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# Towards an Optimised Lean Burn Operating Strategy for an Ammonia-Hydrogen Co-fuelled Spark Ignition Engine

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#### Abstract

Ammonia is now widely considered as a promising renewable fuel, primarily due to favourable storage and transportation characteristics and end use in applications where robust health and safety protocols can always be upheld. In the currently reported work, a thermodynamic single-cylinder spark ignition research engine was fitted with separated gaseous ammonia and hydrogen port fuel injection, with experiments undertaken to improve understanding of the impact of varied co-fuelling upon combustion, performance, fuel economy and emissions. Under stoichiometric conditions with pure ammonia  $(NH_3)$ , it was possible to operate under stable combustion at low-to-medium speeds and medium-to-high engine loads. At the lowest loads, up to ~20% hydrogen (by energy) was required. Engine-out NH<sub>3</sub> emissions remained relatively high across the stoichiometric operating map (~7,000-8,000ppm). An alternative hydrogen co-fuelling lean burn spark-ignition strategy was then developed with the aim of improving engine efficiency and balancing engine-out emissions to be compatible with future use of Selective Catalytic Reduction (SCR) after-treatment technology. This was based upon directly using NH<sub>3</sub> slip as a NOx reductant within an SCR unit and ideally eliminating conventional urea-based fluid injection. Ideally, such SCR systems operate with a fixed "alpha ratio" equal to  $\sim 1$  (where alpha ratio is the ratio of engine-out NH<sub>3</sub>) to NOx on a ppm basis, with a value of unity indicating the ideal amount of reductant to simultaneously consume NH<sub>3</sub> slip and decompose NOx). Several speed and load sweeps were undertaken to evaluate the ideal combinations of hydrogen substitution ratio and relative air-to-fuel ratio ( $\lambda$ ). It was concluded that operating the engine with ~20% hydrogen and slightly lean ( $\lambda$ ~1.2) would result in an ideal alpha ratio of ~1 across the majority of the map, with little variation in alpha ratio or lambda noted with changing engine speed and load. The results indicate, apparently for the first time, the high promise of such a co-fuelling engine operating strategy to enable high engine efficiency with minimised pollutant emissions via existing SCR emissions after-treatment technology. The supplementary hydrogen was noted to also result in small improvements in indicated thermal efficiency of 1-2% compared to baseline stoichiometric operation with 100% ammonia, with accompanying basic calculations indicating this may help offset any penalties from on-board hydrogen production via thermo-catalytic NH<sub>3</sub> cracking. Overall, the work has demonstrated a new engine operating strategy to help overcome the challenges of slow NH<sub>3</sub> combustion and high pollutant emissions via existing diesel engine after-treatment technologies.

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### 1. Introduction

Battery electrified propulsion is widely predicted to become the dominant method of propulsion for light duty ground transport. For longer range heavy transport applications (marine, off-road, freight rail), significant challenges remain around battery energy density, acceptable range and total operating cost. As a result, there has been significant attention is recent years into alternative renewable fuels produced via sustainable hydrogen. Amongst the options, ammonia has been the subject of intensified research in recent years due to highly favourable hydrogen storage characteristics and (ultimately) zero carbon capability. On a volumetric basis, liquid ammonia can store approximately 1.5 times more hydrogen than liquid hydrogen [1] without the need for energy intensive cryogenic storage. In terms of end use, the key challenges include guaranteeing safe use (due to high toxicity attributes), overcoming very slow combustion and controlling key pollutant emissions [2, 3].

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The historical utilisation of ammonia as a fuel in internal combustion engines dates back nearly a century, notably during the 2nd World War [4].

Subsequently to this, intensive research was conducted in the mid-1960s, focusing on experiments within both compression and spark ignition engines.

The high auto ignition temperature of ammonia necessitates extremely high compression ratios, typically around 35:1, for pure ammonia operation in Compression Ignition (CI) engines [5]. Consequently, most studies in CI engines have focused on using a "dual fuel" approach, where a premixed ammonia-air mixture is ignited by a pilot fuel with a low auto-ignition temperature and favourable cetane rating. Diesel, DME, kerosene and amyl-nitrate have been thoroughly researched under dual-fuel mode [6-14].

However, complexities associated with the additional fuel circuit, coupled with challenges in mitigating excessive ammonia "slip" and operating engines under unfavourable throttled conditions (together with the remaining carbon content in the pilot fuel), render this dual-fuel approach less appealing than spark ignition. Pure ammonia can be used in spark ignition engines at significantly lower compression ratios (i.e. nearer to the real-world optimum), as demonstrated by Starkman et al.[15] in the 1960s. Additionally, Pearsall et al. studied the operation of ammonia in both types of engines and recommended a compression ratio in the range of 12-16 as an optimum [14].

Although superior to compression ignition, the relatively poor premixed combustion properties of ammonia (see Table 1) make operating a spark ignition engine with pure ammonia at low loads challenging, especially in larger bore engines typical in heavy transport. Nonetheless, there are several strategies which can be explored, such as increasing the effective compression ratio, utilising higher ignition energy, co-fuelling with faster burning sustainable fuel(s) and supercharging (potentially without charge air cooling). Amongst these solutions, co-fuelling with hydrogen has been the most extensively studied method due to good combustion characteristics as well as the ability of on-board hydrogen production via ammonia thermocatalytic cracking [16-18] plasma assisted cracking [19-21] and electrolysis [22-24].

