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USE OF ELECTROFUEL BLENDS IN HOMOGENEOUS-CHARGE COMPRESSION-IGNITION ENGINES :

AN EXPERIMENTAL FOCUS ON AMMONIA-HYDROGEN

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*To Léa, my love,
for she gave me the strength to accomplish this adventure.*

As far as the energy and global warming issues are concerned: insulate your home, invest green, use your bike, and live in sobriety.

Une société vraiment libre, une société autonome, doit savoir s'autolimiter, savoir qu'il y a des choses qu'on ne peut pas faire ou qu'il ne faut même pas essayer de faire ou qu'il ne faut pas désirer.

Cornelius Castoriadis

New energy cannot be created and high grade energy is being destroyed. An economy based on endless growth is Unsustainable. [...] A species set on endless growth is Unsustainable.

Muse - Unsustainable

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List of publications

CHAPTER 2 is based on the following submission to peer-reviewing:

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Nomenclature

Abbreviations

0D 0-Dimensional

AMP Amplifier

aTDC after Top Dead Center

bb blow-by

BDC Bottom Dead Center

BE Brake Efficiency

BMEP Brake Mean Effective Pressure

bTDC before Top Dead Center

BTE Brake Thermal Efficiency

CA Crank Angle

CA50 Crank Angle at which 50% of the combustion heat has been released.

CAD Crank Angle Degree

CAES Compressed-Air Energy Storage

CCGT Combined-Cycle Gas Turbine

CCS Carbon Capture and Storage

CHP Combined Heat and Power

CI Compression Ignition

CN Cetane Number

<i>COP</i>	Coefficient Of Performance
<i>CR</i>	Compression Ratio
<i>cyl</i>	cylinder
<i>DHN</i>	District Heating Network
<i>DI</i>	Direct Injection
<i>EGAR</i>	Exhaust Gas Air Replacement
<i>EGR</i>	Exhaust Gas Recirculation
<i>EROI</i>	Energy Return On Investment
<i>EVC</i>	Exhaust Valve Closure
<i>EVO</i>	Exhaust Valve Opening
<i>FC</i>	Fuel-Cell
<i>FS</i>	Full Scale
<i>FTIR</i>	Fourier-Transfor Infra-Red spectroscopy
<i>FuelMEP</i>	Fuel Mean Effective Pressure
<i>GT</i>	Gas Turbine
<i>H – B</i>	Haber-Bosch
<i>HCCI</i>	Homogeneous-Charge Compression-Ignition
<i>HHV</i>	Higher Heating Value
<i>HRR</i>	Heat Release Rate
<i>ICE</i>	Internal Combustion Engine
<i>IE</i>	Indicated Efficiency
<i>IEA</i>	International Energy Agency
<i>IMEP</i>	Indicated Mean Effective Pressure
<i>IVC</i>	Intake Valve Closure
<i>IVO</i>	Intake Valve Opening

<i>LC</i>	Least Count
<i>LCA</i>	Life Cycle Assessment
<i>LCOE</i>	Levelised Cost Of Energy
<i>LCOES</i>	Levelised Cost Of Energy and Storage
<i>LHV</i>	Lower Heating Value
<i>LTC</i>	Low Temperature Combustion
<i>LTHR</i>	Low Temperature Heat Release
<i>MFC</i>	Mass Flow Controller
<i>mGT</i>	micro Gas Turbine
<i>MON</i>	Motor Octane Number
<i>MPRR</i>	Maximum Pressure Rise Rate
<i>NDIR</i>	Non Dispersive Infrared Sensor
<i>ON</i>	Octane Number
<i>P2F</i>	Power-to-Fuel
<i>P2F2P</i>	Power-to-Fuel-to-Power
<i>PEM</i>	Proton Exchange Membrane
<i>PHES</i>	Pumped-Hydro Energy Storage
<i>PPC</i>	Partially-Premixed Combustion
<i>ppm</i>	parts per million
<i>PV</i>	Process Value
<i>PZT</i>	Piezoelectric Transducer
<i>RCCI</i>	Reactivity-Controlled Compression-Ignition
<i>RCM</i>	Rapid Compression Machine
<i>RGF</i>	Residual Gas Fraction
<i>RI</i>	Ringling Intensity

<i>RON</i>	Research Octane Number
<i>ROPA</i>	Rate Of Production Analysis
<i>RPM</i>	Rotation Per Minute
<i>SACI</i>	Spark-Assisted Compression-Ignition
<i>SCCI</i>	Stratified-Charge Compression-Ignition
<i>SI</i>	Spark Ignition
<i>SOC</i>	Start Of Combustion
<i>SOE</i>	Solid Oxide Electrolyser
<i>SOEC</i>	Solid Oxide Electrolysis Cell
<i>ST</i>	Shock Tube
<i>SV</i>	Set Value
<i>TDC</i>	Top Dead Center
<i>TSCI</i>	Thermally Stratified Compression Ignition
<i>TWC</i>	Three Way Catalyst
<i>WDI</i>	Water Direct Injection
<i>WOT</i>	Wide Open Throttle

Greek letters

α	Scaling factor for the convection correlations [-]
δ	Ignition delay [s]
γ	Ratio of the heat capacities [-]
ϕ	Equivalence ratio [-]
τ	TDC offset [CAD]
θ	Crank angle position [CAD aTDC]

Symbols

<i>A</i>	Surface [m ²]
----------	---------------------------

B	Bore diameter [m]
c_p	Specific heat capacity at constant pressure [J/mol/K]
c_v	Specific heat capacity at constant volume [J/mol/K]
H	Enthalpy [J/kg]
h	Heat convection coefficient [W/m ² /K]
L	Connecting rod length [m]
m	Mass [kg]
M_m	Molar mass [g/mol]
n	Mole quantity [mol]
p	Pressure [Pa]
Q	Heat exchanged/released [J]
R	Ideal gas constant [J/mol/K]
S	Stroke length [m]
T	Temperature [K]
t	Time [s]
u	uncertainty at a σ confidence level
U_{95}	Uncertainty at a $2\sigma=95\%$ confidence level
V	Volume [m ³]
V_d	Displacement volume [m ³]

Abstract

The energy transition towards major renewable shares comes at many costs and challenges. One of them is the need for massive and long term electricity storage, for which hydrogen, ammonia, methane and methanol produced from water electrolysis, and carbon capture when needed, are being envisioned. A clean and efficient conversion system able to use these specific fuels is yet to be designed. This thesis investigates the Homogeneous-Charge Compression-Ignition (HCCI) engine potential for the clean and efficient use of the four electrofuels and their blends. While achieving multi-fuel operation, the two main challenges to overcome are the inherent low power density of HCCI engines, and the emission of unburned fuel.

First, a numerical investigation of the electrofuels under various HCCI conditions is performed: intake temperature and pressure, fuel blending, fuel loading, and compression ratio variations are studied. Methane and ammonia appear quite resistant to auto-ignition and need to be promoted. For an optimum power density, blending them with hydrogen or methanol, or increasing the compression ratio, seems a better alternative to intake temperature increase. Nevertheless, the possibility of using the four electrofuels in the same engine is demonstrated. Still, the quantitative trade-off linking the compression ratio and other operating conditions regarding power density and pollutant emissions for these blends is to be experimented. Finally, given their uncarbonated aspect, opposed auto-ignition resistance, relative poor knowledge, and high power density potential, the remaining part of this thesis is dedicated to the investigation of the ammonia-hydrogen blend in HCCI engines.

Two preliminary experimental studies are carried out with ammonia and hydrogen. I first used a low compression ratio (15:1) HCCI engine to assess

the limits and potential of ammonia: hydrogen promotion is mandatory under such conditions but ammonia slow kinetics prevent ringing (damaging combustion from extreme intensity) by damping hydrogen combustion through radical sharing, hence allowing higher equivalence ratios. Regarding emissions, ammonia emits above 1000 ppm of NO_x and N_2O is emitted when the combustion temperature is too low. Yet Exhaust Gas Recirculation (EGR) and ammonia loading can be used to mitigate those. I then led a second preliminary study using a Rapid Compression Machine (RCM) to obtain the first auto-ignition data of ammonia and ammonia-hydrogen under low temperature conditions. The existing kinetic mechanisms are shown to be unable to correctly predict ammonia-hydrogen behaviour under these conditions, and improvement directions are suggested. Moreover, ammonia is shown to resist hydrogen promotion for hydrogen concentrations below 20%vol. in the fuel blend.

The gained knowledge is capitalised in the making of an ammonia HCCI test bench at UCLouvain. A compression ratio of 23:1 is selected to allow the full ammonia-hydrogen blending range. The engine is equipped with a UV spectrometer to record unburned ammonia and NO_x emissions. The results indicate that ammonia has a 50% IMEP increase potential compared to hydrogen and slightly outperforms both methanol and methane thanks to its ringing resistance. To avoid any combustion quenching, the combustion temperature must reach at least 1700 K, which is favoured with increased hydrogen fractions and other measures: reduced wall cooling or wall coatings; maximised stroke-to-bore ratio; flat piston with minimised crevices; etc. Finally regarding NO_x emissions, both ammonia and hydrogen could be operated at maximal load without producing thermal- NO_x , however ammonia led to the production of at least 600 ppm of fuel- NO_x with late combustion exceeding 2000 ppm. The use of EGR for a reduced oxygen availability is a promising technique and can provide a two-fold reduction in emissions, yet it requires counter-acting measures for the reduced combustion temperature.

Of course, many questions remain un-answered for the final design of a multi-fuel HCCI application. Yet, I believe this thesis to pave the way to answering those questions by giving numerical and experimental tools as well as reference results.

Besides, many side tasks have been performed and will be included in the text: the successful use of water direct injection for thermal stratification and improved power density; the negligible effect of ozone seeding on ammonia auto-ignition; the development of a methodology to quantify experimental engine measurement uncertainties; and considerations for ammonia low temperature combustion mechanisms improvement.

Foreword

A tale of two possible outcomes

Inspired from "*Collapse*" by Jared Diamond

The Viking expansion across the North Atlantic began in the year 793. After reaching the Faeroe Island and then Iceland, the Vikings finally set foot in southern Greenland around the year 870.

Devoid of any vegetation in most of its areas, Greenland offered yet a few protecting fjords with luxuriant pastures where the Vikings could settle. Despite being fierce sea raiders, Vikings were foremost farmers cultivating wheat and raising livestock. Woodlands became quickly cleared and turned into the necessary pastures to the intensive Viking livestock and wheat economy. Yet all this was done disregarding the fragile Greenland environment. Cleared land was newly exposed to North Atlantic winds, and livestock were crushing any plant or tree regrowth from natural seeding. Massive soil erosion was on its way, preventing from proper wheat growing. By the year 1400, all Viking Greenlanders had starved to death, without the possibility of importing goods or sailing back due to the lack of wood to build boats.

Surprisingly, Icelandic Vikings encountered quite the same environmental problems, but with a different outcome. Icelandic soils being considered more fragile than Greenland ones, deforestation, soil erosion and overgrazing came as well. However, Icelandic Vikings took notice and adopted drastic measures away from their ancestors' culture: giving up on pigs and goats, restricting sheep to a maximal number per acre of land, and establishing pasture rotation management. As a result, the Icelandic Viking society did not collapse, but Iceland still bears today the scars of former massive deforestation and soil erosion.

Le secret d'ennuyer est de vouloir tout dire.

Voltaire

1

Introduction

1.1 Context & Motivation

Just like the Icelandic Vikings noticed they had massively deforested their island, we have noticed the dangerous levels of CO₂ in our atmosphere. Now, it is up to us to do something about it and survive like the Icelandic Vikings, or to do business as usual like Greenlander Vikings and *collapse*.

Our energy consumption impact on the climate, through the *greenhouse* effect of our CO₂ emissions, is not to be demonstrated anymore. The global surface temperature of the Earth is already +1 °C higher compared to stable pre-industrial levels and is expected to reach +4 °C by 2100 if nothing is changed. More droughts, floods, perturbation of ocean currents, hurricanes, soil erosion and other climate-related disasters, massive deaths and population migrations shall arise.

New policies, suggested by most countries after the Paris Agreements of the 2015 COP 21 summit, are not sufficient to diminish our greenhouse gas emissions. According to the world energy model of the International Energy

Agency, see Figure 1.1, following these New Policies will not allow to decrease our global emissions. CO₂ emissions have increased in 2017 and 2018 as the New Policies cannot cope with the increasing world population and quality of living (i.e. *economic growth*).

If we are to maintain the global warming under an acceptable level (below +1.5-2 °C - i.e. near miss of the point of no return), our energy-related greenhouse gas emissions must fall to zero by 2065, see Figure 1.1. Yet the existing and under construction assets in 2018 (power plants, industries, buildings...) will only stop emitting CO₂ around 2060. This leaves us with limited room for manoeuvre, as seen in Figure 1.1, for the transition towards total decarbonisation. It means that we have a CO₂ budget of around 400 GtCO₂ that can still be emitted until 2065. After which all the energy we use, down to the energy used to produce our solar panels and wind turbines, must be green.

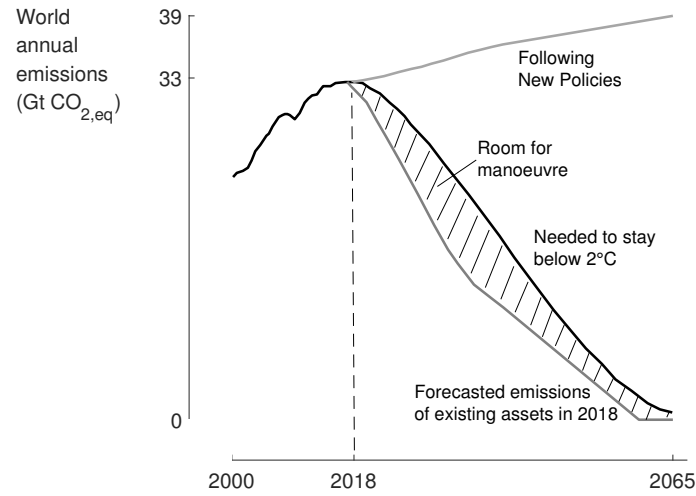


Figure 1.1 – Energy related CO₂ emissions. The existing CO₂ emitting assets leave little space for additional emissions if we want to stay below +2 °C of global warming. The New Policies will not even allow to decrease our emissions. Reproduced from the 2018 World Energy Outlook from the International Energy Agency [1, 2].

In 2018, all the energy-related CO₂ emissions summed up to 33Gt and are split between: electricity production (36%), transport (24%), industries (20%), building heating and cooling (18%), and others (2%). Yet they do not include the meat and dairy livestock related emissions which amounts to 7.1 Gt CO_{2,eq}, or as much as the whole transport sector [3, 4], including nutrition of animals, direct methane emissions, and land use change. This further stresses the critical state we are in.

Nine billion people will be stepping on Earth's surface, by 2050, with ever higher lifestyle expectations. The human civilisation will henceforth need to shift towards sustainability following the path of consumption reduction and maximal renewable integration. This thesis deals with an innovative way to maximise the potential we can extract from renewable energies.

1.1.1 The energy transition towards sustainability

If we are anywhere serious about willing to stay below the +2 °C barrier, every CO₂-saving solution is needed. It includes massive political and individual actions (i.e. a lifestyle change like Icelandic Vikings, such as the way we eat meat, the way we (need to) commute every day, the way we consume disposable items...), but also the energy transition towards renewable energy.

Reaching zero net CO₂ emissions by 2065 means that every joule of energy, down to the energy used to extract minerals or building solar panels, must come from renewable sources. Every joule coming from fossil fuel will have to be compensated by carbon capture and storage. The big question is two-folded: first, is there enough potential for solar, wind, hydro, biomass, geothermal, tidal, wave, and ocean thermal gradient to supply 100% of our primary energy needs? second, can we harvest enough of those by 2065 and keep meeting the (probably) increasing energy demand afterwards? The answer comes two-folded. It is not possible to have a 11 billion human society with living standards being those of the current First World relying 100% on renewable energy. Yet it is technically feasible provided a moderate lifestyle combining sobriety and efficiency. Estimates about the required reduction in primary energy consumption to do so are as various as variable, but a reduction of at least 25% by 2050 seems needed [1, 5, 6].

The energetic profitability of renewables, called Energy Return On Investment (EROI) [7, 8], is decreasing when their worldwide use is increasing. The EROI of a specific technology/primary energy is the ratio of the energy pro-

duced by the technology over its whole lifetime with respect to the energy required by the technology to be constructed, operated, and dismantled. Recent studies, such as the ones from Dupont et al. [7, 8], show the decreasing trend of renewables EROI as they are installed more and more widely, see Figure 1.2. Dupont et al. [8] estimate that the annual world wind and solar energy potential is 720 EJ (or the equivalent of the expected world annual consumption by 2040 [2]) if we restrict ourselves to EROI higher than 8.9. Compared to fossil fuels having an EROI of around 25-30 (which allowed the First World to reach its actual lifestyle), renewables have much lower EROIs with at best 15 for wind turbines and 10 for solar panels. An EROI of 7 to 9 is often considered the minimum required by a society to maintain a quality of life including transportation, nutrition, and minimal education, but not sufficient for high level education, health care, and activities such as arts.

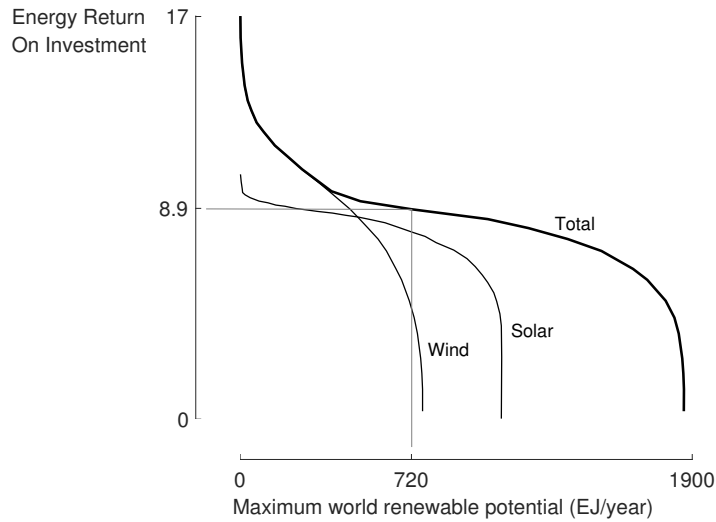


Figure 1.2 – The estimated world potential for solar and wind cannot meet the 720 EJ consumed worldwide by 2040 with an EROI higher than 8.9. These estimates include solar PV and CSP, and wind on-shore and off-shore. Yet they do not include the associated energy-costs with electricity grid modifications and storage facilities. Adapted from [7, 8].

The decrease in EROI with increasing renewable installation is due to the variability in space of the renewable resources, with the best spots being used first, decreased global potential due to over exploitation, and maximal distance to electrical consumers. Finally, those calculations do not take into account that the produced renewable power might be at a place or time where no consumption is needed. Therefore, for such 100% scenarios to be actually achievable, not a single Joule of renewable production must be wasted and storage and transport are needed to move the energy at a place and time where it will be consumed.

1.1.2 Long-term and High-capacity storage: Power-to-Fuel

To deal with the urgent need of renewable, and its limited availability in space and time, any excess electricity must be stored for further use. Moreover, at high renewable shares, the intermittency of renewables will push the electrical grid towards instability and black-out, not mentioning the market price volatility. Storage and restitution are needed to maintain the balance between production and consumption. Limpens et al. [9] showed that a society transitioning from fossil fuels to renewable electricity production cannot cope without storage on a daily basis starting from 30 % of renewable share, and long-term storage starting from 75 % renewable share, see Figure 1.3. With the intermittency and seasonal variability of renewables, we face the need to store huge amounts of electricity. The focus of this thesis lies with affordable and efficient ways of providing long-term storage.

There are two sides to the long-term electricity storage when dealing with high shares ($> 50\%$) of renewables in a given region. The first one is the duration itself given that the excess might occur for consecutive weeks or months. The second is the required storage high-capacity since renewables most often shine and blow equivalently in very large areas. Therefore when a region relies mostly on renewables for its energy supply and faces simultaneous high wind and solar irradiation, it faces generalized and massive excess power with the short-term solution being curtailment.

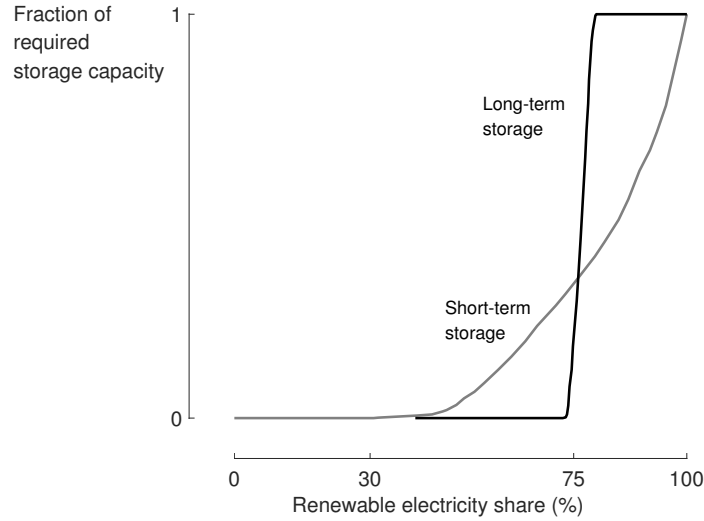


Figure 1.3 – The need for long-term storage arises at 75% of renewable electricity share. This storage is needed to stabilize the electrical grid and to allow for more renewables to integrate the network. Adapted from [9].

For long-term and high-capacity storage, most storage technologies cannot be used. It requires a low discharge rate, a high energy density, and a low price on storage energy capacity. Flywheels, batteries, Compressed-Air Energy Storage (CAES), and Pumped-Hydro Energy Storage (PHES) do possess some of these characteristics, but Power-to-Fuel (P2F) outperforms them in all those categories, see Figure 1.4. P2F consists in the production of a fuel, having as a root hydrogen production from water electrolysis. Excepted for local storage where density and transport concerns are reduced, hydrogen mass storage is economically and energetically expensive. The compression/liquefaction required to maximise the density implies the use of adapted tanks to withstand the pressure/temperature and avoid leakages. Therefore hydrogen is preferably converted to other fuels more convenient for massive storage and handling, and that can be produced efficiently from readily accessible buildings blocks such as nitrogen and carbon dioxide. Among others, one can cite the engine compatible methane, methanol, ammonia, nitromethane, acetic acid, dimethyl ether, and formic acid. Still this thesis will focus, in addition to hydrogen, on methane, methanol and ammonia. As the market for electrofuel is not yet developed,

the main reason to focus on them is that they benefit from a worldwide use and consequent infrastructures: methane can be injected into the natural gas grid without any restriction, and ammonia and methanol are already within the five most produced chemicals worldwide given their dominant use in the fertiliser and chemical industries. Moreover, ammonia is the only simple electrofuel that does not require carbon to be produced and is liquid at a pressure of 9 bar, and methane and methanol are the most easily produced from hydrogen. Therefore, these three fuels and hydrogen will be called the *electrofuels* of interest for the rest of this manuscript although other electrofuels such as nitromethane, acetic acid, dimethyl ether, and formic acid might become of interest due to their different properties (e.g. lower auto-ignition resistance).

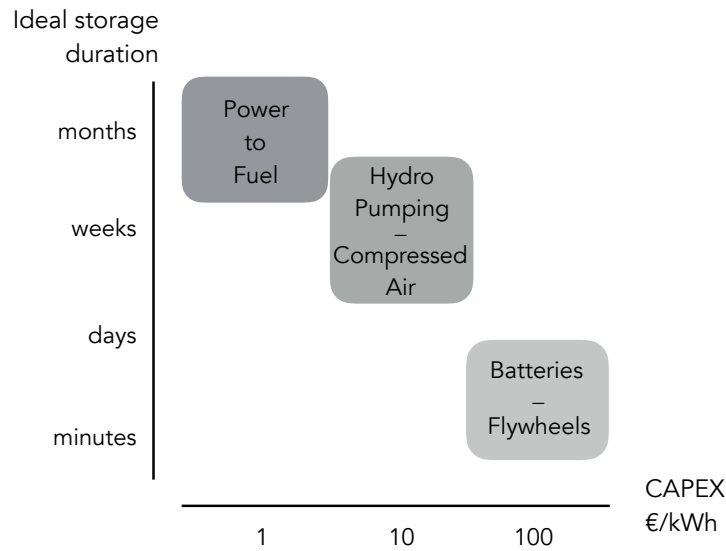


Figure 1.4 – The Power-to-Fuel storage technology is the ideal candidate for long-term storage, due to its low CAPEX (CAPital EXpenditures, i.e. investment costs) for the storage energy capacity. Batteries require frequent charge and discharge, on a daily basis, to reduce their return on investment period because of their huge CAPEX. Adapted from [10–12].

The main disadvantage of P2F compared to other technologies is its rather low efficiency. With an electrolysis efficiency of 70-75 %_{LHV}, i.e. based on hy-

drogen Lower Heating Value (LHV), hydrogen must then be converted back to electricity with an efficiency ranging from 60% for Combined-Cycle Gas Turbine (CCGT) or fuel-cells, to 50% for big engines and 30% for the smallest engines. Moreover, the conversion from hydrogen to any other fuel adds roughly another 80% efficiency. Therefore, the goal of this thesis is to minimise the losses during the conversion of the electrofuels to electricity.

1.1.3 The need for integrated energy systems: decentralized cogeneration units

In light of the previous concerns of limited renewable potential and low EROI, the use we make out of those electrofuels must be the highest: achieving 60 % electrical efficiency in a centralized CCGT is nice, but achieving 95 % total efficiency in a decentralized Combined Heat and Power (CHP) unit is better. Still in order to valorise the generated heat, and considering that low temperature heat is not transported easily, the CHP units need to operate at a decentralized level, see Figure 1.5.

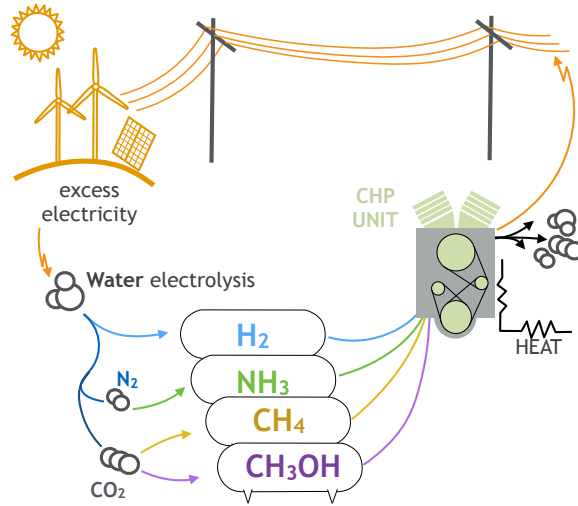


Figure 1.5 – A CHP unit allows the efficient conversion of the four P2F electrofuels into electricity and heat. CHP flexibility between the four fuels is required to provide maximum use and security of supply.

These aspects pledge in favor of integrated systems using decentralized CHPs: an energy system that can valorise today's excess of electricity into tomorrow's need for energy, may it be electricity or heat for the residential or industrial sector. Yet, with higher uncertainty in production (i.e. renewable intermittency), these integrated energy systems need components to ensure the resilience to unforeseen events and to ensure the security of supply. To bring resilience, the decentralized CHP systems shall ideally be multi-electrofuel. In times of exceptional P2F shortages, natural gas obtained from the gas grid would ensure the security of supply, hence the interest for this CHP system to be suited to methane. Being suited to hydrogen seems ideal for times where medium-term storage could be used, in order to have higher conversion efficiencies instead of producing a long-term storage fuel. Finally, for place and time where liquid storage would be favored, the suitability to ammonia or methanol is needed.

A final question we might ask ourselves is : wouldn't it be more profitable to use the electrofuels in existing markets (like the steel industry for hydrogen, the fertilizer industry for ammonia, or the transportation sector with methane in place of CNG)? True, in a first step through the transition, the electrofuels could be used in existing fuel markets to gain momentum, production assets, and therefore reduce their cost of production, or create new markets where they could be sold at higher prices like for transportation. As an example, the fertilizer industry produces annually 180 Mt of ammonia from natural gas, which represents 0.5% of our annual world energy consumption. The potential for electrofuels in existing markets is huge, and is part of our need for near-100 % renewable energy. Eventually, if the near-100% renewable energy mark is not reached (i.e. fossil fuels are still being used), the use of the produced electrofuels in such markets instead of for providing the backup electricity in times of shortages will depend on the market prices and incentives, mainly, with constraints from needed fuel properties in some cases like for the aviation. Yet in the aim of bringing down the costs of the P2F2P concept, and help reaching the near-100% renewable energy mark, this thesis investigates the multi-electrofuel CHP concept.

1.2 The proposed solution

Here is a short description of the characteristics which the CHP unit must comply to. According to a recent review of 40 European district heating networks, their power production and thermal output ranges are 0.3-3 MW_{elec} and 0.1-10 MW_{th} [13]. The CHP unit should therefore be within the 0.3-3 MW electrical range. The highest electrical efficiency is desired (due to the foreseen electrification of the residential heating with heat pumps), still flexibility regarding the electricity to heat ratio produced is desired to allow matching the local demand. The unit shall be multi-electrofuel suited. Finally, pollutant emissions shall be minimized given their threat to local and global health, and the cost of the related after-treatment systems.

1.2.1 HCCI engines as combined heat and power units

A candidate to properly answer the need for a fuel-flexible, 0.3-3 MW_{elec} size CHP unit is the piston engine. Among the many piston engine combustion modes, the Homogeneous-Charge Compression-Ignition (HCCI) engine showcases advantages in terms of the high efficiency - clean operation compromise. This advantage is even stronger in the considered power range, as will be detailed later. The main characteristic of this engine is the combination of high efficiency and low pollutant emissions, already for small size engines. It has a different combustion strategy and phenomenology than conventional Spark Ignition (SI) or Compression Ignition (CI), see Figure 1.6.

First, the mixture is homogeneous and auto-ignites as soon as the compression leads to sufficiently high temperature and pressure. Indeed, no ignition device such as a spark is used, so the combustion onset relies on kinetically-driven auto-ignition. Given the mixture homogeneity, the whole mixture burns at once in a very short amount of time: up to 6 times shorter than for SI-CI. The short combustion duration represents an advantage regarding thermodynamics since more time is spent at high pressure and more energy can be extracted from the chamber to the crankshaft (i.e. closer to the ideal Otto cycle with a combustion at constant volume). Second, this generalised auto-ignition forces

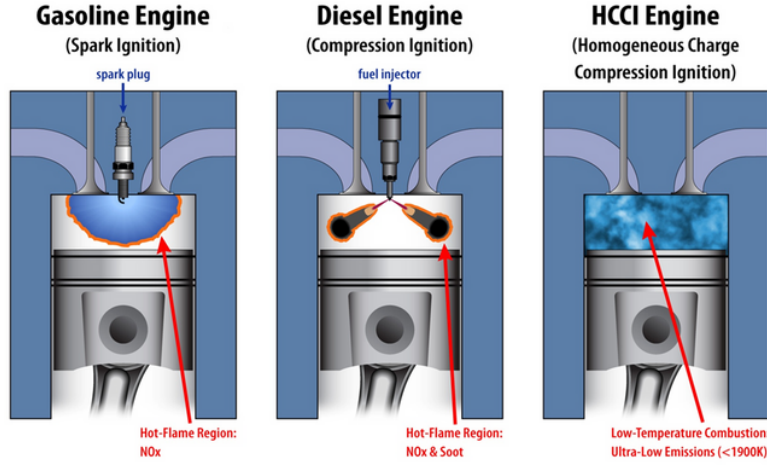


Figure 1.6 – The HCCI combustion is simultaneous across the chamber: the homogeneous mixture ignites at once since it is driven by the compression. Lower equivalence ratios are used to mitigate the combustion intensity, which leads to Low Temperature Combustion. Extremely rich and hot regions that produce soot and NO_x, like in Diesel and Gasoline applications, are avoided. Reproduced from [14].

to reduce the fuel loading (low equivalence ratio) which eventually leads to a reduced mixture heat capacity ratio hence a better thermodynamic efficiency. Third, the mechanism of auto-ignition combined to lean conditions protects from knocking and therefore very high compression ratios can be used, further improving the thermodynamic efficiency. Fourth, this reduction in fuel content leads to what is called Low Temperature Combustion (LTC): no thermal-NO_x and soot emissions, see Figure 1.7. The lower combustion temperature keeps the mixture away from the critical combination of oxygen and high temperatures that leads to the formation of thermal-NO_x. Moreover the absence of any local rich mixture (like in CI engines) prevent any soot production. These reasons explain the potential of HCCI engines for high efficiency and low pollutants, even at low engine sizes.

Regarding efficiencies, 100 kW research-lab HCCI engines showcase 43-45% brake efficiencies [16, 17] which are not met for commercial SI before 1 MW

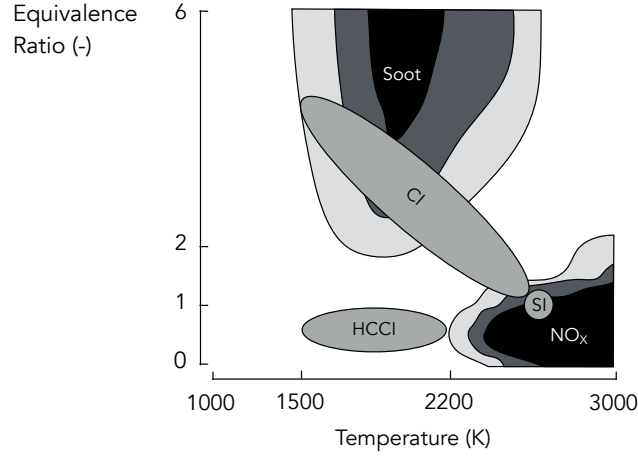


Figure 1.7 – Locally and globally lean HCCI conditions avoid the production of NO_x and soot emissions. Adapted from [15].

size (e.g. 42.8% electrical efficiency for the 1 MW_e Jenbacher type 4 engine, see Figure 1.8), but that are comparable to CI engines. As the brake efficiency increases with engine size (lower relative wall heat losses) and power density (the friction losses will lose weight in the balance) for SI engines (e.g. 50% brake efficiency for the 4.4 MW Wäertsilä 31SG), the same effects apply to the HCCI engines hence explaining its substantial potential for District Heating Networks (0.3-3 MW_e).

Regarding pollutant emissions, the new european regulations covering CHP gas engines in the 1-50 $\text{MW}_{\text{thermal}}$ range only concerns NO_x and SO_x [18]. The limits for NO_x are at 95 mg/Nm^3 for natural gas and 190 mg/Nm^3 for other gaseous fuels, with the former limit for natural gas being at 190 mg/Nm^3 . Current state-of-the-art gas engines cannot reach such NO_x levels without secondary measures (i.e. exhaust gas after-treatment). For example, Jenbacher engines emit 500 mg/Nm^3 of NO_x in their high efficiency mode, but can achieve 250 mg/Nm^3 of NO_x by derating their efficiency by 1.3 percentage point (down from 42.8 to 41.5 % electrical efficiency for the 1 MW_e Jenbacher type 4 engine). Therefore, HCCI engines present a considerable advantage for NO_x emissions since they can avoid the need of supplementary after-treatment systems.

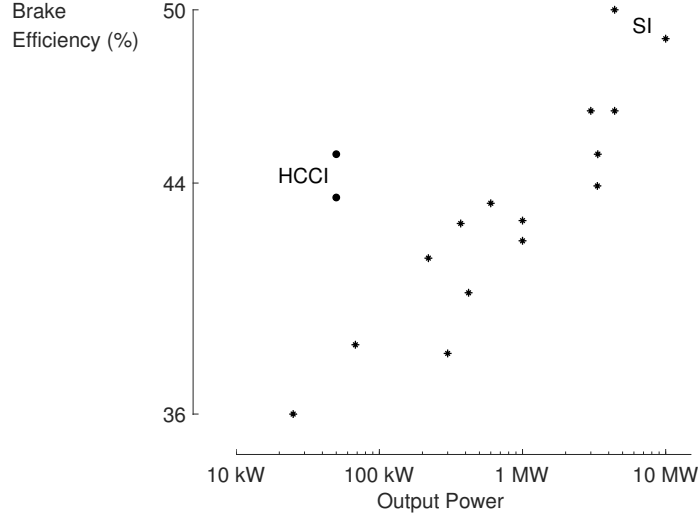


Figure 1.8 – Compared to commercial SI engines inventoried from stationary engine manufacturers (MAN, MWM, Jenbacher, Wärtsilä), a 100kW research HCCI engine showcases an efficiency that is not met for SI before the 1 MW size.

1.2.2 Expected challenges for a multi-electrofuel HCCI engine

All these benefits come, unfortunately, tied to three main issues. The first one is the control of the combustion timing and load. Without any direct control device such as a spark plug or an injector, the combustion timing relies solely on the auto-ignition process driven by the mixture kinetics (temperature and composition). Once the intake valve is closed, the die is cast. Still this issue can be discarded in our stationary application case given the fixed rotational speed and slow evolution of load requirements. However the combustion load control is difficult since a modification of the fuel or the fuel quantity changes the mixture composition and hence its auto-ignition resistance, especially for hydrogen. Moreover, the fuel quantity range between misfire and ringing conditions (i.e. too intense combustion) is narrow in HCCI conditions.

The second disadvantage is the low power output due to the low fuel contents. Higher CAPEX (CAPital EXpenditures, i.e. investment costs) than with SI-CI technologies are to be expected for too low power densities, as well as missing on an even higher efficiency potential due to higher relative friction

losses. This drawback will be a constant source of trade-off and optimisation in this thesis. Moreover, the four electrofuels of interest being resistant to auto-ignition and imposing high intake temperatures, it further lowers the HCCI power density, especially for methane and ammonia.

The third weakness is higher unburned emissions due to the low temperature aspect. For the electrofuels considered, minimizing unburned emissions (and properly characterizing to allow exhaust after-treatment) is a priority given the high toxicity of ammonia and methanol, and the high greenhouse effect of methane. Therefore, for HCCI applications, the avoidance of a NO_x after-treatment system will be to balance with the probable need for a bigger unburned fuel oxidiser system (even though such emissions are not regulated for the time being).

Eventually, the main aspect of integrated energy systems that the CHP unit must meet is the flexibility against fuel source and load. HCCI engines allow to use any fuel, as long as it creates an homogeneous gaseous mixture and that the conditions for auto-ignition are met at the right timing in the cycle. Still the cost and difficulty for meeting such conditions is either badly characterized for the electrofuels of interest and their blends or simply unknown.

These advantages and downsides are inherent to the HCCI concept, and each fuel will influence them in a positive or negative way. It is of interest to characterise them for the four electrofuels of interest. Hydrogen and methane have both been substantially studied under HCCI conditions, but it is not the case for ammonia and methanol, and blends thereof. The HCCI performances with the electrofuels of interest and their blends will be developed and analyzed further under the scope of this thesis.

1.3 Thesis questions & objectives

The scientific questions tackled by this thesis are related to the use of known and unknown electrofuels characteristics and their blends in an HCCI engine. The goal is the design of an electrofuel flexible HCCI engine with primary concerns on power density, efficiency, and pollutant emissions, knowing that the three drawbacks inherent to HCCI engines shall be mitigated since further exacerbated by these particular electrofuels. The initial list of scientific questions for this thesis is as follows:

- What is the kinetic behavior of ammonia under HCCI conditions (the other electrofuels being already well-known)?
- What are the operating conditions (compression ratio and intake conditions) for the electrofuels and their blends to be HCCI-suitable (avoid ringing and misfire)?
- What is the trade-off between multi-electrofuel flexibility and engine performances?
- How and how much do the electrofuels of interest and their blends mitigate/exacerbate HCCI inherent drawbacks?
- Are the conventional methodologies for HCCI power density and pollutant improvement suited to the electrofuels: exhaust gas recirculation, turbo-compression, etc.?

The way to succeed is to double your failure rate.

Thomas J. Watson

2

Electrofuel properties and state-of-the-art for their engine use

This chapter's sections 2.1 and 2.2 are based on the following submission:

Dias, V., Pochet, M., Contino, F., & Jeanmart, H. (2019). *Energy and economic costs of chemical storage*. Submitted to Frontiers in Mechanical Engineering.

As much as it is interesting to know what are the auto-ignition characteristics of the four electrofuels of interest, it is interesting to know how they are obtained and what they eventually produce when burned (energy, pollutants, ...). This chapter traces the story of each fuel, of their electro-production, of their properties (known and unknown regarding HCCI use), of their existing use in piston engines, of the influence of blending them together, and finally of their kinetic mechanisms or lack thereof.

2.1 Production of the electrofuels

The four electrofuels share the common root of water electrolysis for hydrogen production. Depending on the final fuel desired, the last building block might either be nitrogen (for ammonia) or carbon dioxide (for methane and methanol). Of course a wide variety of fuels can be produced from hydrogen (e.g. surrogates for diesel or gasoline), but the more complex the molecule is, the more complex the production process becomes with a reduced efficiency. Just like the Chinese characters for "crisis" (危机) are the combination of the characters for "danger" (危) and "opportunity" (机), the energy crisis we are facing might be the opportunity for us to move towards fuels with simpler molecules for the sectors that cannot be electrified. Simpler fuels are produced more efficiently.

Hydrogen

Hydrogen is obtained with an efficiency of about 70-75%, based on its LHV, for commercialised alkaline electrolyzers. For Proton Exchange Membrane (PEM) and Solid Oxide Electrolyser (SOE) fuel cells, although experimental research demonstrates LHV efficiencies in the range of 60-82% [19], the current commercial applications only manage to reach 55-62% [20], and 67-75% in development [21]. Yet hydrogen is not convenient for massive storage given its very low energetic density of about 10 MJ/Nm³. Hydrogen compression at 700 bar or liquefaction does not reach energetic densities higher than 4 GJ/m³ and 8 GJ/m³. Moreover, it is a very expensive storage solution given the high pressure or low temperature to withstand. The overall efficiency for stored hydrogen is 50-60% of its LHV, with liquefaction or compression [22–24]. Alternatives to compression or liquefaction storage are liquefaction in organic liquid (10 GJ/m³) and absorption in metal hydrides (15 GJ/m³). Yet both of them are still under development and expensive, and they require a specific process to free the stored hydrogen [25–27]. Finally, hydrogen can be inserted into the natural gas network up to 2% in volume, as currently restricted in Europe [28], yet mixing it with a different fuel. Therefore, hydrogen storage is only preferred for mid-term and limited quantity electricity storage and other alternatives are currently needed.

