignition.](image)

Being in the context of mid- and long-term electricity storage with power-to-fuel, our engine must be able to run separately with hydrogen and ammonia. Therefore we will investigate the combustion from full hydrogen to the maximal content in ammonia allowed with a restricted 15.3:1 compression ratio and 473 K intake temperature. After achieving this broad range hydrogen-ammonia combustion, high EGR rate is to be used with ammonia in order to suppress any excess oxygen at the intake and hence limit the formation of fuel-NOx.

For each operating condition we define the EGR rate, \( \alpha \), as the fraction of excess intake air (compared to stoechiometry) that is replaced by exhaust gases. This will be done experimentally by inserting the correct amount of nitrogen and steam before the intake manifold. Our general combustion reaction can be written as follows:

\[
\phi_0 (xH_2 + yNH_3) + \frac{3x + 2y}{4} (O_2 + 3, 76 N_2) + (1 - \alpha) (1 - \phi_0) \frac{3x + 2y}{4} (O_2 + 3, 76 N_2) + 4, 76 \alpha (1 - \phi_0) \frac{3x + 2y}{4} aO_2 + bN_2 + cH_2O \rightarrow aO_2 + bN_2 + cH_2O
\]
The initial equivalence ratio, $\phi_0$, refers to the equivalence ratio when there is no EGR. Still the equivalence ratio is not suited to evaluate the fuel content. Indeed, if EGR is used (following the above definition), the equivalence ratio will increase although the fuel quantity stays the same. At this point, it is common to introduce the Fuel Mean Effective Pressure (FuelMEP) concept:

$$FuelMEP = \frac{m_{fuel} \cdot LHV_{fuel}}{V_c}$$ (1)

which represents the quantity of energy contained in the cylinder per unit volume. FuelMEP is a very interesting parameter as it is more sensitive to the operating conditions. All the experimental conditions tackled in this paper are described in Table 3.

### Results and Discussion

Ammonia has indeed been found to be highly resistant to auto-ignition, see the pressure curves in Figure 2 where the ammonia content is increased with every other intake conditions kept constant (set of experiment # 2, Table 3). Going from 45 to 60 %vol. content in ammonia, the CA50 is pushed back from TDC to 4.4 CAD aTDC. With an increase in ammonia content to 65 %vol. the combustion becomes close to misfire (8.05% of CoVIMEP).

In-cylinder pressure (bar)

![In-cylinder pressure](image)

Figure 2: In-cylinder pressure curves for various NH$_3$:H$_2$ blends. Intake pressure of 1.5 bar and intake temperature of 473 K, set of experiment # 2. Ammonia high auto-ignition delay is observed through a delay of the combustion as the ammonia content is increased.

Seeing the impact of ammonia on auto-ignition delay, the first important fact to quantify is the required intake conditions for ammonia combustion. Figure 3 compares the simulated required intake temperature to the experimental one in order to have the same CA10 for the set of experiment # 1 (Table 3). The required intake temperature difference between simulations and experiments stays below 15 K for the studied range of ammonia content.

![Comparison between experimental data and simulations of the required intake temperature for the set of experiment # 1: various NH$_3$:H$_2$ blends. The required intake temperature difference between simulations and experiments stays below 15 K.](image)

### Engine performances

The interest of this section does not lie in the absolute value of performances but in their variations with increased ammonia content. Since the unburned exhaust gases could not be measured we computed an alternative to the combustion efficiency: the heat release efficiency (HRE). It is defined as the ratio between the released heat and the mixture energy content:

$$CE = \frac{\sum_{\theta=40}^{\theta} HRR(\theta) \cdot \Delta\theta}{m_{fuel} \cdot LHV_{fuel}}$$ (2)

where HRR is the Heat Release Rate (J/CAD) computed from the in-cylinder pressure which is measured every $\Delta\theta = 0.1$ CAD. Figure 4 gives the heat release efficiency against the ammonia content in the fuel mixture. We see that the heat release efficiency first decreases linearly as the ammonia content is increased. The reason for this reducing efficiency is due to ammonia higher auto-ignition requirements than...
that of hydrogen, hence more unburned molecules. An efficiency plateau is reached for ammonia contents higher than 30 %vol.

Figure 4: Heat release efficiency for increasing contents of ammonia and constant CA10 at TDC. Data obtained with the set of experiment # 1. The higher requirements for ammonia auto-ignition lead to more unburned fuel.