Gasoline has also been widely studied as a combustion promoter in ammonia in spark ignition engines, with notable contributions from the CFR research group. Grannell et al. [25] explored the fuelling limits and efficiency of ammonia-gasoline co-fuelling, concluding that ammonia can replace a significant portion of gasoline energy above 4bar net

Indicated Mean Effective Pressure (IMEPn). Their results showed that the required amount of gasoline decreased with increasing speed and load. Interestingly, re-optimising the compression ratio did not improve gasoline displacement or thermal efficiency. Ryu et al. [26] examined the direct injection of gaseous ammonia into a Port Fuel Injected (PFI) gasoline engine and found that extended injection times required for ammonia negated the advantages of direct injection over PFI systems [27]. Haputhanthri et al. [28] studied the combustion of ammonia/gasoline emulsified mixtures and found that ammonia can be dissolved into gasoline using emulsifiers (such as methanol and ethanol) with the resulting composite fuel enhancing engine performance under high-load conditions.

 
 Table 1. Combustion Characteristics of Ammonia, Hydrogen and Gasoline [29-33]

Species	Hydrogen	Ammonia	Gasoline	
Formula	$H_2$	NH <sub>3</sub>	C <sub>8</sub> H <sub>18</sub>	
LHV (MJ/kg)	120	18.8	44.5	
Laminar Burning				
Velocity @ $\lambda = 1$	3.51	0.07	0.58	
(m/s)				
Auto-ignition	773 850	020	502	
Temperature (K)	775-850	930	305	
Research Octane	>100	130	00.08	
Number	>100	130	90-98	
Flammability				
Limit in Air	4.7-75	15-28	0.6-8	
(vol.%)				
Quench Distance	0.0	7	1.09	
[mm]	0.9	7	1.90	
Absolute				
Minimum	0.02	0	0.1	
Ignition Energy	0.02	0	0.1	
(mJ)				

Morch et al. [34] explored dual-fuel ammonia combustion with varying hydrogen substitution levels and identified that a ~10% volume substitution yielded maximum thermal efficiency. Frigo et al. [35] further expanded on this by evaluating ammonia-hydrogen co-fuelling across varying speed/load conditions and observed that whilst hydrogen enrichment improved combustion, the impact on engine load was greater than engine speed. Additionally, this research concluded that ~7% hydrogen energy was required, as a minimum, for stable combustion at full load (increasing to around 11% at part load). The study also considered the feasibility of using waste exhaust gas heat to crack ammonia onboard to produce hydrogen; however, the higher combustion temperatures required for the thermo-catalytic cracker significantly increased NOx emissions [36].



Complementary research by Lhuillier et al. [37] and Mounaïm-Rousselle et al. [38] in modern spark ignition research engines also demonstrated that adding small amounts of hydrogen (~10% volume) significantly improved ammonia combustion, enabling stable engine operation across various loads and engine speeds ranging from 650rpm to 2,000rpm.

A key challenge of using ammonia in internal combustion engines lies in controlling NOx and unburned ammonia emissions. However. SCR systems use ammonia to established decompose NOx into nitrogen and water vapour. This suggests that, with the correct balance of unburned ammonia and NOx entering the SCR system, both emissions can be effectively neutralised at the "tailpipe". Girard et al. [39] investigated the ratio of ammonia-to-NOx in an SCR system and found the ideal ratio, termed "alpha ratio", to be ~1:1 (NH<sub>3</sub>:NOx). The currently reported work describes the experimental research carried out in a modern spark ignited single cylinder engine operating on ammonia and hydrogen, with the aim of understanding optimum conditions for achieving an alpha ratio of 1 over a range of speed and load conditions. This was achieved by varying the ammonia-hydrogen energy ratio in the fuel mix as well as air-to-fuel ratio under which the engine was operated.

### 2. Materials and Methods

#### 2.1 Testbed Setup

The research was conducted using an externally boosted single-cylinder spark ignition engine, derived from the MAHLE Powertrain "Di3" demonstrator engine [40]. This modified engine featured a pent-roof, four-valve cylinder head with a centrally located spark plug and a side-mounted gasoline direct-injector positioned beneath the intake valves, designed for standard E10 gasoline delivery. The engine was modified to allow several different fuels to be used. Ammonia was introduced via port injection, facilitated by an upgraded intake manifold and a prototype port fuel injector. Additionally, the engine incorporated a fully hydraulic independent variable valve timing (VVT) system, allowing precise optimisation of valve timing and overlap. The key specifications of the engine are outlined in Table 2.

Shown in Fig. 1 is a schematic representing the engine intake air system, capable of operating under either naturally aspirated conditions or with boosted intake air via an external compressor (capable of delivering pressures up to 4 bar absolute). To minimise dynamic pressure fluctuations, surge tanks were installed in both the intake and exhaust. Intake

air temperature (45°C), engine coolant temperature (95°C) and oil temperature (95°C) were precisely controlled to within  $\pm$ 1°C.

Table 2. Engine hardware specifications			
Parameters	Value		
Engine Type	Four Stroke Single Cylinder		
	Spark Ignition		
Displaced Volume	400 cc		
Stroke	73.9 mm		
Bore	83 mm		
Compression Ratio	12.39		
Number of Valves	4		
Valvetrain	Dual Independent Variable		
	Valve Timing (40°CA Cam		
	Phasing)		
Fuel Injection	PFI Hydrogen		
Configuration	PFI Ammonia		
Cylinder Head	Pent Roof (High Tumble Port)		
Geometry	Tent Root (Tingii Tuliiole Tort)		
Piston Geometry	Pent Roof with cut-outs for		
Tiston Geometry	valves		
Ignition Coil	Single Fire Coil, 100mJ, 30kV		
Max Power	40 kW (Gasoline)		
Max Torque	96 Nm (Gasoline)		
Max In-Cylinder	120 har		
Pressure	120 0ai		
Max Speed	5,000 rpm		
Boost System	External Compressor (Max		
	4barA)		
Control System	MAHLE Flexible ECU		
Control Software	ETAS INCA		

Set out in Figs. 2 and 3 are the ammonia and hydrogen fuel supply systems respectively. Flow rates were monitored using a Coriolis flowmeter with a maximum error of 1% at the lowest recorded flow rates. Gaseous ammonia was delivered to the engine via a port fuel injector supplied by Clean Air Power, with the ammonia stored in a liquid-vapour equilibrium within a pressurised drum. The pressure differential between the intake manifold and the drum's vapour pressure facilitated ammonia delivery to the engine. To enhance safety, the supply line was equipped with a nitrogen-based purging system and electrically controlled safety valves, enabling rapid isolation of the ammonia supply in emergency scenarios.