Methane

The main P2F route envisioned for methane production is by combining hydrogen and carbon dioxide through the Sabatier process [29]. The overall LHV conversion efficiency from electricity reaches 64%, using carbon capture from coal power plant fuel gases (1.04 GJ/tCO₂). The carbon dioxide could also be captured from the air to make the process independent of a centralised carbon source, yet with a doubled end-product cost from 203 to 406 €/MWh_{fuel, no storage}. Two other routes for renewable methane production are the biomass anaerobic digestion (producing methane and carbon dioxide) and the Fisher-Tropsch process combining hydrogen and carbon monoxide. For storage, methane can either be liquefied (10% penalty on the overall production efficiency) or compressed at 60 bar and inserted into the natural gas network. Mainly the latter solution is envisioned as the penalty on the overall efficiency would be smaller than 5%; it would ensure a direct use/replacement of natural gas fossil fuel; it would provide transportation at the same time; all the combustion systems based on natural gas are compatible with methane.

Methanol

Methanol is liquid at ambient conditions, with an energetic density of 15.6 GJ/m³. Methanol is obtained from CO₂ hydrogenation, as for methane, yet with another equilibrium in terms of reactants and thermodynamic state [30]. The overall LHV efficiency for electricity conversion to methanol is 61%. Methanol bears the same considerations regarding carbon dioxide as methane.

Ammonia

Ammonia is obtained through the Haber-Bosch process by combining hydrogen and nitrogen, which composes around 79%vol. of the air. be captured from the air. This might be its main advantage compared to methane and methanol: it only needs water, air and electricity to be produced. It can consequently be produced practically anywhere, without the need of a carbon source. The overall liquid ammonia production efficiency from electricity currently reaches 50-55% of its LHV [31, 32] but recent research on SOE recovering heat from the Haber-Bosch process shows efficiencies that can exceed 62% LHV [25, 33]. Ammonia is liquefied at just 9 bar or −33 °C, with a density of 13 GJ/m³ and a 0.1% loss in overall efficiency, hence offering a more practical storage vector

than hydrogen for long periods and high capacities. Ammonia is currently the second most produced chemical around the world (mainly for the fertilising industry) and consequently benefits from a wide handling know-how: pressurised or cryogenic storage, liquefied truck-transportation, gaseous pipeline transportation, etc.

Solar thermochemical conversion

A promising alternative to P2F is the direct conversion of solar thermal energy to fuels. This principle uses a concentrated solar tower where oxido-reduction reactions occurs using the various building blocks (H_2O , CO_2 , and N_2) and solar heat as activation energy. Although this concept do not help regarding the excess renewable electricity storage, efficiencies from solar energy to fuel LHV of 30% are claimed and might help creating the new electrofuel market [34].

2.2 LCOES considerations: from electricity to fuel transportation

Each of the four electrofuel having its own production process and preferred storage system, it is of interest comparing them with fair indicators. An energetic and economic point of view are used for the roundtrip energetic efficiencies and the Levelised Cost Of Energy and Storage (LCOES). The LCOES indicator is the ratio of all the lifetime costs (investment and operational costs of charging, discharging, and auxiliary units) over the sum of energy released as output.

Dias et al. [29] recently submitted for publication a comparative LCOES study for the four electrofuels of interests. They used the same processes and LHV efficiencies as the one described above and reported in Table 2.1, as well as state-of-the-art references for investment and operational costs. Apart from the hydrogen stored as a high-pressure gas for which the required tank thickness is enormous, the four other envisioned P2F solutions end up at around 250€/MWh (direct consequence of the major share taken by the electrolyser and electricity purchase), with a slight advantage for methanol [29]. Yet LCOES studies are very speculative and such differences are not significant next to the estimation uncertainties.

Table 2.1 – *Efficiencies and LCOES of the four electrofuels of interest [29]*

	H _{2,gas}	H _{2,liq.}	CH _{4,gas}	CH _{3OH} _{liq.}	NH _{3,liq.}
LHV efficiency (%)	60	50	59	60	52
LCOES (€/MWh)	490	240	260	220	260

To fairly compare P2F to other long-term storage technologies, one must consider the Power-to-Fuel-to-Power (P2F2P) systems that include a final conversion step from P2F to electricity. Despite the lower round trip efficiency of P2F2P compared to other long-term storage solutions, see Table 2.2, LCOES analyses showed that it stays cost-competitive. Jülich did a comprehensive LCOES study comparing PHES, CAES and P2F2P [10]. Using consistent assumptions among the different technologies, she obtained LCOES of 1400 €/MWh_e for PHES, 2400 €/MWh_e for CAES, and 500 €/MWh_e for P2F2P. Yet the P2F2P LCOES of Jülich considered an LCOES for stored-methane of 140 €/MWh, which is only 54% of what Dias obtained. For the discharging unit of P2F2P, Jülich uses CCGT with 58% electrical efficiency and 727 €/kW of investment. Hedegaard and Meibom obtained similar results [12]. When considering Dias results together with a 1-10 MW piston engine as discharging unit having a 50% electrical efficiency and a 727 €/kW investment cost (although for such piston engines the accepted range is 300-600 €/kW), the LCOES of P2F2P would stay lower than that of PHES and CAES, see Table 2.1.

Table 2.2 – *Efficiencies and LCOES of long-term storage technologies [10, 12, 29]*

	PHES	CAES	P2F2P
Roundtrip efficiency (%)	76	55	30 ^a
LCOES (€/MWh _e)	1400	2400	710 ^b

^a Assuming a 60%_{LHV} P2F and a 50% efficient piston engine.

^b Assuming a 250€/MWh P2F LCOES.

Assuming a 50% efficient piston engine.

Maintaining 700€/kW for the conversion unit investment cost.

2.3 Basic properties

A glimpse of the four electrofuels suitability to HCCI mode and their behaviour can already be obtained from their basic properties. Their basic chemical, physical, and combustion properties are compared in Table 2.3.

Table 2.3 – *Electrofuel basic properties*

	Hydrogen	Methane	Methanol	Ammonia
Chemical formula	H ₂	CH ₄	CH ₃ OH	NH ₃
Health hazards (0-4)	0	0	1	3
Environmental hazard (0-4)	1	2	0	2
Boiling point at 1 bar (°C)	-253	-162	65	-33
Flammability in air (%vol)	4-75	5-15	7-36	16-25
Lower Heating Value (kJ/mol)	244	802	639	318
Air-fuel ratio ($\phi = 1$) (mol/mol)	2.4	9.8	6.5	3.6
Laminar burning velocity (m/s)	3.51	0.38	0.36	0.07
Minimum ignition energy (mJ)	0.01	0.28	0.14	8.00
Auto-ignition temperature (°C)	500-585	586	439	657

Health considerations - Ammonia is highly toxic, and its gaseous state at ambient conditions makes it a serious hazard to human health: as 300 ppm are only bearable less than 30 minutes, 2000 ppm will lead to severe damages in 30 minutes of exposure, and 5000 ppm to a quick death. Methanol is also highly toxic with a lethal dose being 1-2 ml per kg of body weight, yet its liquid state make it much less hazardous.

Explosion considerations - From hydrogen's flammability limits in air, and its minimum ignition energy, one understands that it causes high fire/explosion issues. On the other hand, methane and methanol only poses moderate issues, and ammonia barely any issues.

Environmental considerations - Regarding the environment, their impact can be severe as well. Methane has a greenhouse gas effect more than 30

times that of carbon dioxide [35], but its impact on ground atmosphere is quite minor. Ammonia under low concentrations is a source of nutrient (nitrogen) for plants, yet under high concentration it leads to nitrification, acidification and eutrophication of water and soils, as well as fine particles and ammonium in the atmosphere, eventually destabilising the nitrogen cycle [36]. Hydrogen has a minor effect on global warming, yet it promotes ozone production at ground level (hence smog with its health-related issues) and ozone depletion in the stratosphere [37]. On the other hand methanol is infinitely soluble in water and biodegradable [38], and when emitted as a gas has a significantly lower greenhouse gas effect than methane [38]. Of course, these considerations are for unexpected events (e.g. spills) and are not applicable when the compounds stay in their storage or process units. Ammonia and methanol are also corrosive to many materials. Care should be taken when using them: compatible materials must be used.

Combustion considerations - Although the four electrofuels have very different LHV, once their air-fuel ratio is taken into account they have similar engine mixture energy contents. The laminar burning velocity can inform us about the species kinetic reactivity: methane and methanol have similar laminar flame velocities, but hydrogen is largely more reactive and ammonia largely less. On the other hand, the auto-ignition temperature indicates the ease at which a temperature increase will trigger the auto-ignition (different from the flame speed which characterise the combustion propagation after the first ignition). Methanol and hydrogen seem to auto-ignite more easily than methane, which itself ignites more easily than ammonia. This can be partly explained by the compactness of the molecule, as well as the molecule bonds strength. Figure 2.1 represent the evolution of the auto-ignition resistance for various fuels under HCCI conditions, reproduced from [39]. Although ammonia is not represented, the electrofuels of interest are observed to be resistant to auto-ignition compared to longer hydrocarbon molecules, with methane being more resistant than hydrogen and methanol. Finally, the four electrofuels of interest having simple structures, their whole combustion happens in a single stage, i.e. the first radicals obtained after the ignition delay trigger the whole combustion process from branching to termination reactions. The ease of auto-ignition is to be differentiated from the various octane numbers, or knocking

indicators, that encompasses both auto-ignition and kinetic reactivity within the spark-ignition process.

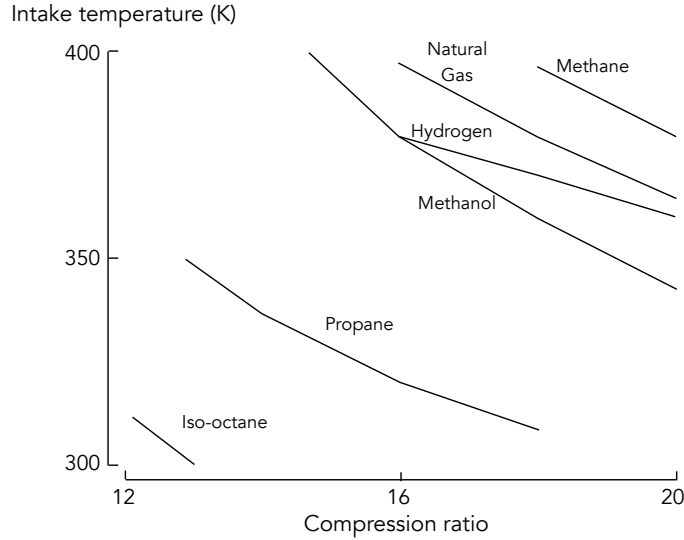


Figure 2.1 – Simulation in a single-zone model of the auto-ignition resistance of various fuels. The HCCI intake temperature is the one required to obtain a start of combustion at the TDC. The resistance is observed to be function of the molecule compactness. Reproduced from [39].

2.4 Basics of piston engines and HCCI engines

This section reports all the basic definitions used in the piston engine community, and uses them to clarify the state-of-the-art. This thesis only considers the case of 4-stroke engines, given their cleaner combustion aspects than 2-stroke engines, and comparable efficiencies in the 0.3-3 MW_{elec} range for stationary applications¹. From the reciprocating motion, the piston position evolves between the Bottom Dead Center (BDC), i.e. maximum cylinder volume, and

¹Due to the limited HCCI power density, a 2-stroke configuration could be beneficial to limit the impact of friction losses, yet it is out of the scope of this study to investigate such application

Top Dead Center (TDC), i.e. minimum cylinder volume. The difference between both is called displacement volume V_d . The main characteristic of an engine is its Compression Ratio (CR), or the extent to which the mixture is compressed, and is defined as:

$$CR = \frac{V_{BDC}}{V_{TDC}} \quad (2.1)$$

A typical pressure curve is reported in Figure 2.2, together with the BDC, TDC, and valve timings. At the Intake Valve Closure (IVC), the cylinder becomes a closed system and the compression begins, eventually leading to the combustion if the auto-ignition conditions are reached. Power is produced during the expansion, mainly until the Exhaust Valve Opening (EVO). There begins the breathing phase, with the exhaust of the combustion gases followed by the admission of the fresh charge. The presented configuration of Intake Valve Opening (IVO) and Exhaust Valve Closure (EVC) denotes a positive overlap. A positive overlap is usually used for a maximised scavenging of the cylinder. A negative overlap is usually performed to trap combustion gases and obtain internal Exhaust Gas Recirculation (EGR).

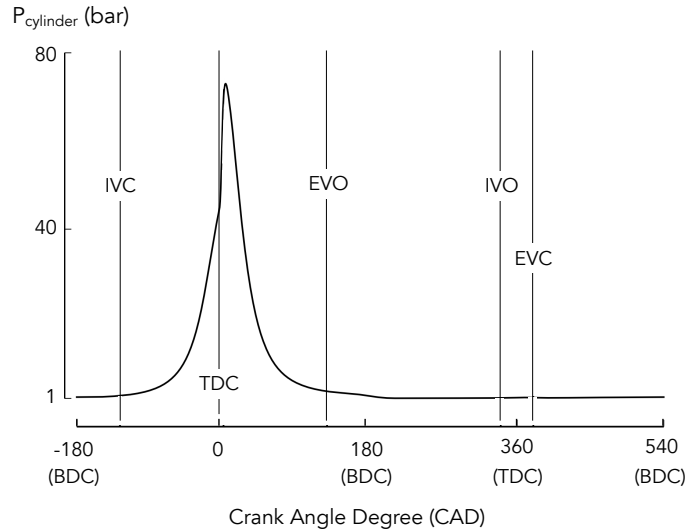


Figure 2.2 – In-cylinder pressure curve for typical HCCI configuration, as a function of the piston Crank Angle (CA).

Integrating the pressure over the volume evolution gives the produced work by the engine (the gas work on the piston). The main parameter used to represent the gross piston work (extracting the pumping losses needed for the breathing phase) is the gross Indicated Mean Effective Pressure (IMEP), which is the performed work per unit of displacement volume:

$$\text{IMEP} = \frac{\int_{-180}^{180} p dV}{V_d \cdot 10^5} \text{ (bar)}. \quad (2.2)$$

If the friction losses (adimensionalised from the displacement volume = FMEP) are taken out from the IMEP, the Brake Mean Effective Pressure (BMEP) is obtained, or a direct image of the engine power density:

$$\text{BMEP} = \text{IMEP} - \text{FMEP} \text{ (bar)}. \quad (2.3)$$

The parameters that represent the engine thermodynamic efficiency (i.e. only considering the combustion quality and timings) and overall efficiencies (i.e. considering in addition power density, so friction-pumping-exhaust losses) are the gross Indicated Efficiency (IE) and the Brake Efficiency (BE):

$$\text{IE} = \frac{\int_{-180}^{180} p dV}{Q_{\text{fuel}}}, \quad (2.4)$$

$$\text{IE} = \frac{4 \cdot \pi \cdot T_{\text{average}}}{Q_{\text{fuel}}}, \quad (2.5)$$

where Q_{fuel} is the quantity of injected fuel energy per cycle, and T_{average} is the average torque produced over an engine cycle. The factor '4' in Equation (2.5) comes from the 4-stroke configuration considered.

Many combustion indicators are computed from the in-cylinder pressure curve. These computations, called *heat release analysis* and detailed in Appendix A.4.1, give the evolution with the CA of the combustion Heat Release (HR), see Figure 2.3. From the HR are defined the combustion timings (CAX), defined as the CA at which X% of the total combustion heat (Q_{gross}) has been released. The derivative of the HR, the Heat Release Rate (HRR), is the combustion intensity and is directly influenced by the fuel reactivity and the combustion timing. The combustion intensity is also often represented by the Maximum Pressure Rise Rate (MPRR), expressed in (bar/CAD), and by the

maximal in-cylinder pressure $P_{\max}$. Both parameters are used for engine dimensioning as they represent the dynamic and static conditions that the engine can withstand. In our case, highly reactive fuels, such as hydrogen, lead to short combustion duration hence intense combustion and limit the power density as the MPRR and/or $P_{\max}$ are quickly reached.

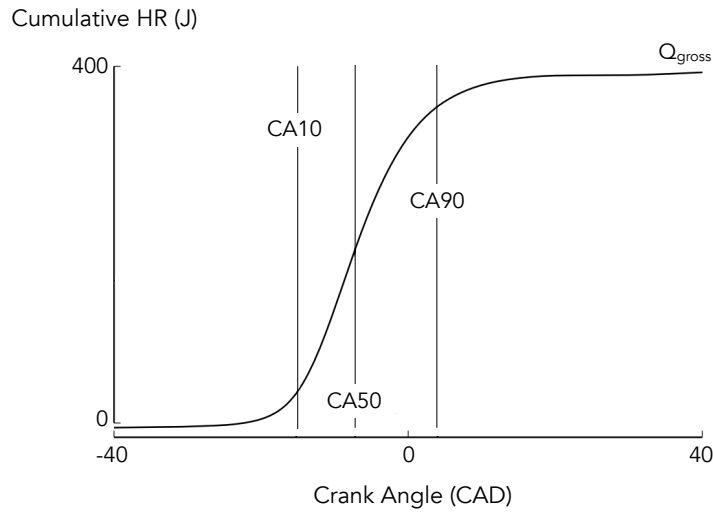


Figure 2.3 – Typical HCCI cumulative heat release obtained from the pressure curve. The combustion timings and HRR are obtained from it. CA10-CA50-CA90 are usually used as reference for the combustion start-mid-end points.

Finally, two phenomena must be defined, characterising ill-operation. First, misfire occurs when the mixture fails to auto-ignite during some cycles. Most of the time it occurs for a too low equivalence ratio or too late combustion. Its most common indicator is the coefficient of variation of the IMEP for N consecutive cycles, for which values above 5% are regarded as unstable (prior to misfire):

$$\text{CoV}_{\text{IMEP}} = \frac{100}{\overline{\text{IMEP}}} \sqrt{\frac{1}{N} \sum_{i=0}^N (\text{IMEP}_i - \overline{\text{IMEP}})^2} . \quad (2.6)$$

On the other hand, too intense combustion will lead to a damaging combustion phenomenon called *ringing*. It occurs when the local/microscopic auto-ignition kernels produce a detonation (supersonic pressure wave due to a critical energy density kernel) instead of a deflagration (subsonic pressure wave). The generated supersonic pressure waves will resonate in the combustion chamber and amplify themselves with other ignition kernels. The pressure oscillations are called ringing from the characteristic noise of the engine. They lead to oscillating mechanical stresses (induced from an oscillating thermal dilatation and contraction) in the engine walls and eventually lead to block failure. The parameter characterising it is the Ringing Intensity (RI) and shall be defined in due time in Chapter 5.

2.5 State-of-the-art

The use of the four electrofuels in piston engines dates back to the most early engine prototypes. Their state-of-the-art SI and CI designs can serve both as reference for the forthcoming thesis research and as shoulders to stand on.

2.5.1 Existing use of the four electrofuels in piston engines

Hydrogen use in piston engines

Hydrogen engines are nearly as old as the piston engine itself. François Isaac de Rivaz invented and patented in 1807 the first hydrogen engine, thirteen years after the petroleum engine of Robert Street, the first patented piston engine. The famous Lenoir engine (1860) was actually running on a mixture containing hydrogen. In 1933, Norsk Hydro was already operating an hydrogen piston engine vehicle using ammonia in-situ reforming.

Modern hydrogen cars are far beyond the laboratory tests. Ford reached in 2001 the step of the hydrogen demonstration vehicle (SI - 14.5:1 - PFI - 2.0L - Ford P2000) that met the Super-Ultra-Low-Emission-Vehicle (SULEV) standards (excepted for NO_x : 0.3g/km) with a 18% reduced fuel consumption compared to gasoline, thanks to hydrogen knock resistance² [40]. Quantum Tecstar modified a Toyota Prius and fully met the SULEV standards and pro-

²Hydrogen is knock resistant in SI engines thanks to its high flame speed, yet its prone to ringing in HCCI engines due to its reactivity and short combustion duration.

duced more than 30 vehicles [41]. This ought to the possibility of using a Three Way Catalyst (TWC) since the mixture is stoichiometric. Still the main hurdle to hydrogen piston engine cars penetrating the market is the hydrogen price at around 10 €/kg (energetically equivalent to 3.6 €/l of gasoline). Some hydrogen fuel cell cars are being manufactured, with mainly the Toyota Mirai (3000 sales per year, with a plan to extend the production lines and reach 20.000 to meet the annual demand). However their price is still prohibitive and the issues regarding their green energy (Life Cycle Assessment (LCA) from cradle to grave) and recycling are to be answered. Finally, the IEA claims the alkaline FC used to be only 45% efficient (stressed by the need for cheaper FC) and the Environmental Protection Agency (United-States) asserted the Mirai to be 3.6 l/100km of gasoline equivalent. As a comparison, the Mazda Skyactiv X performs at 4.4 l/100km (NEDC, against 5.2 for the conventional state-of-the-art gasoline). Yet all of this is beyond the scope of this thesis, as well as the potential for the hydrogen piston engine for the train/maritime sector.

Regarding hydrogen HCCI engines, efforts were kept inside the stationary application since the automotive sector for hydrogen is unclear, even for the SI mode. Hydrogen HCCI engines have successfully been experimented with compression ratios in the 15:1-20:1 range [16, 42, 43] with intake temperatures in the 70-150 °C range. Emissions of NO_x, CO, and HC are kept below 0.1 g/kWh (~10 ppm), yet with around 5000 ppm of unburned hydrogen. Increasing the equivalence ratio from 0.2 to 0.33 allowed a two-fold decrease in unburned hydrogen, yet producing a seven-fold increase in NO_x emissions. At low emissions levels, brake thermal efficiencies of 43% were achieved, slightly over SI performances. Still, for atmospheric intake conditions, maximal engine net IMEPs of 3 bar were found, compared to 5-6bar for hydrogen SI and 10-12 bar for gasoline SI. Therefore for pure hydrogen use (not considering the production and storage aspects), the SI engine might be a preferred choice over the HCCI engine, since it has the possibility to use TWC to reduce its emissions to acceptable levels while having twice the power output of HCCI and therefore (possibly) better brake efficiencies when taking the friction losses into account [44].

Blending another of the electrofuels of interest with hydrogen can help mitigating the drawbacks of hydrogen: storage density, kinetic reactivity, current availability. However, to my knowledge there is no experimental study investigating ammonia, methane or methanol addition in hydrogen SI, CI or HCCI

engines. Instead, given the much higher availability of the other electrofuels (or their difficulty to auto-ignite), it is hydrogen that is usually seen as an additive.

Methane use in piston engines

There is no denying that natural gas is by far the most used gaseous fuel in piston engines. Indeed, thanks to the worldwide use and availability of natural gas, "gas" stationary piston engine units are designed by many (if not all) manufacturers (Jenbacher, Caterpillar, Wärtsilä, MAN, etc.), and "gas" automotive piston engines are widely used over the world (CNG or LNG cars). They are more efficient and cleaner than their gasoline counterparts. Natural gas containing more than 80%vol. of methane, and its combustion properties being close/identical to pure methane, methane can be used in any CNG/LNG car without any modification apart from the spark timing [45]. Due to the higher octane number of methane (higher resistance to auto-ignition) the compression ratio can even be increased (from 9-10:1 to 12:1) to improve the performances without any side effect. Fiveland states that lean-burn SI NG engines allow, at full load, 14-18 BMEP with 38-42% peak brake efficiency (43% according to Tuner [44]) and 75-170 ppm NO_x emissions (1 g/kWh) [46]. Einewall [47] demonstrated/obtained a reduction of 99% in NO_x and 95% in HC emissions (both a 0.1 g/kWh) thanks to a stoichiometric-EGR-TWC mode compared to a lean burn strategy. Yet the efficiency decreased by two points to 39% and CO emissions increased to 1-2 g/kWh.

For CI engines (including HCCI), the fuel auto-ignition resistance being the main parameter regarding engine design, using methane instead of natural gas will impose engine modifications such as intake air temperature or compression ratio. For pure methane HCCI, Fiveland obtained good combustion timings with a 19.8:1 compression ratio and a 170 °C intake temperature, yet low combustion efficiencies of around 91% were obtained [46]. Fiveland associated them to the low combustion temperature (1500-1800 K) and low cylinder pressure (naturally aspirated) that led to mixture quenching at boundary layers and crevice regions. Moreover, they used a truck engine having a diesel piston bowl: the homogeneous charge (contrary to diesel sprays) filled the squish region having a huge S/V ratio so they experienced significant quenching. Under 1500K CO fails to oxidize in CO₂. Christensen et al. [48] obtained for a 17:1/19:1 NG HCCI engine, with constant CA₅₀ around TDC, 3.5/4 bar net IMEP (94% combustion efficiency, 43% net indicated efficiency, 0.01 g/kWh

NO_x, 10 g/kWh HC, 2g/kWh CO) without supercharging and 13/14 bar net IMEP (92% combustion efficiency, 54% net indicated efficiency, 0.01 g/kWh NO_x, 13 g/kWh HC, 4g/kWh CO) with 2 bar of boost. For reasons that will be clarified later, achievable power density is vastly influenced by the fuel used.

Regarding blending opportunities, the hydrogen addition in methane HCCI engines has been studied experimentally, see [49, 50]. The findings show the positive impact of hydrogen addition on the auto-ignition resistance (improved combustion timing control and reduced intake temperature) and on unburned hydrocarbons and combustion efficiency. The negligible impact on NO_x emissions at low load, but increased NO_x emissions at high loads (i.e. thermal-NO_x), has been noticed. Yet these studies are limited in terms of operating conditions and engine design therefore not encompassing the existing trade-off that such blending can impose on the engine design and its performances. Methane has not yet been studied with ammonia or methanol addition in HCCI engines to the best of my knowledge.

Methanol use in piston engines

Methanol is highly resistant to knock, possesses a high flame speed and a low flame temperature, a high heat of vaporisation, and is liquid at atmospheric conditions. It is therefore an excellent SI fuel. Brusstar et al. [51] and Koenig et al. [52] obtained 42% peak brake efficiencies with different engine designs. Both architectures were using turbocharging and EGR dilution to allow stoichiometric operation from low load to high load and hence allowing the use of a TWC. However, emission concerns for methanol need further work as it seems that TWC are converting some of the unburned methanol into formaldehyde, particulate matter seems to be higher than gasoline, and NO_x levels are unclear (sometimes higher sometimes lower than gasoline) [38].

Regarding CI engines, methanol auto-ignites more difficultly than diesel and requires preheating or dramatic compression ratios. It can be used in dual fuel engines -or reactivity-Controlled Compression-Ignition)- where methanol is injected first to create a (partially) premixed mixture that is subsequently ignited through the compression ignition of injected diesel [53]. This technique is mature and used in the marine sector by MAN and Wärtsilä. Another solution is to use a glow plug (i.e. a hot spot) that first leads to a localised reforming of methanol into a mixture of methanol, carbon monoxide and hydrogen that auto-ignites more easily [38]. This is similar to the Spark-Assisted

Compression-Ignition (SACI) concept, also an alternative, yet out of the scope of this thesis [54]. Finally more recent works have resorted to early methanol DI that led to stratified or even homogeneous charge, together with the use of high compression ratios, and EGR, and achieved soot-free stoichiometric combustion (enabling TWC use). Diesel-like efficiencies were obtained with fewer NO_x emissions, yet with reduced combustion efficiency ($\sim 96\%$) [55, 56]. The high power density obtained from the stoichiometric operation would be an advantage over Partially-Premixed Combustion (PPC) and HCCI engines.

Methanol HCCI combustion has been reasonably well studied, with compression ratios ranging from 15.5:1 to 17.5:1 and intake temperatures in the 140-200 °C range [57–60]. Maurya and Agarwal published a comprehensive experimental investigation of a 17.5:1 methanol HCCI engine and reached a peak gross IMEP of 4.9 bar with an equivalence ratio of 0.5 [59]. Such a feat is possible because, compared to hydrogen, methanol kinetic reactivity after auto-ignition is moderate. Indeed, at maximum load the combustion duration stayed above 5 CAD. The intake temperature was 160 °C to allow for an ideal ignition timing, hence a comparable resistance to auto-ignition as hydrogen. The maximum gross thermal efficiency of 45% was reached at an equivalence ratio of 0.33 and 3.8 bar of gross IMEP and decreased below 38% at maximum load due to the impossibility to maintain the SOC close to TDC. At maximum load the RI was of 5 MW/m², at the limit of an acceptable continuous operation. NO_x emissions are below 10 ppm for low loads, yet the threshold temperature of 1800 K for thermal- NO_x emission is crossed for equivalence ratios higher than 0.3 and 100 ppm are emitted at maximum load. Unburned hydrocarbons were quite independent of the load and around 10 g/kWh, while the CO emissions had a five-fold decrease from low to high load to end at 13 g/kWh. Similar results have been obtained in the other studies, and Gharehghani managed, using a turbocharged HCCI engine, to reach a 2 bar of boost [60].

No blending with any of the four electrofuels of interest has been experimented to the best of my knowledge, yet Gharehghani successfully operated natural gas and methanol in the same engine although natural gas needed a 40 °C higher intake temperature to operate at the same combustion timing, rendering lower IMEP (-2 bar) and thermal efficiency (-2% absolute) than methanol, but 10 times lower NO_x emissions [60].

Ammonia use in piston engines

The first recorded successful use of pure ammonia in a locomotive dates back in 1822 by Sir Goldsworthy Gurney. The first ammonia piston engine powered car was realised by Casale Ltd. in 1905, an endeavour that ended up with a patent in 1935. Other noticeable elements are the Belgian ammonia-fed bus fleets during World War II; the military efforts in the 1960's to design ammonia suited SI engines that could reach acceptable performances; the patent filed by Caterpillar in 2008 for ammonia fed power systems; and the publicly recognised interest in ammonia fuelled piston engines by at least 9 stakeholders including Toyota and Siemens [61].

Ammonia has been studied in SI and CI piston engines more recently, to provide clean and efficient alternative fuel engines. For SI engines, Koike et al. [62] studied ammonia-hydrogen blends with various engine speeds and loads. A compression ratio of 14:1 was sufficient to achieve pure ammonia operation at high loads. The raw emissions of unburned ammonia and NO_x were around 4500 ppm each, yet a conventional TWC allowed to lower both emissions below 200 ppm. The effectiveness of the TWC for stoichiometric ammonia mixtures has also been demonstrated by Grannell et al. [63], with a dual fuel gasoline-ammonia engine operating at 30% and 37% of IE for an IMEP of 4 bar and 12 bar, respectively [64]. Frigo et al. [65] obtained, using a 10.7:1 SI engine, brake efficiencies of 26% with continuous in-situ catalytic reforming of part of the ammonia into hydrogen to obtain the right flame propagation speed. Duynslaegher et al. [66] took the advantage of ammonia slow kinetics and resistance to auto-ignition to use a SI engine with a compression ratio of 15:1 and 17:1 and achieved pure ammonia operation, yet with high NO_x emissions and unburned fractions of hydrogen and ammonia.

Regarding CI engines, many studies showed that without increasing the compression ratio a promotion fuel was always necessary to allow for ammonia auto-ignition (hydrogen, diesel, DME, etc. [67–69]) and that ammonia fraction had to be limited to avoid additional NO_x emissions at high loads because the thermal- NO_x would add to the fuel- NO_x [70]. Gray et al. [71] showed that a compression ratio of 35:1 was necessary to auto-ignite ammonia with ambient intake conditions. Additionally, Gray et al. [71] performed a compatibility study of ammonia with the engine lubricating oil, and ammonia and its combustion products presents no substantial compatibility problem (maintained composition and physical properties).

To the best of my knowledge, prior to this thesis ammonia had never been used in HCCI engines except for one unique experiment: Van Blarigan [72] demonstrated pure ammonia combustion in a 40:1-60:1 compression ratio HCCI free piston engine without preheating, yet leaving all pollutant, performance and operational questions unanswered. Even though such compression ratios lead to high friction losses it demonstrates the possibility of ammonia HCCI cold operation and highlights the interest of higher compression ratios.

Regarding blends, none of them has never been investigated under HCCI conditions, contrary to SI engines as reported above. Additionally, as ammonia is soluble in gasoline and than methanol improves ammonia solubility in gasoline, Haputhanthri experimented without any change in engine performances the addition of up to 11%vol content ammonia in M10 grade gasoline (i.e. 3% energetic content) [73].

2.5.2 Multifuel abilities of other engine modes

SI engines using fuel blends have been studied for decades. Yet the research for fuel-flexible SI engines is more recent, and complex. The complexity comes from the high deviations in flame speed created by fuel blending, with the the knocking and pollutant creation phenoma being tied to the flame propagation inside of the combustion chamber. The case of hydrogen for fuel blending is peculiar given its extreme flame speed requiring lower compression ratios in order to avoid knocking and being able to boost the engine. Still, laboratory SI engines manage some fuel-flexibility if non-optimal conditions are tolerated. Lhuillier et al. [74] performed a comprehensive investigation of the possible use of ammonia, ammonia-hydrogen blends and methane in an unchanged 10.5:1 PSA engine. They managed to achieve pure ammonia operation with only a 50 °C intake temperature and obtained similar results to previous studies: 7.2 bar IMEP with a 37% indicated efficiency and 92-95% combustion efficiency (20.000 ppm NH_3 and H_2) with 3000 ppm NO_x (fuel and thermal combined). In the same 10.5:1 PSA engine, they achieved with methane a higher IMEP (+0.7 bar), lower NO_x (-1000 ppm), and better combustion efficiency (+1%-2% absolute) compared to ammonia. Finally, Lhuillier at al. [75] also investigated hydrogen seeding in ammonia: from 0% to 15% only minor changes where noticed in the engine performance, but when pushing the hydrogen seeding further the performances gradually degraded to eventually ending up misfiring with an hydrogen content of 60%vol. This proves the ammonia-methane fuel flexibil-

ity of the SI engine to some extent, yet showing the strong impact of a fixed compression ratio on the pollutant emissions and on the achievable hydrogen blending range. Other studies obtained similar results regarding hydrogen-methane and hydrogen-ammonia blends: limited hydrogen blending ratio to $\sim 40\text{-}50\%$ vol. for methane and natural gas [76, 77] and $\sim 60\text{-}70\%$ vol. for ammonia [78]. Resorting to variable compression ratios engines is often highlighted as a must for multifuel SI engines [78]. Regarding the compression ignition mode for the electrofuels of interest, or advanced compression ignition modes like HCCI, no multi-electrofuel study is to mention, to the best of my knowledge, apart from the single Diesel-electrofuel (CNG, DME, methanol, methane, ammonia) studies already mentioned.

2.5.3 Power density considerations

For a thermodynamic optimum (i.e. IE-wise), the CA10 happens right before the TDC and the combustion is the shortest possible. For an overall optimum (i.e. BMEP-wise), the CA10 is delayed and the combustion duration increased (through reduced intake temperature, EGR, thermal stratification, etc.) in order to decrease the MPRR and $P_{\max}$ and allow for higher fuel contents, hence higher power density. A trade-off is to be found as a too late combustion will eventually diminish the BE through the IE. Moreover, a later combustion happens at a lower temperature, with the associated risk of unburned emissions. Yet it comes at hand when turbocharging (or increasing the compression ratio) is used to maximise the power density (i.e. BE) and risks breaking the thermal- NO_x threshold, or MPRR- $P_{\max}$. Dec et al. [79] successfully operated a gasoline HCCI engine (being prone to auto-ignition, see isooctane in Figure 2.1) with 2 bar of boost from a turbocharger and obtained 16.3 bar of IMEP, a good stability, no ringing, improved combustion efficiency ($\sim 99\%$), and no NO_x ($\leq 0.05 \text{ g/kg}_{\text{gasoline}}$). To achieve it, EGR down to stoichiometric conditions was necessary, see Chapter 5, with CA50 around 19 CAD aTDC. Using a 14:1 CR, the required intake temperature went down from 130°C to 60°C , with an available exhaust temperature before the turbocharger of $150\text{-}200^\circ\text{C}$, enough to provide a 2 bar of boost. Generally, the same remarks for increasing the boost hold true for increasing the compression ratio since higher pressure and temperature are obtained. The question for the electrofuels of interest is as follows: is their kinetic reactivity compensating for their higher auto-ignition resistance compared to gasoline?

2.5.4 Why not using SI engines, or other technologies?

Based on the above literature review, and based on the maturity that some technologies have with the use of the electrofuels of interest, a legitimate question would be: is the HCCI engine the ideal technology for the multi-electrofuel CHP concept envisioned ?

Based on the latest developments in SI technology using the electrofuels of interest, their efficiency for comparable power outputs is somewhat smaller compared to HCCI engine. Yet the main discriminant for SI engine in the integrated energy system vision is its lower in-situ fuel flexibility while maintaining maximal performances (and therefore pledging in favor of the HCCI engine). Although SI engines can be designed more easily than HCCI engines for almost any fuel, and with higher load flexibility, the obtained design itself is less resilient than the HCCI concept to a change in fuel properties. Deviations in flame speed and auto-ignition properties quickly leads to unavoidable knocking and high pollutant emissions. Regarding CHPs on the market, they can be purchased for various types of fuel (natural gas, CNG, biogas, etc), yet each single unit is not fuel-flexible. However the time frame must be considered regarding the CHP multi-electrofuel concept. If the concept was to be put on duty tomorrow, the SI technology would be selected, yet at the expense of a reduced in-situ fuel flexibility and efficiency. Yet the HCCI potential for higher efficiency, and stronger flexibility and resilience, cannot be ignored if the CHP concept is on a mid-long-term frame, which is the case. Finally, the argument of pollutant emissions is to be nuanced. Indeed, untreated SI engine emissions can be quite high, however TWC prices are not that prohibitive and very good performances have been obtained with the four electrofuels of interest [38, 41, 47, 62]. On the other hand, although HCCI applications can avoid the need for NO_x after-treatment systems, it might not be the case for their unburned emissions. The final part of this thesis will be devoted to investigating the extent of these unburned emissions as well as possible mitigation techniques to help less expensive after-treatment systems.

Direct injection is an option where the timing of injection will dictate the type of combustion strategy obtained. Early injection renders a -close to- HCCI engine as the gaseous fuel would have the time to completely mix with its surrounding air. On the other hand a late injection renders a diffusion combustion

(slower hence higher power densities achievable) and lower unburned emissions but high NO_x and soot emissions. Intermediate injection timings leads to PPC, regarded by many as the highest potential for engine efficiency since it renders slower combustion rates than HCCI and therefore solves the issue of power density. Yet PPC tends to produce more NO_x and soot than HCCI, and is still in an early phase of research. Therefore it represents a high opportunity of hybridization for the considered CHP HCCI engine when peak power would be desired.

Other hybrid technologies of low temperature combustion are being studied to mitigate HCCI shortcomings, the three main being SACI (the technology used, in particular, by Mazda to achieve the world first HCCI passenger-car engine) and Stratified-Charge Compression-Ignition (SCCI). The SACI principle is based on the prior spark-ignition of a local stoichiometric region that consequently leads to the auto-ignition of the rest of the chamber being in lean conditions. It is halfway between SI and HCCI in terms of power density, controllability and pollutants. It is necessary to solve passenger-car related issues such as transient phases or cold starts. The SCCI principle can be achieved in many ways: usually with fuel stratification through direct injection and therefore similar to the PPC concept, or unusually (because more difficult) through thermal stratification. The latter is of high interest to this thesis and the Section 6.2.2 will investigate the impact of Water Direct Injection (WDI) on the thermal stratification and performances of the HCCI concept. Regardless of the implementation, the stratification allows a staging/damping of the combustion and therefore allows higher power densities without impacting substantially the pollutants. Finally, the RCCI principle allows a somewhat different combustion behavior compared to HCCI through the direct injection of a given fuel during the end of compression to trigger the auto-ignition of an homogeneous or partially-premixed fuel-air mixture. This concept is highly compatible with the current multifuel application as the direct injection can be processed with both gaseous and liquid fuels to give an additional control parameter and help when the fuel blending ratio needs to be varied. It helps mitigating the combustion intensity (hence renders higher power densities) yet with the associated cost of an even lower combustion efficiency due to the close-wall mixture being at a lower equivalence ratio. Many of these hybrid modes can be of great help in specific cases (e.g. cold starts, varying blending ratio, increased power output, decreased unburned emissions, etc.), yet this is out of the scope of this thesis

as a primary and rigorous evaluation of the behaviour of the multifuel HCCI concept is necessary to then highlight the needs for improvement and possible applications of alternate combustion modes in specific configurations.

Finally alternatives exist to piston engine for CHP units. The two other main protagonists are the gas turbine and the Fuel-Cell (FC). The gas turbines (in the 0.01-10 MW range) are cleaner than their piston engine counterparts before the after-treatment systems (including unburned emissions and NO_x even when using ammonia), highly suited for methane applications, have already been used with ammonia-hydrogen [80] or ammonia-methane blends [81] without posing material compatibility issues, with methanol being considered a superior turbine fuel by General Electrics [82]. Yet when using mixture of electrofuels, the blending ratios had to be kept within specific ranges in order to guarantee the combustion stability (e.g. 70%vol. of ammonia when blended with hydrogen and 30%vol. when blended with methane [80, 81]). Dual-fuel technologies exists to broaden the blending ratios, such as double nozzle injection or even swirl or flameless combustion [83–85], yet they are still under research. Finally their efficiencies are smaller (25-41% electrical, with heat recovery, [86]) compared to HCCI engines for given power outputs. Fuel-Cells (FC) on the other hand are more efficient and research is being performed to achieve fuel flexibility. PEM FC currently reach 50-55% electrical efficiency when fed with hydrogen [21, 87] and a recent review claims that 60% is at reach [88]. SOFC achieve somewhat lower figures of 45-55% electrical efficiency, and are suited to the use of the various electrofuels of interest, yet only in laboratories [21, 89–91]. FC high investment costs (more than 4000 €/kW compared to 500 €/kW for piston engines [92–94]) as well as overall environmental impact and poisoning issues are holding them back. The multi-fuel aspect of FC is being studied as well. PEM are using pre-reformers (heated catalyst - 3000 €/kW [93]), but SOFC on the other hand can rely on their high operational temperatures to perform direct internal reforming with limited performances reductions [95]. Moreover, a game changer would be the reversibility of the FC into an electrolyser for the P2F. Research is being performed to experimentally achieve reversibility and multifuel ability and therefore cut the environmental impact and investment costs in two.