Regarding the IMEP over FuelMEP ratio (i.e. the indicated efficiency), the obtained data for the set of experiment # 1 is displayed in Figure 5. We observe a continuous decrease in indicated efficiency for an increase in ammonia content. This is partly due to heat release efficiency and partly due to the heat losses. Indeed, as the CA50 was kept constant, intake temperature was increased for increased ammonia content, hence higher heat losses. Moreover, the combustion duration being longer for a higher ammonia content, the IMEP will be automatically lower since the output work will move away from optimum (i.e. instantaneous combustion just after the TDC). The combustion duration goes linearly from 4.4 CAD aTDC for pure hydrogen to 7 CAD aTDC for 60 %vol. in ammonia.

Figure 5: Indicated efficiency for increasing contents of ammonia and constant CA10 at TDC. Data obtained with the set of experiment # 1. Both heat release efficiency and heat losses impact the obtained indicated efficiency for increasing ammonia concentration.

Although these efficiencies are acceptable for a research engine, they could be optimised, particularly regarding the heat release efficiency. Indeed, the piston bowl is not optimised for HCCI conditions, hence a poor heat release efficiency that indicates a decaying combustion efficiency for increasing ammonia contents. Unfortunately the exhaust measurement tools were unfit to detect unburned hydrogen and ammonia. Moreover, no wall temperature measurement could be performed. Therefore, a complementary study should be done to trace the reasons for this seemingly low combustion efficiency.

Influence of the oxygen availability on the fuel-\(\text{NO}_x\) emissions

Using hydrogen and ammonia, the only pollutant that can be emitted is \(\text{NO}_x\). For pure hydrogen the measured \(\text{NO}_x\) emissions were below 10 ppm. This indicates that the maximal in-cylinder temperature was always kept below the thermal \(\text{NO}_x\) limit of 1800 K, which has been confirmed during the post processing of the data. Yet, as soon as some ammonia was added to the mix, the \(\text{NO}_x\) concentration was above several thousands ppm whereas the global in-cylinder temperature did not increase. Therefore these emissions find their origins in the nitrogen contained in ammonia, as expected, which is set free as soon as the combustion starts. As explained in the previous sections, EGR can be used to reduce the oxygen excess and hence penalize the incomplete combustion pathway of ammonia. We display in Figure 6 the \(\text{NO}_x\) emissions against various EGR rates, for the set of experiments # 3 and 4.

Figure 6: Fuel-\(\text{NO}_x\) emissions against EGR rate for a 20 %vol. Data obtained with the set of experiments # 3 and 4. Oxygen availability has a large impact on fuel-\(\text{NO}_x\) formation.

Here again the absolute values cannot be compared between the two set of experiments as they were done with different equivalence ratios, different intake pressures and different CA50. But the decreasing trend with an increase in EGR rate is significant. Moreover, with 80 % of EGR, the actual equivalence ratio is only around 0.5. Therefore there
is still a lot of excess oxygen is such conditions. Unfortunately the evaporator was used to produce the steam of the synthetic EGR was not powerful enough to evaporate the water flow needed to simulate a 100 % of EGR. Theoretically, no fuel-NO\textsubscript{x} would be produced in such conditions as no excess oxygen would be available but an impact on the combustion efficiency should be expected. Indeed, for the set of experiment \# 3, two points of heat release efficiency were lost when going from no EGR to 60% EGR. 

Conclusions

A conventional 15.3:1 effective compression ratio HCCI engine has been used to burn various mixtures of hydrogen and ammonia. Using the maximal intake pressure (1.5 bar) and the maximal intake temperature (480 K) possible, the engine was able to operate efficiently with an ammonia content up to 57 \%vol. Due to the very high auto-ignition resistance of ammonia, higher concentrations in ammonia led to poor combustion and finally misfire. For similar operating conditions, the heat release efficiency of ammonia was found to be around 5 points lower than that of hydrogen. Then the very high intake temperature required to auto-ignite ammonia was inducing substantial heat losses and consequently reduced the IMEP. Finally, the fuel-NO\textsubscript{x} emissions induced by ammonia could be effectively reduced through the use of EGR to reduce the oxygen availability. The main conclusions of this paper regarding the findings are:

- Higher compression ratios and intake pressure should be used with ammonia in order to minimize the required intake temperature and hence maximize the IMEP and efficiency.
- Ammonia combustion efficiency must be studied thoroughly as it seems to be a major drawback.
- Full EGR could be used to cancel fuel-NO\textsubscript{x} emissions. Still, it will require strategies to compensate for the induced loss in combustion efficiency.

A conventional light duty compression ignition engine, operated in HCCI mode is suited for the use of small fractions of ammonia with hydrogen (up to 20-30 \%vol.). Yet for higher concentrations of ammonia higher compression ratios and intake pressures are recommended.

Acknowledgments

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References