Fig. 3. Schematic of the Hydrogen supply line



Hydrogen was supplied to the engine through a dedicated port fuel injector also provided by Clean Air Power, similarly to the setup for ammonia. The hydrogen was stored in bottles at an initial pressure of 172 bar and fed into a hydrogen manifold. To ensure precise delivery, the pressure was regulated in two stages; the first regulator reduced manifold pressure to 50 bar, optimising accuracy for Coriolis flowmeters (maximum error within 1%), while the second regulator further reduced the pressure to a maximum of 20 bar for the limitations of the port fuel injector (PFI). Hydrogen was injected during the intake stroke, minimising residence time in the intake manifold. Further details including injection timing and feed pressures are provided in Table 4 and discussed in subsequent sections of the report. Safety measures included the installation of flashback arrestors and electrically controlled safety valves to isolate and vent the system during emergencies.

Dynamic pressures in the intake and exhaust runners were measured using piezoresistive transducers. Cylinder pressure was recorded using a piezoelectric pressure transducer paired with a matching amplifier, both calibrated in-situ to industry standards via a dead weight tester. Engine-out emissions were analysed using a suite of dedicated analysers capable of measuring standard emissions (NOx,  $CO_2$ , CO, THC, and  $O_2$ ) as well as ammonia "slip" emissions. Detailed specifications for all analysers are provided in Table 3.

Data acquisition was conducted through a custombuilt system developed with National Instruments hardware and software.

- Steady-state parameters including temperature, pressure, and flow rates were measured at a sampling rate of 10 Hz.
- Pressure data from the transducers was captured at a resolution of 0.2 Crank Angle Degrees (CAD) using an optical encoder, which was pre-synchronised with a capacitive probe. For each test, 300 cycles of pressure data were recorded.
- Mass fractions burned were evaluated qualitatively using one-dimensional heat release analysis.

Tuble 5. Details of Elimbolon Thatysets			
Gas	<b>Operating Principle</b>	Dynamic Range	Accuracy / Error (%)
NOx	Chemiluminescence	0-1,000 ppm	Better than +1% range or $\pm 0.2$
			ppm whichever is greater.
$O_2$	Non -Dispersive Infrared Spectroscopy	0 -5 %, 0 -10 %, 0 -25 %	±0.01 %O2.
NH <sub>3</sub>	Tuneable Diode laser Spectrometry	1ppm -10,000 ppm	±2% of Full Scale Deflection
TUC	Flame ionisation detector	0-10,000 ppm	Better than $\pm 1$ % range or $\pm 0.2$
Inc			ppm whichever is greater.
CO CO.	Non -Dispersive Infrared Spectroscopy	100-10,000 ppm	Better than $\pm 1$ % of range or
$CO, CO_2$ I		or 1-100 %	$\pm 0.5$ ppm whichever is greater.
N <sub>2</sub> O	Non -Dispersive Infrared Spectroscopy	0-1,000ppm	0.5% of range or 1% of reading

#### Table 3. Details of Emission Analysers

#### 2.2 Test Plan

Since practical applications of ammonia are expected to be in low-to-medium speed heavy duty engines, the test points were selected to cover typical operating regimes of these engines (e.g. from 1,000-2,600rpm and varied loads). Baseline experiments were conducted on running the engine at stoichiometric conditions with spark timing optimised for maximum brake torque, while hydrogen co-fuelling was minimised to maintain stable combustion. This stability was defined by keeping the coefficient of variation in the net Indicated Mean Effective Pressure (CoV NIMEP) below 3%. An initial hypothesis suggested that operating the engine slightly rich might enhance NH<sub>3</sub> displacement due to a marginally higher laminar burning velocity. However, this approach proved ineffective, as attempts to run slightly rich at

the substitution ratio limit resulted in frequent misfires. This outcome was attributed to a low relative air-to-fuel ratio and the significant reduction in the ratio of specific heats, which negated any small gains in laminar burning velocity. These effects are consistent with theoretical predictions previously inferred from the chemical modelling work of Kobayashi et al. [41].

Common engine settings used for the tests are summarised in Table 4. Although valve timing remained fixed, adjustments to overlap were necessary at 1,000rpm, where it was reduced from 37 to 24 Crank Angle Degrees (CAD). This modification addressed significant ammonia slip observed at low speeds and high boost pressures, caused by excessive cylinder scavenging under these conditions.



Further to the baseline tests, experiments were conducted by varying the air fuel ratio under pure ammonia operating conditions followed by varying the hydrogen substitution under optimal lambda conditions. This is described in detail in previous research [42] on which the current report expands upon for context.