To summarize, many other technologies could play (now or later) a significant role in specific configurations of the energy transition. Yet we evaluated higher the opportunities and suitability of the HCCI engine to resilient CHP

multi-fuel energy systems, and worth the investment of a whole PhD Thesis, if not more.

2.6 Existing electrofuel kinetic mechanisms

Although the goal of this thesis is to achieve an experimental study of the use of the four electrofuels of interest in an HCCI architecture, performing numerical investigations of the associated questions is of interest. Numerically, preliminary results can be obtained rapidly, and economically. Moreover, thanks to the simulations flexibility, a deeper understanding of the fuels behaviour can be obtained by modifying the simulations conditions, modifying any fuel property, etc.

The kinetic mechanisms used to model the combustion of each of the four fuels must be valid under HCCI conditions, i.e. regarding ignition delay and for high pressures (>10 bar), intermediate temperatures (~ 900 - 1200 K) and low equivalence ratios (<0.6).

The chemistry of hydrogen is always included in methane, methanol, and ammonia since hydrogen appears during their normal combustion. Therefore no mechanism for pure hydrogen is needed, as one from the other fuels can be used. Even though a consensus about the higher performance of the 2013 mechanism from K  romn  s et al. [96] for hydrogen ignition delay has been reached in the community, the results from the mechanisms of NUIG, Konnov, GRI, and Li have been reviewed to give equivalent or close results in the whole temperature (900-2500 K), pressure (0.2-90 atm) and equivalence ratio (0.1-4) ranges [97].

Still, it must be noted that kinetic mechanisms are based, eventually, on a multitude of molecular reactions for which the rate coefficients have been experimentally measured or estimated from *ab Initio* calculations, and the many mechanisms available are often based on the same reaction rate coefficients. Therefore, with the improvement of measurements and calculations techniques, it can occur that some influential reaction rate coefficients or new reactions come to be refuted, debated, or added. This is currently (~ 2017 - 2018) the case for the hydrogen mechanism with the termolecular $H+O_2+R$ reaction [98], that led to the creation of a new hydrogen mechanism by Konnov [99]. All this, of course, is out of the scope of this thesis yet is worth being

mentioned given the use that will be made of kinetic mechanisms (Chapter 3) and research performed on them (Chapter 4).

For methane, among all the existing mechanisms, the NUI Galway [100], USC 2.0 [101] and GRI 3.0 [102] have been tested against ignition delay at high pressure (18 bar) and in lean conditions (equivalence ratio of 0.5) in a shock tube [103]. Moreover the mechanisms of AramcoMech [104] and GRI 3.0 have been tested against ignition delay at 30 bar and with an equivalence ratio of 0.5 in a shock tube and in a Rapid Compression Machine (RCM) for a mixture of 70%vol. methane and 30%vol. hydrogen [105]. Among the two validation studies, the best performing mechanisms were USC 2.0 and AramcoMech for both methane and hydrogen. USC 2.0 has been selected for this thesis given its smaller size.

For methanol, Burke et al. [106] validated their own Mech15.34 mechanism and the mechanism of Li et al. [107] against ignition delay in a shock tube and a RCM at an equivalence ratio of 0.5 and at 30 bar. A recent comparison study from Feng et al. [108] used the experimental RCM measurements from Burke et al. [106] and the shock tube experiments from Noorani et al. [109] at 10 bar, 1070-1760K, and 0.5 and 1.0 of equivalence ratio to compare four actual methanol kinetic mechanisms and obtained that the Mech15.34 and the Li et al. mechanisms were the best performing under HCCI conditions. The mechanism from Li et al. was chosen for this thesis given its compactness.

Ammonia kinetic mechanisms

Given the extensive work performed on ammonia kinetic mechanisms in this thesis, it deserves a separated and more detailed section. More importantly, prior to 2018 there were no experimental data of ammonia auto-ignition under HCCI-relevant conditions. This sub-section gathers the existing kinetic studies prior to, and after, 2018 and their related conditions of validity.

Most studies on ammonia kinetics were performed for the nitrogen (NO_x) chemistry or the DeNO_x process [110–115], including solid fuel combustion leading to ammonia emission and other nitrogen species formation [116, 117]. These studies, although realised at a range of temperatures including those of LTC (1100 - 1400 K), are not related to any equivalence ratio concept since ammonia is viewed as an exhaust treatment additive. Regarding ammonia oxidation in flames, several studies have been performed, from the reaction rate investigations to the global mechanism behaviour, under close to stoichiometric

conditions and at high temperatures (> 1500 K) [111, 113, 118, 119]. It is only recently that two studies on the ignition delay of ammonia at high pressures and under lean conditions have been performed. Mathieu and Petersen performed measurements, and developed a kinetic mechanisms based on them, of ammonia ignition delays in a shock tube up to 30 bar, with an equivalence ratio of 0.5, but under diluted conditions and from 1560 K to 2455 K [120]. Song et al. [121] measured ammonia oxidation in a laminar flow reactor at up to 100 bar, at an equivalence ratio of 0.2, but between 450 K and 925 K. The two main applications and origins of development for the early studies being the DeNOx process and the combustion in Spark Ignition (SI) engine, and the latter studies being performed out of the HCCI range, it is therefore legitimate to question their suitability for ammonia ignition delay under LTC mode.

This knowledge gap pushed me to pursue in October-November 2017 a dedicated experimental investigation of ammonia (and ammonia-hydrogen blends) auto-ignition in a RCM under high pressures, intermediate temperatures, and lean conditions. That study will be the subject of Chapter 4, where the experimental results will be compared to the existing (prior to and after 2018) ammonia kinetic mechanisms.

In parallel to that research, two original experimental research on ammonia kinetic study have been led. He et al. [122] performed RCM experiments of diluted (70%) ammonia-hydrogen mixtures (hydrogen in the 5-20%vol. range) under 20-60 bar, 950-1150 K, and 0.5-2 of equivalence ratio. Shu et al. [123] performed shock tube experiments for ammonia under 20-40 bar 1100-1600 K, and 0.5-2 of equivalence ratio. Both these studies will be complementary to the one led during this thesis in the quest for an HCCI suited ammonia mechanism.

2.7 Outlook: structure of the thesis to address the state-of-the-art

This concludes a broad literature review on the potential and existing knowledge for the four electrofuels use in a (multi-fuel) HCCI engine.

Based on the energetic and economic aspects of stored P2F, there is no clear winner among the four electrofuels of interest. The reality is more complex, as for the coming energy mix: there is no unique solution but rather different technologies that are inter-connected to make a globally resilient solution. The Netherlands and the USA have existing ammonia pipelines; many harbours are

equipped for methane and methanol storage and transport; many countries in the world have existing natural gas pipelines; hydrogen pipelines are emerging; the liquid state of methanol and ammonia is ideal when no pipelines are available; hydrogen and ammonia do not require carbon dioxide to be produced.

Regarding the possibility of a single architecture allowing the use of the four fuels, their auto-ignition resistances being rather apart from each other, technical challenges shall arise and an overall high performance seems compromised. Yet no study has ever been performed for the four fuels under the same conditions. Therefore, a preliminary numerical study will be performed about the four electrofuel use within the same conditions. Expected operating conditions and ideal blends shall be the aim of Chapter 3.

For decentralised applications, it is clear that the ammonia-hydrogen blend shows potential given its non-carbonated aspect (production and pollution). Moreover, hydrogen and ammonia being at the two extremes of the auto-ignition range, having an engine suited to them ensures the applicability of natural gas use in case of needs, from the grid, to provide resilience to the system. Lastly, if methane allows as high power outputs as gasoline thanks to its auto-ignition resistance, the possibly higher potential for ammonia is to be investigated first. Therefore, the rest of this thesis is devoted to the investigation of the ammonia-hydrogen blend.

Nevertheless, the knowledge of ammonia behaviour under HCCI conditions being poor, it seemed necessary to first investigate its fundamental properties. Therefore, Chapter 4 is devoted to filling that gap, through the experimental use of a RCM and comparison with the predictions of existing kinetic mechanisms.

Finally, building on the gained knowledge, the ammonia-hydrogen blend is experimented in a specifically designed engine architecture for which the results are reported in Chapter 5.

The global objective is to put the multi-electrofuel HCCI concept on the map: potential (efficiency, power density, pollutants), ideal blends, main hurdles, and most needed works. Although ammonia-hydrogen is the only blend that this thesis covers extensively, Chapter 6 gathers all the ideas, concepts, or sometimes even research basis that I had during these four years on other multi-electrofuel HCCI concerns. These include, among others, experimental results of HCCI thermal stratification through water direct injection for improved power density, and oxy-combustion considerations for methane and

2.7. Outlook: *structure of the thesis to address the state-of-the-art* 43

methanol.

You don't start out writing good stuff. You start out writing crap and thinking it's good stuff, and then gradually you get better at it.
That's why I say one of the most valuable traits is persistence.

Octavia E. Butler

3

The four electrofuels under HCCI conditions: a numerical investigation

This chapter is a further-developed version of the following publication:
Pochet, M., Dias, V., Jeanmart, H., Verhelst, S., & Contino, F. (2017). *Multifuel CHP HCCI Engine towards Flexible Power-to-fuel: Numerical Study of Operating Range*. Energy Procedia, 105, 1532-1538.
<http://doi.org/10.1016/j.egypro.2017.03.468>

In order to determine if a single engine design could be used to burn the four electrofuels of interest and their blends, or if particular blends show more potential, a HCCI single zone model has been developed. This model particularity is to accurately predict the required intake conditions for a given mixture to auto-ignite at the desired Crank Angle (CA) timing. This chapter studies the influence of the intake conditions (equivalence ratio, temperature, and pressure) and the compression ratio on the fuel auto-ignition. Results show

that a single engine design (i.e. compression ratio) is suitable for the use of the four electrofuels provided that a sufficient intake temperature is provided, yet decreasing the power output for auto-ignition resistant fuels. Fuel blending has strong promoting effects in the case of hydrogen and methanol addition into ammonia and methane. This allows for a significant increase in the IMEP through a reduction of the required intake temperature. Yet the generally low IMEP requires further work on increased equivalence ratios, on increased intake pressure, and the ringing risks associated with them.

However, engine performance estimations can be imprecise when using single-zone models. Moreover, using the same engine for fuels having too different auto-ignition resistances (e.g. ammonia and hydrogen) asks for wide variations in intake temperatures that might be counter-efficient to reach or that would impact the engine power output. These limitations are highlighted and the need for higher accuracy simulations or even experiments is expressed. The results of this chapter are used to design the experimental setup of Chapter 5.

3.1 A single-zone model for auto-ignition prediction

Operating an HCCI engine raises a constraint on the mixture suitability for auto-ignition. Having no spark or direct injection, the mixture auto-ignition depends solely on its kinetics, and therefore on the compression ratio and intake conditions (temperature, pressure and mixture composition). The objective of this preliminary study on the required HCCI conditions is to investigate the link between the numerous intake conditions and the resulting auto-ignition for the four electrofuels and their blends.

The studied ranges for the variables of interest are shown in Table 3.4. The range for the compression ratio goes from usual values for compression-ignition engines ($\sim 15:1$) up to values that would allow the auto-ignition of hydrogen and methanol, the two most reactive fuels, without pre-heating the intake charge ($\sim 25:1$). The intake pressure ranges from atmospheric up to 2 bar (absolute pressure). Since a turbocharger is preferred to provide the intake pressure, higher intake pressures than 2 bar are hard to obtain in HCCI engines given their low exhaust temperatures due to lean conditions. Moreover, the four electrofuels being resistant to auto-ignition, they still required a final heat recovery (i.e. after the turbocharger) to increase their intake temperature.

The HCCI turbocharging limits will be investigated in Section 3.3.4. Regarding the intake temperature, it must be chosen so that even ammonia and methane will auto-ignite in the less favorable conditions. The rotational speed is fixed at 1500 RPM since our interest lies in stationary applications.

Table 3.1 – *Engine parameter ranges used for the investigation.*

Parameter	Range	Step
Compression ratio	15:1 - 25:1	2.5
Intake pressure (bar)	1 - 2	0.5
Equivalence ratio	0.2 - 0.4	0.1
Intake temperature (K)	≥ 300	variable

Given the high number of combinations to assess, a single-zone model has been chosen to save computational time when assessing the auto-ignition feasibility of each fuel in all the operating conditions, similarly to what has been done in [124]. Moreover, a single-zone model is particularly suited to simulate HCCI conditions given the quasi-homogeneity of the mixture and given that the fluid dynamics only plays a limited role in the auto-ignition of an homogeneous charge.

The model has been built using the open-source code OpenFOAM-3.0.x. OpenFOAM is a c++ based code relying on finite volume methods to solve ordinary differential equation problems. Alternatives like in-house models or CANTERA could have been used, yet the choice for OpenFOAM is linked to its built-in CHEMKIN package solving the kinetic aspects of combustion problems. The CHEMKIN package, comprehensively explained in [125], was used "as is" and its functioning can be summarised as follows: when provided with the local mixture composition and thermodynamic state (pressure and temperature), it computes the consumption/production of every species based on the reaction rate coefficients provided for each reaction composing the mechanism of interest. The model developed in this chapter is in charge of computing the evolution of the thermodynamic state inside of the engine cylinder, based on an imposed piston motion and on the CHEMKIN results for species evolution and consequent heat release, see Figure 3.1. This model derivation, validation and use is reported in the following sections.

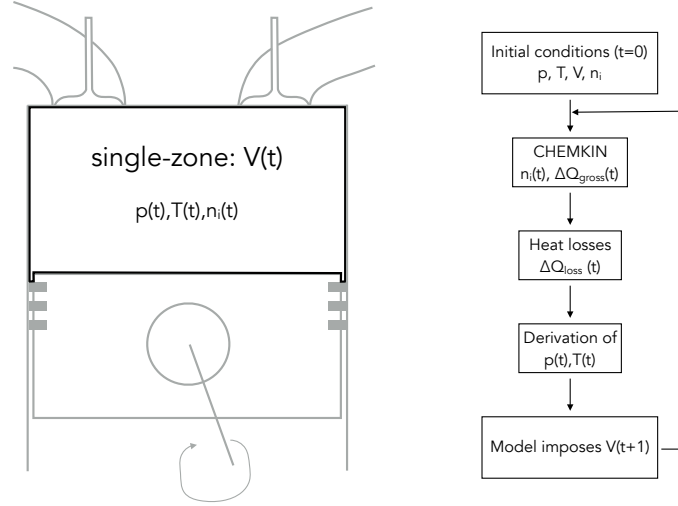


Figure 3.1 – The single-zone model assumes a unique volume V , evolving with time t , that composes the whole combustion chamber. The model makes the use of the CHEMKIN package and the first law of thermodynamics to compute the evolution of the closed system.

The kinetic mechanisms used for this thesis have been detailed in Section 2.6. For methane and hydrogen, the USC 2.0 mechanism was used [101]. For methanol, the mechanism from Li et al. [107] is used. Finally, the mechanism from Mathieu and Petersen is used for ammonia [120].

Eventually, as the heat release is obtained, the CA10 is defined as the start of combustion and if the CA10 happens within an acceptable range $[-3, 7]$ CAD aTDC, the obtained intake conditions are deemed appropriate.

3.1.1 Physical and mathematical derivation of the model

Several 0-dimensional HCCI studies have already been performed, using either a single-zone [126, 127] or a multi-zone [127–129] description of the cylinder. The phenomenon of interest in this study being the auto-ignition timing, a precise model for the combustion was not needed. Therefore, a single-zone approach was deemed sufficient. Still for a correct prediction of the ignition-timing the temperature inhomogeneity inside the combustion chamber needs to be taken

into account. The four electrofuels of interest being single-stage ignition fuels, their auto-ignition will occur first where the temperature is higher: the core zone. The exact methodology to estimate the core temperature along the cycle is described in Section 3.1.3. Finally, the model uses a differentiate form of the conservation of energy together with chemical kinetic mechanisms, and it imposes the closed system volume evolution related to the piston motion, as is explained throughout this section.

The single-zone model assumes a closed system between the BDC before compression and the BDC after expansion, as well as no residual gases being left in the cylinder. Regarding the model itself, it follows the first law of thermodynamics for a closed system in which the mixture is assumed to behave like an ideal gas, see Equation (3.1). Then, separating the heat exchange between the gross heat release, Q_{gross} , and the heat losses, Q_{loss} , yields the equation resolved at every time step by the OpenFOAM solver:

$$dU = nc_v dT = \delta Q_{gross} + \delta Q_{loss} - p dV \quad (3.1)$$

where U is the internal energy of the mixture, n is the number of moles trapped in the cylinder, c_v is the mixture specific heat capacity at constant volume, p is the in-cylinder pressure and V is the instantaneous chamber volume. The heat production Q_{gross} is given by the built-in CHEMKIN package. The mixture specific heat capacity at constant pressure, c_p , is in turn obtained at every time step from the weighted average of the respective species specific heat capacities computed from the JANAF polynomial correlations.

The wall heat losses are represented by an equivalent convection transfer for the entire exchange surface area A :

$$\delta Q_{loss} = h \cdot A \cdot (T - T_{wall}) \cdot dt \quad (3.2)$$

where h is the coefficient of convective heat transfer ($\text{W/m}^2/\text{K}$). The wall temperature, T_{wall} , is imposed 10K higher than the coolant temperature. The increment in temperature is computed from the enthalpy increment as $dT = dU/(nc_v)$, the pressure is obtained from the ideal gas law and the system volume variation is given by the piston motion. The accuracy of the results will depend on the accuracy of the initial conditions and on the correctness of the core temperature estimation. The following section is devoted to determining these parameters.

3.1.2 Initial conditions determination

Representing a real engine by a single-zone closed-system model requires the initial conditions to be such that the simulated thermodynamic state is the same as the experimental one once the cylinder becomes a closed system i.e. at IVC. Therefore the CAD at which the model starts is important. An obvious choice would be to start the simulation at IVC. Yet it is difficult and prone to error to choose values for p_{IVC} and T_{IVC} when only the intake values are measured or given as constraints. Moreover many effects that influence p_{IVC} and T_{IVC} depend on the engine and operating conditions. Therefore it is more interesting to set the simulation start at BDC and to study the variations that can occur between the intake measurements and the BDC values.

Due to the fact that the intake valves close later than BDC, the piston will start its compression when the valve is still open. Therefore a modelled compression in a closed system starting at BDC should over-estimate the in-cylinder pressure. To investigate that, an isentropic compression is compared to 100 consecutive experimental pressure cycles in Figure 3.2. The pressure cycles were obtained with the HCCI engine from Université d'Orléans, described in Table 3.2, and running under methanol [57]. The coefficient of variation in IMEP for these 100 cycles was 1.2%. The isentropic compression is obtained with p_{BDC} fixed at the mean intake pressure of the 100 cycles. JANAF polynomials were used to update the isentropic coefficient along the compression. It can be concluded from Figure 3.2 that an IVC happening before 157 CAD before Top Dead Center (bTDC) has a negligible effect on the pressure during compression compared to the span observed for 100 consecutive experimental cycles. In such cases the intake pressure can be used for p_{BDC} .

Next, T_{BDC} has to be estimated as it is different from the temperature measured in the intake manifold. This is due to the mixing with residuals gases, gas dynamic effects, and heat exchanges. Based on the method of Sjöberg and Dec [130], Contino et al. [131] determined the influence of these three phenomena for the Orléans HCCI engine and obtained the following correlation valid in the 40–200 °C intake temperature range with a cooling system at 90 °C (with an estimated overall error of 10%):

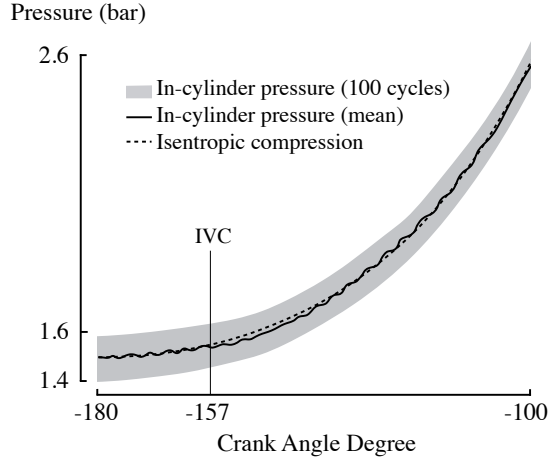


Figure 3.2 – Influence of the IVC occurring after BDC on the filtered in-cylinder pressure during the early compression. The influence of such IVC timing is negligible compared to the cycle-to-cycle variations. The CoV_{IMEP} for these 100 cycles is 1.2%

Table 3.2 – Engine specifications used for the single-zone model calibration

Engine model	PSA DW10
Displacement, V_c	499 cc/cylinder
Stroke, S	88 mm
Bore, D	85 mm
Connecting rod length, L	145 mm
Geometric compression ratio, CR	16:1
Effective compression ratio, CR_e	15.39:1
Intake Valve Closing (CAD)	157 before TDC
Coolant temperature	95 °C

$$T_{BDC} = 0.652 \cdot T_{intake} + 138 \text{ (K)} \quad (3.3)$$

Although this relation is only valid for the engine considered, it gives a qualitative idea of the phenomenon for similar engines. Moreover, HCCI combustion results obtained on that engine will be used to calibrate the single-zone

model.

Finally, the effective compression ratio must be taken into account as it influences the pressure rise during compression. Therefore to compute pressure evolution a simulated TDC volume being different from the geometric one was used: $V_{\text{TDC, simu}} = V_c / (CR_e - 1)$ with a simulated cylinder volume going from V_{BDC} to $V_{\text{TDC, simu}}$.

3.1.3 Simulating the experimental core temperature through modified heat losses

For the single-zone model to properly estimate the CA10, having calibrated heat losses is mandatory. As the HCCI auto-ignition is triggered in the hotter core zone of the cylinder for single-stage ignition fuels (it may arise in a different way for two-stage ignition fuels [132]), the objective for the single-zone model is thus to correctly describe the evolution of the core temperature. Yet in a single-zone model, the temperature is a scalar representative of the whole bulk gas. Thereby, using the heat loss model described in Equation (3.2) will slow down the temperature rise of the entire mixture at the same rate. However, in a real compression it is the boundary layer that exchanges heat with the walls. This leads to a hotter core zone which conventional single-zone models cannot depict. Indeed, usual correlations (such as Woschni's or Hohenberg's) used to represent the convection coefficient h of Equation (3.2) renders a correct cycle-overall heat dissipation through the walls [133], but they do not influence correctly the core temperature.

By modifying the scaling factor, α , of the usual convection correlations, Broekaert et al. [133] tried to fit simulated losses to experimental losses measured from an HCCI engine. Among the different correlations that were modified, Hohenberg's was chosen in our case since it can be used with a simple single-zone model:

$$h = \alpha \cdot \left(\frac{p}{10^5} \right)^{0.8} \cdot V^{-0.06} \cdot T^{-0.4} \cdot \left(\frac{S \cdot RPM}{30} + 1.4 \right)^{0.8} \quad (3.4)$$

Broekaert et al. [133] observed that the original scaling factor ($\alpha = 130$) produces an over-estimation of the heat losses during the entire HCCI cycle. By decreasing the scaling factor they managed to obtain a correct estimation of the wall heat fluxes at TDC, but observed a small underestimation of the heat losses during the compression stroke. Nevertheless, in our case, such

small underestimation induces a higher in-cylinder temperature: the result sought for in this study. This type of correction on the convection coefficient must therefore be tested with the developed single-zone model and calibrated against experimental combustion curves to allow an accurate estimation of the auto-ignition timing, see Section 3.2.1.

3.2 Calibration and validation of the model against experimental data

For the model to accurately depict the ignition timing, the scaling factor of the heat loss model must be modified, as explained in Section 3.1.3, and calibrated against detailed experimental data. Finally the model with the selected scaling factor will be used to assess its precision in estimating the ignition timing of independent HCCI configurations reported in the literature.

3.2.1 Calibration of the heat loss scaling factor

For this calibration procedure, two sets of data were obtained with the Orléans HCCI engine, described in Table 3.2. They correspond to methanol combustion and to the combustion of a mixture of methane and hydrogen (i.e. hythane) [50, 57]. These two sets of experiments had a CA10 of 0.4 CAD and 9.1 CAD, respectively. Figure 3.3 displays the estimated CA10 by the single-zone model as a function of the scaling factor. The ideal scaling factor for the CA10 estimation was found to be $\alpha = 59$ for methanol and $\alpha = 72$ for hythane. A unique scaling factor for different operating conditions could not be found, although the fuel should not have a substantial impact on it. This is due to the fact that CA10 is highly sensitive to the core temperature and therefore highly sensitive to the wall temperature and T_{BDC} . The reason why the best fit for hythane was higher than the one for methanol is that the water coolant temperature for the hythane experiments was 7 K lower than the temperature used to derive Equation (3.3). Therefore, the estimated T_{BDC} from Equation (3.3) is higher than the actual one, hence the need for a higher heat loss for a proper CA10 estimation. Moreover, determining a mean wall temperature among the piston, the cylinder liner and the cylinder head temperatures based only on the coolant temperature will always be prone to errors. Nevertheless a small error in the CA10 estimation by the single-zone model is acceptable regarding the

goal which is to know if particular conditions induce auto-ignition of a specific fuel. A good trade-off can thus be found with $\alpha = 65$, rendering a CA10 estimation error of 1 CAD for the methanol case and of 2 CAD for the hythane case.

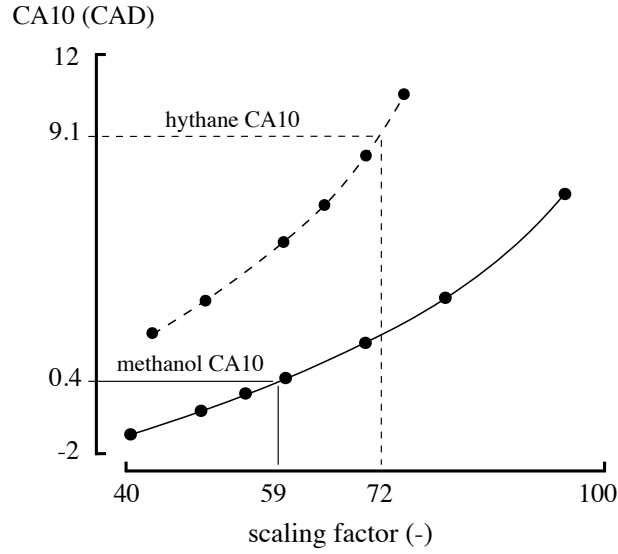


Figure 3.3 – Influence of the convection coefficient scaling factor on the estimated CA10. A good trade-off can be found with $\alpha = 65$.

3.2.2 Validation of the single-zone model

To assess the model validity, two other experimental configurations from the literature are used. The first one is a methane HCCI engine experimented by Neshat et al. [127] and the second one is a methanol HCCI engine experimented by Maurya et al. [59]. Neshat et al. provide the geometric compression ratio only but they give pressure and temperature conditions at the IVC. Therefore, there is no need for the effective compression ratio and the HCCI combustion can be simulated starting at IVC using the developed model. Maurya et al. provide the intake temperature and pressure only. Therefore the effective compression ratio is used this time to simulate the HCCI combustion starting

from the BDC. The estimated and experimentally measured CA10 values are given in Table 3.3. In both cases the estimated CA10 is within 2 CAD of the correct value, hence an error around 5 K in intake temperature, which is acceptable regarding the study objective. The model accuracy is guaranteed only for similar cases: single-stage ignition fuels used in high compression ratio HCCI engines ($>15:1$) having bore over stroke ratios close to 1.

Table 3.3 – *Validity of the model for CA10 estimation of literature experimental data.*

Study	Parameters	CA10 (bTDC)	
		measured	estimated
Neshat et al. [127]	IVC = 146 CAD bTDC	2.5	3.7
	$p_{\text{IVC}} = 1.515$ bar		
	$T_{\text{IVC}} = 441$ K		
	CR = 21.5:1		
Maurya et al. [59]	IVC = 162 CAD bTDC	0.5	2.5
	$p_{\text{BDC}} = 1.013$ bar		
	$T_{\text{BDC}} = 420$ K (from Eq. 3.3)		
	$CR_e = 16.2:1$		

3.3 Results and discussions

This section reports the parametric study results of Table 3.4: the operating conditions and engine compression ratio influence on the electrofuels ignition timing. From the discussion above it is clear that the compression ratios used in this section should be considered as effective compression ratios for real engines. Moreover, Equation (3.3) is used to compute T_{BDC} from the intake temperature. The results are discussed regarding their implications on a multi-fuel HCCI engine, and regarding their limitations.

3.3.1 Influence of compression ratio, intake pressure and equivalence ratio

The required intake temperatures under which the four electrofuels can be burned in the same naturally aspirated engine are displayed in Figure 3.4 as a function of the compression ratio, so that the CA10 happens at TDC. The study is limited to 25:1 in compression ratio, as barely no intake heating is required anymore for hydrogen and methanol, and as higher compression ratios would decrease the power density due to a limited equivalence ratio from the increased combustion intensity, see Figure 5.18.

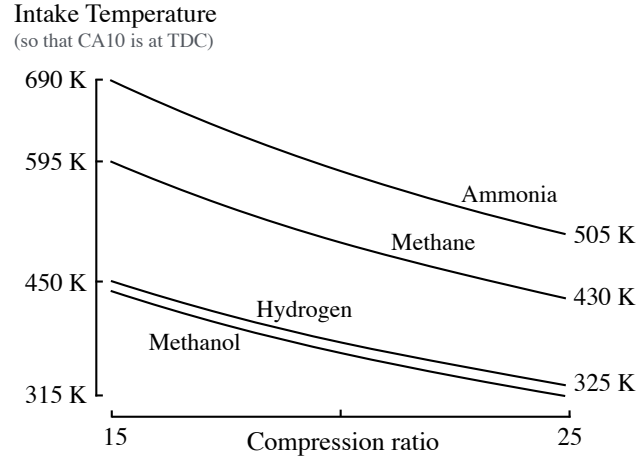


Figure 3.4 – Required intake temperature for having a proper combustion of the fuels (i.e. CA10 at TDC) for various compression ratios. Conditions are naturally aspirated with an equivalence ratio of 0.3. Methane and ammonia are particularly resistant to auto-ignition, an image of their high ignition delays.

Knowing the required intake temperature to auto-ignite a fuel in given conditions is interesting for the reader willing to design such an engine. Still it is not adequate to characterize the auto-ignition tendency of a fuel alone, set free from the engine influences like heat losses and valve timing. In that regard, the temperature reached at 15 CAD bTDC, T_{-15} , is more linked to the

mixture auto-ignition tendency [131]. The T_{-15} reached when the CA10 is at TDC are displayed in Figure 3.5 as a function of the compression ratio.

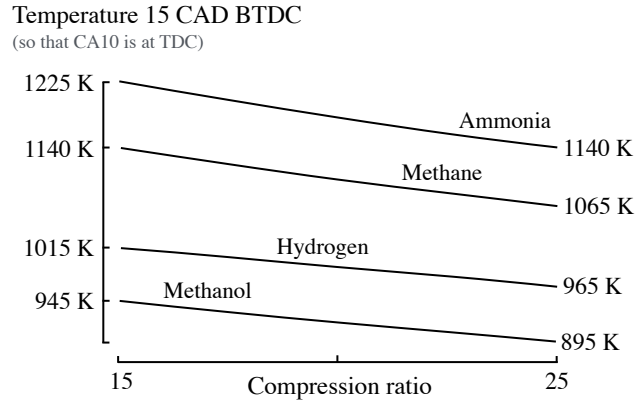


Figure 3.5 – T_{-15} attained by the fuels for having a proper combustion of the fuels (i.e. CA10 at TDC) for various compression ratios. Conditions are naturally aspirated with an equivalence ratio of 0.3.

The use of a low compression ratio for ammonia and methane should be discarded because of the excessively high intake temperatures, and T_{-15} , required. Furthermore, the higher the intake temperature, the more critical the following issues will become: (1) providing high intake temperature is difficult and prone to heat losses, (2) the mixture density will decrease, hence a lower IMEP and (3) the TDC temperature will be so high that the LTC zone might be exceeded and therefore thermal- NO_x might be produced. Therefore higher compression ratios should be used to reduce the required intake temperature for a desired T_{-15} .

Even for high compression ratios, ammonia and methane are very resistant to auto-ignition and it would be beneficial to reduce their required intake temperature for the three above-mentioned reasons. For that aspect, rising the intake pressure has a substantial effect on the intake temperature, see Figure 3.6. A 2 bar intake allows to reduce the intake temperature by 60 K for ammonia and by 50 K for methane. Moreover, Christensen et al. [48] showed

the ringing abatement with increased in-cylinder pressure as the energy contained in the pressure wave oscillations is inversely proportional to pressure. Another advantage of a higher intake pressure is the increased fuel content in each cycle hence a direct increase in IMEP. Yet the disadvantage associated with a high in-cylinder pressure is higher friction losses.

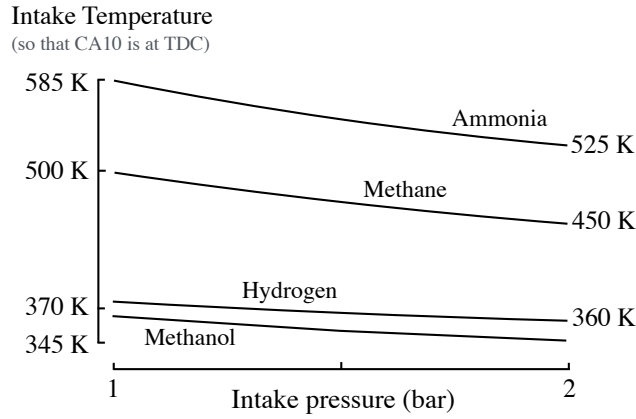


Figure 3.6 – Required intake temperature for having a proper combustion of the fuels (i.e. CA10 at TDC) for various intake pressures. Engine compression ratio and equivalence ratio are 20 and 0.3, respectively. Methane and ammonia are particularly sensitive to intake pressure.

The effect of the intake pressure on T_{-15} is the same as on the required intake temperature, see Figure 3.7.

An increase in the equivalence ratio has an influence on the required intake temperature that is opposed to the objective, but rather small as shown in Figure 3.8. As the four fuels are single-stage ignition fuels (no low-temperature heat release), the equivalence ratio only affects significantly the mixture heat capacity, but not the kinetics. Still, this model does not take into account that increasing the equivalence ratio in a running engine increases its thermal

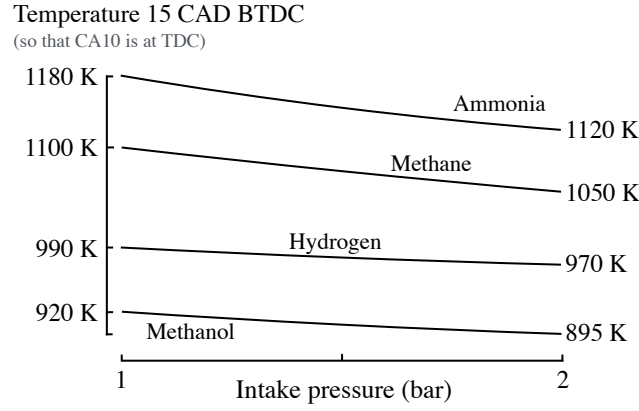


Figure 3.7 – T_{-15} attained by the fuels for having a proper combustion of the fuels (i.e. CA10 at TDC) for various intake pressures. Engine compression ratio and equivalence ratio are 20 and 0.3, respectively.

load (i.e. higher temperature at the start of compression for a given intake temperature), hence a reduced auto-ignition resistance. Moreover, increasing the equivalence ratio is highly beneficial to the IMEP. Therefore, the only constraint on an increasing equivalence ratio will be the ringing apparition, as the MPRR and the maximal in-cylinder pressure will increase.

3.3.2 Operating range: electrofuels sensitivity to intake temperature

Ideal engine operation (i.e. good combustion efficiency and low pollution) can be obtained at different CA10 depending on the fuel and the load. Given the short combustion duration under HCCI conditions (~ 5 -10 CAD), the CA10 is most of the time situated between -3 and 7 CAD after Top Dead Center (aTDC). An early CA10 (before TDC) leads to a fast and intense combustion (i.e. close to Otto optimum), and a late CA10 (after TDC) to a decreased combustion intensity and peak temperature, for the same fuel quantity. Delaying the combustion is often used in piston engine applications to allow for higher fuel contents while staying ringing/knocking safe with acceptable maximal pressures. Depending on the objective (efficiency or power output), the

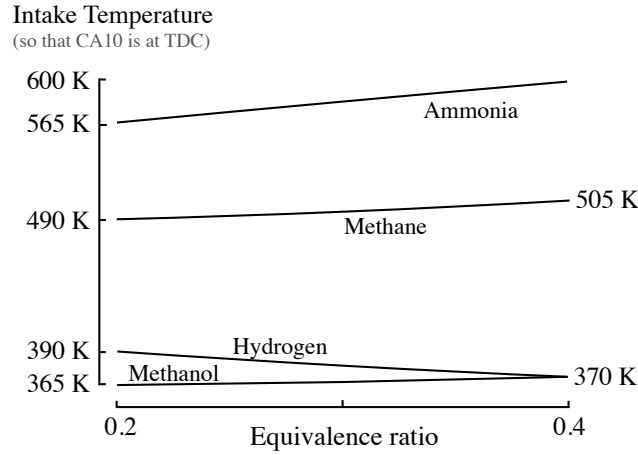


Figure 3.8 – Required intake temperature for having a proper combustion of the fuels (i.e. CA10 at TDC) for various equivalence ratios. Engine compression ratio and intake pressure are 20 and 1 bar, respectively. The fuels are rather insensitive to equivalence ratio regarding auto-ignition resistance.

engine must be able to switch from early to late CA10 and vice versa. The necessary intake conditions to obtain such early, mid and late CA10 (occurring at -3, 2, and 7 CAD aTDC respectively) for the multi-fuel HCCI concept are given in Figure 3.9. To control the fuels from late to early CA10, the variation in intake temperature is about 50K for methane and ammonia, and about 30K for methanol and hydrogen. Still, between mid and late CA10 the temperature variation is only 15K for methane and ammonia, and 10K for methanol and hydrogen. Conventional temperature control systems based on a type-K thermocouple linked to the intake heater by a PID controller are precise within $\pm 2\text{K}$ [43, 57]. This shows that a combustion timing control based on intake temperature is feasible for stationary applications.

3.3.3 Fuel blending influence on auto-ignition

Having several fuels at hand does not mean that they have to be used separately: one can think of mixing them to obtain more interesting properties. For example, a strategic reserve of hydrogen or methanol could be used to promote

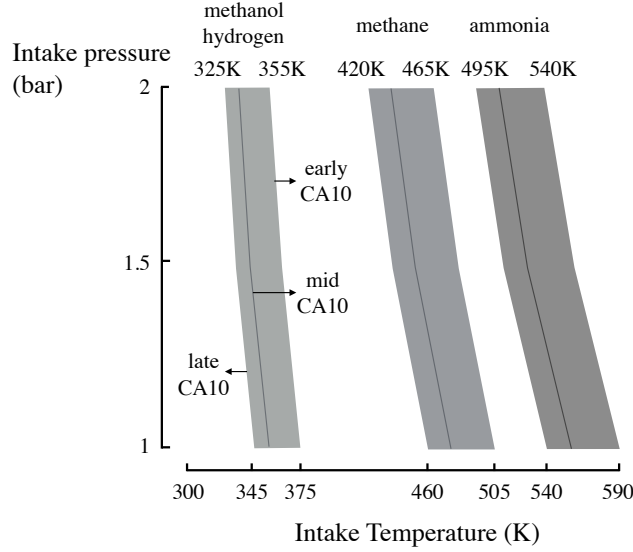


Figure 3.9 – Required intake pressure and temperature to auto-ignite the four different fuels with an early, mid, or late CA10 (-3, 2, and 7 CAD aTDC respectively). Engine conditions are 20:1 compression ratio and 0.3 of equivalence ratio. Combustion timing control based on temperature seems feasible given the usual control precision of $\pm 1\text{-}2\text{K}$.

the combustion of methane and ammonia and reduce the required intake temperature. Also, ammonia could be used to damp the combustion of hydrogen and avoid ringing. Figure 3.10 depicts the influence of hydrogen and methanol addition (in %vol.) to ammonia or methane. The promotion effect is always observed but it is stronger and non linear for hydrogen addition to ammonia and methanol addition to methane. At this point, it must be stated that using the kinetic mechanisms for fuel blends for which they were not specifically validated is only done in order to get general trends since substantial errors could be obtained. For instance, small proportions ($\sim 10\%$ vol.) of hydrogen are simulated to produce a steep promotion of ammonia, although we will observe a less sudden promotion in the experimentations of Chapter 4. For the methanol-methane blend the Mech15.34 mechanism [106] was used since the Li et al. [107] mechanism does not provide a detailed chemistry for methane combustion, hence somewhat smaller values for the intake temperature. Unfortunately, no kinetic mechanism that could correctly handle mixtures of ammonia and methanol was found.

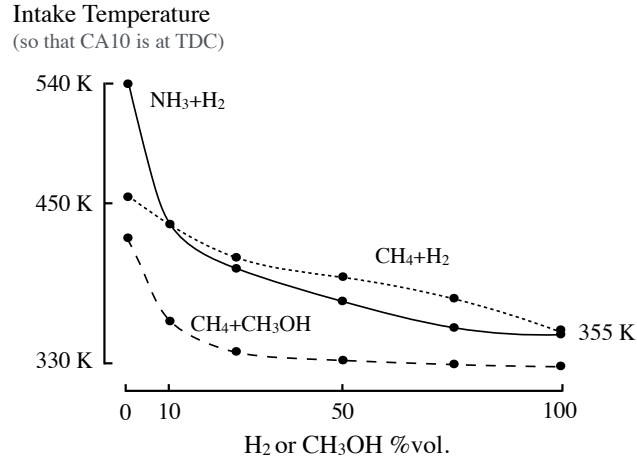


Figure 3.10 – Influence of hydrogen and methanol addition on the auto-ignition resistance of methane and ammonia. Engine parameters are: 20:1 compression ratio, 2 bar intake pressure and 0.4 of equivalence ratio. The promotion effect is not linear and depends on the fuel combination, not only on the promoter.