<b>Table 4.</b> Engine settings for substitution tests			
Settings	Values		
Operating			
Temperature	90 °C		
(Coolant & Oil)			
Spork Timing	Maximum Brake Torque		
Spark Thining	(MBT)		
Air-fuel Equivalence	1		
Ratio	1		
H <sub>2</sub> Injection Start			
Angle	220 CAD BIDCI		
Ammonia Injection			
End Angle	400 CAD BIDCI		
Inlet Air	40 <sup>0</sup> C		
Temperature	40 C		
Ammonia Rail	2.5 harG		
Pressure	5-5 0alG		
Ammonia Feed	27.0 $20.0$		
Temperature	27 C-30 C		
Hydrogen Feed	2 6 har C A		
Pressure	2-0 bard A		
<sup>a</sup> Crank Angle Degrees			
<sup>b</sup> Before Top Dead Centre Firing			

#### 3. Results and Discussion

#### 3.1 Baseline spark ignition stoichiometric maps

Set out in Fig. 4(a) is the percentage of ammonia energy in the fuel mix (energy basis) with which the engine can operate stably at different speed-load conditions. Low speed and high load conditions are more favourable to stable ammonia combustion due to increased time and higher in-cylinder temperatures respectively. Stable operation (CoV <3%) of the engine away from this region necessitated hydrogen addition, with the maximum demand of hydrogen recorded at the lowest load and highest engine speed in the test region (2,600rpm-3bar IMEPn). Compared to previous studies conducted with E10 co-fuelling, ~50% more ammonia substitution can be achieved with hydrogen co-fuelling indicating the improvement in combustion properties enabled using hydrogen [43, 44].

Analysing the data, it is evident that while incylinder temperature and turbulence help improve the combustion of ammonia, its significance is reduced when compared to the time available for combustion. This was indicated by the engine being able to operate in a stable manner with pure ammonia at low-speed low-load conditions (with low in-cylinder temperature and turbulence; longer time available for combustion) as opposed to highspeed high-load conditions (with high in-cylinder temperature and turbulence; shorter time available for combustion) where hydrogen co-fuelling is required for stable operation.

Furthermore, the isolines tend to follow a hyperbolic curve shifting from being nearer horizontal at lower loads to becoming nearer vertical as the speed increases. The vertical isolines indicate the insensitivity of hydrogen required to in-cylinder temperatures for stable combustion, potentially implying that hydrogen's role is more an ignition promoter than a combustion promoter.

A similar trend was observed with the studies conducted with gasoline co-fuelling [43, 44], where the addition of gasoline had a greater impact on reducing the initial combustion duration (0-10% mass fraction burned). Likewise, the horizontal shift of the isoline indicates the sensitivity of ammonia combustion to burned mixture inside the cylinder, this can be further examined by analysing the results of engine pressure ratio given in Fig. 4(c).

The engine pressure ratio expressed in Equation 1 is defined as the ratio of intake to exhaust manifold pressure and indicates the effectiveness of in cylinder scavenging at the various test points. As seen in Fig. 4(c), at load points where the isolines are nearer horizontal, the intake manifold pressure is lower than the exhaust resulting in the engine retaining significant levels of burned mass compared to higher load conditions where boosted operations lead to better scavenging. This suggests the presence of burned mixtures which have significant impact, slowing down the combustion requiring more hydrogen to compensate for this.

$$Engine \ Pressure \ Ratio$$

$$= \frac{Intake \ manifold \ pressure}{Exhaust \ manifold \ pressure}$$
(1)

The NOx and unburned ammonia emissions from the tests are plotted in Fig. 4(d) and Fig. 4(e) respectively. Previous studies using the same engine hardware [43, 44] found that NOx emissions are considerably lower when running on pure NH<sub>3</sub> compared to pure gasoline (E10), under the same operating conditions.





**Fig. 4.** Maps from baseline stoichiometric tests (a) Maximum ammonia substitution [%] (b) exhaust gas temperature [<sup>0</sup>C] (c) engine pressure ratio [-] (d) NOx emissions [ppm] (e) Unburned ammonia emissions [ppm] (f) Alpha ratio [-].



In contrast to conventional fuels, NOx emissions from ammonia operation tend to decrease with increase in engine load especially at high engine speeds where the co-fuelling with hydrogen results in higher NOx at lower engine loads potentially due to higher in-cylinder temperature (indicated by the exhaust gas temperature plots in Fig. 4(b)) increasing the thermal NOx formation. Compared to the co-fuelling region, NOx emissions in the pure ammonia operating region tend to increase initially with engine load before dropping down. The initial increase of NOx emissions in the pure ammonia operating region could explained as a combined effect of an increase in temperature and reduction in in-cylinder residuals from the increase in engine pressure ratio. This can be further analysed by comparing the data with that of engine pressure ratio in Fig. 4(c), the NOx peaks at the same region where the engine pressure ratio is ~1, where the lack of residuals from increased in-cylinder scavenging and higher temperature results in higher NOx. While the temperature increases further with an increase in load, the higher temperature could also enable the non-catalytic reduction of NOx by ammonia, while this hypothesis needs to be experimentally proven, the variation of unburned ammonia emissions set out in Fig. 4(e) could be an indicator to understand this as the unburned ammonia emissions should also reduce in tandem with NOx emissions.

Comparing the unburned ammonia emissions to that of NOx, it can be observed that similarly to NOx emissions, unburned ammonia emissions tend to reduce with an increase in load, with the highest values recorded at low speed and load conditions. Furthermore, both NOx the relative variation of data from load point to load point is similar. For example, at 1,800rpm the recorded NOx and unburned ammonia for the various load tends to reduce or increase as load increases, suggesting that ammonia is potentially consumed to reduce NOx. While this further adds evidence to the hypothesis of noncatalytic reduction of NOx, it should be noted that the variation of NOx is very small to come to a concrete conclusion without further experimentation.