3.3.4 Limits of intake temperature supply when turbocharging

To be feasible and efficient, the stationary engine unit will need to provide the necessary intake conditions (temperature and pressure) by itself. This can be done, without reducing the electrical efficiency, by recovering the exhaust enthalpy using a turbo-compressor and a heat exchanger, see Figure 3.11. Using the temperature and pressure given by the OpenFOAM model at the exhaust valve opening as an input (T_4, p_4) , and the desired engine intake pressure and temperature as a constraint (T_3, p_3) , one can answer the question: is the energy content before the turbine enough to feed the compressor and leave a sufficiently high energy content at the exhaust to pre-heat the intake? The intake heater is placed before the compressor in order to be able to benefit from the lowest exhaust temperature possible.

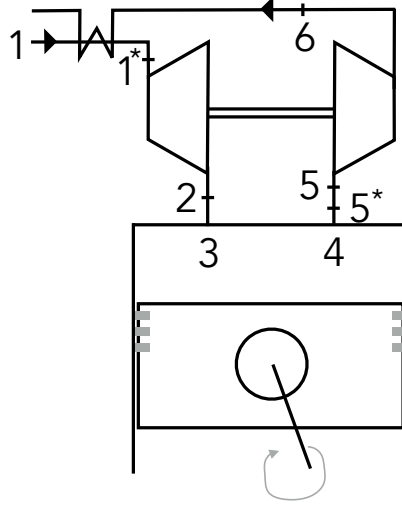


Figure 3.11 – Representation of a turbo-compressor coupled at the HCCI engine to provide the desired intake pressure, as well as a heat exchanger to reach the required engine intake temperature solely from the turbo exhaust heat recovery.

Assuming an ideal gas behaviour from the exhaust mixture, the following set of equation is derived to model the turbocharger coupling to the single-zone model. The compressor isentropic efficiency is defined as:

$$\eta_{si,C} \triangleq \frac{W_{m,C,s}}{W_{m,C}} \simeq \frac{h_{2,s} - h_1^*}{h_2 - h_1^*} \simeq \frac{T_{2,s} - T_1^*}{T_2 - T_1^*} \simeq \frac{\left(\frac{p_2}{p_1^*}\right)^{(1-1/\gamma_C)}}{\frac{T_2}{T_1^*} - 1}, \quad (3.5)$$

where γ_C is the ratio of the mean specific heat capacities at the compressor, $p_2 = p_3$ is the desired intake pressure and T_2 is such that the desired intake temperature is reached in T_3 , taking the admission process into account (heat exchange, mixing with residual gas and dynamic effects), see the methodology from Sjöberg et al. [130] fully derived in Appendix A.4.4. Eventually, taking the safe value of $\eta_{si,C} = 74\%$, Equation (3.5) gives us T_1^* that must be achieved from the intake pre-heating.

The exhaust process from the cylinder through the valve is assumed to be an irreversible expansion of the gas against a constant pressure $p_5 = p_2 = p_3$, giving:

$$\begin{aligned}
dU &= -pdV \\
mc_v(T_5^* - T_4) &= -p_5(V_4 - V_5^*) \\
mc_v(T_5^* - T_4) &= -mR^*T_3 + mR^*T_5^* \\
c_pT_5^* &= R^*T_3 - c_vT_4 .
\end{aligned} \tag{3.6}$$

The temperature before the turbine being obtained, taking into account a 10% heat exchange (ϵ_{exch}) with the exhaust manifold beign at an assumed 100 °C, from:

$$T_5 = (1 - \epsilon_{\text{exch}})T_5^* + \epsilon_{\text{exch}}373 . \tag{3.7}$$

If one assumes the power balance between the compressor and the turbine yet with a mechanical efficiency of 95% (η_{mec}), the temperature at the turbine exhaust is given by:

$$mc_{p,C}(T_2 - T_1^*) = \eta_{\text{mec}}mc_{p,T}(T_5 - T_6) . \tag{3.8}$$

Finally, assuming a pinch of 30 K at the gas-phase heat exchanger, and a minimal exhaust temperature of 100 °C to avoid condensation, the following inequality describes if the available energy content of the exhaust flow surpasses what must be given at the intake pre-heating:

$$\begin{aligned}
E_{\text{available}} - E_{\text{needed}} &> 0 \\
mc_{p,\text{exch},\text{cold}}(T_6 - 30 - 373) &> mc_{p,\text{exch},\text{hot}}(T_1^* - T_1) ,
\end{aligned} \tag{3.9}$$

where $c_{p,\text{exch},\text{cold}}$ and $c_{p,\text{exch},\text{hot}}$ are the two streams respective average heat capacities of the heat exchanger.

If the exhaust flow energy content is higher than the energy required to heat the intake mixture, then the HCCI engine can be operated without external burner or heat supply. For hydrogen and methanol, all the considered intake conditions are achievable with this system, as demonstrated by Dec et al. [79] for gasoline. On the other hand, methane and ammonia cannot be operated in any condition because they require intake temperatures that are too high in comparison to the energy available at the exhaust. Figure 3.12 reports the evolution of the minimal equivalence ratio required as a function of the operated intake pressure and compression ratio. As a consequence, the achievable equivalence ratio with ammonia or methane (i.e. resistance to ringing, behaviour of

exhaust emissions, etc.) is a crucial question for the technical feasibility and efficiency of such a system. Indeed, equivalence ratios higher than 0.4 might lead to knocking or to the production of thermal- NO_x .

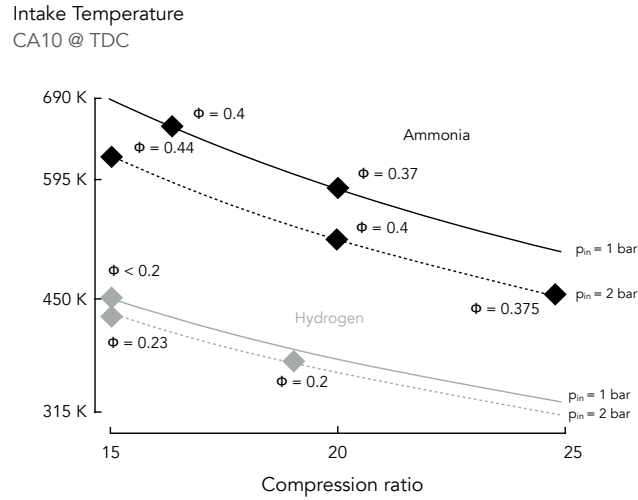


Figure 3.12 – Depending on the compression ratio and the intake pressure, the required equivalence ratio to provide enough enthalpy at the turbine outlet for reaching the intake temperatures is indicated at the diamonds. Hydrogen conditions are globally reached for equivalence ratios higher than 0.2, but equivalence ratios of about 0.4 are required for ammonia.

As an example, to have enough energy available at the exhaust to pre-heat the intake in order to eventually reach the desired intake temperature for ideal ignition timing, in the case of a 20:1 compression ratio with a 2 bar intake pressure the ammonia equivalence ratio has to be higher than 0.4. In that case, the obtained temperature states are as follows:

3.4 Outlook and conclusion

HCCI operating conditions have been studied for an intake pressure ranging from 1 to 2 bar, for an equivalence ratio ranging from 0.2 to 0.5, and for a

Table 3.4 – Temperature states for the turbocompressed single-zone model in the case of a 0.4 equivalence ratio ammonia run with a 2 bar intake and a compression ratio of 20:1.

T_1	T_1^*	T_2	T_3	T_4	T_5^*	T_5	T_6	$E_{\text{available}}$	E_{needed}
(K)	(K)	(K)	(K)	(K)	(K)	(K)	(K)	(J/cycle)	(J/cycle)
293	399	507	469	847	647	620	509	77	79

compression ratio ranging from 15:1 to 25:1 for the use of the four electrofuels of interest. The developed single-zone model features a heat loss model calibrated for a proper estimation of the auto-ignition timing of single-stage ignition fuels in HCCI engines having a high compression ratio ($> 15:1$) and a bore over stroke ratio close to 1. The model has been validated using experimental results from the literature with an accuracy of ± 2 CAD. Generally, the HCCI mode is shown able to burn the four electrofuels within a single engine design, as long as the provided intake temperature and/or compression ratio lead to sufficiently high temperatures at the end of compression (T_{-15}). The major findings and conclusions are:

1. Ammonia and methane are much more resistant to auto-ignition than methanol and hydrogen. Roughly, ammonia requires 80K more at the intake than methane and 180K more than methanol and hydrogen to auto-ignite.
2. Regarding the intake pressure, the higher the better considering that it increases the IMEP and reduces the required intake temperature (hence further increasing the IMEP).
3. The choice of the engine compression ratio will be a trade-off between allowing the auto-ignition of ammonia and methane within achievable intake temperatures, and preventing hydrogen and methanol from ring-ing.
4. CA10 control and combustion delaying for combustion intensity reduction are achievable through intake temperature reduction.
5. Hydrogen and methanol promote ammonia and methane, respectively, in a non-linear way: the main part of the promotion happens when the additive is in minor proportions. A 10-30%vol. content of the promoter

seems to provide half of the promotion. Therefore, storing strategic reserves of hydrogen or methanol, or proceeding to a partial ammonia or methane reforming to hydrogen to promote their combustion shows a great interest.

Even though these results were obtained with tools elaborated for HCCI conditions (single-zone model and kinetic mechanisms), they require experimental investigations. Indeed, many parameters are left uncovered in this chapter: combustion efficiency, combustion duration and timing, pollutant emissions, IMEP, ringing, maximum pressure limit, EGR, etc. Most importantly the mutual interactions between those parameters is to study. Although the way to maximise HCCI engine power density is relatively well established, see the reference publication from Dec et al. [79] reported in Section 2.5, simply the basic performances for electrofuel blends in HCCI engines are yet to be obtained.

Thinking of the goal of a single engine architecture, the ammonia-hydrogen blend seems a good candidate to investigate first due to their auto-ignition resistances span covering those of methane and methanol. Moreover their non-carbonated aspect together with hydrogen fast kinetics and ammonia slow kinetics might render interesting complementary features. Still, due to ammonia relative poor kinetic knowledge, a first fundamental study is performed in Chapter 4 in order to gain insight into its potential HCCI behaviour and to help better plan its experimental investigation. Such experiments would help to better comprehend the existing trade-offs regarding compression ratio, efficiency, ringing, or emissions, as well as give a proof concept of the multi-fuel HCCI system. Chapter 5 shall be devoted to that endeavour.

Regarding the CHP concept, further studies are required for HCCI engines regarding cold start and technically reaching the intake temperature and pressure using turbo-compressors and heat exchangers. Yet it is out of the scope of this thesis.

The problem in this business isn't to keep people from stealing your ideas; it's making them steal your ideas!

Howard Aiken

4

A fundamental characterisation of ammonia under HCCI conditions

This chapter is based on the following publication:

Pochet, M., Dias, V., Moreau, B., Foucher, F., Jeanmart, H., & Contino, F. (2018). *Experimental and numerical study, under LTC conditions, of ammonia ignition delay with and without hydrogen addition*. Proceedings of the Combustion Institute, 37, 621-629. <http://doi.org/10.1016/j.proci.2018.05.138>

Ignition delay times for ammonia are not available at relevant HCCI conditions. This lack of fundamental kinetic knowledge leads to uncertain ignition delay predictions by the existing ammonia kinetic mechanisms and prevents from determining optimal HCCI operating conditions. Using a Rapid Compression Machine (RCM), the ignition delays of ammonia with hydrogen addition (0%, 10%, and 25%vol.) have been studied under HCCI conditions: low equivalence ratios (0.2, 0.35, 0.5), high pressures (43 bar and 65 bar) and low

temperatures (1000 - 1100 K). This chapter presents the comparison of the experimental data with simulation results obtained with five kinetic mechanisms found in the literature. It then provides a sensitivity analysis to highlight the most influencing reactions on the ignition of the ammonia-hydrogen blends.

The obtained range of ignition delays for pure ammonia and for the ammonia-hydrogen blends prove their suitability for HCCI engines. Still the hydrogen addition must be greater than 10%vol. to produce a significant promotion of the ignition delay. The two best performing mechanisms still predict too long ignition delays for pure ammonia, while the delays become too short for ammonia-hydrogen blends. A third mechanism captures correctly the relative influence of hydrogen addition, but is globally over-reactive. Through the sensitivity analysis, H_2NO has been identified as the main cause for the under-reactive pure ammonia kinetics and N_2H_x has been identified as the main cause for globally over-reactive ammonia-hydrogen mechanisms.

4.1 A rapid compression machine for auto-ignition delay determination

RCM are experimental devices that allow to measure the auto-ignition delay of a given mixture in stable and homogeneous conditions. The device is characterised by the rapid compression of a mixture, typically using a piston, followed by the sudden stop in compression (within a few milliseconds), see Figure 4.1, hence ensuring (quasi) steady thermodynamic conditions during the auto-ignition delay. The ignition delay is measured by the time between the end of the compression and the peak of pressure rise rate. Still some imperfections exist in a RCM, which influence the measurement of the ignition delay, and shall be detailed when later dealing with them.

4.1.1 The RCM setup from Université d'Orléans

The experimental set-up used in this study is the single piston RCM of the PRISME laboratory in Université d'Orléans, see Figure 4.2. The functioning principle is based on the RCM at the Argonne National Laboratory [134], see

4.1. A rapid compression machine for auto-ignition delay determination 71

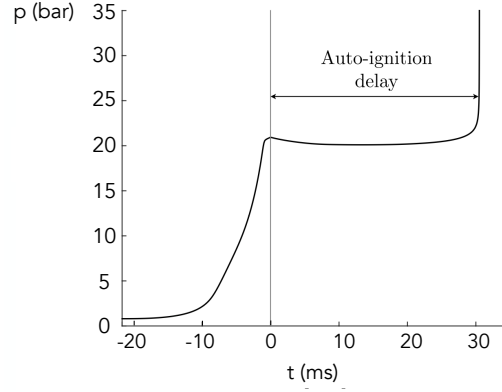


Figure 4.1 – Ignition delay measured from the typical reactive pressure evolution in a RCM. Adapted from [134].

Figure 4.2. The combustion chamber piston is linked by a shaft to a bigger piston, which accelerates the whole system when suddenly connected to a 4 bar air vessel. The system is hydraulically stopped when the lock mounted on the shaft reaches the end of the stroke and creates a concealed air pocket. From the shaft motion, the combustion piston compresses the mixture to investigate.

The piston geometry of this machine (see Figure 4.3) is based as well on the design of the RCM at the Argonne National Laboratory [134]. The high crevice volume allows the absorption of the boundary layer to minimize the formation of a roll-up vortex during the compression. Following the crevice validation methodology of Bourgeois et al. [135], the crevice volume is 13% below the conservative volume that guarantees the absence of a vortex. In the case where small vortices would develop near the crevice region, given that neither ammonia nor hydrogen has a negative temperature coefficient region, there would be no effect on the ignition delay as the auto-ignition onset would still happen in the core region. The whole RCM characteristics are summarised in Table 4.1.

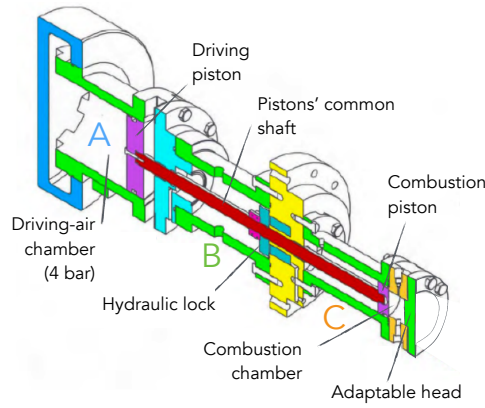
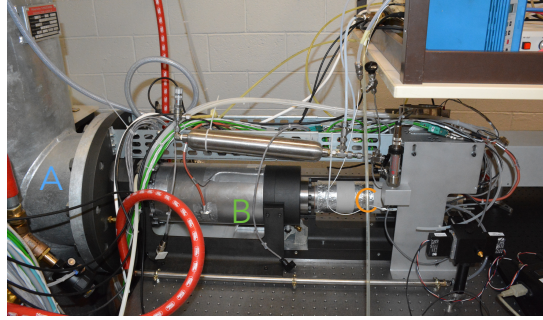


Figure 4.2 – The RCM setup at the PRISME laboratory. From left to right: A) the 4 bar driving vessel, B) the shaft housing containing the deceleration device, C) the combustion chamber. Schematic reproduced from [134].

Experimental procedure and uncertainty considerations

Several sensors as well as the experimental procedure affect the obtained ignition delay, δ , which is defined as the time between the end of the compression (i.e. maximum compression pressure) and the combustion MPRR:

$$\delta = t_{\text{MPRR}} - t_{P_c} . \quad (4.1)$$

To carry out a shot with the RCM, first the mixture has to be prepared. The preparation vessel is first vacuummed and then filled by each of the desired gases, in sequence. To do so, a specifically calibrated mass flow controller (BROOKS Cori-Flow M13V10I) is used to deliver each gas, starting from a null flow rate each time and stopping at the desired partial pressure of the vessel. The mass

4.1. A rapid compression machine for auto-ignition delay determination⁷³

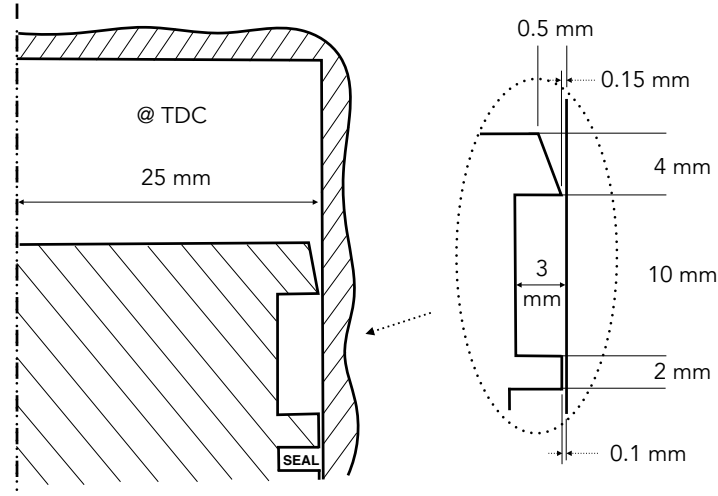


Figure 4.3 – Design of the RCM piston at the PRISME laboratory.

Table 4.1 – RCM main characteristics

Bore - Stroke	50 - 300 mm
Compression time	35 ms
Time $p_{\max}/2$ to $p_{\max}$ (t_{50})	4 ms
Max. piston velocity	11.5 m/s
Piston acceleration	1500 m/s ²
Acceleration time	15 ms
Piston deceleration	4500 m/s ²
Deceleration time	5 ms
Crevice volume	4.82 cm ³
Compression ratio	24.34:1
Intake temperature	20-110 °C

flow controller has an accuracy of $\pm 1\%$ on the flow rate and $\pm 0.2\%$ on its full range (i.e. systematic error). Then, the piston is put in backwards position and the combustion chamber is vacuumed. The combustion chamber is then filled with the prepared mixture until the intake pressure reaches the desired value. The vessel and intake pressure sensors are KELLER PAA-33X/80794

piezoelectric transducers having an accuracy of ± 0.2 mbar and a repeatability of ± 0.1 mbar in the 0-5 bar range. Finally, the piston is accelerated thanks to the driving vessel, then automatically decelerated when reaching the hydraulic lock system. The mixture subsequently auto-ignites if the required thermodynamic conditions have been reached. Regarding the in-cylinder pressure acquisition, a piezoelectric AVL QH32C transducer having a linearity of $\pm 0.2\%$ and an accuracy of $\pm 1\%$ is used. The charge amplifier, a KISTLER 5011, induces an error smaller than 1% on the current received. The pressure signal has a sampling frequency of 20 MHz and is filtered through a normalised Butterworth cut-off frequency of 0.03. For non-reactive shots, the intake temperature is measured as well using a type K thermocouple with an accuracy of ± 1 K.

Even though deriving the measurement uncertainty of the ignition delay, equivalence ratio, and in-cylinder temperature and pressure is out of the scope of this chapter, the repeatability uncertainty of the machine is derived hereafter. Two sets of five measurements for both short and long ignition delays have been performed. For the five repeated points of mixture #1 with passivation and with intake pressure and temperature set at 1075 mbar and 89 °C, the mean ignition delay is 36.83 ms. The standard deviation is $s = 1.00$ ms. For an assumed normal distribution of the ignition delay population, the sample drawn follows a Student's t distribution and the repeatability uncertainty on the mean ignition delay at a confidence level of 95% (U_{95}) is:

$$U_{95} = \pm t_{4 \text{ dof}}^{0.05/2} \frac{s}{\sqrt{5}} = \pm 1.1 \text{ ms} .$$

These five repeated conditions were obtained with a variability in compression pressure and temperature of ± 0.4 bar and ± 1.5 K, respectively. For the same mixture at an intake pressure and temperature of 1100 mbar and 115 °C, the mean ignition delay is 8.63 ms. Following the same procedure, the repeatability uncertainty on the mean ignition delay with a confidence level of 95%, for a sample of five measurements, is $U_{95} = \pm 0.5$ ms. For this sample the variability in compression pressure and temperature was of ± 0.3 bar and ± 1.0 K, respectively.

To assess the uncertainty related to the preparation of a new mixture (e.g. after the vessel has been emptied), five shots drawn from two mixture preparation are compared. The intake conditions are set again at 1075 mbar and 89 °C (i.e. late ignition delay), but this time the obtained standard deviation is $s = 1.35$ ms and the related uncertainty on the mean is $U_{95} = \pm 1.5$ ms.

4.1. A rapid compression machine for auto-ignition delay determination⁷⁵

Using a Welch F test with a confidence level of 0.01, there is no statistical difference shown between the two mean ignition delays of the two mixture preparation.

Ammonia adsorption on the RCM walls

Ammonia adsorbs with time on stainless steel, which might decrease the actual equivalence ratio of the mixture between consecutive shots [120]. For that reason the liner of the RCM has been coated with chrome to minimize the contact with steel. Moreover, the mixture reservoir (made out of stainless steel 304) was passivated following the procedure of Mathieu and Petersen [120]: reservoir filling with pure ammonia at a pressure of 133 mbar for 5 minutes followed by a complete vacuuming for 5 more minutes. To test the influence of passivation, the reservoir has been filled with mixture #1 a first time without, and a second time with prior passivation and five consecutive shots have been made each time. For a Welch F test with a confidence level of 0.01, there was no statistical difference between the two samples mean ignition delay or a decay in ignition delay. Still the passivation was used for all experiments.

4.1.2 The adiabatic effective core volume method for RCM simulation and post-processing

With well designed RCM crevices, assuming uniform temperature and chemical composition in the core zone, outside of the boundary layer, is a valid hypothesis [136]. Therefore a 0-dimensional model can be used to represent the thermodynamic state in this zone (i.e. the hottest region, relevant for the chemical kinetics). This model will be used to predict the ignition delay with the kinetic mechanisms and compare them to the obtained experimental results. The widely-used model of the *effective adiabatic core volume* has been implemented to capture this core zone. It is thoroughly derived in [136, 137], yet a brief derivation is given here. The mixture in the rapid compression machine being trapped (neglecting blow-by), one can start from the conservation of energy in a closed system,

$$dU = nc_v dT = \delta Q - p dV , \quad (4.2)$$

where U is the internal energy of the mixture, n is the number of moles trapped in the cylinder, c_v is the mixture specific heat capacity at constant volume, p is

the in-cylinder pressure and V is the instantaneous chamber volume. Assuming the mixture to behave like an ideal gas, Equation (4.2) can be rearranged to:

$$\frac{c_v}{R}d(pV) = \delta Q - pdV \quad , \quad (4.3)$$

and, finally using the Mayer relation $R = c_p - c_v$ with $\gamma = \frac{c_p}{c_v}$ the ratio of the specific heat capacities of the cylinder mixture, one obtains:

$$\frac{dp}{p} = -\gamma \frac{dV}{V} + \delta Q \quad . \quad (4.4)$$

If Non-Reactive shots are considered (for which we have an in-cylinder pressure measurement, p_{NR}) where the oxygen is replaced by nitrogen to avoid combustion, we obtain $\delta Q = 0$ inside the adiabatic core zone. Therefore, using:

$$\frac{dp_{NR}}{p_{NR}} = -\gamma \frac{dV_e}{V_e} \quad , \quad (4.5)$$

renders V_e the *effective* volume evolution of the adiabatic core region that follows the exact compression of the Non-Reactive shot, which is isentropic. Figure 4.4 compares the geometric volume evolution to the effective volume for a neat ammonia mixture with an equivalence ratio of 0.35. As can be seen in Figure 4.4, the heat losses are implicitly taken into account by the *effective volume* since it is slightly higher than the geometric one during compression, and that it expands during the post-compression period. This *effective volume* allows as well to take machine-related effects into account (such as piston rebound after the end of compression) and eliminate imperfections (such as small roll-up vortices).

The effective volume is eventually used as the constraint of a specifically developped single-zone model, similar to the one developped in Chapter 3. Using the experimental mixture composition, and intake temperature, volume and pressure as initial conditions, the model follows the effective volume evolution to render the isentropic compression described by Equation (4.4). The simulated pressure and temperature will evolve until they trigger the mixture kinetics (simulated using the CHEMKIN package) and render $\delta Q > 0$. Once the combustion is triggered, the adiabatic core volume model is no longer valid.

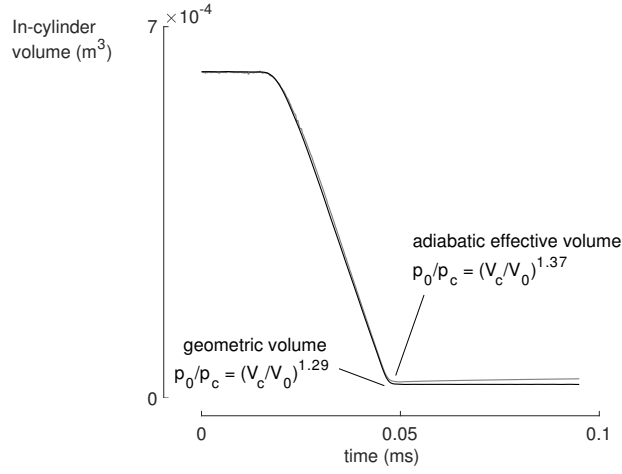


Figure 4.4 – The effective volume of the adiabatic core is always slightly higher compared to the geometric one, indicating for the machine wall heat losses.

Yet the combustion being quasi-instantaneous in a single-zone model, the portion of the ignition delay spent outside of the validity range is negligible.

Any modification to the mixture composition, intake pressure or temperature, or compression ratio influences the adiabatic core volume (i.e. the heat losses), and therefore requires a new Non-Reactive shot to be realised in order to properly simulate the new conditions.

4.2 Existing ammonia mechanisms

Many mechanisms have been built to represent ammonia oxidation kinetics. The two main applications and origins of development for these mechanisms are the DeNOx process and the combustion in SI engine. However it is legitimate to question their suitability for ammonia ignition delay under HCCI conditions.

Based on the fundamental ammonia combustion studies detailed in Section 2.6, the five most advanced and diverse mechanisms were selected for comparison with the obtained RCM experiments. Their validated conditions of use are reported in Figure 4.5.

The first mechanism is the one of Konnov and De Ruyck (**KD, 127 species - 1207 reactions**) [118]. It is a H/N/O model tested for ammonia and hydrogen oxidation, ignition and flame structure at high temperatures [119]. This

mechanism has been modified by Duynslaegher et al. to better match ammonia flame structures at low pressures, close to stoichiometric conditions and for hydrogen molar fractions from 5 to 12% [119]. Still, Mathieu and Petersen have shown that the original KD mechanism performed better for ammonia ignition delay at 30 atm and high temperatures than the modified version from Duynslaegher et al. [120].

The second mechanism, by Zhang et al. (**ZH, 44 species - 251 reactions**) [138], is an H_2 /syngas/ NO_x mechanism based on the ammonia sub-mechanism from Mathieu and Petersen [120] and the NNH sub-mechanism of Klippenstein et al., [115]. The ammonia sub-mechanism is based on lean ammonia shock tube ignition delays at medium to high pressures (1.4, 11, and 30 bar) and high temperatures (1560 - 2455 K) [120]. The NNH sub-mechanism has been built for the DeNO_x process and validated at medium temperatures (1000 - 1500 K) [115]. Compared to Mathieu and Petersen mechanism, the **ZH** mechanism has been further validated for various hydrogen combustion conditions, hence the choice for that mechanism.

The third mechanism, also based on the NNH sub-mechanism of Klippenstein et al., is the mechanism of Song et al. (**SO, 34 species - 204 reactions**) and is modified according to their high pressure (30 and 100 bar) and low temperatures (450-925 K) ignition delays for lean to stoichiometric ammonia mixtures [121].

The fourth mechanism is the one of Dagaut-Kéromnès (**DK, 43 species - 271 reactions**). It is based on the Dagaut and Nicolle work [114] on the reduction of NO_x by ammonia under lean conditions and on the H_2 -CO work of Kéromnès et al. [96] on hydrogen ignition delay at elevated pressures, both performed in the LTC temperature range. The DK mechanism has been validated by Li et al. [139] for stoichiometric ammonia-hydrogen flames and for the Mathieu and Petersen pure ammonia ignition delay data.

The final selected mechanism is from Nakamura et al. (**NK, 38 species - 232 reactions**) [140]. It is based on the Miller and Bowman DeNO_x mechanism [112], and completed with: the H_2 - NH_x - NO_2 - N_2O chemistry of Mathieu and Petersen [120], the H_2 -CO chemistry of Kéromnès et al. [96], and the N_2H_x chemistry of Konnov and De Ruyck [118]. Nakamura et al. describe their mechanism as a "bridge between the Mathieu and Petersen mechanism at high temperatures and the KD mechanism at low temperatures" [140].

The five mechanisms (KD, ZH, SO, DK, NK) are used regardless of the

in-cylinder pressure, hence considering the molecular reactions to happen by binary collisions, except for modelled third body reactions. The experimental in-cylinder maximum pressures are below 80 bar for the compression pressure of 43.4 bar and below 110 bar for the compression pressure of 65.5 bar.

Two Mechanisms that did not existed at the time of the study deserve to be mentioned. First, Glarborg et al. did a comprehensive review of the mechanisms for NO_x emissions, including ammonia combustion for the DeNO_x process, and suggested a new global mechanism with 151 species and 1398 reactions [141]. Second, Otomo et al. (32 species, 213 reactions) improved Song et al. mechanism by modifying NH₂, HNO, and N₂H₂ reactions, yet it has only been validated at high temperatures and equivalence ratios above those of interest for HCCI conditions.

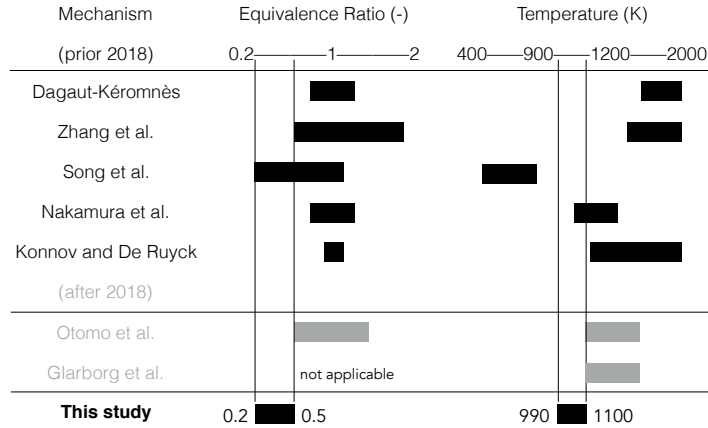


Figure 4.5 – None of the existing ammonia mechanisms are covering the temperature and equivalence ratio regions of interest for HCCI engines.

4.2.1 Operating conditions

To achieve different compression pressures and temperatures, the intake pressure is varied between 400 mbar and 1250 mbar, and the intake temperature between 60 °C and 110 °C (the maximum achievable by the setup). Moreover

argon is used to replace part of the inert nitrogen to help achieving higher compression temperatures with moderate intake temperatures. The mixtures used during the experimental campaign are detailed in Table 4.2. To help achieving higher compression temperatures with moderated intake temperatures, argon is used to replace part of the inert nitrogen. For mixtures #2-4, argon replaces 15%vol. of the nitrogen, and for mixture #5 it replaces 20%vol of the nitrogen.

Table 4.2 – Molar fractions of the different mixtures used

Mixture	1	2	3	4	5
NH ₃ :H ₂ (%vol.)	100:0	100:0	90:10	75:25	100:0
ϕ	0.2	0.35	0.35	0.35	0.5
NH ₃ (%)	5.31	8.93	8.29	7.25	12.29
H ₂ (%)	-	-	0.92	2.42	-
O ₂ (%)	19.89	19.13	19.07	18.98	18.43
N ₂ (%)	74.80	61.15	60.96	60.66	55.43
Ar (%)	-	10.79	10.76	10.70	13.86

4.3 Experimental Results

In this section experimental and numerical ammonia ignition delays are reported as a function of temperature, pressure, equivalence ratio, and hydrogen addition. Finally a sensitivity analysis is performed to improve the prediction of the best mechanisms.

4.3.1 Pure ammonia ignition delay: temperature and pressure dependencies

Pure ammonia ignition delay as a function of the compression temperature is depicted in Figure 4.6. Given the obtained range of ignition delays (3 - 30 ms), these measurements show the suitability of pure ammonia use in a pre-heated intake ($\sim 170^\circ\text{C}$, due to the absence of argon in a real situation) LTC engine with a compression ratio of 25:1. Regarding the mechanisms, SO and DK (both

originating from the DeNOx process study at a mid-range temperature) capture ammonia ignition delays best, while KD is over-reactive (as observed by Mathieu and Petersen [120]) and ZH under-reactive. Finally NK is over-reactive as well and very similar to KD, although based on a DeNOx mechanism. This might be an evidence of the predominance of the N_2H_x chemistry for pure ammonia conditions.

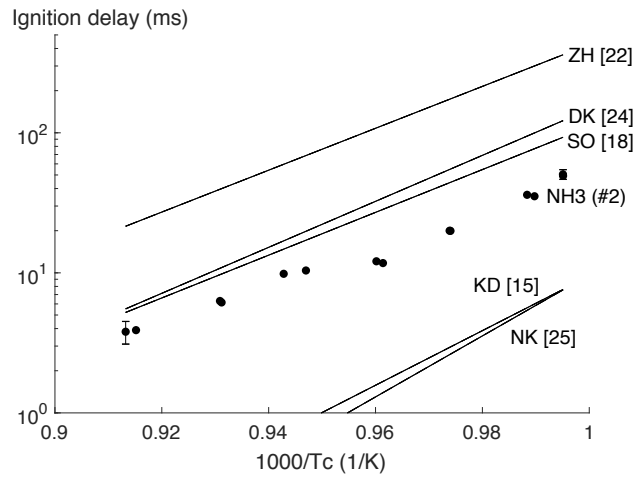


Figure 4.6 – Experimental and numerical ammonia ignition delays as a function of the compression temperature, and for an equivalence ratio of 0.35 and a compression pressure of 65.5 bar (mixture #2). None of the mechanisms correctly predict the measured ammonia ignition delay.

Figure 4.7 shows the influence of the pressure at the end of compression on ammonia auto-ignition. As the pressure increases, ammonia ignition delay experiences a marked decrease. This highlights the interest of a high compression ratio or a boosted LTC engine operating with ammonia. Regarding the mechanisms, their error on the ignition delay estimation increases with the compression pressure, except KD, stressing out the fact that they were not obtained for high pressure ammonia oxidation.

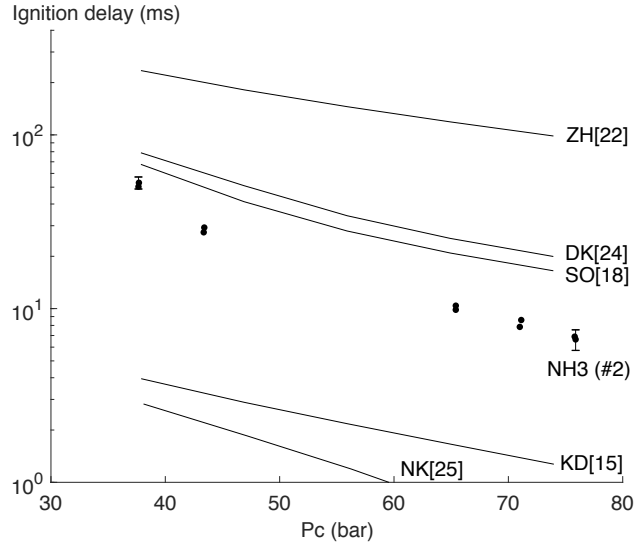


Figure 4.7 – Experimental and numerical ammonia ignition delay as a function of the compression pressure, and for an equivalence ratio of 0.35 and with a fixed intake temperature of 353 K (mixture #2).

4.3.2 Influence of hydrogen addition on ammonia ignition delay

The evolution of the ammonia ignition delay with hydrogen addition is shown in Figure 4.8. The evolution of the ignition delay with the compression temperature is not observed to be influenced by the hydrogen fraction (i.e. the same variation in ignition delay is obtained for a given change in compression temperature). Moreover, the impact of hydrogen addition on the ignition delay seems to be highly dependent on the hydrogen concentration: a small quantity of hydrogen addition seems to have a limited influence on the ignition delay, but increasing the hydrogen fraction up to 25% induces a considerable reduction in the ignition delay. Therefore to promote ammonia under LTC conditions, and allow lower intake temperatures to be used, substantial amounts of hydrogen are required. Regarding the mechanisms at 10%vol. hydrogen, ZH and SO are now over-reactive, and DK is highly over-reactive. KD is so reactive that the modelled combustion happens entirely during the compression. Therefore

this mechanism will no longer be used for the rest of this study. Contrary to KD, NK is only slightly over-reactive with some hydrogen content, meaning that the NH_3 sub-mechanism of Mathieu and Petersen that has been added to NK captures qualitatively well the hydrogen-ammonia interactions. Finally, the over-reactivity of the three best mechanisms (SO, ZH, and NK) decreases substantially at 25%vol. of hydrogen content.

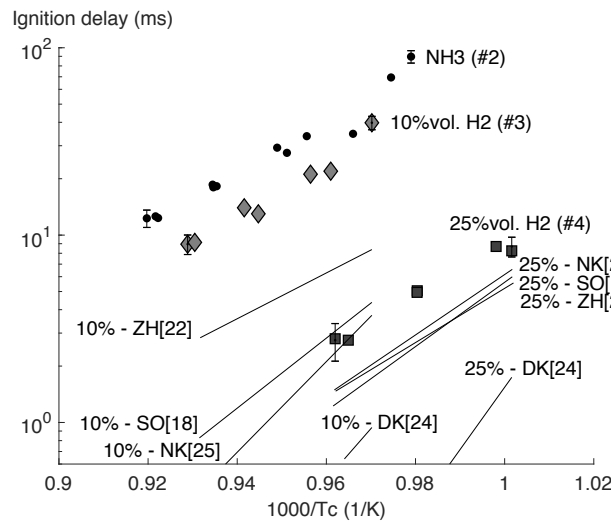


Figure 4.8 – Experimental and numerical ammonia-hydrogen ignition delays at an equivalence ratio of 0.35 and a compression pressure of 43.4 bar (mixture #2,3,4).

To better grasp the influence of hydrogen addition, Figure 4.9 reports the evolution of the experimental and modelled ignition delays as a function of the hydrogen %vol. Results for NK, SO, and ZH mechanisms are plotted for the experimented mixtures, as well as for 2 and 5%vol. hydrogen content. These two points can only serve a qualitative purpose as they have been simulated from the effective core volume of the neat ammonia run, even though with the correct compression temperature and pressure. For a blend of fuels, it is generally observed that the logarithm of the obtained ignition delay is linearly correlated to the molar fraction of the respective fuel ignition delays, as for the hydrogen-methane case [142]. As observed in Figure 4.9, the experimental

results of the ammonia-hydrogen blend do not follow this empirical rule for the first few %vol. of hydrogen added, meaning that the radical pool created by the early hydrogen auto-ignition is not sufficient to trigger ammonia kinetics. Such behaviour is obtained, solely, by the NK mechanism, although globally over-reactive. The global over-reactivity of NK might be brought by the N_2H_x chemistry of KD. According to SO and ZH predictions, only a small fraction of hydrogen is required to induce a much earlier auto-ignition. This implies that either the pure ammonia chemistry under LTC conditions is not well captured or that the hydrogen-ammonia interactions are too strong, since the ammonia sub-mechanism is globally under-reactive. An in-depth sensitivity analysis is necessary to distinguish the base mechanism responsible for a correct ammonia reactivity and the base mechanism responsible for correct hydrogen-ammonia interactions.

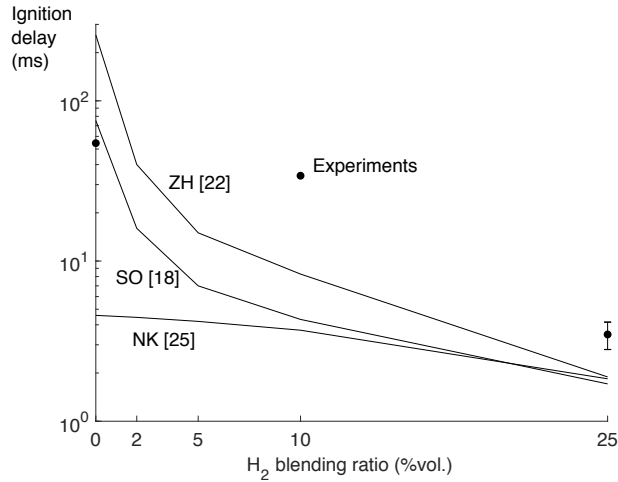


Figure 4.9 – Ignition delay as a function of the hydrogen content %vol., at an equivalence ratio of 0.35, a compression temperature of 1031 K and a compression pressure of 43.4 bar (mixture #2,3,4).