Analysing the unburned ammonia emissions alone, it can be observed that the engine emits a significant amount of unburned ammonia in the exhaust, with the lowest recorded value remaining higher than 5,000ppm albeit values tend to reduce with engine speed. While the presence of hydrogen does play a role in this reduction, higher engine temperature seems to have an impact in dictating the unburned ammonia emissions, with higher values recorded at lower speeds with more hydrogen in the fuel mix. These results are comparable to previous studies published by Lhuillier et al. and Mounaïm-Rousselle et al. [37, 45] using similar engines and under similar operating conditions ( $\lambda$ , MBT). As explained above, ammonia can reduce NOx and is used as a reagent in SCR after-treatment systems. Moreover, higher temperatures can aid the oxidation of ammonia within the catalyst as determined by Girard et al. [39] in conventional diesel engines utilising "AdBlue". The study also suggests an optimum ratio (for SCR) of NH<sub>3</sub> to NOx, termed as "alpha ratio" to be 1, with the value increasing to 2 for high temperature operation.

Figure 4(f) illustrates the variation of alpha ratio in the test region. The actual alpha ratio for the test condition ( $\lambda$ =1, MBT) is considerably higher than what is required for the proper operation of an SCR, potentially requiring an additional ammonia oxidation catalyst to remove the excess ammonia after the SCR system. As seen from Fig. 4, onboard hydrogen infrastructure (either via storage or an ammonia cracker) is essential to enable the engine to operate across the whole test area. However, running the engine at these stoichiometric conditions would result in significant amounts of unburned ammonia in the exhaust requiring not only NOx after treatment but also ammonia oxidation catalysts to remove the excess ammonia downstream of the NOx after-treatment systems. The next section provides an overview of an alternative lean burn operating strategy, derived with the aim of optimising the engine-out emissions of unburned ammonia and NOx by using hydrogen to enhance the combustion when lean.

# 3.2 Constant Load Air-to-Fuel Ratio Sweeps with Fixed Hydrogen

Set out in Fig. 5(a) are the engine-out NOx (solid lines) and NH<sub>3</sub> (dashed lines) emissions results obtained during relative air-to-fuel ratio sweeps and a fixed engine speed of 1400rpm and at fixed loads of 10, 14 and 16 bar IMEPn. Shown in Fig. 5(b) are the corresponding values of alpha ratio. All the data was obtained with a fixed ammonia to hydrogen cofuelling ratio of 80:20 by energy (with 20% H<sub>2</sub>) with optimised spark timing at every site (MBT). While it was possible to operate the engine on pure ammonia at these speeds and loads, the intent of these experiments were to understand the impact of fixed H<sub>2</sub> co-fuelling on alpha ratio at varying air-tofuel ratio, with the H<sub>2</sub> optimised for the first initial load case (10bar) to optimise alpha ratio and thereafter held constant.

Observing Fig. 5(a), it can be concluded that operating the engine slightly lean ( $\sim\lambda$ =1.2) results in peak engine-out NOx and minimised NH<sub>3</sub> slip. Both trends are associated with increased in-cylinder gas temperatures and higher oxygen availability.





**Fig. 5.** Results of engine air to fuel ratio sweeps at fixed engine loads showing a) engine-out NOx and NH<sub>3</sub> emissions b) associated alpha ratio (with the blue shaded area indicating the ideal control zone for SCR operation c) indicated thermal efficiency and d) exhaust gas temperature.

A key point to note is that the results were relatively insensitive to varied engine load with a fixed hydrogen percentage of 20%. The blue shaded area in Fig. 5(b) indicates the zone in which it would be possible to attain the ideal alpha ratio (or slightly lower to allow precision control via some small additional injection of ammonia directly into the exhaust to ensure ideal conditions in real applications). Set out in Fig. 5(c) are corresponding values of indicated thermal efficiency. Operating the engine at  $\lambda = 1.2$  enabled improved efficiency of ~2% c.f. the prior stoichiometric operating strategy. Further gains were attained up to  $\lambda \sim 1.4$  without adverse impact on alpha ratio. However, as shown in Fig. 5(d), operation at  $\lambda \sim 1.2$  results in reduction in exhaust gas temperatures of ~50°C, reducing further with excess air ratio. It is important to note that single cylinder engines usually incur lower exhaust gas temperatures than practical multi-cylinder variants. Nonetheless, the reduction in temperature must be traded off in future applications to ensure effective SCR conversion can be achieved at the lowest engine speeds and loads. A further point to make is that the alpha ratio remains relatively flat when varying lambda between 1.2 to 1.4 and that such variation presents an additional variable to help control SCR operating temperatures in real engines.

Shown in Fig. 6(a) are measurements of engine-out N<sub>2</sub>O. Under the limited conditions evaluated, the results indicate that lean operation only results in significant increase in N<sub>2</sub>O emissions beyond  $\lambda$ =1.4. N<sub>2</sub>O is a highly potent greenhouse gas that has a 100-year global warming potential (GWP<sub>100</sub>) of 273 [46]. This means that it must be reduced but it is also important to provide context relative to fossil fuel emissions. Note the relatively low  $N_2O$ concentrations observed of ~30-50ppm (8,000-13,650ppm CO<sub>2-eq</sub>) at stoichiometric conditions compared with the typical 12-14% CO<sub>2</sub> (120,000-140,000 ppm) typically measured in the exhaust of modern engines operating with fossil fuels. For context, ~100ppm of N<sub>2</sub>O equates to >90% equivalent decarbonisation on a global warming impact basis assuming green ammonia and hydrogen are utilised in place of gasoline in this engine. Figure 6(b) shows repeat values of alpha ratio obtained from the engine running on pure ammonia. The excessive ammonia slip from pure ammonia operation results in a significant increase in alpha ratio, such that the optimum alpha ratio is not



achieved at any point in the lambda sweep. SCR systems can temporarily store some ammonia within the catalyst bed and hence high alpha ratio values might be tolerated for short periods of time in some practical applications, depending on the size and initial state of the catalyst and overall operating cycles. However, this would not present a viable operating strategy without some additional  $NH_3$  "clean up" catalyst and potential trade off with increased tailpipe emissions of  $N_2O$ .