4.3.3 Influence of the equivalence ratio on ammonia ignition delay

Figure 4.10 shows the evolution of the pure ammonia experimental ignition delay as a function of the equivalence ratio. There is a small dependence of the ignition delay on the equivalence ratio. However, for a given temperature, the variability of the ignition delay is close to the respective uncertainty regions. This result implies that a perturbation created by a small change in the equivalence ratio could easily be handled by an engine control system. Yet the reasons for a possible equivalence ratio leading to a higher ammonia reactivity under LTC conditions, and its variability with the temperature, is still an open question.

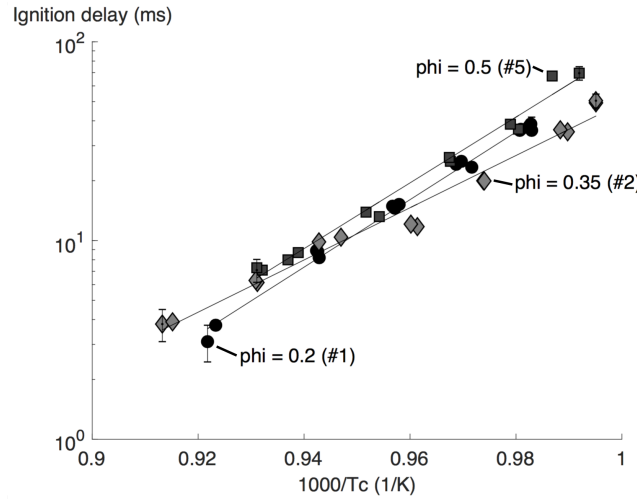


Figure 4.10 – Experimental ammonia ignition delays, and their linear regressions, as a function of the equivalence ratio and at compression pressure of 65.5 bar.

4.3.4 Sensitivity analysis of the kinetic mechanisms: pure ammonia and ammonia hydrogen blends

Three mechanisms with different origins and reactivity will be used for the sensitivity analysis: ZH (under-reactive, based on ammonia oxidation at high

temperature), SO (under-reactive, based on DeNO_x at low temperature), and NK (over-reactive, based on ammonia oxidation at high temperature). The sensitivity analysis will be performed on the OH radical at its peak timing, as it has been shown to produce very similar results to a sensitivity analysis on the ignition delay [120]. The sensitivity analysis is done using the OpenSMOKE++ software [143, 144]. Reactions with a normalized sensitivity coefficient lower than 0.2 are discarded.

The two first sensitivity analyses are performed for mixtures #2,3,4 (at 1075 K, 50 bar) and with the mechanisms ZH and SO to extract the reactions responsible for an under-reactivity with pure ammonia and an over-reactivity for ammonia-hydrogen blends. The raw results of the sensitivity analysis are reported in Figure 4.11. Out of the influencing reactions, the only ones that would promote the ignition delay of pure ammonia and reduce (or not influence) the reactivity of ammonia-hydrogen blends are the same for both mechanisms, see Tables 4.3 and 4.4. Four of the highlighted reactions are common to both mechanisms and three of them are linked to the H₂NO chemistry. Therefore the H₂NO chemistry seems to play a significant role in the under-reactivity of pure ammonia and over-reactivity of hydrogen-ammonia auto-ignition. Moreover, the rate coefficients of these reactions are not well known: they have been established solely by estimations or *ab Initio* calculations. All these elements seem to pin the H₂NO chemistry as a potential direction for ammonia mechanism improvement under LTC conditions.

Table 4.3 – Details for the ZH reactions that could improve both ignition delay estimations for pure ammonia and ammonia-hydrogen blends.

#	Reactions	Ref.	Method
1	$\text{HO}_2 + \text{H}_2\text{NO} = \text{H}_2\text{O}_2 + \text{HNO}$	[145]	Estimation
2	$\text{H}_2\text{NO} + \text{NO}_2 = \text{HNO} + \text{HONO}$	[146]	Estimation
3	$\text{O}_2 + \text{NH}_2 = \text{O} + \text{H}_2\text{NO}$	[115]	<i>ab Initio</i>
4	$\text{HONO} + \text{NH}_2 = \text{NO}_2 + \text{NH}_3$	[147]	<i>ab Initio</i>

The third sensitivity analysis, still performed for mixtures #2,3,4 (at 1075 K, 50 bar), is done on the over-reactive NK mechanism, see Figure 4.12 for the

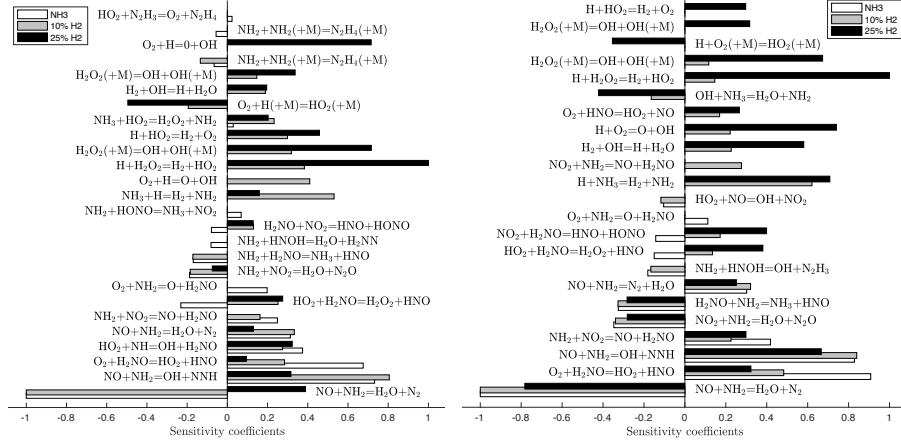


Figure 4.11 – Relative sensitivity coefficients of the SO (left) and ZH (right) mechanisms. Sensitivity analyses for mixtures #2,3,4 (at 1075 K, 50 bar).

Table 4.4 – Details for the SO reactions that could improve both ignition delay estimations for pure ammonia and ammonia-hydrogen blends.

#	Reactions	Ref.	Method
1	$\text{HO}_2 + \text{H}_2\text{NO} = \text{H}_2\text{O}_2 + \text{HNO}$	[145]	Estimation
2	$\text{H}_2\text{NO} + \text{NO}_2 = \text{HNO} + \text{HONO}$	[121]	Estimation
3	$\text{O}_2 + \text{NH}_2 = \text{O} + \text{H}_2\text{NO}$	[115]	<i>ab Initio</i>
5	$\text{HNOH} + \text{NH}_2 = \text{H}_2\text{O} + \text{H}_2\text{NN}$	[145]	Estimation
4	$\text{HONO} + \text{NH}_2 = \text{NO}_2 + \text{NH}_3$	[148]	<i>ab Initio</i>

raw results. Out of the influencing reactions, only the ones that can explain a general over-reactivity without impacting the relative reactivity between the three blends are kept, see Table 4.5. To do so, only the reactions having higher sensitivity coefficients for pure ammonia are kept. From the obtained reactions, #6,9,10 must be discarded since their rate coefficients are identical to those of the SO and ZH mechanisms. Reactions #12,13 are interesting in the sense that they present different rate coefficients than the ones used in all the other mechanisms, hence a source of over-reactivity. Finally, reactions #7,8,11 belong to the N_2H_x chemistry and are potential candidates for improvement. Indeed, reactions #7,11 do not appear in the other mechanisms, and reaction #8 has different rate coefficients than in the other mechanisms. Even though obtained experimentally, the conditions were not representative of the LTC mode: at-

mospheric temperature and pressure for reaction #7 and rich and atmospheric pressure, but medium temperatures, for reactions #8,11. This led Nakamura et al. to state " N_2H_x chemistry has not been well studied compared with other nitrogen chemistry" [140]. Therefore the pure ammonia over-reactivity of NK can be attributed mainly to the N_2H_x chemistry coming from the over-reactive KD mechanism.

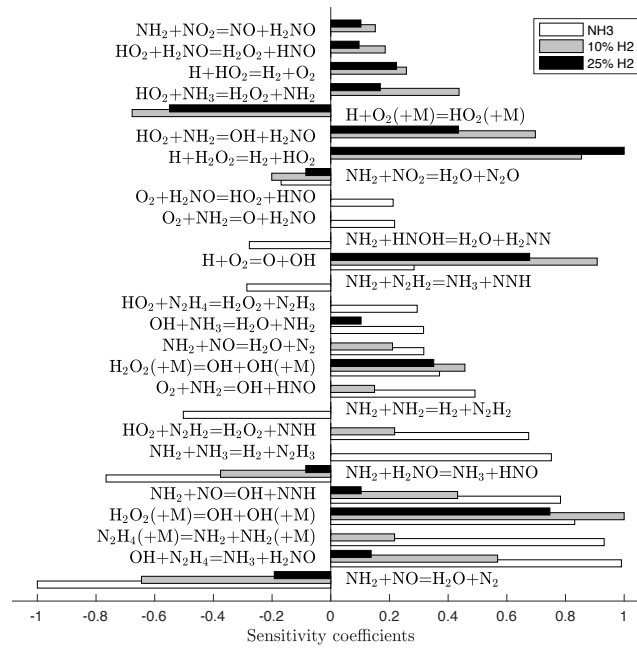


Figure 4.12 – Relative sensitivity coefficients of the NK mechanism sensitivity analysis for mixtures #2,3,4 (at 1075 K, 50 bar).

Table 4.5 – Details for the NK reactions that could damp the general reactivity without impacting the relative difference between the blends.

#	Reactions	Ref.	Method
6	$\text{NH}_2 + \text{NO} = \text{H}_2\text{O} + \text{N}_2$	[115]	<i>ab Initio</i>
7	$\text{OH} + \text{N}_2\text{H}_4 = \text{NH}_3 + \text{H}_2\text{NO}$	[149]	Experiment
8	$\text{N}_2\text{H}_4 (+ \text{M}) = 2 \text{NH}_2 (+ \text{M})$	[118]	Empiric fit
9	$\text{NH}_2 + \text{NO} = \text{OH} + \text{NNH}$	[115]	<i>ab Initio</i>
10	$\text{NH}_2 + \text{H}_2\text{NO} = \text{NH}_3 + \text{HNO}$	[121]	Estimation
11	$\text{HO}_2 + \text{N}_2\text{H}_2 = \text{H}_2\text{O}_2 + \text{NNH}$	[140]	Empiric fit
12	$\text{O}_2 + \text{NH}_2 = \text{OH} + \text{HNO}$	[115]	<i>ab Initio</i>
13	$\text{NH}_2 + \text{NO}_2 = \text{H}_2\text{O} + \text{N}_2\text{O}$	[150]	Empiric fit

4.3.5 Limitations of existing ammonia mechanisms and reactions

In this sub-section, the recent mechanisms of Glarborg et al. [141] and Otomo et al. [151] that did not exist at the time of this initial study, as well as modified versions of the mechanisms from Nakamura et al. and from Song et al. are compared with the neat ammonia RCM ignition delay data.

Figure 4.13 depicts the under-reactivity of both new mechanisms and the barely improved predictions from the two modified mechanisms. For the new mechanisms, this is no surprise given that the mechanism from Glarborg et al. is based on a review of the nitrogen chemistry between 1100 K and 1400 K and that the mechanism from Otomo et al. is an update of the mechanism from Song et al. regarding the NH_2 , HNO , and N_2H_2 reactions for higher temperatures and equivalence ratios than HCCI conditions. Regarding the new versions of Nakamura et al. and of Song et al. , they were obtained by modifying the reactions highlighted in Section 4.3.4 using any other reaction rate found in the literature, and eventually selecting the best performing (combinations). These modified mechanisms do not perform significantly better than the original versions, see Figures 4.6 and 4.13, indicating that the existing reaction rate coefficients in the literature are not adequate for the LTC conditions. Even though such improvement strategy is quite dubious, it is often used to indicate that the existing knowledge on a specific reaction is insufficient, if that reaction is known to be responsible for the estimation error of a mechanism in given conditions.

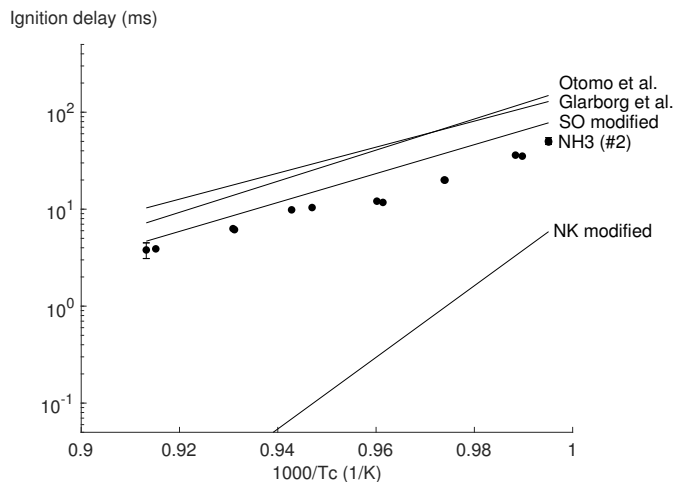


Figure 4.13 – Both the new mechanisms from Glarborg et al. [141] and from Otomo et al. [151] cannot capture neat ammonia ignition delays in the LTC region (mixture #2). The modified mechanisms from Song et al. and Nakamura et al. do not perform significantly better than the original versions, indicating that the existing reaction rate coefficients in the literature are not adequate for the LTC conditions.

4.4 Outlook and conclusion

Ignition delays for neat ammonia and minor fractions of hydrogen addition (10 and 25%vol.) have been experimentally obtained in a RCM at high pressures (43 and 65 bar), low temperatures (1000 - 1100 K), and under lean conditions (0.2, 0.35, and 0.5 of equivalence ratio). These results are currently being used for the improvement of ammonia kinetic mechanisms in several research groups (to my knowledge: Orléans & Cottbus universities, Polimi & ULB universities, Tohoku university).

Three out of the five mechanisms evaluated were found under-reactive for ammonia auto-ignition (DeNOx-based mechanisms), and two over-reactive (flame-based mechanisms), stressing out the need for an adapted ammonia kinetic mechanism to LTC pressures and temperatures. A sensitivity analysis allowed to identify H_2NO as a possible cause for pure ammonia under-reactivity in the three DeNOx-based mechanisms, and the N_2H_x chemistry as the cause of

the two over-reactive mechanisms. These compounds have been identified and should serve as a first step towards an ammonia-hydrogen LTC mechanism.

The ignition delays obtained for ammonia-hydrogen blends prove their suitability for high compression ratio LTC engines ($\sim 25:1$ for pure ammonia). Such value allows to minimize the intake temperature and consequently the heat losses despite the high compression ratio. Moreover, no ringing has been noticed during these experiments, even at equivalence ratios of 0.5, which ought solely to the low intensity observed for ammonia combustion.

With hydrogen addition, fractions higher than 10%vol. were required to induce a significant promotion of the ignition delay. This implies the need for a substantial hydrogen reserve or direct ammonia reformer at the engine intake if promotion is needed.

Finally no significant influence of the equivalence ratio was measured on the ignition delay although a smaller ignition delay is observed both experimentally and numerically at an equivalence ratio of 0.35.

Future works should focus on the improvement of the ammonia mechanisms under LTC conditions. A possible starting point might be the fundamental characterisation of the reactions involving the H_2NO and N_2H_x species, under the specific HCCI conditions.

It is not because things are difficult that we do not dare, it is because we do not dare that they are difficult.

Lucius Annaeus Seneca

5

Experimentation of ammonia-hydrogen HCCI engines

This chapter is based on the following publication and submission:

- Pochet, M., Truedsson, I., Foucher, F., Jeanmart, H., & Contino, F. (2017). Ammonia-Hydrogen Blends in Homogeneous-Charge Compression-Ignition Engine. SAE Technical Paper 2017-24-0087.
<http://doi.org/10.4271/2017-24-0087>
- Pochet, M., Jeanmart, H., & Contino, F. (2019). *Towards an ideal ammonia-hydrogen HCCI engine: combustion, load and emission performances*. Submitted to Frontiers in Mechanical Engineering.

We have seen in the previous chapters that, although ammonia high resistance to auto-ignition forces the use of high intake temperatures, ammonia had a high resistance to ringing hence possibly allowing the use of a high compres-

sion ratio, a high equivalence ratio, and a high intake pressure. This chapter investigates the extent of this potential.

Ammonia can also be ideally promoted by hydrogen. Hydrogen is known to be prone to ringing, especially at high compression ratios, yet it is to be assessed to which extent, and under which blending ratios, ammonia can damp hydrogen reactivity. Increasing the compression ratio increases the thermodynamic efficiency and allows the use of ammonia with reduced intake temperatures, but increases the friction and heat losses as well through higher in-cylinder pressures, and potentially decreases the achievable equivalence ratios. Therefore a trade-off is to be found for the ideal compression ratio.

Hydrogen has already shown its HCCI suitability with brake efficiencies higher than 40% under small scale HCCI conditions (~ 20 kW, naturally-aspirated) [16, 42]. Still there is very little knowledge about clean and efficient ammonia use in HCCI conditions. The only prior ammonia experiment under LTC conditions is the one from Van Blarigan that used a free-piston HCCI engine with 40:1+ compression ratios to achieve auto-ignition of neat ammonia without pre-heating and without ringing behaviour [72]. Also, ammonia equivalence ratios as high as 0.5 have been successfully operated during this thesis work using a RCM with a 24.3:1 compression ratio, without experiencing ringing, see Chapter 4. However, regarding HCCI power density, it is still unclear whether its high equivalence ratio potential can compensate for its need of high intake temperature. For that aspect, the evolution with the ammonia-hydrogen blending ratio of the hydrogen promotion on ammonia, and of the ammonia propensity to damp hydrogen reactivity shall be crucial.

Ammonia being a nitrogen based fuel, its combustion is expected to release unbounded nitrogen atoms that, in the presence of oxygen, lead to the production of NO_x . On the other hand, hydrogen combustion under HCCI conditions is usually NO_x -free. Indeed, as it is a low temperature combustion process, the conditions for the emission of thermal- NO_x are not met. When adding ammonia to the mixture, nitrogen radicals will spontaneously appear from ammonia combustion hence no need for high temperatures to split the nitrogen molecules contained in the air. Therefore fuel- NO_x will be produced. A first step will be to investigate influencing control parameters on NO_x production and, second, possible mitigation techniques. Usual temperature reduction techniques will be helpless as they only influence thermal- NO_x emissions. Still, high EGR rates will be performed to evaluate the oxygen availability impact on fuel- NO_x for-

mation from ammonia combustion. Several studies have shown that decreasing the oxygen excess was effective in reducing the NO_x intermediate molecules to N_2 [116, 152].

In this chapter, the potential performances and emissions of the ammonia-hydrogen HCCI engine are assessed, using two different effective compression ratios: 15:1 and 22:1. The performances (combustion efficiency, indicated thermal efficiency, output power, etc.) and emissions (NO_x , unburned NH_3) are investigated as a function of the main control parameters: intake temperature, ammonia-hydrogen blending ratio, equivalence ratio, and EGR.

These are the tackled questions in this chapter to give us guidelines for the ideal ammonia HCCI engine design:

- What are the required conditions to have a proper ignition timing for the whole ammonia-hydrogen blending range?
- What are the related performances (i.e. combustion efficiency, power density, and indicated efficiency, ...), load range (i.e. achievable equivalence ratios), misfire region and ringing region?
- How much are the NO_x emissions increased by ammonia?
- Are the reaction pathways evolving as a function of the combustion timing and EGR?
- How does all the previous results evolve with the ammonia-hydrogen blending ratio?

5.1 Experimental setups & methodology

5.1.1 Setups description

The results reported in this chapter have been obtained on two different setups. The first setup, based in the PRISME laboratory at Université d'Orléans, has a PSA DW10 diesel engine retrofitted to a single-cylinder engine and has been used for various studies on HCCI combustion, see for example [57, 124]. The diesel injector has been replaced by a piezoelectric pressure sensor, and the fuels are admitted at the intake to allow HCCI conditions. The second setup, based in the iMMC laboratories of UCLouvain, is equipped with a Yanmar L100V single-cylinder engine specifically modified for ammonia use at a high compression ratio. The diesel injector has also been replaced by a piezoelectric

pressure sensor, the fuel mixture is induced by MFC, and the piston bowl has been filled through welding to render a higher effective compression ratio (22:1) and reduce the required intake temperature for ammonia operation. The choice for this particular compression ratio, as well as other operating aspects of that engine, is described in Section 5.3. Both setups are displayed in Figure 5.1 and have their engine characteristics summarised in Table 5.1.

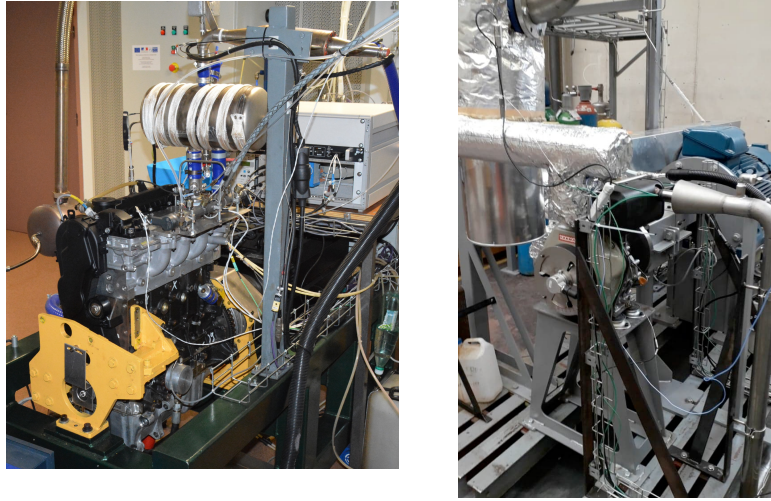


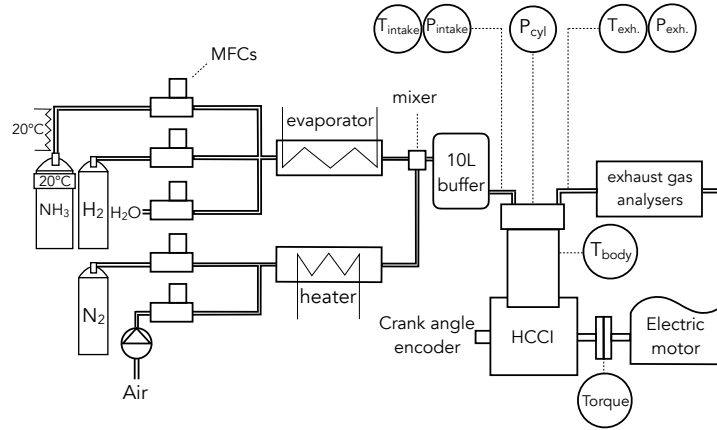
Figure 5.1 – HCCI setups from Orléans PRISME laboratories (left) and from UCLouvain (right).

The piping and instrumentation diagram of both Orléans and UCLouvain setups are identical in their bottle-MFC-heater-mixer-engine-sensors schematisation, which has been schematised in Figure 5.2.

Both setups benefit from two injection lines, one for air and inert species and one for fuel and water. The combined use of an air line as well as nitrogen and water allows to emulate EGR conditions. The chosen EGR composition

Table 5.1 – Engines specifications

	UOrléans	UCLouvain
Engine	Water-cooled Four-cylinder converted to single-cylinder	Air-cooled Single-cylinder
Make	PSA DW10	YANMAR L100V
Displacement volume, V_c	499 cm ³	436 cm ³
Bore	85 mm	86 mm
Stroke	88 mm	75 mm
Connecting rod length	145 mm	145 mm
Geometric compression ratio	16.1:1	23.0:1
Effective compression ratio	15.3:1	21.9:1
Piston shape	Diesel bowl	Flat
Rotational speed	1500 RPM	1500 RPM
IVC	157 CAD BTDC	127 CAD BTDC
EVO	140 CAD ATDC	127 CAD ATDC

**Figure 5.2** – UCLouvain setup designed for ammonia-hydrogen combustion, exhaust analysis, and synthetic EGR conditions. The Université d’Orléans setup is identical.

is respective to the specific operating conditions (fuel blend, equivalence ratio and residual gas fraction) yet assuming a complete combustion and no pollutant formation. All the gaseous and liquid in-trant flow rates are controlled by respective mass flow controllers. Each line has a separate heater allowing to reach the desired intake temperatures or evaporating the induced water for EGR purposes. Both admission lines are merged at a gas mixer (using a venturi effect) which is connected to a 10 liter buffer tank. The venturi sections are designed to maximise the homogeneity for given flow ranges of the two streams, and the buffer ensures further homogenisation and decreases the intake pressure fluctuations due to the intake valve motion. The intake pressure (influenced by the total flow rate of the mixture) and exhaust pressure are measured in the intake and exhaust manifolds. The intake, exhaust and cylinder-wall temperature measurements are done by type K thermocouples. Apart from setting the desired respective flow rates and intake temperature, nothing more is done to control the HCCI combustion. Regarding outputs, the in-cylinder pressure is measured by a relative piezoelectric transducer flush-mounted in the cylinder-head. The crank angle is acquired every 0.1 Crank Angle Degree (CAD) and synced with the in-cylinder pressure signal. Finally, the exhaust oxygen, ammonia and NO_x concentrations are measured using a UV spectrometer for the UCLouvain setup, and the NO_x concentration is measured using an IR spectrometer for the Orléans setup. All the controls and acquisitions were performed by a National Instruments Compact Rio 9022 real-time controller operated with the LabView environment. The used sensors are summarised in Table 5.2 and the related uncertainties on the engine inputs and outputs are detailed in Section 5.1.2 for the UCLouvain setup.

In this chapter EGR is applied with the aim of replacing all the excess intake air to reach effective stoichiometric conditions. Therefore a new definition is used for the EGR. We define the Exhaust Gas Air Replacement (EGAR) as the fraction of the excess intake air that is replaced by exhaust gases (same mole quantity at the same temperature). Therefore a 100% EGAR means that the mixture is in effective stoichiometric conditions. The general equation for ammonia-hydrogen combustion considered in this chapter is therefore written as follows:

Table 5.2 – Sensors equipping both setups

	UOrléans	UCLouvain
Gas inputs	Brooks SLA-585X	Brooks SLA-585X
Water input	Coriflow M14	Coriflow M14
P _{intake}	Kistler 4075A	Kistler 4260
Thermocouples	K-junction	K-junction
P _{cylinder}	Kistler 6043A	AVL GH15D
NO _x emissions	Horiba MEXA 7000	Thetys EXM 400
NH ₃ emissions	-	Thetys EXM 400
Lambda sensor	-	Bosch LSU 4.9

$$\begin{aligned}
& \phi_0 (x\text{NH}_3 + y\text{H}_2) \\
& + \phi_0 \frac{3x + 2y}{4} (\text{O}_2 + 3,773 \text{N}_2) \\
& + (1 - EGAR) (1 - \phi_0) \frac{3x + 2y}{4} (\text{O}_2 + 3,773 \text{N}_2) \\
& + 4,76 EGAR (1 - \phi_0) \frac{3x + 2y}{4} \frac{a\text{O}_2 + b\text{N}_2 + c\text{H}_2\text{O}}{a + b + c} \\
& \longrightarrow a \text{O}_2 + b \text{N}_2 + c \text{H}_2\text{O}
\end{aligned} \tag{5.1}$$

where ϕ_0 is the equivalence ratio without considering the recirculated oxygen by the EGAR. It must be mentioned that hydrogen and ammonia have comparable engine mixture energy content. For example, for an equivalence ratio of 0.3, a neat hydrogen mixture possesses a 21.5 kJ/mol energy content compared to a 20.7 kJ/mol for neat ammonia. Therefore, mentioning the operated equivalence ratio regardless of the blending ratio is a good image of the mixture energy content used.

5.1.2 Data post-processing, and uncertainty analysis of the engine inputs and outputs

One cannot rush into internal combustion engine experiments hoping the obtained results to be of high quality and representative of the reality. The acquired raw data needs some post-processing steps before being suited for the engine performance analysis. The whole post-processing process used is described in details in Appendix A, but is listed here. The in-cylinder pressure

signal must be filtered and pegged to correct for noise and relativity of measurement. Then, the TDC offset, the effective compression ratio, and the blow-by are computed and accounted for in the heat release analysis. The methodology used to compute the effective in-cylinder temperature is based on the work of Sjöberg et al. [130] (and extended in Appendix A) and an illustration of the correlation between T_{in} and T_{BDC} is reported in Figure 5.3. Finally, the heat losses are calibrated to obtain a flat cumulative gross heat release curve before and after the combustion.

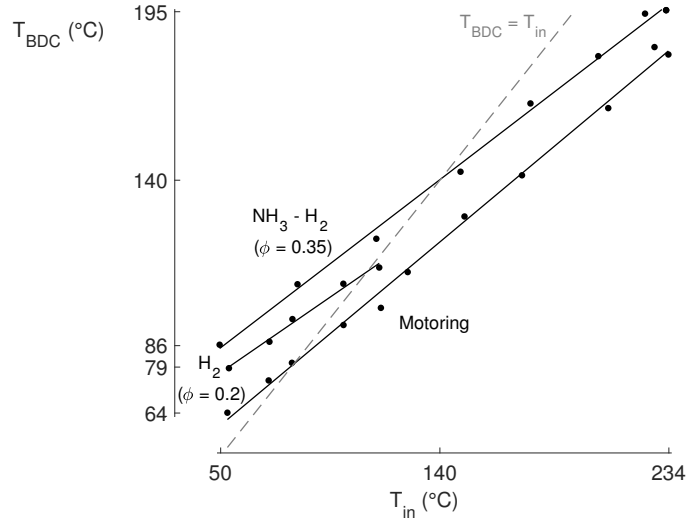


Figure 5.3 – Post-processed effective temperature at BDC as a function of the intake temperature. The impact of the RGF temperature and wall heat exchange on the BDC temperature can be observed.

For the UCLouvain test bench, the uncertainties on the engine inputs and outputs of interest are obtained following the whole methodology developed in Appendix A. This methodology accounts for the impact of sensors, post-processing methodology, and engine setup. The methodology has not been used for the UOrléans data, yet given the similar setup configuration, engine characteristics, and sensor specifications, the uncertainty ranges can be assumed similar. The maximal and minimal uncertainties of the engine inputs and outputs

(encompassing sensor calibrations, the acquisition system, the post-processing, and the statistical analysis data) encountered during the whole UCLouvain study are reported in Table 5.3. Given that the obtained uncertainties were fairly constant throughout the experimental runs, the uncertainty ranges shall not be reproduced on every figure.

Table 5.3 – *Relative uncertainties at a 95% confidence level for every parameter of interest. Ranked in ascending order and expressed in %, except for the CAX that are absolute U95 uncertainties.*

	Best	Worst	Average
T_{intake}	0.3	0.6	0.4
P_{max}	0.9	2.1	1.1
IMEP	1	11	1.5
FuelMEP	1	8	2
T_{BDC}	2	2	2
HRR_{max}	1	9	2
MPRR	1	10	3
RI	2	11	4
$T_{-15 \text{ CAD}}$	3	6	4
T_{max}	3	4	4
NH_3 ratio	3	16	5
Exhaust NO	3	25	6
Unburned NH_3	4	33	7
Exhaust NO_2	10	30	12
CA_{10} (CAD)	0.0	0.8	0.3
CA_{50} (CAD)	0.0	2.4	0.3
CA_{90} (CAD)	0.6	8.0	2

5.2 Low CR experimental results (Orléans setup)

As a preliminary study, the HCCI setup from Orléans has been used. The ammonia fraction in the fuel could be varied from 0 to 61%vol., the intake pressure from 1 to 1.5 bar, the equivalence ratio from 0.2 to 0.3, and the

EGAR from 0 to 80%. Finally, the intake temperature was varied to maintain a constant CA50 of 4 CAD aTDC $\pm$ 1 CAD.

5.2.1 Implications of ammonia resistance to auto-ignition

The experimental required intake temperatures such that the CA50 occurs at 4 ± 1 CAD aTDC for various hydrogen-ammonia blends are depicted in Figure 5.4. The various runs are performed at constant FuelMEP of 8.5 bar. The experimental results are compared to simulations performed using the developed single-zone model in Chapter 3, together with the Mathieu and Petersen mechanism [120]. The limited test bench intake pressure (1.5 bar) and temperature (210 °C) did not allow to operate with an ammonia volumetric content higher than 61% (for CA10 occurring at TDC). This fact highlights the promoting effect of hydrogen on ammonia. Yet above such a concentration in ammonia the resistance to auto-ignition increases in an exponential way.

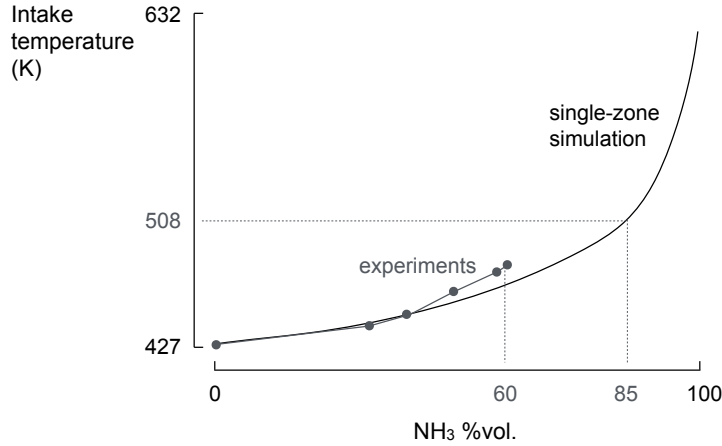


Figure 5.4 – Required intake temperatures for various hydrogen-ammonia blends such that the CA10 occurs close to TDC. Both ammonia resistance to auto-ignition and hydrogen promotion effects are observable.

Through the following simulations we show that the promotion of ammonia thanks to hydrogen is not only due to the heat released from hydrogen

combustion but as well due to the radicals created. Among the various starting reactions that can consume ammonia molecules, the ones involving either the O, the H, or the OH radical have a reaction rate coefficient one order of magnitude greater than the others. Using the same single-zone model as previously, the evolution (production and consumption) of the various radicals and intermediate species right before the combustion onset can be obtained, see Figures 5.5 and 5.6. The first case is for neat hydrogen and the second one for 40%vol. ammonia content. Both cases have the same combustion timing. Looking at the various kinetic mechanisms for ammonia and hydrogen, OH is the main radical responsible for the combustion initiation. A OH peak is observed at the time of peak HRR and CA50, as has been proven and used in [120] and Chapter 4. Looking at hydrogen kinetics in Figure 5.5, H_2O_2 is formed in the early initiation of combustion, followed by HO_2 . Both molecules accumulation is then rapidly consumed to form OH, which triggers the main combustion.

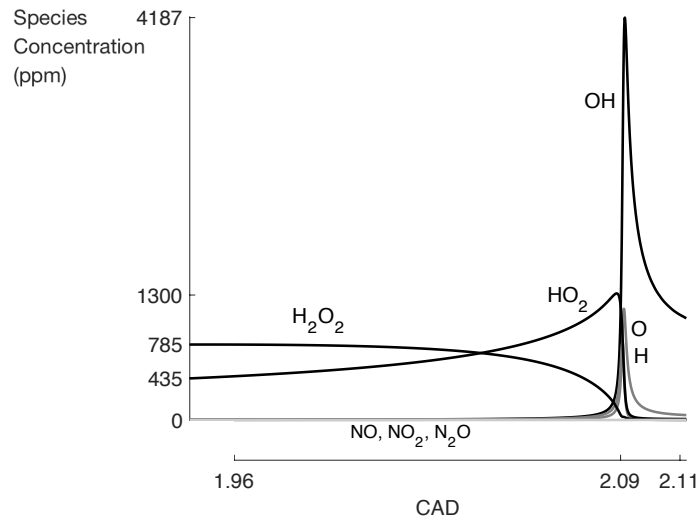


Figure 5.5 – Intermediate species evolution for neat hydrogen. During the initiation phase, a pool of H_2O_2 and HO_2 is formed, which is eventually consumed for the OH production. Obtained using the HCCI single zone model developed in Chapter 3 together with the mechanism from Mathieu et al. [120].

Many differences can be highlighted with the radicals evolution for the ammonia-hydrogen combustion case, see Figure 5.6. First, OH and HO₂ peaks are smaller. Then, a significant quantity of intermediate species is formed (e.g. HNO, HONO, HO₂ ...), all consuming OH radicals for their production and decomposing into other non-reactive intermediate species. Consequently, ammonia and hydrogen molecule combustion is intertwined as they share their radicals, but it is damped as the general combustion follows a higher number of steps.

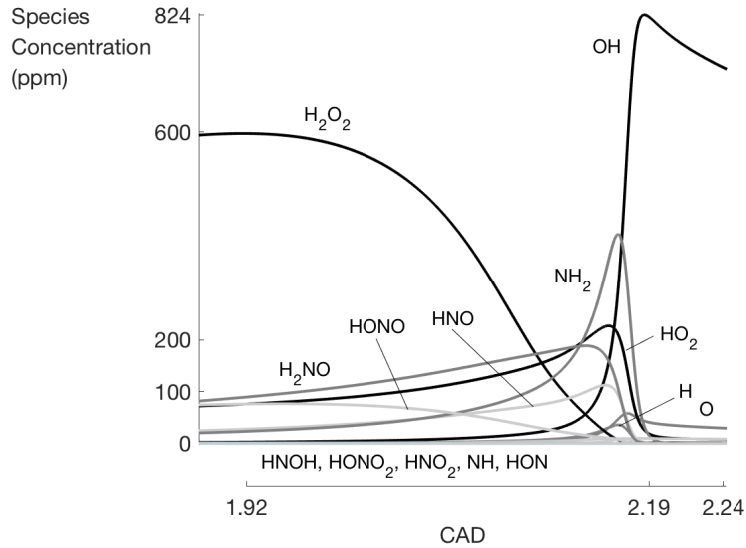


Figure 5.6 – Intermediate species evolution for 40%vol. ammonia content. A lower OH peak is observed, together with a significant amount of non-reactive intermediate species being formed. Obtained using the HCCI single zone model developed in Chapter 3 together with the mechanism from Mathieu et al. [120].

These effects concerning radicals sharing can be observed from the experiments on the HRR curves, shown in Figure 5.7. Three mixtures are being

displayed: pure hydrogen, 32%vol. in ammonia content and 61%vol. in ammonia content, all having the same CA50 thanks to a different intake temperature. A common and smooth heat release can be observed for the three cases. As the ammonia content increases, both slopes of the HRR tends to decrease: at the beginning of the combustion the HRR increases more slowly as the hydrogen radicals are being captured by ammonia molecules and its intermediate species, and at the end of the combustion the HRR decreases more slowly due the radicals sharing and the genuinely lower reaction rate coefficients of ammonia intermediate reactions.

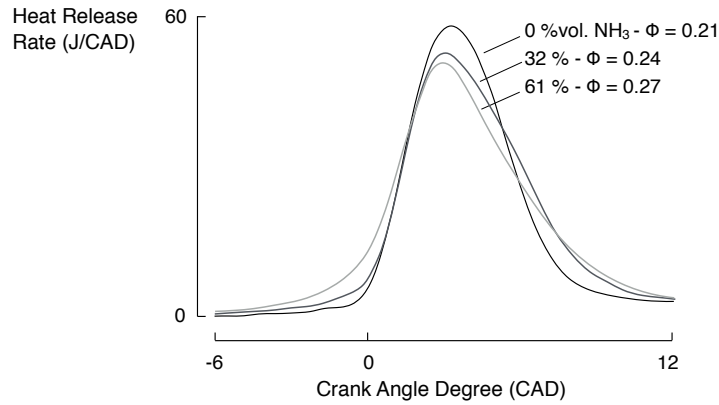


Figure 5.7 – Heat Release Rate curves for various hydrogen-ammonia blends. The combustion intensity decreases with ammonia share.

These radicals sharing effects translate into a major influence: an increased combustion duration. Figure 5.8 displays the influence of the ammonia content on the combustion duration for constant and increasing equivalence ratios as the ammonia fraction in the fuel blend is increased. For both cases the combustion duration increases with the ammonia proportion. The effect is so strong that even when the equivalence ratio is increasing, the combustion duration (and HRR, see Figure 5.7) are decreasing.

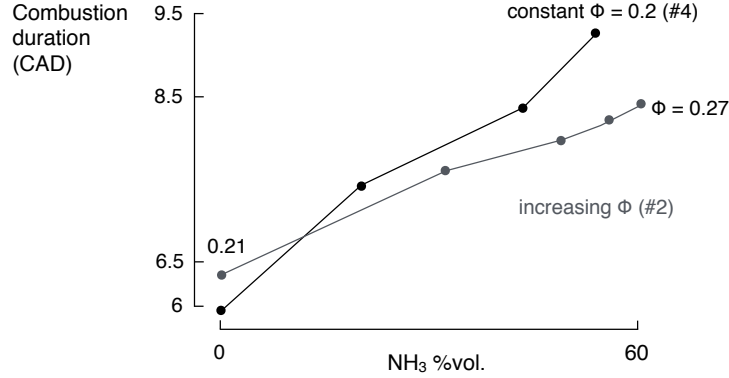


Figure 5.8 – Combustion duration as a function of the ammonia content when the fuel content is increased as the ammonia content is increased, the combustion duration increases.

The combustion damping effect of ammonia can be explained through the evolution of the intermediate species formation with the increase in ammonia fraction, see Figure 5.9. As first indicators, the peak concentration of OH, of $\text{H}_2\text{O}_2 + \text{HO}_2$, and of the remaining ammonia intermediate species are used. As a second indicator, the CAD time between the OH peak and the H_2O_2 peak, $\Delta_{\text{time,OH-H}_2\text{O}_2}$, is used. As the ammonia fraction increases, the OH and $\text{H}_2\text{O}_2 + \text{HO}_2$ peaks are decreasing. The essential radicals for fuel combustion are decreasing in concentration: OH concentration is divided by four with the first 15%vol. ammonia content while the $\text{H}_2\text{O}_2 + \text{HO}_2$ concentration is decreasing quite linearly. Ammonia non-reactive intermediate species pool reaches a plateau after 15%vol. ammonia content.

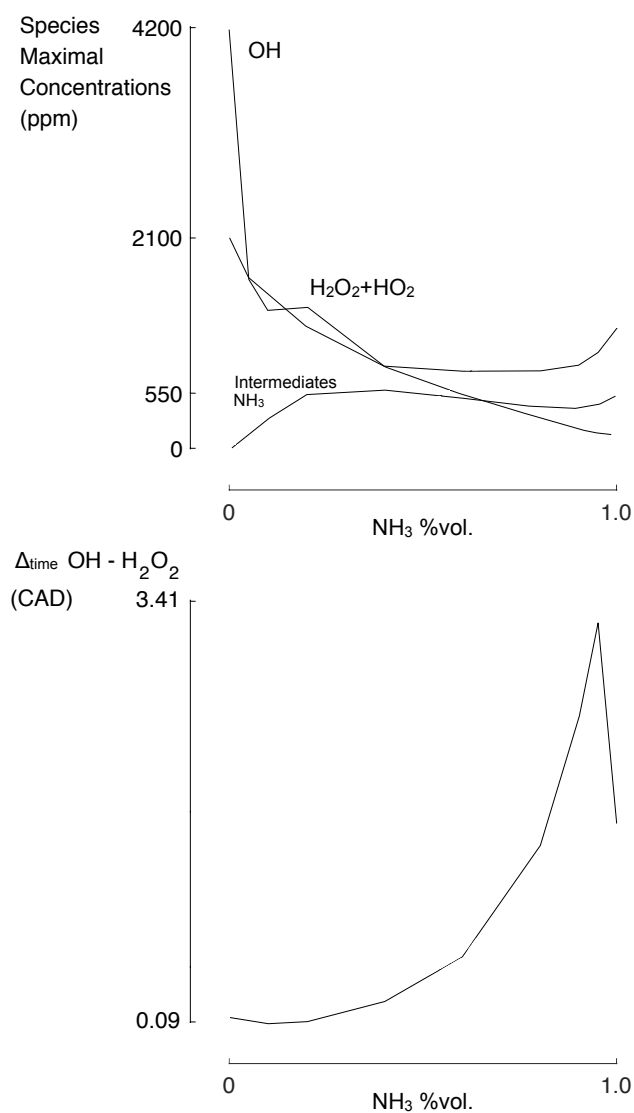


Figure 5.9 – The OH and $\text{H}_2\text{O}_2 + \text{HO}_2$ peak concentrations are rapidly decreasing with the ammonia fraction, while the pool of ammonia non-reactive intermediate species is being formed. The initiation period between H_2O_2 and OH formation is extended.

5.2.2 Ammonia resistance to ringing

The power output of hydrogen HCCI engines is restricted due to the limited equivalence ratios used to avoid ringing. The easiest way to reduce hydrogen ringing for a given equivalence ratio is to delay its combustion later in the cycle to enforce a longer combustion duration. Yet, this solution leads to a non optimal cycle and it is therefore not ideal for extended operation times. In the considered configuration, the longer combustion duration for hydrogen-ammonia blends can be exploited to reduce the ringing issues related to hydrogen. Moreover, as the ringing results in resonating in-cylinder pressure waves, studies have shown the interest of increasing the in-cylinder pressure to diminish the intensity contained in the pressure waves and hence to decrease ringing [153, 154]. These two points have been studied and the results are described below.

Figure 5.10 displays the RI and FuelMEP against Maximum Pressure Rise Rate (MPRR) of many ammonia-hydrogen blends. The RI is the power flux contained within the pressure waves, a function of the maximal amplitude of the pressure signal filtered between 4 and 25 kHz and of the maximal in-cylinder pressure [154]. The RI considered is often the averaged value over 100 consecutive cycles. Above 5.5 bar/CAD of MPRR a correlation between the RI and the MPRR for the four operating conditions can be clearly seen. This could be considered as the ringing apparition limit although such levels are far below the 2 MW/m² limit evaluated by Eng as damaging for the engine. Two results can be drawn from the evolution of the MPRR as a function of the FuelMEP. Firstly, by comparing the influence of the intake pressure for neat hydrogen, it can be seen that for an identical MPRR, the condition with a higher intake pressure allows a higher FuelMEP. Therefore increasing the intake pressure allows to increase the energy content inside the cylinder while avoiding ringing. Secondly, looking at the operational conditions with ammonia, as the ammonia proportion is increased, the MPRR decreases. Moreover, for the operating condition where the equivalence ratio is increased (0.21-0.27) together with the ammonia fraction (0-61%), the MPRR still decreases as a result from the radicals sharing and the lengthening of the combustion duration. Therefore this radicals sharing allows an un-correlation between the FuelMEP and the MPRR and consequently allows for high power densities in the ringing-safe region

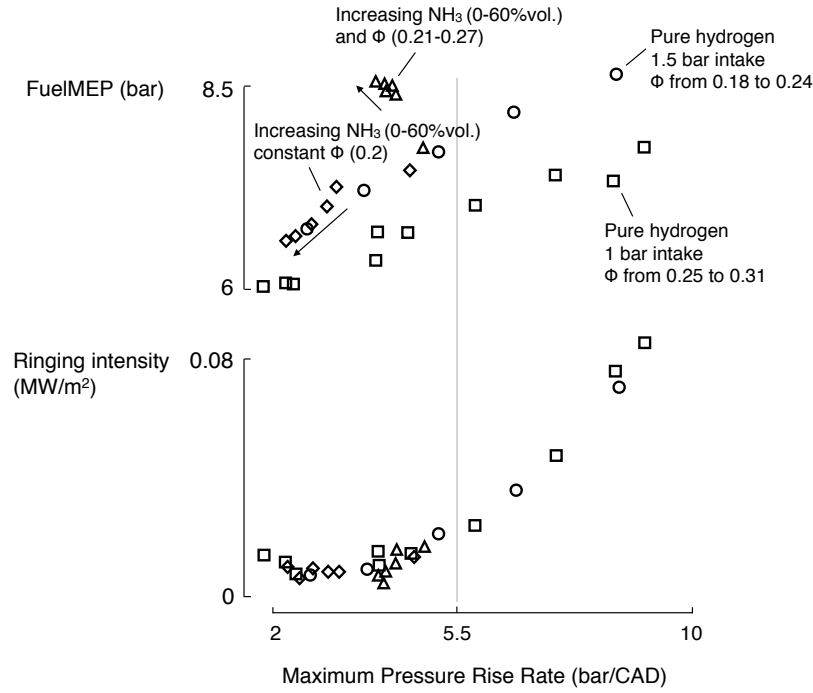


Figure 5.10 – Ringing amplitude and FuelMEP as a function of MPRR. Ringing and MPRR are shown to be correlated. An increased intake pressure allows higher FuelMEP for the same MPRR and ammonia presence reduces the MPRR for the same FuelMEP.

5.2.3 Ozone seeding impact on ammonia auto-ignition

Many oxidising chemical species (e.g. ozone, nitric oxide, nitrogen dioxide, etc.) have been used to promote HCCI auto-ignition [39]. When used as additives, these species will decompose during the compression phase and eventually help produce oxidising compounds such as OH to trigger (i.e. reduce the ignition delay of) the mixture auto-ignition. Depending on the fuel and on the oxidising compound used, the promotion based on the CA10 will vary around 5 to 15 CAD for a 50 ppm addition [39, 50, 57]. The double interest with such promotion technique is that, in addition to triggering the combustion through early OH production, the main combustion phase duration is not altered for identical CA50 (i.e. through intake temperature variation) [155]. For ammonia, this means that the ringing reduction potential could be maintained.

Ozone was investigated for the promotion of ammonia in this research for two reasons. First, ozone is among the most powerful oxidisers for HCCI combustion and the most easily produced as it only requires air and electric discharges between two electrodes. Second, the experimental setup at Université d'Orléans is equipped with all the required material for such investigation given their leading role in the study of ozone promotion [50, 57, 155–157]. By supplying a constant 5 NL/min of pure oxygen in an ozone generator (ANSEROS COM-AD-01), and controlling the applied frequency of electric pulse discharges, the ozone seeding concentration can be controlled. The ozone generator is calibrated with a ± 0.1 ppm accuracy using a ANSEROS MP-6060 analyzer [50]. Separately, pure nitrogen was admitted to the engine in order to maintain the correct oxygen/nitrogen concentration. Ozone has been seeded from 0 to 140 ppm while operating on neat hydrogen or various ammonia-hydrogen ratios. The results are reported for the neat hydrogen and 40%vol. ammonia cases in Figure 5.11. One can observe the considerable onset promotion on neat hydrogen combustion, and the practically negligible effect with ammonia in the fuel blend. The same result is observed with any ammonia-hydrogen blending ratio, from 20%vol. to 60%vol. ammonia content. The single-zone model predictions using the Mathieu and Petersen mechanism [120] for ammonia and Halter et al. [156] sub-mechanism for ozone are in contradiction with the experiments and predict a strong promotion with ammonia.

The ozone promotion effect seems to be cancelled by ammonia, even for minor ammonia fractions in the fuel blend. Given the limited extent of these results, no definitive conclusion can be drawn. Yet, as for hydrogen reactivity damping, ammonia intermediate species seem to play a role in this ozone-effect cancellation. This curious observation asks for further experiments and might give more insight into the functioning process of ammonia kinetics and intermediate species. Finally, a different result could be obtained with another oxidant, such as hydrogen peroxide (H_2O_2) or nitric oxide (NO).

5.2.4 Engine output parameters

In this subsection, the engine combustion efficiency, IMEP, and NO_x emissions are analysed. The reason for gathering them in the same subsection is because

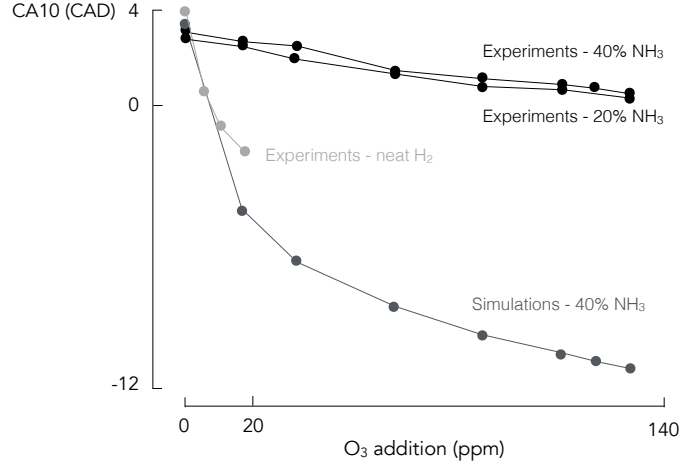


Figure 5.11 – Ozone seeding impact on the ignition timing of various ammonia-hydrogen mixtures. The promotion on hydrogen is lost when ammonia is added. The kinetic mechanism predictions are in contradiction with the experiments.

the obtained combustion efficiency, influencing both the IMEP and NO_x emissions, was to be around 75%. Due to that extremely low combustion efficiency, the following results have to be interpreted with care regarding conclusions on ammonia-hydrogen HCCI engines.

Combustion efficiency

The obtained combustion efficiency as a function of the ammonia blending ratio is depicted in Figure 5.12. The combustion efficiency has been derived for that engine from the energy closure of the Heat Release Rate (HRR) analysis:

$$\text{Combustion Efficiency} = \frac{\sum_{\theta=-40^{\circ}\text{CAD}}^{40^{\circ}\text{CAD}} \text{HRR}(\theta) \cdot \Delta\theta}{m_{\text{fuel}} \cdot \text{LHV}_{\text{fuel}}} \quad (5.2)$$

That method for combustion efficiency determination, although somewhat uncertain ($U_{95} \simeq \pm 10\%$, see Appendix A.4.12), allows to highlight the malfunctioning of the combustion process. The reason for such a low combustion efficiency derives from the piston shape. The HCCI engine from the PRISME laboratories is still equipped with its original piston. Being a diesel engine, the piston possesses a bowl at its top surface's center. Close to TDC, the piston's top surface gets right below the firedeck such that the mixture between both

is pushed towards the bowl. The region outside the bowl is termed the *squish area*. In a diesel configuration, the fuel is injected at the end of compression and towards the bottom of the bowl so that the flow from the squish region towards the bowl maintains the fuel within it during the combustion. In our HCCI configuration, the air and fuel mixture is initially filling the whole combustion chamber. During the combustion the squish area is therefore still filled with fuel. HCCI being a low temperature combustion mode, and the squish area possessing a huge surface of heat exchange, the mixture in the squish area is subject to quenching.

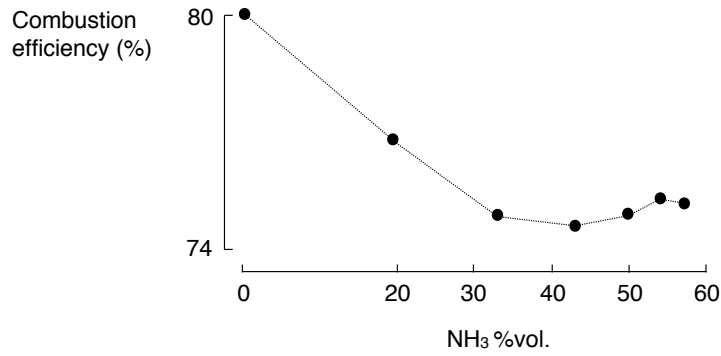


Figure 5.12 – The combustion efficiency is between 70% and 80% regardless of the ammonia blending ratio. The unburned fraction is due to the squish area containing part of the mixture. The slightly higher combustion temperature from hydrogen helps preventing some of the squish area quenching.

The low combustion efficiency is flawing all the other engine outputs in the sense that they are not quantitatively representative for other ammonia-hydrogen HCCI engines. Still, from comparative analysis and simulations, some findings shall be extracted from the obtained IMEP and NO_x emissions with the Orléans HCCI engine.

IMEP comparisons

Even though highly impacted by the combustion efficiency, the obtained IMEP can be compared to other results from the same engine. That exact engine from

the PRSIME laboratories has already been experimented on neat methanol and methane slightly promoted by hydrogen (5-20%vol.). Figure 5.13 compares, for specific MPRR and CA50 points, the optimal IMEP obtained for the four electrofuels of interest in their maximal concentration achievable in that engine. The lower combustion intensities of methane, methanol and ammonia compared to hydrogen are highlighted. Ammonia seems to have a higher power density potential than methanol, and the interest of boosted conditions is further highlighted (example case of methane).

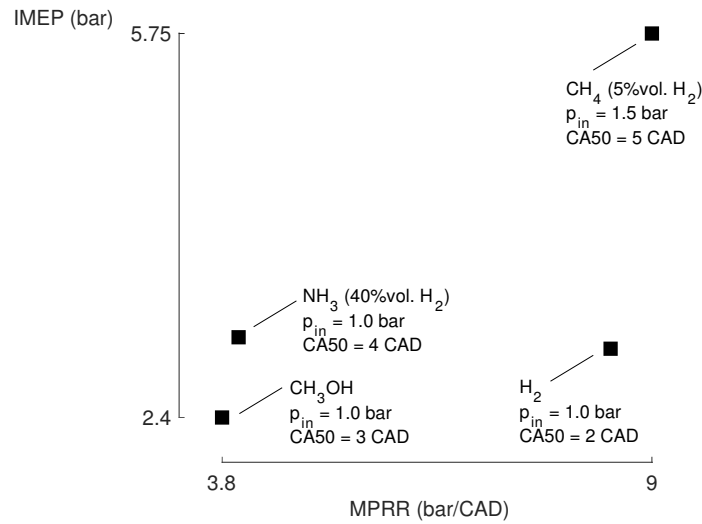


Figure 5.13 – Comparison of the best IMEP obtained for the four electrofuels of interest in the Orléans HCCI engine as a function of the MPRR. Ammonia seems to have the highest IMEP potential.

From another perspective, Figure 5.13 is close to achieve the desired goal of multi-electrofuel HCCI engine. Apart from methane and ammonia that fall short from being operated neat, the Orléans HCCI engine demonstrates the concept feasibility. Still, it remains to clarify the ideal operating conditions for each blend (compression ratio, intake pressure, blending ratio).

NO_x considerations

The NO_x emission concentration is measured using an IR spectrometer. Since ammonia and NO_x present some interferences in their IR absorbance spectrum, specific wavelengths are selected for the measurements to minimize the interferences. For pure hydrogen conditions, the measured NO_x emissions were constantly below 6 ppm. This low NO_x level can be explained by the low maximal in-cylinder temperature in the order of 1100-1400 K, well below the thermal-NO_x limit of 1800 K. Yet, as soon as some ammonia was added in the mixture, a surge of NO_x emissions above several thousands ppm was observed, see Figure 5.14, whereas the global in-cylinder temperature did not increase. Therefore these emissions are not linked to the thermal route but they find their origin in the nitrogen contained in ammonia, which is set free as soon as the combustion starts.

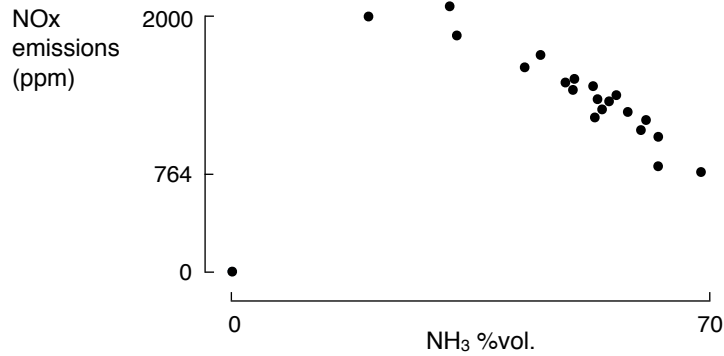
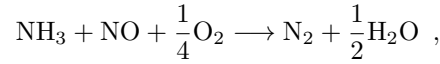


Figure 5.14 – Measured NO_x emissions as a function of the ammonia mixture content. NO_x are emitted as soon as some ammonia is added in the mixture, yet the emissions decrease below 1000 ppm as the ammonia fraction is above 60%.

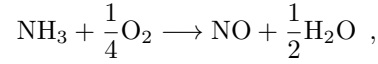
A decrease in NO_x emissions can be seen in Figure 5.14 with an increase in ammonia proportion. Due to the poor combustion efficiency, the exhaust ammonia content ranges from 5000 to 12000 ppm (for an initial ammonia blending ratio ranging from 20 to 60%vol). This increasing exhaust ammonia content, with decreasing NO_x measurement, indicates no interference is taking place in

the spectrometer, yet do not justify the observed trend for NO_x either. Two hypothesis are formulated to explain the decreasing NO_x trend.

The first hypothesis is the in-cylinder NO_x reduction from NH_3 molecules, more commonly know as DeNOx process or Selective Non-Catalytic Reduction. In the 1030-1360 K temperature region and in the presence of oxygen, the reduction reaction:



overtakes the oxidation reaction:



to find a new equilibrium point [158]. In our case, such temperature region occurs between 15 and 40 CAD aTDC. Although a 1000 ppm NO_x concentration takes about 0.05 second (or 10 times the 15-40 CAD time span) to be *fully* reduced [150], given the ammonia to NO_x ratio up to 15 due to the poor combustion efficiency, this DeNOx process might play a role in the observed decreasing NO_x emissions with increasing ammonia fuel blending ratio.

The second hypothesis is linked to the production of N_2O instead of NO_x . For runs where the maximal combustion temperature do not reach 1400 K, the N_2O that is produced during ammonia combustion is not reduced (this point is further detailed in Section 5.3.6). Since the obtained maximal combustion temperature for these experiments has been decreasing far below 1400 K, see Figure 5.15, the transfer from NO_x to N_2O emissions is to be expected. This hypothesis is strengthened by the fact that N_2O do not absorb in the 1500-2000 cm^{-1} infrared range where the main absorbance peaks of NO and NO_2 are located.

As explained in the introduction, EGAR can be used to reduce the oxygen availability. The fuel- NO_x formation is known to linearly reduce with an increasing equivalence ratio, reaching only 10% of their maximal value for stoichiometric conditions [116]. Figure 5.16 displays the NO_x emissions against various EGAR rates. The fuel content being maintained at 20%vol. of ammonia, the EGAR is the reason for an increased effective equivalence ratio. The

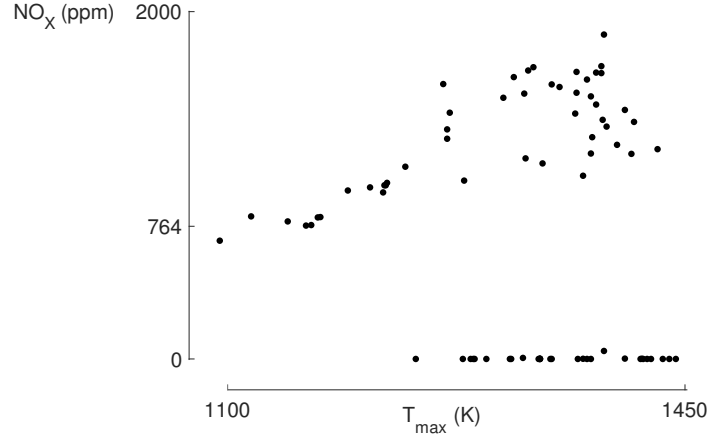


Figure 5.15 – The obtained decrease in maximal combustion temperature, as the ammonia blending ratio is increased, is correlated with the decrease in NO_X emissions.

NO_X 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 of NO_X emissions with an increase in EGAR rate is significant. Being outside of the thermal NO_X zone, the reduced NO_X production can be attributed to the reduced oxygen availability. Unfortunately the evaporator used to produce the steam of the synthetic EGAR was not powerful enough to evaporate the water flow needed to emulate a 100% EGAR.

This qualitative trend has been verified through the simulation of a 20%vol. ammonia content with up to 100% EGAR, see Figure 5.17. The simulated results give a similar response to EGAR as the experiments. With full EGAR the fuel-air mixture was at stoichiometry, therefore the NO emissions were reduced to 89 ppm (no NO_2). However, the production of N_2O was predicted by the model for combustion temperatures below 1400K, on which EGAR had only a limited effect. Still, this point has to be verified experimentally because of the limited representativity of a single-zone model on emissions, as well as the lack of validity of the mechanisms in the conditions of interest. Moreover, an

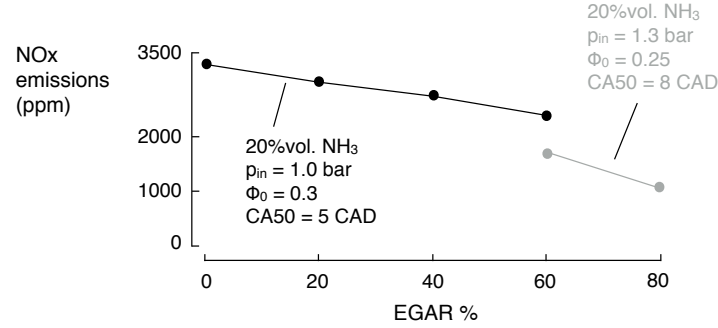


Figure 5.16 – NO_X emissions as a function of the EGAR rate. Reduced oxygen availability reduces the formation of NO_X .

impact on the combustion efficiency should be expected with such high rates of EGAR. Indeed, two percentage points of combustion efficiency were lost when going from no EGAR to 60% EGAR. If this decrease in combustion efficiency were to be observed with a proper piston geometry, then the use of high EGAR rates would not seem to be a more effective solution than an after-treatment system (Selective Catalytic Reduction) that would take care of NO_X emissions and unburned ammonia.

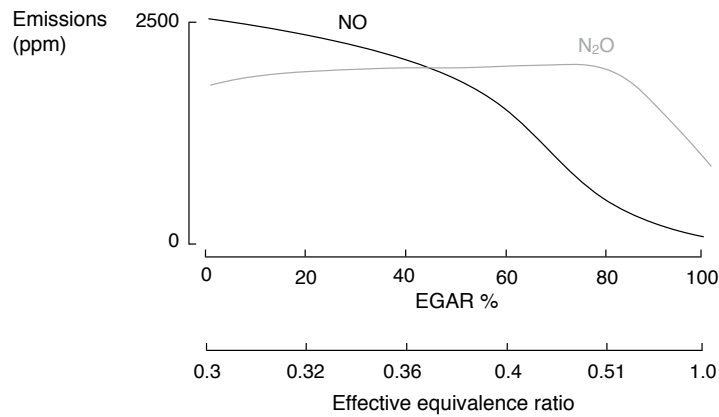


Figure 5.17 – Single-zone simulations of the production of NO and N_2O , for a 20%vol. ammonia content. Going towards stoichiometric conditions allows to reduce the NO_X production to 89 ppm but the N_2O production is still substantial.

5.2.5 Conclusions from the low CR experiments

The expected high power density for ammonia in HCCI engines has been demonstrated. Yet higher compression ratios must be used, and a quantitative determination of the power density evolution with the ammonia-hydrogen blending range and constrained MPRR and $P_{\max}$ is of interest.

The EGAR shows potential for a reduced oxygen availability, hence reduced fuel- NO_x emissions, yet its impact on combustion temperature must be balanced using higher intake pressures instead of simply increasing the intake temperature. Concerns about the possible emission of N_2O for too low combustion temperatures is raised. Finally, 100% EGAR conditions should be aimed at to observe the experimental implications on the other engine outputs.

Finally, the role the intake pressure can play for increasing the ringing resistance has been highlighted. This adds to the positive impact of high intake pressure on increased power density and combustion efficiency. It is to mention that increasing the compression ratio leads to the same benefits through an increased compression pressure and temperature.

5.3 High CR experimental results (UCLouvain)

In this section, the influence of the ammonia-hydrogen blending ratio on the combustion and performance aspects is studied, in addition to the impact of fuel loading, intake temperature, and EGR. Finally, based on these results, and using kinetic single-zone modelling to highlight the underlying causes of the observed phenomena, I propose guidelines for the ideal ammonia HCCI engine.

Compression ratio selection

One of the main goals of this research being the achievement of neat ammonia HCCI engine, the compression ratio had to be raised so that ammonia could auto-ignite at TDC with the test bench maximal supply intake temperature of 240°C . Using the HCCI single-zone model developed in Chapter 3, the evolution of the required T_{BDC} as a function of the engine compression ratio is obtained, see Figure 5.18. The kinetic mechanism used for this preliminary

study is the one from Song et al. [121] that has been shown to render the best results for ammonia auto-ignition under LTC conditions, see Chapter 4. According to these simulations, a compression ratio of 22:1 is required in order to achieve neat ammonia operation with a T_{BDC} of 230 °C. Yet, it can be seen from Figure 5.3 that our limited 240 °C intake temperature test bench can, in fact, only produce a 200 °C T_{BDC} due to the cooling during the admission. Therefore, in order to achieve neat ammonia operation in our test bench, the effective compression ratio would need to be 27:1.

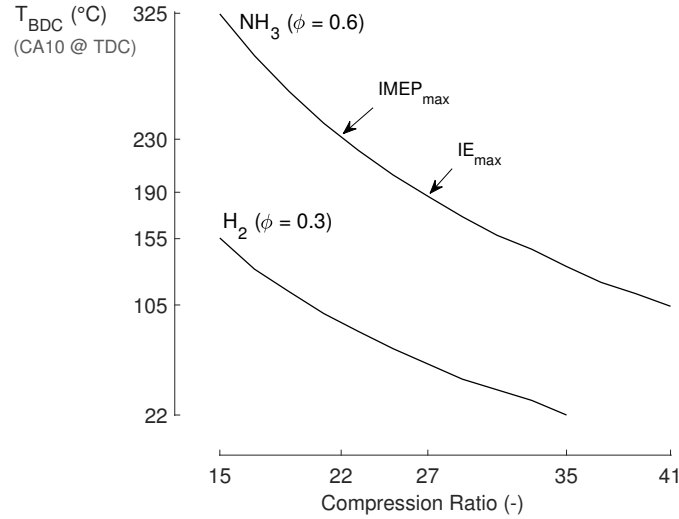


Figure 5.18 – Ammonia-hydrogen CR - ϕ - T_{BDC} iso-curves. For the engine constraints of 120 bar of P_{max} and MPRR of 12 bar/CAD, the highest achievable IMEP is obtained at 22:1 and the highest IE at 27:1. Further increasing the CR decreases the achievable equivalence ratio and increases the wall heat losses.

Regarding the engine power density, the simulations above have been performed to also compute the work produced. For each compression ratio point, the equivalence ratio is optimised under the engine constraints of a maximal in-cylinder pressure of 120 bar and MPRR of 12 bar/CAD. This was made possible by fitting the single-zone model combustion to a Wiebe function-shaped

combustion with a duration of 8 CAD. For this set of compression ratios, and knowing that the required intake temperature decreases with it, the optimal IMEP is reached at 22:1 since at higher compression ratios the equivalence ratio must be limited in order to meet the engine constraints and at lower compression ratios the high T_{BDC} outweighs the higher equivalence ratios. The optimal IE is reached at 27:1 of compression ratio, when the heat losses start to surpass any gain in piston work.

Regarding the Brake Efficiency (BE), it is dictated by the Indicated Efficiency (IE) as well as the friction losses. Due to the impact of an increased compression ratio on the in-cylinder temperature (i.e. increased heat losses and reduced IMEP) and pressure (i.e. increased friction losses), it is generally accepted for Diesel engines that the optimal compression ratio is in the 15-17:1 range. Yet in our configuration of auto-ignition resistant fuels the ideal compression shall be higher, for two reasons. First, the current study is for naturally aspirated HCCI engines having globally lower temperature and pressures than Diesel engines, hence lower friction losses. Second, given that the intake temperatures must be vastly increased compared to Diesel, the consequent IMEP is vastly reduced. This explains the shift of the ideal compression ratio to higher values despite the consequent tax in friction and wall heat losses. For example, switching from 17:1 to 27:1 allows to decrease the required intake temperature for ammonia from 300 °C to 190 °C, rendering a 25% increase in mixture density. To put the IMEP gain from a reduced intake temperature in perspective with the increased friction losses from the increased compression ratio, the simple but widely used Chen-Flynn friction model can be used [159–162]:

$$FMEP(bar) = A + B \cdot P_{\max} + C \cdot U + D \cdot U^2, \quad (5.3)$$

where FMEP (bar) is the Friction Mean Effective Pressure, U is the mean piston speed (m/s), and B the coefficient for maximal in-cylinder pressure lying in the 0.005-0.01 range [162]. The increased $P_{\max}$ for an increased compression ratio from 17:1 to 27:1 leads to an increased FMEP between 0.3 and 0.6 bar, therefore about half the IMEP gain in a first approximation. For these reasons, the optimal BE efficiency would be found with a somewhat lower compression ratio than 27:1. In the case of a heavy-duty and turbocharged engine, the reduction in required intake temperature together with increased achievable equivalence ratio, increased friction and wall heat losses would further reduce

the optimal compression ratio.

Still, for the considered experiments, the goal is the operation of neat ammonia requiring a 27:1 compression ratio. But given that the engine YANMAR L100V valve lift do not allow for geometric compression ratios higher than 23:1, the chosen geometric compression ratio has been limited to 23:1. The piston bowl has been filled through welding and then machined on the top to render a flat piston. The analysis of the newly machined piston under motoring conditions revealed an effective compression ratio of 21.9:1. For more information on the determination of the effective compression ratio and the difference with the geometric compression ratio, see Appendix A.3.3. The choice for a flat piston is explained as they are better suited to HCCI engines given that they minimize the piston crevice volume, and therefore the unburned fuel, for a given compression ratio and stroke-to-bore ratio [163, 164].

5.3.1 Experimental campaign

Aiming at stationary applications, a constant 1500 RPM is applied. Although neat ammonia operation was aimed at, the ammonia share could only be varied from 0 to 95%vol given the compression ratio and limited intake temperature. In order to have a map of the engine operating range, each blending ratio is assessed from misfire to ringing conditions by variation of the equivalence ratio. For this study, misfire is considered as a CoV_{IMEP} (Coefficient Of Variation of the Indicated Mean Effective Pressure, see Equation (2.6)) higher than 5% or a combustion efficiency lower than 90%. Synthetic EGAR will be applied with the aim of replacing the excess intake air. Finally, the intake pressure is set at atmospheric conditions and the intake temperature is controlled in each run to maintain a CA50 (Crank Angle at which half of the fuel energy has been released) of 4 CAD aTDC, unless stated otherwise. A summary of the operating conditions used in this paper is given in Table 5.4.

5.3.2 Temperature-Pressure regions

As a first indicator of ammonia resistance to auto-ignition, the supplied BDC temperature throughout the experimental campaign is observed to increase exponentially with the increase in ammonia fraction in the fuel blend, see Figure 5.19. Low fractions of ammonia have no significant impact on the auto-ignition resistance of the whole mixture given the slow rise in BDC temperature.

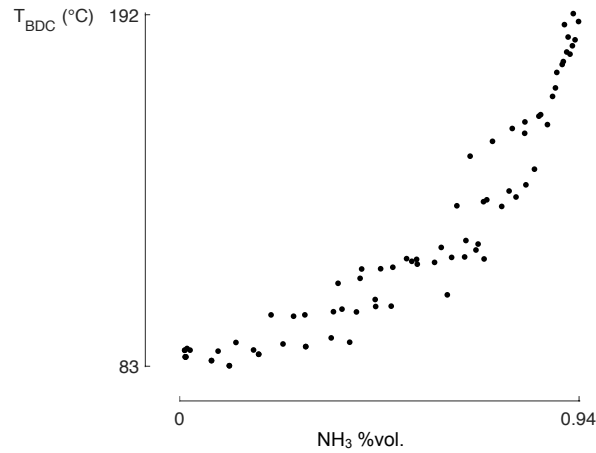
Table 5.4 – Recorded operating conditions. All were operated at 1500 RPM and 1 atm intake pressure.

Run (#)	T _{in} (°C)	NH ₃ (%vol.)	ϕ (-)	EGAR (%)
All	50 - 240	0 - 95	0.1 - 0.65	0 - 100
1	175	37 - 77	0.22	0
2	50 - 205	0 - 91	0.25 - 0.38	0
3	52, 177	0, 92	0.26, 0.65	0
4	82	0 - 50	0.15 - 0.38	0
5	175	0.21 - 0.82	0.23	0, 50, 80
6	131	0.33, 0.24	0.18, 0.26	0 - 0.95

- indicates a continuous range

, indicates specific points

The increased resistance starts to appear at around 15%vol. of ammonia and then increases non-linearly, yet according to the RCM experiments of Chapter 4 the rise in ignition delay should be tapering off reaching neat ammonia.

**Figure 5.19** – The required BDC temperature to allow 0-4 CAD CA50 timings is increasing exponentially with the ammonia fraction in the fuel, from 50 °C to 235 °C in terms of supplied intake temperature.

A better indicator of the auto-ignition resistance can be obtained from the encountered temperature and pressure 15 CAD before the TDC, T_{-15} and P_{-15} [131]. These indicators take further account of the mixture heat capacity, wall heat exchanges, gas dynamics, and other phenomena at play during the compression. For the transition from neat hydrogen to 95%vol. ammonia, T_{-15} is increasing non-linearly and P_{-15} is strongly decreasing, see Figure 5.20.

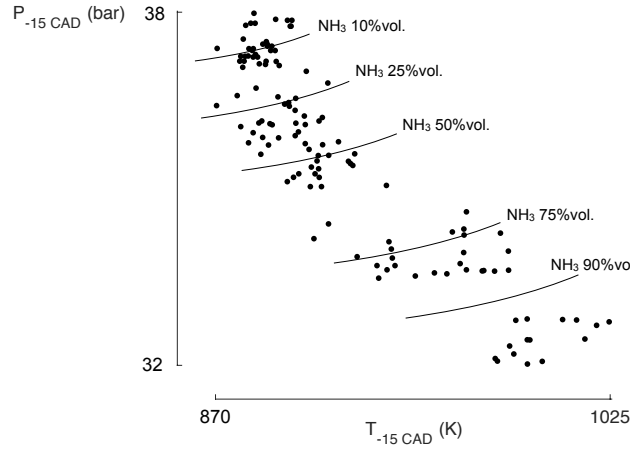


Figure 5.20 – Pressure and temperature region 15 CAD before TDC for CA50 between -2 CAD and 6 CAD. The resistance to auto-ignition of ammonia and its high heat capacity value explain why T_{-15} is increasing and P_{-15} is decreasing with higher ammonia fractions. Iso-lines for ammonia blending ratios are highlighted.

The reason for an increase in T_{-15} originates from the increased intake temperature, but the P_{-15} evolution derives at two-thirds from the increased heat exchange (less in-cylinder mass and increased temperature difference) and at one-third from the high heat capacity of ammonia, $c_{p,\text{NH}_3,293\text{K}} = 35.2 \text{ J/mol/K}$, compared to hydrogen, $c_{p,\text{H}_2,293\text{K}} = 28.8 \text{ J/mol/K}$. Not only the heat capacity of ammonia is higher than that of hydrogen, but it grows much faster with temperature: $c_{p,\text{NH}_3,1000\text{K}} = 56.5 \text{ J/mol/K}$ compared to $c_{p,\text{H}_2,1000\text{K}} = 30.2$

J/mol/K, see Figure 5.21. The higher the ammonia loading is, the slower and lower the pressure and temperature will rise, therefore requiring increased BDC temperatures to allow ammonia auto-ignition.

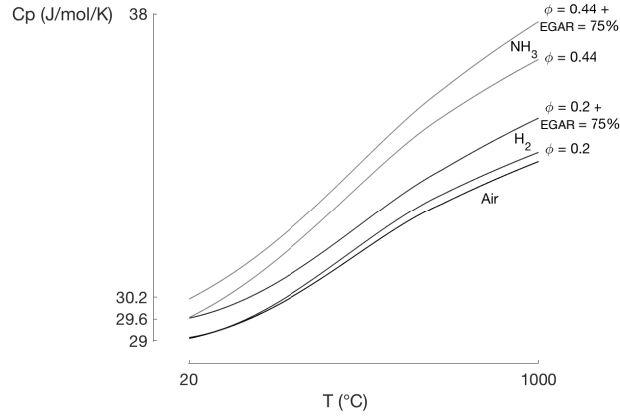


Figure 5.21 – The heat capacity of a typical ammonia engine mixture is higher, and increasing faster with temperature, than air, hydrogen engine mixture, and hydrogen engine mixture with 75% of EGAR.

5.3.3 Achieved IMEP: influence of the ammonia fraction and equivalence ratio

Increasing the ammonia fraction allows to reach significantly higher equivalence ratios thanks to ammonia combustion damping properties, hence a higher gross IMEP potential, see Figure 5.22. From neat hydrogen to 95%vol. ammonia fraction, a 67% increase in IMEP has been obtained, with more than three quarter of that increase happening between 15%vol. and 50%vol. of ammonia. Indeed, the required BDC temperature (see Figure 5.19) only increased after 15%vol. of ammonia but its final exponential increase is counter-balancing the IMEP gain from the achievable equivalence ratios. Nevertheless, Figure 5.22 can be a deceptive representation of the reality, as it hides many operating conditions to the reader.

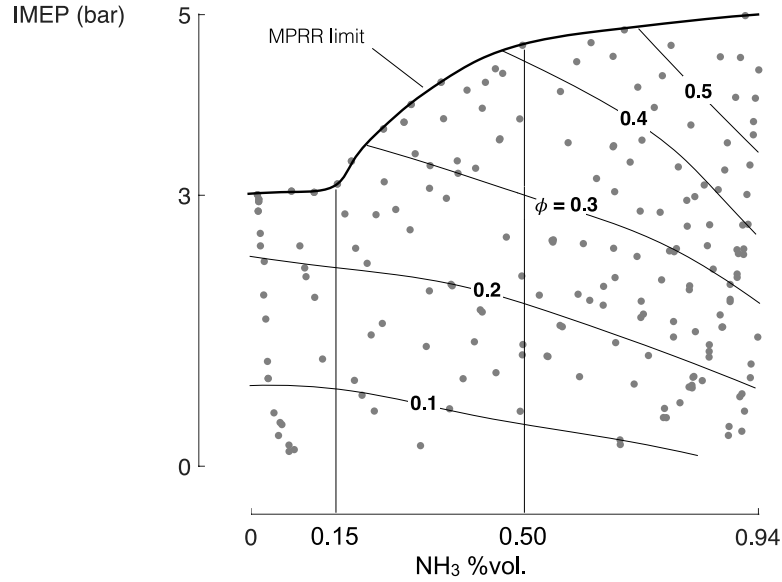


Figure 5.22 – Obtained IMEP as a function the ammonia blending ratio, with iso-lines for the equivalence ratios being highlighted. By increasing the ammonia fraction in the fuel blend, the equivalence ratio can be increased for a maintained MPRR. A jump of 67% in gross IMEP is consequently obtained with a 94%vol. ammonia content compared to neat hydrogen. The increase in IMEP is noticed only after 15%vol. in ammonia fraction, but tapers off after 50%vol. ammonia.

A more explicit view of the IMEP potential and limitations is obtained by plotting it against the MPRR, see Figure 5.23. As the equivalence ratio is increased to maximise the IMEP, the MPRR rises as well. Yet, as the MPRR rises above 10 bar/CAD, the heat and friction losses soar, eventually limiting the IMEP. We observe that ammonia helps reaching a higher IMEP for the same MPRR, meaning that ammonia damps the overall combustion rate.

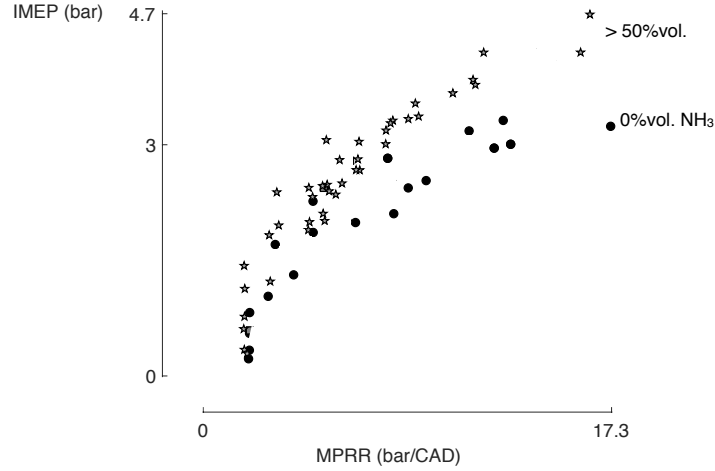


Figure 5.23 – *IMEP as a function of the MPRR for CA50 in the 2-6 CAD range. Most of the IMEP rise occurs between 15%vol. and 50%vol. of ammonia, and then tapers off due to heat and friction losses). Ammonia allows higher IMEP due to a reduced MPRR.*

As the MPRR further increases, ringing appears and the heat losses are further exacerbated. The engine is considered to be actively ringing when the RI, a function of the maximal amplitude of the pressure signal filtered between 4 and 25 kHz and averaged for 100 consecutive cycles [154], is higher than 2 MW/m². I chose this threshold level from the ringing noise generated by the engine. It corresponds to the safety level selected initially by Eng [154]. We observe that ammonia prevents ringing conditions and Figure 5.24 shows that 25%vol. ammonia concentrations are enough to significantly reduce the RI for a given MPRR. Given the relative uncertainty of $\pm 4\%$ on the RI, these are significant results. Moreover, given that increasing the intake pressure helps reducing the RI (see [165]), operating a heavy-duty engine would represent a considerable advantage for ammonia as it could accept the higher intake pressures that would allow further increased fuel loadings.