Fig. 7. Variation of alpha ratio for various  $H_2$  fuel ratios at different  $\lambda$  for 6bar and 14bar IMEPn

# 3.3 Varied Hydrogen Substitution Mapping at Constant Speed

Set out in Fig. 7 is the variation of alpha ratio for low and medium engine loads with varied hydrogen composition in the fuel mix and at varied equivalence ratio. In general, the isolines for alpha ratio exhibit a parabolic curve, with a minimum around  $\lambda$ =1.2. Furthermore, the value of alpha ratio reduces with increased hydrogen in the fuel mix. At least 20% hydrogen (by energy fraction) is required to achieve an alpha ratio of 1 at  $\lambda$ =1.2, this remained true regardless of the engine load. A better understanding of alpha ratio can be realised by analysing the variation of unburned ammonia and NOx in the same region.

The variation of unburned ammonia in the exhaust for both loads are given in Fig. 8. An increase in hydrogen in the fuel mix reduces unburned ammonia in the exhaust. This is at least partially due to having less ammonia in the fuel mix, and hydrogen



potentially aiding the combustion of ammonia in the crevice volumes by virtue of its low quench distance. For a constant hydrogen fuel percent, the unburned ammonia in the exhaust increases as the air fuel equivalence ratio ( $\lambda$ ) increases, however, this effect is only observed at lower hydrogen concentrations. At higher hydrogen concentrations, the isolines tend to become more horizontal with a minima between  $\lambda = 1.1$  and 1.2. This could be due to the lean limit extension of hydrogen at higher concentrations compared to lower concentrations where the lean limit is closer to stoichiometric conditions. Comparing the two load conditions, it can be observed that the higher temperature operation at 14bar IMEPn reduces the unburned ammonia slightly to the 6bar IMEPn case, however, this effect is minimal compared to the impact of hydrogen.

The lack of variation of unburned ammonia with  $\lambda$ suggests that the minimum trend of alpha ratio at  $\sim\lambda$ =1.2 is governed more by the NOx emissions given in Fig. 9. As seen in the figure, NOx emissions peak at  $\lambda$ =1.2 for a given hydrogen concentration due to the higher combustion temperature and sufficient oxygen available for the NOx formation to occur. Increasing the hydrogen concentration increases the NOx emissions by 2,000ppm as the concentration of hydrogen is increased from 0%-50% at  $\lambda$ =1.2. The higher temperature (and potential reduction in residual burned gases) increases the NOx emissions under high load emissions, peaking at 5,000ppm between  $\lambda$ =1.2 and 1.3. In both cases, NOx emissions are also independent of hydrogen concentration between  $\lambda = 1.0 \& 1.2$ , with the isolines near vertical in this region, which could be due to insufficient or stratified oxygen availability for peak NOx formation.



Fig. 8. Variation of unburned  $NH_3$  emissions for various  $H_2$  fuel ratios at different  $\lambda$  for 6bar and 14bar IMEPn

Figure 10 illustrates the variation of CoV of IMEPn for the test region for both engine loads. As seen in the figure, the CoV is stable closer to stoichiometric conditions, with the stability decreasing at higher values of  $\lambda$ . While the addition of hydrogen improves the CoV, enabling stable operation at higher loads, the effect is more pronounced at 14bar IMEPn. This could be attributed to low combustion temperature at 6bar IMEPn deteriorating the stability at higher  $\lambda$ .

The combustion stability can be further analysed using the Lowest Nominal Value of IMEPn (LNV of IMEPn) which is defined in Equation (2) below,

# LNV of IMEPn = $\left(\frac{Minimum of IMEPn}{Average IMEPn}\right) * 100$ (2)

Figure 11 shows that the LNV of IMEPn tends to remain above 95% (deemed as stable for SI combustion) in most regions with hydrogen with the exceptions being the higher  $\lambda$  test points at 6bar IMEPn where the engine was operating close to the combustion stability limit. The LNV value below 89 indicates partial burning cycles, which increases the average amount of unburned ammonia in the exhaust as discussed above.





**Fig. 9.** Variation of NOx emissions for various  $H_2$  fuel ratios at different  $\lambda$  for 6bar and 14bar IMEPn



Fig. 10. Variation of CoV of IMEPn for various hydrogen fuel ratios at different  $\lambda$  for 6bar and 14bar IMEPn



Fig. 11. Variation of LNV of IMEPn for various hydrogen fuel ratios at different  $\lambda$  for 6bar and 14bar IMEP.





Fig. 12. Variation of spark timing for various hydrogen fuel ratios at different  $\lambda$  for 6bar and 14bar IMEPn







Fig. 14. Variation of 10-90% MFB [in CAD] for various hydrogen fuel ratios at different  $\lambda$  for 6bar and 14bar IMEPn





**Fig. 15**. Variation of ITE for various hydrogen fuel ratios at different  $\lambda$  for 6bar and 14bar IMEPn

The impact of hydrogen addition on the combustion can be further examined by analysing the variation of key combustion metrics across the test region. Shown in Fig. 12 below is the variation of spark advance needed to achieve MBT spark timing at various points in the test region. As seen from the figure, the addition of hydrogen speeds up the combustion and reduces the spark advance needed to achieve MBT spark timing.

Compared to the effect of increasing hydrogen in the fuel mix, the increase in  $\lambda$  is less sensitive on the spark advance as indicated by the isolines being more horizontal in the graph. As expected, increasing the load speeds up the combustion requiring ~4CAD less of spark advance to achieve MBT spark timing for the same hydrogen substitution and  $\lambda$ .