More than knowing the IMEP limitations and drivers, it is interesting to understand how ammonia damps the combustion. Increasing the ammonia fraction in the fuel blend while maintaining the intake temperature and equivalence ratio (set #1) delays the combustion, see Figure 5.25.

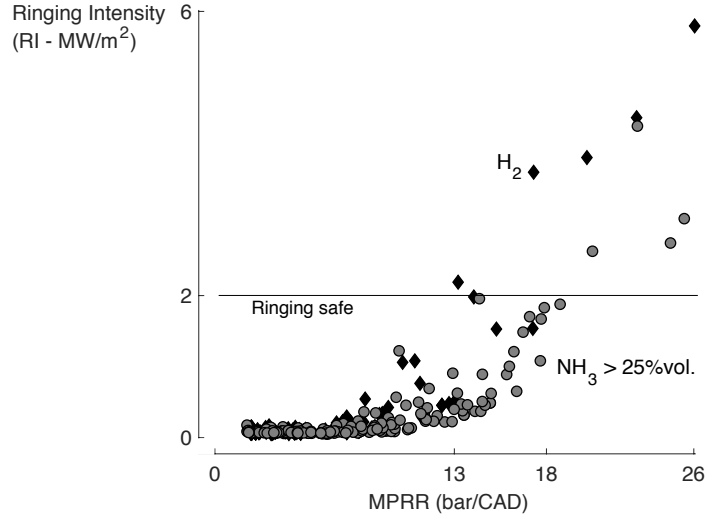


Figure 5.24 – The RI is correlated to the MPRR. Ammonia reduces the onset threshold and the slope of the correlation.

This delay arises both from ammonia slower kinetics and from its higher heat capacity leading to lower T_{-15} and P_{-15} . To rigorously characterise the damping effect, the HRR for an increased ammonia fraction and constant CA50 and FuelMEP (set #2) are plotted in Figure 5.26. Ammonia can create a two-fold reduction in MPRR, with a combustion duration increase from 3 CAD to 7 CAD. Again, we observe that low fractions of hydrogen and low fractions of ammonia do not have significant effects on the heat release rate. In terms of ignition process, ammonia has a much longer initiation and termination period than hydrogen, hence a wider HRR. During that initiation period, some heat is released yet it is not sufficient to trigger the bulk auto-ignition. Similarly, the start and end of the HRR are less sharp. This long initiation period could be explained from the radical analysis performed in Section 5.2.1: a lot of OH radicals are consumed to convert NH_3 to NH_2 and other non-reactive intermediates prior to the main combustion. Compared to neat hydrogen combustion, the OH peak value for ammonia-hydrogen is ten times lower, see Figures 5.5 and 5.27.

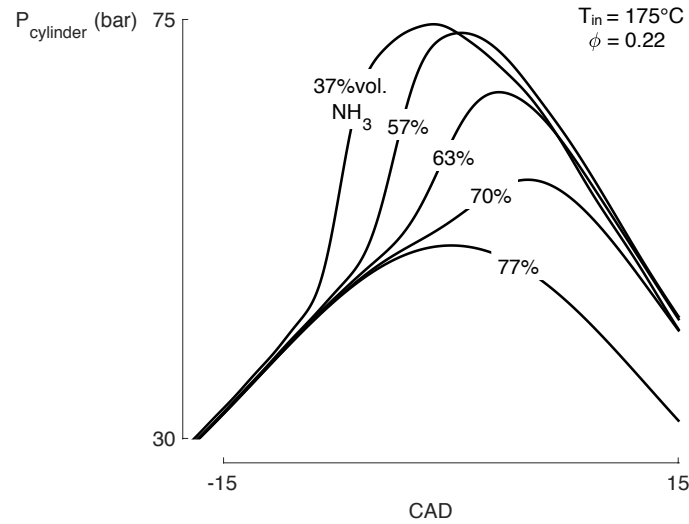


Figure 5.25 – The combustion is delayed as the ammonia fraction is increased in the set #1, with constant equivalence ratio and intake temperature.

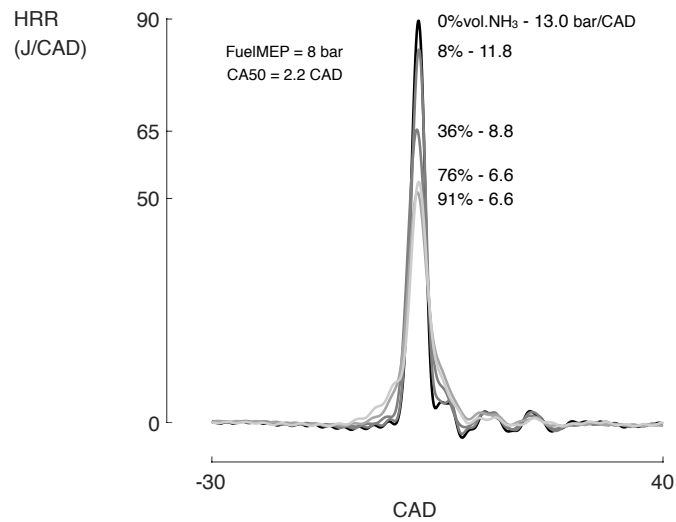


Figure 5.26 – HRR evolution for set #2 having constant FuelMEP and CA50 as the ammonia fraction is increased from 0% vol. to 91% vol. The maximum HRR and MPFR are reduced by half and the tails of the HRR are getting wider.

With equivalent MPRR and similar combustion timings, the set #3 gathers the highest IMEP that were achieved with neat hydrogen and with ammonia-hydrogen blends: 3.2 bar and 5.0 bar, respectively, see Figure 5.27.

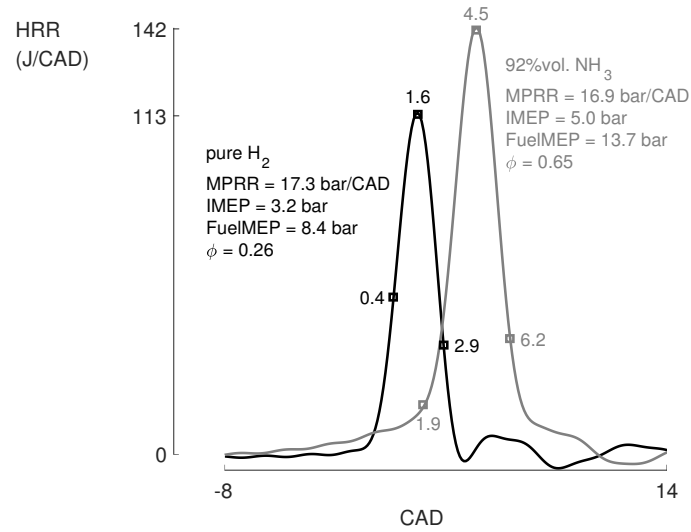


Figure 5.27 – For set #3 with equivalent MPRR, ammonia possesses a much longer initiation period than hydrogen, during which some heat is released but too few to trigger the bulk auto-ignition. The CA10, CA50 and CA90 are marked by squares on the HRR curves. For equivalent ignition timing and combustion duration, ammonia allows to increase the IMEP by more than 50% without impacting the indicated efficiency.

Finally, the obtained indicated efficiency as a function of the ammonia content is observed to stay constant for the maximal IMEP points (i.e. MPRR > 9 bar/CAD), see Figure 5.28. This result might seem counter intuitive since the heat capacity of ammonia has been shown to be higher and increase faster with temperature than hydrogen, see Figure 5.21. Moreover, due to the higher intake temperature used with ammonia, heat losses undergo an absolute increase. Still, in a relative point of view, the heat losses do not increase as fast

as the gain in produced indicated work thanks to the higher equivalence ratios allowed by ammonia. This fact derives from the longer combustion durations observed with ammonia and similar combustion temperatures (see upcoming Section 5.3.5), despite the increased IMEP.

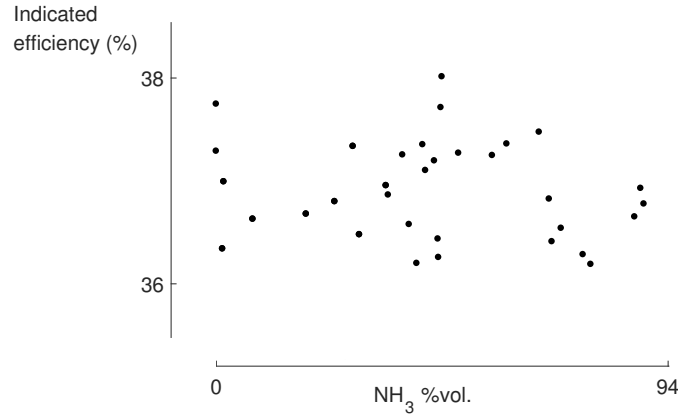


Figure 5.28 – Obtained indicated efficiency as a function of the ammonia blending ratio, for all the operating conditions with a $MPRR > 9$ bar/CAD (i.e. $\sim$ optimised IMEP). Under these ideal IMEP conditions, the indicated efficiency is observed to be independant of the ammonia blending ratio.

5.3.4 Increased operating range and combustion timing control

The load range potential has already been assessed in Figure 5.22, but we need to assess the ease with which such range can be obtained (i.e. the engine controllability). The experimental set #4 is operated with a constant intake temperature of 82°C while the IMEP rises from 1.6 bar to 3.8 bar through an increased ammonia flow rate, see Figure 5.29. When the ammonia fraction is increased while the hydrogen flow rate is maintained, the combustion duration decreases by 50%. Therefore the high FuelMEP prevails over ammonia slow kinetics in that case. Moreover, although the total fuel flow rate and ammonia fraction increase (and therefore the RGF temperature), the start of combustion

remains the same due to a higher mixture heat capacity and longer ignition delay.

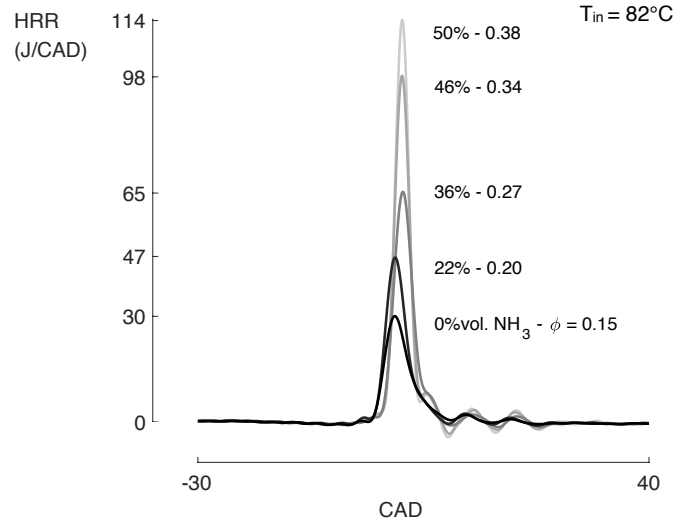


Figure 5.29 – Simply increasing the ammonia flow rate while maintaining the intake temperature and hydrogen loading (set #4) can lead to a constant combustion timing, although the load has been more than doubled.

A deeper understanding is obtained through simulations with a classic RCM single-zone effective adiabatic core volume model, see its development in Chapter 4. Two cases have been studied: for the first one, the volume evolution of the RCM shot simulation as been fitted to showcase an effective compression ratio of 21.7:1 yet with a compression time of 35 ms and a second-half compression time of 4 ms, as in Chapter 4. For the second case, the compression temperature and pressure have been fixed to 956.22 K and 75.57 bar, the ones obtained in the first case for neat hydrogen at an equivalence ratio of 0.2. For both cases, the ignition delay evolution has been studied as a function of an increase in ammonia fraction with equivalence ratios ranging from 0.2 to 0.5, see Figure 5.30. These results show that, for the first case study, the ammonia-hydrogen blending ratio can be adapted to control both the combustion timing

and engine load thanks to the competing effects of equivalence ratio kinetics, heat capacities and ignition delay resistances. Thanks to the second case study, one can see that for the kinetic effect alone, increasing the ammonia fraction increases the ignition delay and increasing ammonia equivalence ratio decreases the ignition delay. Therefore in the first case the increase in ignition delay with the equivalence ratio is only due to the heat capacity of ammonia, and not to the kinetics.

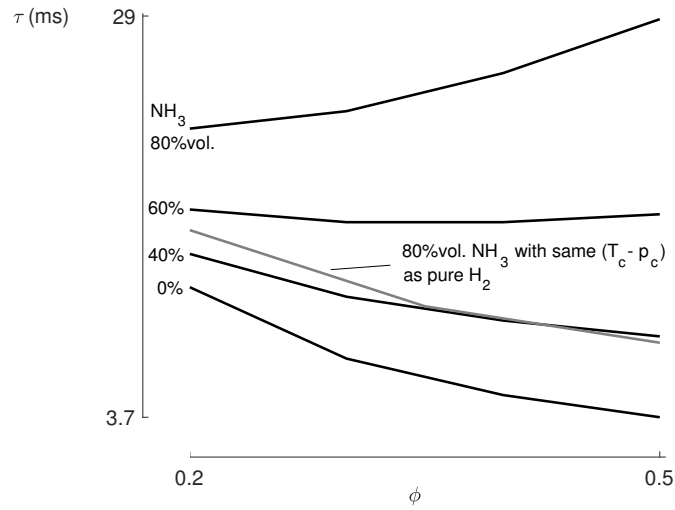


Figure 5.30 – The ignition delay increases when the fuel loading is increased with an ammonia share higher than 60%vol., according to single zone effective adiabatic core volume RCM simulations. Yet when the heat capacity effect of ammonia is cancelled by forcing the compression temperature and pressure, the ignition delay decreases with an increase in fuel loading.

Finally the hydrogen promotion threshold is sharp and should be considered when operating the engine, given the general control uncertainty and stability. The threshold concentration, which depends on the operating pressure and temperature conditions, is given in Figure 5.31.

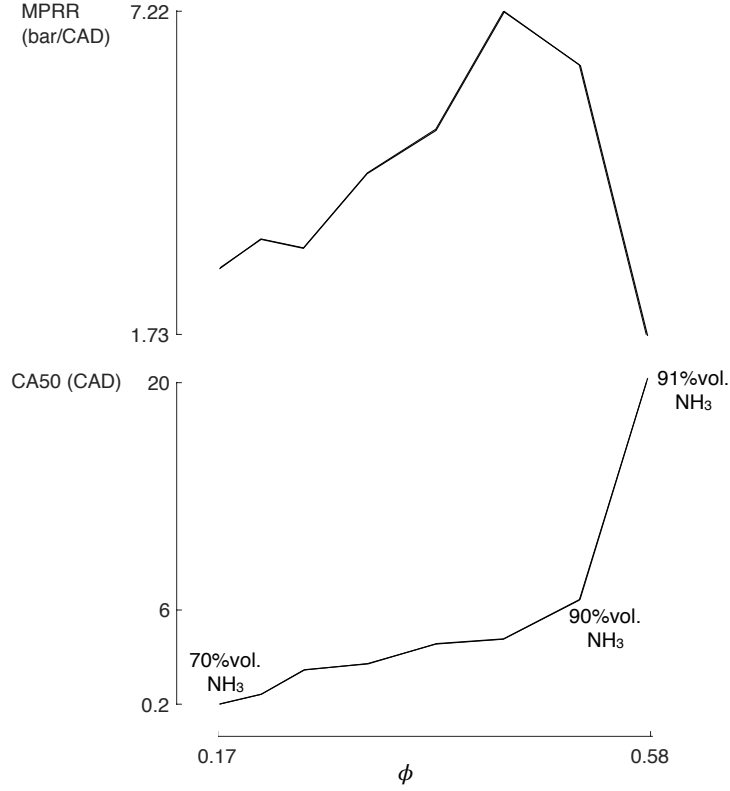


Figure 5.31 – The ammonia auto-ignition promotion by hydrogen stops suddenly at a threshold concentration, which depends on the operating pressure and temperature conditions.

5.3.5 Ammonia combustion efficiency

A major driver for the ideal engine design is the combustion efficiency, as it impacts both the overall efficiency and the pollutants emissions. The unburned ammonia fraction, defined as:

$$\text{Unburned NH}_3 = \frac{\dot{n}_{\text{NH}_3, \text{exhaust}}}{\dot{n}_{\text{NH}_3, \text{intake}}} , \quad (5.4)$$

represents the combustion efficiency and was observed roughly constant with the evolution of the ammonia fuel fraction, see Figure 5.32. We observe the unburned ammonia percentage to span between 5% and 15%, with a strong correlation with the maximal combustion temperature iso-lines. These iso-lines are obtained from the runs themselves: all the dots located below the 1600 K

line have a maximal combustion temperature above 1600 K. To maintain the lowest possible unburned percentage, the maximal in-cylinder temperature has to rise with the ammonia fuel fraction, if not the unburned quantity can double. An increase in maximal in-cylinder temperature from 1500 K to 1800 K is required to maintain a 5% unburned fraction when shifting from neat hydrogen to 95% of ammonia fraction. A 5% unburned fraction represents an ammonia exhaust concentration going from 0 to 6000 ppm depending on the ammonia fuel blending ration. Still, the uncertainty on the maximal temperature being around 4% (or approximately $\pm 70\text{K}$), care should be taken regarding the values of these limit temperatures.

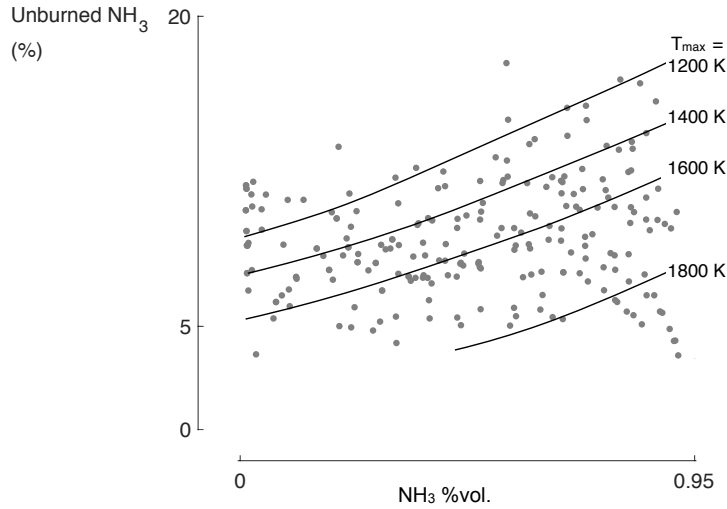


Figure 5.32 – The ammonia unburned fraction is correlated to the ammonia fuel fraction and the maximal combustion temperature ($T_{\max}$, highlighted by iso-lines). It does not go below 5% because of the crevices.

Regardless of the combustion temperature, no combustion has been observed with an unburned ammonia percentage below 5%. This is due to the high crevice volume that represents, at TDC, 4.85% of the chamber volume, and 3.64% of the chamber volume 10 CAD away from TDC. Indeed, the engine

being initially designed for diesel direct injection in the piston bowl, the piston crevices were not minimised and are 7 mm high and 1 mm thick.

Additionally, the extremely low Stroke-to-Bore ratio of this engine ($S/B=0.87$) leads, together with a high compression ratio, to a *pancake* combustion chamber that has an extremely high heat exchange area. In our case, the clearance height at top dead center is only 3.3 mm, against a bore diameter of 86 mm. To minimise the heat exchange area (i.e. maximise the Volume-to-Surface area), the Stroke-to-Bore ratio has to be maximised (e.g. heavy-duty). This will help as well to increase the mean crevice temperature.

Another factor to consider is that operating on neat ammonia might not be ideal. Of course it is of interest to study neat ammonia, yet the impact it has on the intake temperature and combustion efficiency must be taken into consideration. Ammonia can readily be promoted by hydrogen continuously produced from ammonia reforming within an intake cracker. Using a Ruthenium-based catalyst, Frigo et al. [166] obtained an ammonia conversion efficiency to hydrogen and nitrogen ranging from 0 to 100% with a catalyst switch from 200 to 500 °C. Without catalysis, the conversion efficiency of ammonia in a blank reactor at 500 °C falls to around 40% [167]. Therefore, hydrogen promotion should not be disregarded based on hydrogen supply concerns only.

If one assumes that any additional unburned ammonia percentage to the $V_{\text{crevice}}/V_{\text{chamber}}$ ratio at the CA90 is linked to a wall quenching phenomenon, a quenching thickness can be computed, see Figure 5.33. The close match of the correlation validates the CA90 choice as the reference point after which the unburned fuel is not converted anymore.

The quenching thickness evolution can be explained through the maximal in-cylinder temperature, see Figure 5.34. The rather spread correlation is explained by the range of ammonia fuel fractions considered. This graph tells us that, in order to significantly avoid quenching in the 1 mm thick crevices, the temperature inside must reach at least 1700 K. Given the range in in-cylinder temperature required to make a difference in combustion efficiency, simply increasing the engine wall temperature by a couple of dozen degrees won't affect it directly, although it will affect the combustion timing and consequently the maximal in-cylinder temperature. Integrating that in addition to the long combustion duration, an early CA10 is preferred for ammonia combustion.

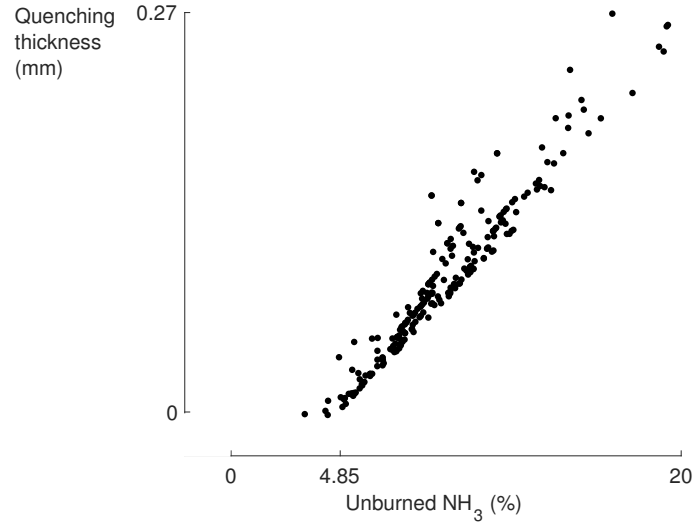


Figure 5.33 – The quenching thickness spans from 0 to 0.27 mm as the unburned ammonia fraction increases from 4.85% to 20%.

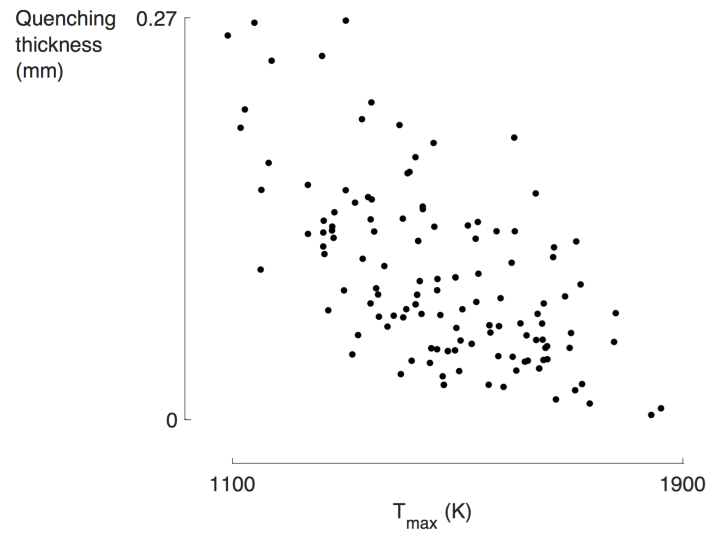


Figure 5.34 – Quenching thickness evolution with the maximal combustion temperature. A maximal combustion temperature above 1700 K shall help minimizing the crevice unburned fuel given the crevice thickness.

5.3.6 NO_x emissions from ammonia

The NO_x emission concentration is measured using a UV spectrometer. Since ammonia and NO_x present some interferences in their UV absorbance spectrum, specific wavelengths are selected for the measurements to minimize the interferences. Further details regarding interference and the calibration of the spectrometer are given in Appendix A.3.7.

Compared to the low NO_x levels (~ 50 ppm) that we observed for neat hydrogen, as soon as ammonia was fed to the engine, the NO_x levels rose to above 1000 ppm and kept increasing with the ammonia intake content, see Figure 5.35. These results are associated with $\text{CA}_{50} = 4 \pm 2$ CAD and maximal combustion temperatures above 1400 K.

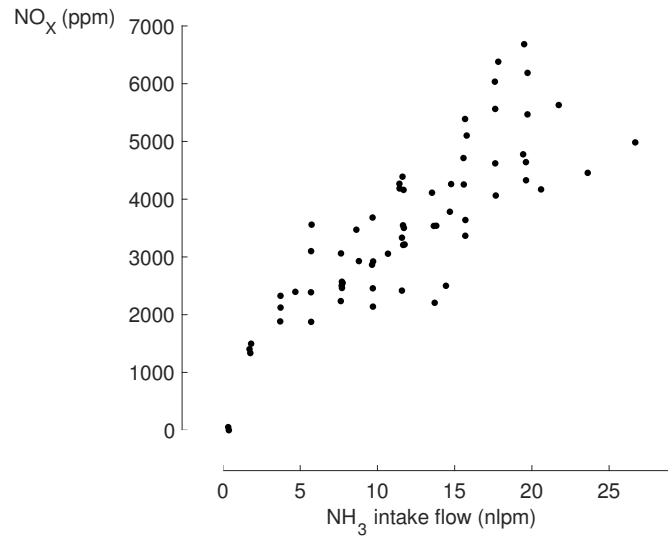


Figure 5.35 – NO_x emissions as a function of the ammonia intake flow, for $\text{CA}_{50} = 4 \pm 2$ CAD and maximal combustion temperatures above 1400 K. As soon as ammonia is blended with hydrogen NO_x emissions appear above 1000 ppm, and keep increasing with the ammonia fuel flow, here expressed in normal liters per minute (nlpm).

This result is opposed to the observation made on the Orléans engine where the x emissions were decreasing with the ammonia content, see Figure 5.14. The reason for that comes with the combustion temperature for the present runs being above 1400 K, hence avoiding the production of N_2O instead of NO_X , and increasing in temperature with the ammonia fuel content since the IMEP was constantly pushed to a maximum, compared to the Orléans runs being strictly below 1400 K since the engine was not pushed in IMEP. Away from abnormal combustion (production of N_2O and possible DeNO_x phenomenon happening with the unburned ammonia) a clear correlation is observed between NO_X exhaust concentration and ammonia intake content.

To further investigate the possible N_2O production from ammonia HCCI combustion, the following test is performed: starting from a 50%vol. ammonia fuel blend (8 nlpm of ammonia), the intake temperature is progressively reduced. The obtained NO emissions are displayed in Figure 5.36 and are observed to increase with a decreasing maximal combustion temperature below 1450 K.

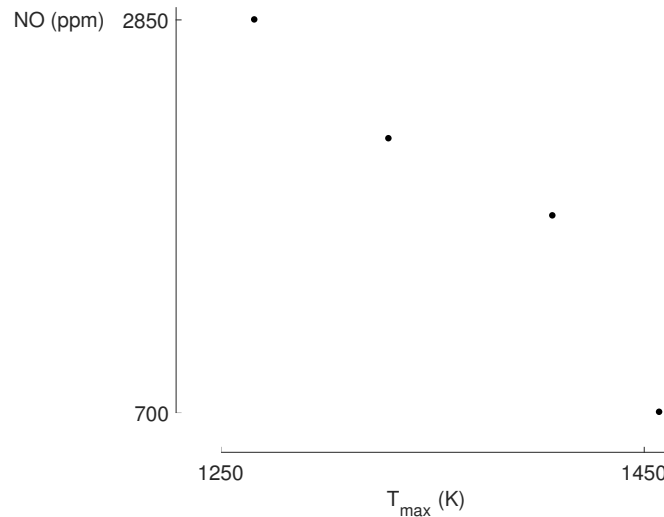


Figure 5.36 – For a maintained ammonia and hydrogen intake flow rate of 8 nlpm and decreasing intake temperature, the NO emissions start to soar when the maximal combustion temperature decreases below 1400 K.

It is not the NO formation that is impacted when decreasing the maximal combustion temperature below 1400 K, but rather the decomposition of N_2O . N_2O is known to form in low temperature and lean environments [168], but when the combustion temperature fails to reach the 1400 K barrier, the N_2O pool formed is never reduced, see Figure 5.37. As the N_2O molecules absorb UV in a wide wavelength range (including 190-230 nm), the selected width from 214 to 216 nm for NO measurement in our UV spectrometer was probably measuring N_2O in the present case.

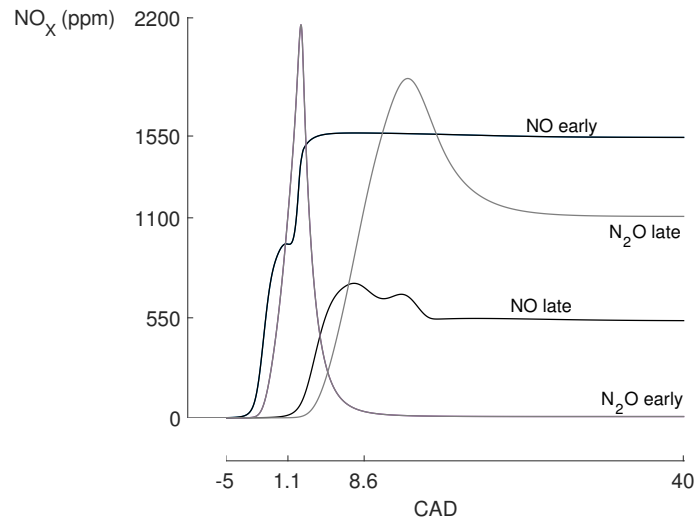


Figure 5.37 – NO and N_2O production-consumption curves for an early and a late combustion. The late combustion happens below 1400 K which is insufficient to reduce the pool of N_2O . Simulation results obtained with the previously used single-zone model with the kinetic mechanism from Mathieu et al. [120].

EGR impact on NO_x emissions

To fully characterise the EGR impact on the engine emissions, one must look at all the NO_x compounds and the combustion efficiency. For early combustion

timings (i.e. sufficient combustion temperatures), the EGR can have up to a three-fold reduction effect on the NO emissions, see Figure 5.38. Yet EGR lowers the combustion temperature hence meeting the N_2O threshold more easily. Moreover, considering the high impact of EGR on the mixture heat capacity, in addition to that of ammonia, it becomes a hurdle to achieve auto-ignition and maintain combustion temperatures that minimize the quenching thickness. As a consequence, EGR was not able to further increase the IMEP of the ammonia-hydrogen blends. Finally, the EGR negatively impacts the NO_2 emissions, see Figure 5.39. The global impact of EGR is therefore negative if no combustion temperature enhancing technique (such as turbocharging) is used.

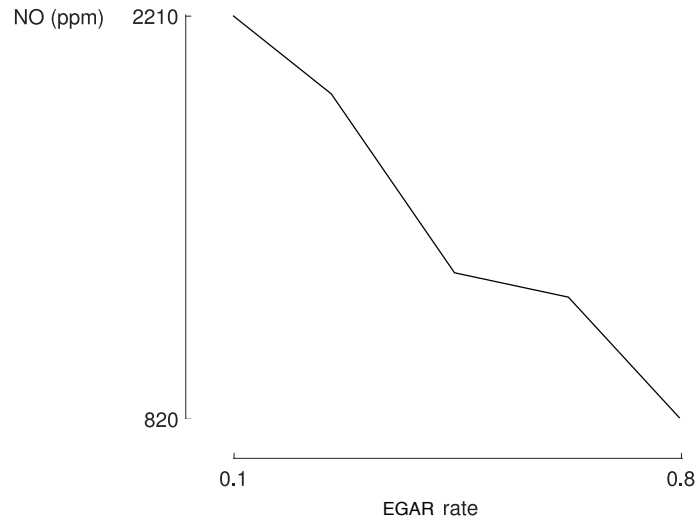


Figure 5.38 – A factor three in NO reduction can be achieved thanks to EGR, for early combustion timings (i.e. prior to the N_2O threshold).

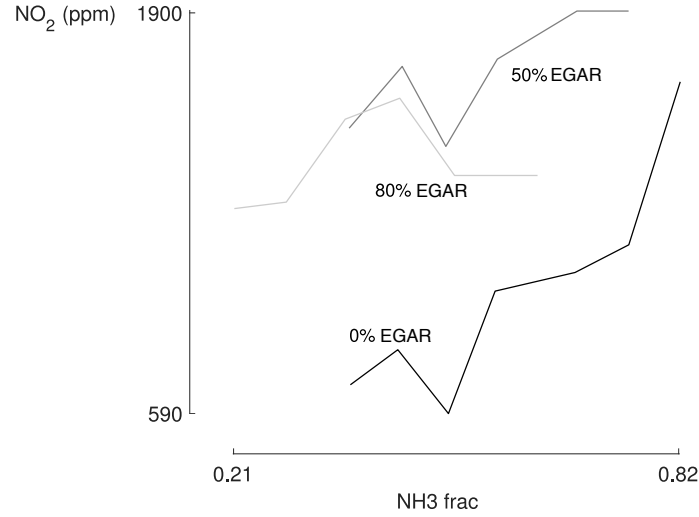


Figure 5.39 – NO_2 emissions increase as the ammonia fraction is raised, and the EGR impacts them negatively.

5.3.7 Exhaust emissions confronted to pollutant regulations

For the considered 0.3-3 MW_e power range in this thesis, there exists only one directive regarding pollutant emissions: the Medium Combustion Plant Directive (MCPD - for thermal output between 1 and 50 MW [18]). This directive only regulate NO_x and SO_x emissions for stationary engines. Yet as SO_x would only be emitted from the lubricating oil used in the electrofuel HCCI engine only the NO_x regulation will be investigated here.

The NO_x level to comply to is 190 mg/Nm^3 for new liquid or gaseous fuel engines running more than 1500 hours per year. A concentration of 190 mg/Nm^3 of NO_x is equivalent to 142 ppm of NO or 93 ppm of NO_2 , yet the measured mixture must be on a dry basis with a 15%vol. O_2 content. In the performed experiments, water and oxygen accounted together for one quarter of the global exhaust, varying between 23%vol. and 28%vol. depending on the ammonia-hydrogen blending ratio and equivalence ratio used.

For the case of neat hydrogen operation, since the measured NO_x emissions stayed below 50 ppm, the corrected value for oxygen and water content would reach close to 70 ppm, well below the MCPD legal value hence avoiding the

need for any after-treatment systems. With ammonia added in the fuel blend, the measured NO_x emissions being always above 500 ppm, an after-treatment system shall be needed.

The other pollutants observed through this experimental campaign (unburned H_2 , unburned NH_3 , and N_2O) are not regulated, under the MCPD or even under the Industrial Emission Directive (IED - including MCPD and installations with thermal power output above 50 MW [169]). Still, the Best Available Techniques (BAT) report on large combustion plants (published by the european Joint Research Center with the aim of providing an evidence-based scientific support to the European policy-making process) mentions typical values for ammonia exhaust concentration in the order of 3-20 mg/Nm^3 (i.e. < 26 ppm) for biomass combustion plants or processes using an ammonia-based DeNO_x process. It is therefore to expect that similar ammonia emission regulations would appear in the case an ammonia market for stationary applications would appear. No mentions of specific values for N_2O and H_2 are made in the BAT report. Regarding road vehicles, the EURO VI standard for heavy-duty diesel vehicles limits NH_3 emissions to 10 ppm to avoid ammonia slip from the DeNO_x system, yet it does not mentions H_2 and N_2O . One must look at the US road legislation to find a limit of 133 mg/kWh (~ 10 ppm) for N_2O emissions [170].

5.3.8 After-treatment measures to reduce NO_x emissions

In the case of ammonia HCCI combustion, the MCPD NO_x regulations of 190 mg/Nm^3 (i.e. 142 ppm of NO or 93 ppm of NO_2) are not met. To reduce NO_x emissions, various after-treatment techniques could be used provided that specific exhaust conditions are supplied.

Three Way Catalytic converters (TWC) can be used to convert NO_x emissions with conversion efficiencies above 95%, yet requiring stoichiometric operations and exhaust temperatures above 300-350 °C to reach such efficiencies. The reason for mentioning the use of TWC for a lean ammonia HCCI engine is that they have been shown to render equivalent conversion efficiencies for NH_3 in addition to NO_x emissions [62]. For further information on the possible stoichiometric operation of a HCCI engine, refer to Section 6.2.

Selective Catalytic Reduction (SCR) can be used whatever the oxygen concentration to reduce NO_x and N_2O , with conversion efficiencies at 100% for the temperature window 300-450 °C, still requiring the use of an ammonia-based

substance to obtain the following ratio in the exhaust mixture: $\frac{[\text{NH}_3]}{[\text{NO}_x]} \simeq 1$ [171]. In practice, the NH_3 to NO_x ratio is slightly higher than 1 to ensure total NO_x conversion and an Ammonia Oxidizer (AMOX) catalyst is therefore used to convert the ammonia leftovers from the SCR [170]. The need for ammonia is usually seen as a drawback since ammonia has to be supplied, still in our specific ammonia HCCI application it can be seen as an advantage as the unburned ammonia can be used to reduce the NO_x in the SCR. For the performed experimental campaign, the obtained exhaust temperature (measured in the non-insulated exhaust manifold) evolved from 180 °C for neat hydrogen to 330 °C for 95%vol. ammonia content. Also, with a constant combustion efficiency of 95%, the ammonia exhaust concentration evolved from 0 to 6000 ppm hence evolving accordingly to the NO_x concentration, see Figure 5.35. With an improved crevice design hopefully rendering a two-fold reduction in unburned fuel, some NH_3 shall be added to maintain the ammonia to NO_x ratio. The use of a SCR to perform a combined NH_3 - NO_x reduction is therefore at reach for the considered application, coupled to an AMOX.

Lean NO_x Trap (LNT) can be used whatever the oxygen exhaust concentration to adsorb NO and NO_2 , and uses frequent rich-combustion cycles to regenerate the trap by reducing NO_x to nitrogen and water with an average 2% fuel economy cost. LNT reach a total NO_x adsorption-conversion when used at 250 °C. Still, LNT only achieve partial N_2O adsorption-conversion and generate NH_3 as a bi-product during the regeneration. However, recent studies have shown practical evidence of the beneficial combination of LNT and SCR in series: as the NO_x reduction is split between the LNT and SCR, the fuel penalty can be mitigated compared to pure LNT, the ideal operation temperature of both systems is more flexible and in the 200-300 °C range (which is of interest in the considered HCCI configuration), and total conversion of NO_x - N_2O - NH_3 is achieved [172, 173].

5.4 Outlook and conclusion

In this chapter, the ammonia-hydrogen blend has been successfully experimented in HCCI engines having a 15:1 and a 22:1 compression ratio. For the given 12 bar MPRR and 120 bar P_{max} constraints, the ideal CR regarding power density for ammonia was 22:1. Using a heavy duty engine would allow the use of a higher compression ratio without forcing to limit the equivalence

ratio, hence reaching better global efficiencies and power densities. Although the ammonia-hydrogen fraction did not influence the IE significantly, the other engine outputs were greatly modified by the blending ratio.

First, ammonia slow kinetics and radical exchange with hydrogen allow to damp the combustion intensity at ammonia fractions as low as 20%. Further increasing the ammonia share allowed to reach higher equivalence ratios and IMEP. A global 50% increase in IMEP compared to neat hydrogen is possible, with 5.0 bar. Moreover, given the used compression ratio, hydrogen was closer from its ideal power density CR than ammonia.

For a maximised ammonia combustion efficiency, the main operating parameter to consider is the maximum combustion temperature (and limited gradient towards the engine wall). It is enhanced through high fuel loads, obtained from turbocharging and high equivalence ratios. To avoid bulk quenching, maximum combustion temperatures of 1600 K were required for neat hydrogen and 1800 K for neat ammonia. Such conditions were met for 50 and 90%vol. ammonia fraction under 4.5 and 5.0 bar IMEP, respectively, and allowed combustion efficiencies of 95%. The remaining unburned emissions were shown to be linked to the crevice volume, as it was estimated to 5% of the TDC volume. Parameters that are to consider to limit crevice unburned emissions are a minimised crevice volume and a high stroke-to-bore ratio.

Other noticeable results can be mentioned. Regardless of the engine MPRR and $P_{\max}$ constraints, increasing the cylinder pressure for a given heat release helps reducing the ringing intensity, e.g. through the intake pressure or compression ratio. For maximal combustion temperatures below 1400 K, N_2O is being produced, which must be avoided at all costs given its greenhouse effect 298 times stronger than CO_2 . Finally, the ammonia-hydrogen blending ratio selection is a practical and faster way of load and combustion timing control than through intake temperature variation.

As soon as ammonia was present in the fuel, fuel- NO_x emissions above 1000 ppm have been observed, and further increasing with the intake ammonia flow rate up to 7000 ppm. Still, these emissions were decreasing with a reduced oxygen availability produced by replacing excess intake air by exhaust gases (more than a two-fold reduction when using 80% EGAR). Yet EGR impacted other combustion aspects: overall reactivity and combustion efficiency. Moreover, given the regulations on NO_x emissions for medium scale stationary engines (< 150 ppm), resorting to the the use of EGR might be useless if that level

cannot be reached and that a SCR or LNT treatment would be needed anyway (although smaller), unless effective stoichiometric conditions can be reached (with acceptable combustion temperatures to avoid N_2O formation and render good combustion efficiency) where drastically less expensive TWC could be used to reduce the remaining NO_x particles.

Finally, the ideal ammonia-hydrogen blending ratio is a complex trade-off decision. 75% of the IMEP increase potential happens before 50%vol. of ammonia content in the fuel. Also, the higher the hydrogen fraction the lower the required maximal combustion temperature to avoid bulk quenching and the lower the required intake temperature. Finally, hydrogen can readily be obtained from ammonia catalysis at the engine intake.