The Mass Fraction Burned (MFB) data can be used understand how hydrogen improves the to combustion in the engine. Figure 13 shows the variation of 0-10% MFB data. The improvement in the mass fraction burned from the additional hydrogen seems to be more significant between 0 and 20% H<sub>2</sub> as illustrated by the proximity of the isolines. Beyond this, the addition of hydrogen has reducing impact on the MFB values for both loads, with the stagnation more prominent at higher load conditions. In contrast to 0-10% MFB, the variation in the 10-90% combustion duration remains relatively similar across the test region, as seen in Fig. 14. This correlates to prior research [42-44] which shows that ammonia slows down combustion in the flame initiation phase significantly but has a much lower effect during the latter stages of burning.

Even though the variation of 10-90% MFB is relatively small, the data shows that the 10-90% MFB is more sensitive to the hydrogen energy mix than  $\lambda$ . This sensitivity is illustrated in the 6bar IMEPn data, where the isolines show a hyperbolic shifting from being horizontal near trend stoichiometric conditions, to vertical as the lambda increases. While this trend is less structured in the high load conditions, the data shows a similar trend against  $\lambda$  where the transition occurs moving closer to stoichiometric conditions and the increase in hydrogen concentration in the fuel mix. This variation in the data could be due to an air-quenching effect, slowing down combustion at higher  $\lambda$ conditions

One of the challenges of using hydrogen to optimise emissions is the efficiency penalty that needs to be accounted for to produce the required hydrogen onboard. Lean operation was selected to minimise the impact of this penalty and can be observed in the data of Indicated Thermal Efficiency (ITE) shown in Fig. 15. As seen in the figure, the operating efficiency improves with an increase in  $\lambda$ , this is mainly due to increased ratio of specific heats in the unburned mixture and the reduction in heat losses to the cylinder walls by virtue of cooler combustion. Furthermore, at lower  $\lambda$ , the efficiency is less sensitive to the amount of hydrogen and operates more as a function of mixture equivalence ratio. This suggests that increasing the hydrogen beyond the optimum amount would be detrimental to the overall efficiency of the system.

To understand if the 2% improvement in efficiency achieved by operating the engine at  $\lambda$ =1.2 with 20% hydrogen (over stochiometric) is sufficient to negate the efficiency penalty of producing hydrogen from



ammonia onboard, an energy balance analysis was undertaken. The analysis assumed a worst-case scenario in which all the heat energy required to decompose ammonia into hydrogen comes from burning ammonia. By calculating the excess ammonia consumed to produce the heat and adding it to the total fuel consumption, a revised efficiency value was calculated, which was then compared with the ITE values from Fig. 15.

The energy balance equation to calculate excess ammonia consumed is given in Equation 3.

Energy consumed to produce 
$$H_2$$
 (3)  
=  $\dot{m}_{excess} * LHV * \eta$ 

Where  $\dot{m}_{excess}$  is the excess ammonia consumed, LHV is the lower heating value of ammonia and  $\eta$  is the efficiency of system which was assumed conservatively of 70%. The total power required to produce hydrogen can be further calculated by adding the energy required to heat the necessary ammonia to the decomposition temperature with the enthalpy of decomposition of ammonia. The equation to calculate the total power consumed is given in Equation 4.

Energy consumed to produce 
$$H_2$$
 (4)  
=  $[\dot{m}_H * C_p * \Delta T] + [\dot{m}_H * \Delta H_f]$ 

Where  $\dot{m}_H$  is the mass flow of ammonia required to produce the necessary hydrogen, Cp is the specific heat capacity of ammonia and  $\Delta T$  is the temperature difference to which ammonia should be heated to. The energy consumed during the decomposition of ammonia is given by the product of ammonia mass flow and enthalpy of formation of ammonia. The excess ammonia flow required can be calculated by combining Equation 3 and 4 as given in Equation 5.

$$\dot{m}_{excess} = \frac{\left[\dot{m}_H * C_p * \Delta T\right] + \left[\dot{m}_H * \Delta H_f\right]}{LHV * \eta} \tag{5}$$

Except for  $\dot{m}_H$ , all other values in Equation 5 are constants with  $\Delta T$  assumed to be 600K and  $\eta$  to be 70%, these values are given in Table 5 below.

**Table 5.** Values of various parameters taken into consideration for revised efficiency calculation

Parameter	Notation	Value	Unit
Specific heat	Cp	2.175	kJ/kg K
capacity of			
ammonia			

Temperature	$\Delta T$	600	K
difference			
Enthalpy of	$\Delta H_{\rm f}$	2695	kJ/kg
decomposition			
Lower heating	LHV	18.8	MJ/kg
value of			
ammonia			
Efficiency of	η	70	%
decomposition			

The revised indicated thermal efficiency can be calculated by adding the excess ammonia consumed to produce hydrogen into the efficiency calculation as given in Equation 6.

$\eta_{revised}$		(6)
_ (	Indicated Power	
$-\sqrt{(Fuel)}$	energy consump + ṁ <sub>excess</sub> ) * LHV)	
* 100		

The variation of the calculated revised efficiency and the exhaust gas temperature is shown in Figs. 16 and 17, respectively. Unlike the ITE curves in Fig. 15, the revised efficiency is more sensitive to the hydrogen energy fraction in the fuel mix. The values of efficiency decrease with increase of hydrogen, as more ammonia is consumed to produce the hydrogen. As expected, running under lean conditions minimises the efficiency penalty associated with hydrogen production. As a result, the engine can operate with comparable efficiency to the stoichiometric-minimum hydrogen point at  $\lambda$ =1.2 and 20% hydrogen, with the latter offering viable engine-out emissions for the SCR.

Furthermore, it should be noted that the revised efficiency could be improved considerably by taking advantage of exhaust gas waste heat or possibly future catalysts that can decompose ammonia at lower temperatures. As illustrated in the data of exhaust gas temperatures in Fig. 17, the exhaust gas temperature is around  $400^{\circ}$ C for both loads. This suggests that there should be sufficient exhaust gas temperature to help preheat ammonia considering the tests were performed in a single cylinder engine as opposed to a multicylinder engine that should generate significantly higher exhaust gas temperatures.





Fig. 16. Variation of revised ITE for various H<sub>2</sub> fuel ratios at different  $\lambda$  for 6bar and 14bar IMEPn



Fig. 17. Variation of Exhaust gas temperature for various hydrogen fuel ratios at different  $\lambda$  for 6bar and 14bar IMEPn

#### 4. Conclusions

The currently reported work involved experiments to develop a novel lean burn spark ignition ammonia-hydrogen co-fuelling strategy, with the ultimate aim of demonstrating that such an approach would enable high engine operating efficiency with the potential to also adopt existing SCR emissions after-treatment systems in the future to help control key pollutants.

Initial experiments involved benchmarking the engine under stoichiometric operation as a baseline Results demonstrated that operating the engine at lambda 1 is viable, with appropriately minimised supplementary hydrogen when required to improve

combustion stability at low speeds and loads. However, as engine speed increased at a given load it was found that increasingly higher amounts of hydrogen were required, attributed to the presence of residual burned mixture at low loads or the slow burning of ammonia at higher speeds. Operating the engine under these conditions resulted in excessive ammonia slip.

Further studies were undertaken at varied air-to-fuel ratios at constant load, with results from these tests indicating that operating the engine with ~20% hydrogen substitution at  $\lambda$  1.2 to 1.4 resulted in equivalent engine-out NOx and unburned ammonia emissions (i.e. the ideal alpha ratio of ~1). Furthermore, the ideal operating conditions



remained relatively similar regardless of engine load (inferring the need for simpler engine calibration) and offered better thermal efficiency than stoichiometric operation with similar amounts of hydrogen. While operating lean reduces the exhaust gas temperature (which could have an adverse impact on aftertreatment system efficiency), values remained within viable limits for effective SCR operation (despite the use of a single cylinder, which typically run colder exhaust temperatures than multi-cylinder real world engines). Another challenge with operating the engine under lean conditions was the slight increase in N<sub>2</sub>O by ~10ppm (2730ppm CO<sub>2-eq</sub>) from stoichiometric conditions until  $\lambda$ =1.4. Whilst N<sub>2</sub>O is a potent greenhouse gas with a GWP<sub>100</sub> of 273, at these concentrations, its impact is small compared to the CO<sub>2</sub> emissions from the engine operating on fossilderived hydrocarbon fuel (e.g. gasoline). To summarise, the overall reduction in GHG impact was >90% across the entire engine operating map (without any N<sub>2</sub>O after-treatment).

Further experiments were conducted at different hydrogen substitution ratios and air-to-fuel ratios, to understand the general related impact of varied H<sub>2</sub> on combustion, performance, fuel economy and emissions at two engine loads (1400rpm-6bar IMEPn and 1400rpm-14bar IMEPn). It was observed that the addition of hydrogen improved the alpha ratio mainly due to an increase in engine-out NOx emissions from the higher temperature combustion. Hydrogen also enabled stable operation of the engine at leaner conditions, with the initial phase of combustion (0-10% MFB) becoming faster with an increase in hydrogen regardless of air-tofuel ratio. Compared to the initial phase of combustion, the air-to-fuel ratio had a much more significant impact on the combustion duration, especially when operating beyond  $\lambda$ =1.2.

It was concluded that lean operating conditions enabled higher thermal efficiency compared to stoichiometric conditions. Thermal efficiency also remained less sensitive to hydrogen energy fraction, with the operation of the engine at  $\lambda$ =1.2 and 20% hydrogen resulting in a 2% improvement in thermal efficiency. Since the efficiency calculation did not account for the energy consumed to produce hydrogen, a revised efficiency was estimated by assuming all the power required to decompose ammonia into hydrogen came from consuming excess ammonia. While the revised efficiency decreased the efficiency at all hydrogen co-fuelling points, the calculated efficiency when operating with an alpha ratio of 1 was similar to stoichiometric operation i.e. with lean operation effectively negating the losses of the ammonia cracking and with the additional benefit of vastly improved

engine-out emissions. Future work will involve investigating practical impacts from ammonia cracking e.g. the impact of returning a mix of nitrogen and hydrogen on combustion together with practical effects such as cracker waste heat recovery in the engine. Overall, the work has demonstrated the high promise of using relatively small amounts of hydrogen under lean burn conditions to assist combustion, performance, fuel economy and emissions control in future four-stroke spark ignited ammonia engines.

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#### **Conflicts of Interest**

The authors declare no conflict of interest.

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#### Definitions

CAD : Crank Angle Degree NH<sub>3</sub>: Ammonia **NOx :** Oxides of Nitrogen SI : Spark Ignition **LHV**: Lower heating Value **ITE**: Indicated thermal efficiency **MFB** : Mass Fraction Burned CoV: Coefficient of Variance **E10 :** Gasoline with 10% ethanol CI: Compressed Ignition **DI:** Direct injection **PFI**: Port fuel Injection **BTDC** : Before Top dead centre **BTDCf** : Before Top dead centre firing **MBT**: Maximum Brake Torque **ppm**: parts per million **IMEPn** : Net Indicated Mean Effective Pressure



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