The future depends on what you do today.

Mahatma Gandhi

6

Conclusion and outlook for the HCCI multi-electrofuel concept

6.1 Conclusion

With the forthcoming need for multi-electrofuel cogeneration units to provide resilience and efficiency to high renewable-share energy systems, the potential of HCCI engines is investigated.

The electrofuels considered (hydrogen, methane, methanol, and ammonia) are obtained from the excess renewable electricity storage, with the only additional building blocks being water, air, and CO₂. The choice to investigate the HCCI piston engine originates from its inherent high-efficiency and low-pollutant (NO_x and soot) aspects. However, it was uncertain whether both advantages would hold for an engine using various blends of the electrofuels considered. Moreover, the HCCI mode possesses two drawbacks, which have been continuous points of attention during this thesis: the low combustion effi-

ciency and the low power density. Although hydrogen, methane and methanol had already been experimented and simulated under HCCI conditions, it was not the case of ammonia.

The first task performed is the experimental characterisation of ammonia ignition delay under HCCI-like conditions in a rapid compression machine, together with hydrogen seeding (0, 10, and 25%vol.). Ammonia is shown to be resistant to auto-ignition compared to hydrogen, which is itself resistant to auto-ignition compared to gasoline. However ammonia is observed to be also resistant to ringing. Then, the 7 most advanced ammonia kinetic mechanisms are shown unable to correctly predict the measured ammonia behaviour under HCCI conditions. This part is concluded by suggesting improvement paths for the kinetic mechanisms of ammonia based on various sensitivity analysis and comparisons to the ammonia-hydrogen experimental ignition delays.

To meet the objective of a multi-fuel engine, before investigating the performance of such an engine, the required engine design (i.e. compression ratio) and operating conditions (intake temperature and pressure, and equivalence ratio) are needed. A numerical investigation of the electrofuels and their blends is performed using a specifically developed HCCI single-zone model able to correctly predict the ignition timing. Methane and ammonia are shown resistant to auto-ignition compared to hydrogen and methanol, but blending them together shows a strong promotion of their auto-ignition propensity. For example, for a compression ratio of 20:1 and a proper ignition timing, hydrogen and methanol require a 100 °C intake temperature, methane 230 °C and ammonia 315 °C. Although the impact of the various operating conditions on the multi-electrofuel and blending feasibility is quantified, the engine performances in terms of efficiency or pollutant emission is to be experimented.

Ammonia and hydrogen being non-carbonated and at the extremes of the auto-ignition resistance range for the electrofuels considered, that blend is experimented first. Two HCCI engines are used (15:1 and 22:1 compression ratio) to investigate the potential of ammonia for increasing the engine power density. Indeed, ammonia's resistance to ringing might (or not) compensate for its need for high intake temperature regarding power density. With a 200 °C intake temperature, the ammonia fraction in the fuel blend could reach 50%vol. and

90%vol. depending on the compression ratio. The results indicate that ammonia has a 50% IMEP increase potential compared to hydrogen, with a maximum IMEP measured at 5.2 bar and a 4.4 bar IMEP already obtained with a 50%vol. ammonia fuel blend. For comparison, under similar conditions (naturally aspirated, CA50 around TDC, same MPRR and $P_{\max}$, without EGR), the typical IMEP achievable for methane, methanol and gasoline are 4.0 bar, 4.9 bar, and 5.8 bar, respectively, see Section 2.5. The hydrogen combustion damping performed by ammonia is shown to originate from a radical sharing process. To avoid any combustion quenching, the combustion temperature had to reach at least 1700 K for a 50%vol. ammonia fuel blend and 1800 K for a 90%vol. ammonia fuel blend. Regarding NO_x emissions, both ammonia and hydrogen could be operated at maximal load without producing thermal- NO_x , however ammonia led to the production of at least 1000 ppm of fuel- NO_x , which increased to 6000 ppm when the ammonia blending ratio reached 95%vol. For combustion temperatures below 1400 K the large emission of N_2O as been demonstrated. The use of EGR for a reduced oxygen availability was shown effective by providing a two-fold reduction in fuel- NO_x emissions, yet it requires counter-acting measures for the reduced combustion temperature and it did not allow to reach the regulations on NO_x emissions for medium scale stationary engines (< 150 ppm). Therefore an additional SCR or LNT unit would still be needed (yet compatible with the simultaneous reduction of unburned ammonia) unless effective stoichiometric conditions can be reached where drastically less expensive TWC could be used for both ammonia and NO_x reduction.

Of course many questions remain un-answered for the final design of a multi-fuel HCCI application. First, a three fuel configuration could not be experimented, even though methane and methanol lie within ammonia and hydrogen in terms of auto-ignition resistance, nor could the ammonia-methanol or ammonia-methane blends be tested. The former blends would have allowed a reduction in required intake temperature, with a better power density regardless of the blending ratio, as well as a possible promotion from ozone seeding. Second, although the positive impact of a higher intake pressure was experimented, it was not assessed in union to EGR to mitigate its negative effects on the combustion efficiency. Finally, a heavy-duty configuration could not be experimented although it would have been ideal for ammonia (and other ringing resistant fuels such as methane or methanol) given that its optimal power density would be met at higher compression ratios, closer to the optimal global

efficiency. Still, this thesis paves the way to answering those questions by giving numerical and experimental tools as well as reference results.

6.2 Outlook

It shall be as frustrating for you to have only a glimpse of interesting research topics as it has been to me not having enough time to investigate their various aspects.

6.2.1 Optimising the engine architecture for any electro-fuel blend

Similarly to the design performed in Chapter 5, the compression ratio can be optimised so that any given fuel, under the given engine constraints of $P_{\max}$ and MPRR, will render optimal BMEP or BE. The whole design of an architecture for multiple fuels and blending ranges comes down to the question: what are the different fuels that must be operable? and more precisely which level of power density is desired under each blending ratio? For example, in the case of ammonia-hydrogen, although the main goal was the use of neat ammonia, if the design was to be suited to neat hydrogen operation with an acceptable IMEP of 3 bar, no CR higher than 22:1 could be used.

Whatever the fuel to use, these three engine design choices are for certain. First, a flat piston should be used to minimise the crevice volume. Second, heavy-duty engines should be preferred given their higher resistance to cylinder pressure and combustion intensity. Third, the highest intake pressure possible should be used, provided through turbo compression. Indeed, a high intake pressure will increase the resistance to ringing, increase the power density faster than the combustion intensity, and recover exhaust enthalpy. Moreover, the intake pressure can have a significant impact on the auto-ignition resistance as well: one bar boost intake pressure can promote the auto-ignition of ammonia as much as increasing the compression ratio from 22:1 to 27:1, as obtained from the same single-zone model developed in Chapter 3. Eventually, the gain in combustion intensity that even the heavy-duty could not withstand would ideally be compensated by EGR or other damping techniques, see Section 6.2.2.

The next two design choices are tied to a trade-off. First, high stroke-to-bore ratios should be used to minimise the relative importance of piston

crevice volume and possible boundary layer quenching for non-optimal combustion temperatures. Still, for a doubled TDC clearance height, a doubled stroke is needed which shall double the mean piston speed and consequently increase the friction losses. Of course, the combustion efficiency must prevail on the friction losses when using toxic or environmentally-impacting compounds such as methane or ammonia, but the presence of an after-treatment system might influence the trade-off. Second, to maximise the power output the engine rotational speed is ideally increased¹, although it increases the friction losses and consequently reduces the engine lifetime. To find the optimal stroke length and rotational speed for the electrofuels considered, further investigations are required. Still, given the propensity of ammonia and methane for unburned emission production, and given their toxic and environmental aspects, higher stroke-to-bore ratios and rotational speeds than usual should be used.

Finally, an after-treatment system able to effectively deal with the various types of pollutants met in the multi-electrofuel HCCI concept considered must be studied. The challenges to overcome are the diluted, non-stoichiometric, and low temperature exhaust with the presence of unburned fuel (all linked to the HCCI concept), as well as the presence of fuel-NO_x in the case of ammonia combustion or varying exhaust composition in the case of varying fuel blends. In the case where effective stoichiometric conditions are achieved in a systematic and stable manner through EGAR, and that the combined heavy-duty, turbocompressed, and high equivalence ratio operations manage to compensate for the reduced combustion efficiency, then a three way catalytic converter might be used in place of a more expensive selective catalytic reduction system.

6.2.2 Water Direct Injection (WDI)

This section reports the main results of the following master thesis:

Collette, T., Gatin, A. (2019) Increasing HCCI power density through thermal stratification: Impact of water direct injection. Ecole polytechnique de Louvain, UCLouvain. Promoter: Jeanmart, Hervé.

<http://hdl.handle.net/2078.1/thesis:19574>

¹This holds true for stationary applications. Yet, the intentionally low rotational speed of maritime applications could match with ammonia slow HCCI combustion to allow for even higher equivalence ratios.

Although the combined effects of turbocharging and EGR have proved efficient for high power density achievement, see [79], an alternative might be of interest for several reasons. First, as observed with ammonia, low reactivity fuels tend to render unstable operations as the EGR is pushed to effective stoichiometric conditions (although ammonia-EGR was not assessed with turbocharging to increase the combustion temperature). Second, for very reactive fuels such as hydrogen, EGR is not sufficient by itself to compensate for the reactivity gain with an increased equivalence ratio. Finally, better power densities might be obtained with new techniques.

The HCCI combustion principles have become more and more understood through the use of optical engines. Two independent groups (Sandia National Laboratories, and Lund University) have highlighted the crucial role of thermal charge stratification is the occurrence of the auto-ignition process [15, 174–177]. Besides the naturally occurring HCCI thermal stratification (that can be enhanced through piston and admission-port shaping), the main technique currently pursued for stratification is fuel stratification, as in PPC engines with late or sequential injections [178]. Yet, this deteriorates the global emissions due to the presence of rich and high temperature zones. There would be an interest in achieving direct modification of the thermal stratification.

Thinking about hydrogen high reactivity that would ideally be damped by a strong thermal stratification, the idea came to me that the evaporation enthalpy of water could play that role. Indeed, if directly injected into the cylinder during the late compression, water could create a pattern of affected and non-affected regions hence a thermal stratification. Moreover, water being readily recovered from hydrogen exhaust gases, this makes of it the ideal candidate for hydrogen damping. Yet the same idea had already emerged in the mind of Benjamin Lawler, whom as proved the technical feasibility of water direct injection, which creates what he calls Thermally Stratified Compression Ignition (TSCI). Using a combination of EGR (up to effective stoichiometric conditions) and WDI, he increased an hydrogen HCCI gross IMEP from 2 to 5 bar and combustion efficiency from 95.5 to 98.5%. However he increased the NO_x emissions from 0 to 4 g/kg of fuel. Due to the high EGR amounts, only small quantities of water were injected ($\sim 0\text{--}10$ mg/cycle) [179].

WDI being a novel idea with potential, it is worth at least a parallel investigation/confirmation to Lawler works. Moreover, it is of interest assess-

ing the WDI impact alone (without EGR) as it possesses considerable differences/advantages compared to EGR: it does not affect significantly the ignition delay, it does not require significant increases in intake temperatures, it allows cycle-to-cycle control, and it might be less detrimental to low-reactivity fuel cycle-instabilities. Being only indirectly related to my thesis research, I offered the subject for a master thesis investigation. Collette and Gatin [180] successfully investigated and analysed the impact of WDI on neat hydrogen HCCI combustion in the UCLouvain HCCI test bench (flat piston, 22:1 effective CR), by installing a BOSCH HDEV 5.2 direct injector in the firedeck. They studied the impact of the variation of injection timing, injection pressure, injection duration, and injection profile on the combustion.

After having optimised the injection timing, profile, and pressure, Collette and Gatin performed a set of 4 comparative runs. They increased simultaneously the equivalence ratio from 0.2 to 0.5 and the injected water mass from 0 to 72 mg/cycle, see Figure 6.1. The intake temperature was maintained at 80 °C in order to observe the influence of WDI on the ignition delay. We can notice the net IMEP for neat hydrogen increase from 2 to 4.3 bar, although we know from Chapter 5 that the maximal gross IMEP for hydrogen with ideal combustion timings to be 3.2 bar. The increase in power density with WDI is close to that obtained with ammonia: ~45%. Still, judging by the MPRR reported in Figure 6.1, the potential for WDI is even higher since no ringing was obtained under these conditions. The equivalence ratio could have been further increased, ideally with a modification of the intake temperature to maintain an ideal combustion timing. Still, for the installation used, the effect of WDI is observed to taper off for injected masses higher than 50 mg/cycle, indicating that the stratification is gradually being replaced by an overall charge cooling.

To conclude on the potential for WDI, the NO_x emissions stayed below 100 ppm for all the operated conditions, indicating that the thermal-NO_x barrier was not crossed. Unfortunately, the measurements on the combustion efficiency were not workable due to an issue with the lambda sensor.

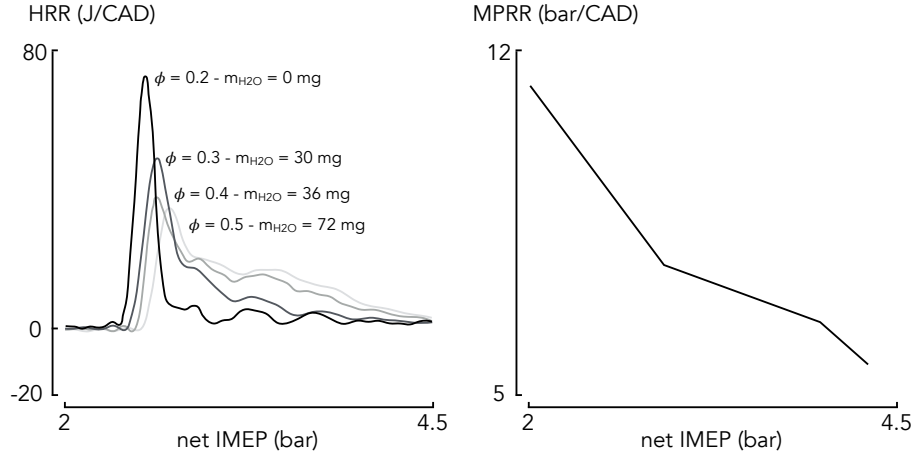


Figure 6.1 – For a simultaneous increase in equivalence ratio and injected mass, the HRR is observed to be elongated and skewed towards the end due to the thermal stratification. For the same operating conditions, the MPRR is observed to decrease with the IMEP, indicating that the WDI potential for power density is high.

6.2.3 Oxygen valorisation and oxy-combustion

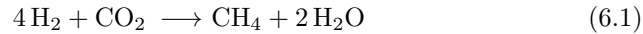
This subsection briefly discusses the possible uses of oxygen addition in the HCCI-CHP multi-electrofuel system. Indeed, from the P2F electrolysis, substantial amounts of oxygen are produced as a by-product. It can be used to improve the HCCI system in interesting ways.

For a maintained fuel content, if nitrogen is replaced by oxygen then the mixture ignition delay and combustion duration shall be influenced. As studied numerically by Li et al. [181] for laminar flames, an oxygen fraction increase from 21 to 30% more than doubles the flame speed, increases the flame temperature by 300 K, and halves the flame thickness (all being an image of the mixture reactivity). Translated to HCCI engines, this poses both advantages and disadvantages. For auto-ignition resistant fuels (such as ammonia or methane) a potential for power density improvement is present through reduced intake temperatures. Yet, for the generally intense HCCI combustion, the admissible fuel loadings shall be limited due to an intensified heat release. As the latter consequence shall prevail to the first one regarding power density, combustion damping techniques (e.g. EGR or WDI) must be used if high power densities

are desired with oxygen addition.

Apart from possibly decreasing the auto-ignition resistance, two configurations for the use of oxygen might be of interest. First, if oxygen is used in place of air and that the engine is operated at stoichiometry, an oxy-combustion is obtained with the sole exhaust gases being water and CO₂, apart from unburned fuel. Second, when EGR is pushed to the limit, as in the experiments of Dec et al. or of Chapter 5, and that a stoichiometric effective equivalence ratio is obtained, the combustion efficiency is observed to decrease. If the nitrogen is replaced by oxygen, even though EGR will serve the same damping purpose, the effective equivalence ratio will not get too close from the stoichiometry and an optimal combustion efficiency can be maintained.

The case of oxy-combustion deserves additional explanations. The conversion from hydrogen to methane through the Sabatier process has a very high efficiency, yet requires CO₂:



For 100 kWh of methane, 5.2 kWh of electricity are necessary to harvest the required CO₂ from a post-combustion coal power plant [182]. To obtain a pure CO₂ stream, the exhaust gases of stoichiometric oxy-combustion only need to be condensed. Moreover, doing so on the decentralised CHP units will provide a set of decentralised pure CO₂ sources. Finally, the whole P2F2P system using stoichiometric oxy-combustion in an HCCI engine can be operated in a closed system, apart from the electricity input and output. This is depicted in Figure 6.2 for the case of methane.

The challenge of such a system is to manage the huge reactivity of HCCI oxy-combustion. To the best of my knowledge, it has never been suggested, so high the HRR would be. Yet, using EGR to produce an effective stoichiometry but with an acceptable fuel quantity is technically feasible within the suggested closed system, see Figure 6.2. In a second step, in order to achieve higher power densities, the amount of EGR required to achieve the effective stoichiometry can ideally be reduced through the use of WDI, hence higher equivalence ratio allowed. Of course, a smart management of the turbocharger and the intake temperature would make the system more mature. I highly recommend this whole concept to be investigated thoroughly, given the potential outcome.

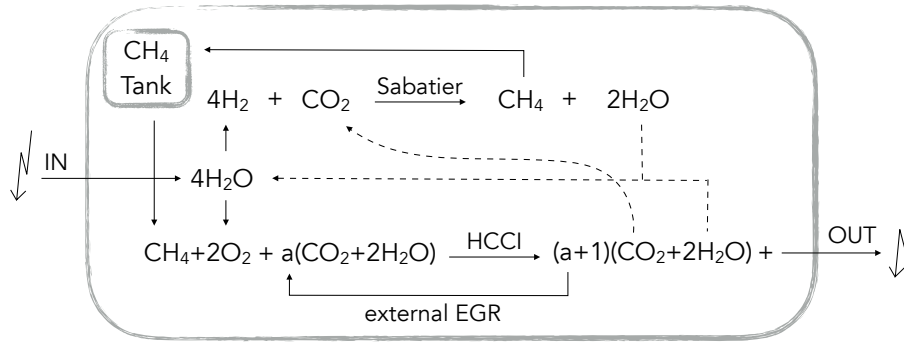


Figure 6.2 – P2F2P system performing the storage of excess electricity into methane and further use in an stoichiometric oxy-combustion HCCI engine. This system uses in a closed cycle the pure oxygen production from the water electrolysis and recovers the pure CO_2 from condensing the exhaust. The amount of EGAR applied to the engine (i.e. 'a' moles) is tuned to control the reactivity and intensity of the combustion.

Bibliography

- [1] IEA. World Energy Outlook 2016. Technical report, International Energy Agency, Paris, 2016.
- [2] IEA. World Energy Outlook 2018. Technical report, International Energy Agency, Paris, 2018.
- [3] P. Gerber, H. Steinfeld, B. Henderson, A. Mottet, C. Opio, J. Dijkman, A. Falcucci, and G. Tempio. Tackling Climate Change Through Livestock - A global assessment of emissions and mitigation opportunities. Technical report, Food and Agriculture Organization of the United Nations, Rome, 2013.
- [4] A. J. McMichael, J. W. Powles, C. D. Butler, and R. Uauy. Food, livestock production, energy, climate change, and health. *The Lancet*, 370:1253–1263, 2007.
- [5] A. négaWatt. Scénario négaWatt 2017-2050. Technical report, 2017.
- [6] E. Dupont, H. Jeanmart, and L. Possoz. Transition énergétique et (dé)croissance économique. *Regards Economiques*, 135:1–26, 2017.
- [7] E. Dupont, R. Koppelaar, and H. Jeanmart. Global available wind energy with physical and energy return on investment constraints. *Applied Energy*, 209(July 2017):322–338, 2018.
- [8] E. Dupont, R. Koppelaar, and H. Jeanmart. Global available solar energy under physical and energy return on investment constraints. *Applied Energy*, 257(September 2019):113968, 2020.
- [9] G. Limpens and H. Jeanmart. Electricity storage needs for the energy transition : An EROI based analysis illustrated by the case of Belgium. *Energy*, 152:960–973, 2018.

- [10] V. Jülch. Comparison of electricity storage options using levelized cost of storage (LCOS) method. *Applied Energy*, 183:1594–1606, 2016.
- [11] A. B. Gallo, J. R. Simões-Moreira, H. K. Costa, M. M. Santos, and E. Moutinho dos Santos. Energy storage in the energy transition context: A technology review. *Renewable and Sustainable Energy Reviews*, 65:800–822, 2016.
- [12] K. Hedegaard and P. Meibom. Wind power impacts and electricity storage - A time scale perspective. *Renewable Energy*, 37(1):318–324, 2012.
- [13] S. Buffa, M. Cozzini, M. D. Antoni, M. Baratieri, and R. Fedrizzi. 5th generation district heating and cooling systems : A review of existing cases in Europe. *Renewable and Sustainable Energy Reviews*, 104(February):504–522, 2019.
- [14] D. Flowers, W. Pitz, S. Aceves, J. Edman, N. Killingsworth, M. Mcnenly, M. Mehl, T. Piggott, M. Sarathy, C. Westbrook, and R. Whitesides. Simulation of High Efficiency Clean Combustion Engines and Detailed Chemical Kinetic Mechanisms Development. Technical report, Laurence Livermore National Laboratory, 2011.
- [15] J. E. Dec. Advanced compression-ignition engines à understanding the in-cylinder processes. *Proceedings of the Combustion Institute*, 32(2):2727–2742, 2010.
- [16] J. M. Gomes Antunes, R. Mikalsen, and A. P. Roskilly. An investigation of hydrogen-fuelled HCCI engine performance and operation. *International Journal of Hydrogen Energy*, 33(20):5823–5828, 2008.
- [17] J. Hyvönen, C. Wilhelmsson, and B. Johansson. The Effect of Displacement on Air-Diluted Multi-Cylinder HCCI Engine Performance. *SAE Technical Paper 2006-01-0205*, 206.
- [18] J. officiel de l’Union européenne. DIRECTIVE (UE) 2015/2193 DU PARLEMENT EUROPÉEN ET DU CONSEIL du 25 novembre 2015 relative à la limitation des émissions de certains polluants dans l’atmosphère en provenance des installations de combustion moyennes. Technical report, 2015.

- [19] O. Schmidt, A. Gambhir, I. Staffell, A. Hawkes, J. Nelson, and S. Few. Future cost and performance of water electrolysis : An expert elicitation study. *International Journal of Hydrogen Energy*, 42(52):30470–30492, 2017.
- [20] M. Radenka and Y. Haoran. Proton Exchange Membrane Water Electrolysis as a Promising Technology for Hydrogen Production and Energy Storage. In *Nanostructures in Energy Generation, Transmission and Storage*, chapter 6, pages 95–109. IntechOpen, 2018.
- [21] C. Lamy. From hydrogen production by water electrolysis to its utilization in a PEM fuel cell or in a SO fuel cell: Some considerations on the energy efficiencies. *International Journal of Hydrogen Energy*, 41(34):15415–15425, 2016.
- [22] M. Gardiner. DOE Hydrogen and Fuel Cells Program: Hydrogen Storage. *U.S Department Of Energy*, pages 1–6, 2009.
- [23] D. Teichmann, W. Arlt, and P. Wasserscheid. Liquid Organic Hydrogen Carriers as an efficient vector for the transport and storage of renewable energy. *International Journal of Hydrogen Energy*, 37(23):18118–18132, 2012.
- [24] H. Wang, X. Zhou, and M. Ouyang. Efficiency analysis of novel Liquid Organic Hydrogen Carrier technology and comparison with high pressure storage pathway. *International Journal of Hydrogen Energy*, 41(40):18062–18071, 2016.
- [25] G. Cinti, D. Frattini, E. Jannelli, U. Desideri, and G. Bidini. Coupling Solid Oxide Electrolyser (SOE) and ammonia production plant. *Applied Energy*, 192:466–476, 2017.
- [26] R. Aslam, K. Müller, M. Müller, M. Koch, P. Wasserscheid, and W. Arlt. Measurement of Hydrogen Solubility in Potential Liquid Organic Hydrogen Carriers. *Journal of Chemical and Engineering Data*, 61(1):643–649, 2016.
- [27] E. R. Morgan. *Techno-Economic Feasibility Study of Ammonia Plants Powered by Offshore Wind*. PhD thesis, University of Massachusetts - Amherst, 2013.

- [28] E. Consultant, Hespul, and Solagro. Etude portant sur l'hydrogène et la méthanation comme procédé de valorisation de l'électricité excédentaire. Technical report, 2014.
- [29] V. Dias, M. Pochet, F. Contino, and H. Jeanmart. Energy and economic costs of chemical storage. *Submitted to Frontiers in Mechanical Engineering*, 2019.
- [30] K. Atsonios, K. D. Panopoulos, and E. Kakaras. ScienceDirect Investigation of technical and economic aspects for methanol production through CO₂ hydrogenation. *International Journal of Hydrogen Energy*, 41(4):2202–2214, 2016.
- [31] European Commission. Reference Document on Best Available Techniques (BAT) for the Manufacture of Large Volume Inorganic Chemicals à Ammonia, Acids and Fertilisers. Technical Report August, 2007.
- [32] M. Matzen, M. Alhajji, and Y. Demirel. Technoeconomics and Sustainability of Renewable Methanol and Ammonia Productions Using Wind Power-based Hydrogen. *Journal of Advanced Chemical Engineering*, 5(3), 2015.
- [33] Insitute for Sustainable Process Technology. Power to Ammonia. Technical report, 2017.
- [34] H2020 Project. Sun to Liquid.
- [35] M. Huijbregts, Z. Steinmann, P. Elshout, G. Stam, F. Verones, M. Vieira, A. Hollander, M. Zijp, and R. van Zelm. ReCiPe 2016 - A harmonized life cycle impact assessment method at midpoint and endpoint level Report I: Characterization. Technical report, National Institute for Public Health and the Environment, 2016.
- [36] Air Pollution Information System. Ammonia.
- [37] M. Z. Jacobson and D. M. Golden. Hydrogen Effects on Climate, Stratospheric Ozone, and Air Pollution Investigators. *Global Climate Energy Project STANFORD UNIVERSITY*, March, 2004.
- [38] S. Verhelst, J. W. Turner, L. Sileghem, and J. Vancoillie. Methanol as a fuel for internal combustion engines. *Progress in Energy and Combustion Science*, 70:43–88, 2019.

- [39] S. M. Aceves, D. Flowers, J. Martinez-frias, F. Espinosa-loza, W. J. Pitz, and R. Dibble. Fuel and Additive Characterization for HCCI Combustion. *SAE Technical Paper 2003-01-1814*, 2003.
- [40] S. J. Szwabowski, S. Hashemi, W. F. Stockhausen, R. J. Natkin, L. Reams, D. M. Kabat, and C. Potts. Ford Hydrogen Engine Powered P2000 Vehicle. *SAE Technical Paper 2002-01-0243*, 2018.
- [41] S. Verhelst and T. Wallner. Hydrogen-fueled internal combustion engines. *Progress in Energy and Combustion Science*, 35(6):490–527, 2009.
- [42] O. Stenlås, M. Christensen, R. Egnell, and B. Johansson. Hydrogen as Homogeneous Charge Compression Ignition Engine Fuel. *SAE Technical Paper 2004-01-1976*, 2004.
- [43] M. Mohamed Ibrahim and A. Ramesh. Investigations on the effects of intake temperature and charge dilution in a hydrogen fueled HCCI engine. *International Journal of Hydrogen Energy*, 39(26):14097–14108, 2014.
- [44] M. Tuner. Review and Benchmarking of Alternative Fuels in Conventional and Advanced Engine Concepts with Emphasis on Efficiency , CO₂ , and Regulated Emissions. *SAE Technical Paper 2016-01-0882*, 2016.
- [45] F. Zhou, J. Fu, D. Li, J. Liu, C.-f. F. Lee, and Y. Yin. Experimental study on combustion , emissions and thermal balance of high compression ratio engine fueled with liquefied methane gas. *Applied Thermal Engineering*, 161(September 2018):114125, 2019.
- [46] S. B. Fiveland, R. Agama, B. Johansson, M. Christensen, J. Hiltner, F. Mauss, and D. N. Assanis. Experimental and simulated results detailing the sensitivity of natural gas hcci engines to fuel composition. *SAE Technical Papers*, 2001-01-36(August):1–12, 2001.
- [47] P. Einewall, P. Tunestål, and B. Johansson. Lean Burn Natural Gas Operation vs . Stoichiometric Operation with EGR and a Three Way Catalyst Reprinted From : SI Combustion and Direct Injection SI Engine Technology. *SAE Technical Paper 2005-01-0250*, 2018.
- [48] M. Christensen, B. Johansson, P. Amnéus, and F. Mauss. Supercharged Homogeneous Charge Compression Ignition. *SAE Technical Paper 980787*, 1998.

- [49] D. Yap, A. Megaritis, S. Peucheret, M. Wyszynski, and H. Xu. Effect of Hydrogen Addition on Natural Gas HCCI Combustion. *SAE Technical Paper 2004-01-1972*, 2004.
- [50] J.-B. Masurier, F. Foucher, G. Dayma, and P. Dagaut. Effect of Additives on Combustion Characteristics of a Natural Gas Fueled HCCI Engine. *SAE Technical Papers. 2014-01-2662*, 2014.
- [51] M. Brusstar, M. Stuhldreher, D. Swain, and W. Pidgeon. High Efficiency and Low Emissions from a Port-Injected Engine with Neat Alcohol Fuels. *SAE Technical Paper 2002-01-2743*, 2002.
- [52] A. Koenig, W. Lee, and W. Bernhardt. Technical and Economical Aspects of Methanol as an Automotive Fuel. *SAE paper no 760545*, 1976.
- [53] J. Coulier and S. Verhelst. Using Alcohol Fuels in Dual Fuel Operation of Compression Ignition Engines : A Review. In *28th CIMAC World Congress*, Helsinki, 2016.
- [54] J. Vavra, S. V. Bohac, L. Manofsky, G. Lavoie, and D. N. Assanis. Knock in Various Combustion Modes in a Gasoline-Fueled Automotive Engine. *ASME 2011 Internal Combustion Engine Division Fall Technical Conference*, 134(August 2012):441–450, 2011.
- [55] K. Hikino and T. Suzuki. Development of Methanol Engine with Autoignition for Low NO_x Emission and Better Fuel Economy. *SAE Technical Paper 891842*, 1989.
- [56] G. Roberts, B. Johnson, and C. Edwards. Prospects for High-Temperature Combustion , Neat Alcohol-Fueled Diesel Engines. *SAE International Journal of Engines*, 7(1), 2014.
- [57] J. B. Masurier, F. Foucher, G. Dayma, and P. Dagaut. Ozone applied to the homogeneous charge compression ignition engine to control alcohol fuels combustion. *Applied Energy*, 160:566–580, 2015.
- [58] C. Zhang and H. Wu. Combustion characteristics and performance of a methanol fueled homogenous charge compression ignition (HCCI) engine. *Journal of the Energy Institute*, 89(3):346–353, 2016.

- [59] R. K. Maurya and A. K. Agarwal. Experimental investigations of performance, combustion and emission characteristics of ethanol and methanol fueled HCCI engine. *Fuel Processing Technology*, 126:38–48, 2014.
- [60] A. Gharehghani. Load limits of an HCCI engine fueled with natural gas , ethanol , and methanol. *Fuel*, 239(April 2018):1001–1014, 2019.
- [61] A. Valera-Medina, H. Xiao, M. Owen-Jones, W. I. David, and P. J. Bowen. Ammonia for power. *Progress in Energy and Combustion Science*, 69:63–102, 2018.
- [62] M. Koike, H. Miyagawa, T. Suzuoki, and K. Ogasawara. Ammonia as a Hydrogen Energy Carrier and Its Application to Internal Combustion Engines. *Journal of the Combustion Society of Japan*, 58(184):99–106, 2016.
- [63] S. M. Grannell, D. N. Assanis, D. E. Gillespie, and S. V. Bohac. Exhaust emissions from a stoichiometric, ammonia and gasoline dual fueled spark ignition engine. In *Proceedings of the ASME Internal Combustion Engine Division*, pages 1–7, Milwaukee, 2009.
- [64] S. M. Grannell, D. N. Assanis, and S. V. Bohac. The operating features of a stoichiometric, ammonia and gasoline dual fueled spark ignition engine. In *Proceedings of ASME International Mechanical Engineering Congress and Exposition*, pages 1–13, Chicago, 2006.
- [65] S. Frigo and R. Gentili. Analysis of the behaviour of a 4-stroke Si engine fuelled with ammonia and hydrogen. *International Journal of Hydrogen Energy*, 38(3):1607–1615, 2013.
- [66] C. Duynslaegher. *Experimental and numerical study of ammonia combustion*. PhD thesis, UCLouvain, 2011.
- [67] A. A. Boretti. Novel heavy duty engine concept for operation dual fuel H₂-NH₃. *International Journal of Hydrogen Energy*, 37(9):7869–7876, 2012.
- [68] A. J. Reiter and S. C. Kong. Demonstration of compression-ignition engine combustion using ammonia in reducing greenhouse gas emissions. *Energy Fuels*, 22(5):2963–2971, 2008.

- [69] K. H. Ryu, G. Zacharakis-Jutz, and S.-c. Kong. Effects of Fuel Compositions on Diesel Engine Performance Using Ammonia-DME Mixtures. *SAE Technical Paper 2013-01-1133*, 2013.
- [70] A. J. Reiter and S.-c. Kong. Combustion and emissions characteristics of compression-ignition engine using dual ammonia-diesel fuel. *Fuel*, 90(1):87–97, 2011.
- [71] J. T. Gray, E. Dimitroff, N. T. Meckel, and R. D. Quillian. Ammonia Fuel â Engine Compatibility and Combustion. *SAE Technical Paper 660156*, 1966.
- [72] P. Van Blarigan. Advanced Internal Combustion Engine Research. *2000 U.S DOE Hydrogen Program Review*, (November):639–656, 2000.
- [73] S. O. Haputhanthri. Ammonia Gasoline Fuel Blends : Feasibility Study of Commercially Available Emulsifiers and Effects on Stability and Engine Performance. *SAE Technical Paper 2014-01-2759*, 2014.
- [74] C. Lhuillier, F. Contino, and V. Universiteit. Combustion Characteristics of Ammonia in a Modern Spark-Ignition Engine. *SAE Technical Paper 2019-24-0237*, 2019.
- [75] C. Lhuillier, P. Brequigny, F. Contino, and C. Rousselle. Performance and Emissions of an Ammonia-Fueled SI Engine with Hydrogen Enrichment. *SAE Technical Paper 2019-24-0137*, 2019.
- [76] F. Ma and Y. Wang. Study on the extension of lean operation limit through hydrogen enrichment in a natural gas spark-ignition engine. *International Journal of Hydrogen Energy*, 33:1416–1424, 2008.
- [77] G. A. Karim, I. Wierzb, and Y. Al-Alousi. Methane-hydrogen mixtures as fuels. *International Journal of Hydrogen Energy*, 21(7):625–631, 1996.
- [78] C. S. Mørch, A. Bjerre, M. P. Gøttrup, S. C. Sorenson, and J. Schramm. Ammonia/hydrogen mixtures in an SI-engine: Engine performance and analysis of a proposed fuel system. *Fuel*, 90(2):854–864, 2011.
- [79] J. E. Dec and Y. Yang. Boosted HCCI for High Power without Engine Knock and with Ultra-Low NOx Emissions - using Conventional Gasoline. *SAE International Journal of Engines*, 3(1):2010–01–1086, 2010.

- [80] A. Valera-medina, M. Gutesa, H. Xiao, D. Pugh, A. Giles, B. Goktepe, R. Marsh, and P. Bowen. Premixed ammonia/hydrogen swirl combustion under rich fuel conditions for gas turbines operation. *International Journal of Hydrogen Energy*, 44(16):8615–8626, 2019.
- [81] E. C. Okafor, K. D. K. A. Somarathne, N. Iki, T. Tsujimura, H. Furutani, and H. Kobayashi. Control of NO_x and other emissions in micro gas turbine combustors fuelled with mixtures of methane and ammonia. *Combustion and Flame*, 211:406–416, 2020.
- [82] G. P. Paper. Feasibility of Methanol as Gas Turbine Fuel. Technical report, 2001.
- [83] T. Zornek, T. Monz, and M. Aigner. Performance analysis of the micro gas turbine Turbec T100 with a new FLOX-combustion system for low calorific fuels. *Applied Energy*, 159:276–284, 2015.
- [84] R. Calabria, F. Chiariello, P. Massoli, and F. Reale. A Biogas Fuelled Micro Gas Turbine Using Dual-Fuel Approach. In *Proceedings of the ASME Turbo Expo*, pages GT2018–76667, Oslo, 2018.
- [85] N. Iki, O. Kurata, T. Matsunuma, T. Inoue, T. Tsujimura, H. Furutani, H. Kobayashi, A. Hayakawa, and E. Okafor. No X Reduction in a Swirl Combustor Firing Ammonia for a Micro. In *Proceedings of the ASME Turbo Expo*, pages GT 2018–75993, Oslo, 2018.
- [86] Siemens. Siemens gas turbine portfolio. Technical report.
- [87] Hydrogenics. HyPM [®] Fuel Cell Power Modules.
- [88] T. Özgür and A. C. Yakaryılmaz. A review : Exergy analysis of PEM and PEM fuel cell based CHP systems. *International Journal of Hydrogen Energy*, 43:17993–18000, 2018.
- [89] M. Rokni. Thermodynamic analysis of SOFC (solid oxide fuel cell)-Stirling hybrid plants using alternative fuels. *Energy*, 61:87–97, 2013.
- [90] G. Cinti, U. Desideri, D. Penchini, and G. Discepoli. Experimental analysis of SOFC fuelled by ammonia. *Fuel Cells*, 14(2):221–230, 2014.

- [91] M. Liu, R. Peng, D. Dong, J. Gao, X. Liu, and G. Meng. Direct liquid methanol-fueled solid oxide fuel cell. *Journal of Power Sources*, 185:188–192, 2008.
- [92] LAZARD. Lazard’s levelized cost of energy analysis - version 11.0. Technical Report November, 2017.
- [93] IEA. Technology Roadmap - Hydrogen and Fuel Cells. Technical report, International Energy Agency, 2015.
- [94] A. Kirubakaran, S. Jain, and R. K. Nema. A review on fuel cell technologies and power electronic interface. *Renewable and Sustainable Energy Reviews*, 13:2430–2440, 2009.
- [95] P. Leone, A. Lanzini, and R. Borchiellini. Operation of a solid oxide fuel cell under direct internal reforming of liquid fuels. *Chemical Engineering Journal*, 191:349–355, 2012.
- [96] A. Kéromnès, W. K. Metcalfe, K. A. Heufer, N. Donohoe, A. K. Das, C. J. Sung, J. Herzler, C. Naumann, P. Griebel, O. Mathieu, M. C. Krejci, E. L. Petersen, W. J. Pitz, and H. J. Curran. An experimental and detailed chemical kinetic modeling study of hydrogen and syngas mixture oxidation at elevated pressures. *Combustion and Flame*, 160(6):995–1011, 2013.
- [97] C. Olm, I. Gy, R. Pálvölgyi, T. Varga, T. Nagy, H. J. Curran, and T. Turányi. Comparison of the performance of several recent hydrogen combustion mechanisms. *Combustion and Flame*, 161(9):2219–2234, 2014.
- [98] M. P. Burke and S. J. Klippenstein. Ephemeral collision complexes mediate chemically termolecular transformations that affect system chemistry. *Nature Chemistry*, (August):1–5, 2017.
- [99] A. A. Konnov. Yet another kinetic mechanism for hydrogen combustion. *Combustion and Flame*, 203:14–22, 2019.
- [100] E. L. Petersen, D. M. Kalitan, S. Simmons, G. Bourque, H. J. Curran, and J. M. Simmie. Methane/propane oxidation at high pressures: Experimental and detailed chemical kinetic modeling. *Proceedings of the Combustion Institute*, 31 I(1):447–454, 2007.

- [101] H. Wang, X. You, A. Joshi, S. Davis, A. Laskin, F. Egolfopoulos, and C. Law. USC Mech Version II. High-Temperature Combustion Reaction Model of H₂/CO/C₁-C₄ Compounds, 2007.
- [102] G. Smith, D. Golden, M. Frenklach, N. Moriarty, B. Eiteneer, M. Goldenberg, C. Bowman, R. Hanson, S. Song, W. Gardinier, V. Lissianski, and Z. Qin. GRI-Mech 3.0.
- [103] Y. Zhang, Z. Huang, L. Wei, J. Zhang, and C. K. Law. Experimental and modeling study on ignition delays of lean mixtures of methane, hydrogen, oxygen, and argon at elevated pressures. *Combustion and Flame*, 159(3):918–931, 2012.
- [104] W. K. Metcalfe, S. M. Burke, S. S. Ahmed, and H. J. Curran. A hierarchical and comparative kinetic modeling study of C₁- C₂hydrocarbon and oxygenated fuels. *International Journal of Chemical Kinetics*, 45(10):638–675, 2013.
- [105] N. Donohoe, A. Heufer, W. K. Metcalfe, H. J. Curran, M. L. Davis, O. Mathieu, D. Plichta, A. Morones, E. L. Petersen, and F. Güthe. Ignition delay times, laminar flame speeds, and mechanism validation for natural gas/hydrogen blends at elevated pressures. *Combustion and Flame*, 161(6):1432–1443, 2014.
- [106] U. Burke, W. K. Metcalfe, S. M. Burke, K. A. Heufer, P. Dagaut, and H. J. Curran. A detailed chemical kinetic modeling, ignition delay time and jet-stirred reactor study of methanol oxidation. *Combustion and Flame*, 165:125–136, 2016.
- [107] J. Li, Z. Zhao, A. Kazakov, M. Chaaos, F. Dryer, and J. Scire. A Comprehensive Kinetic Mechanism for CO, CH₂O, and CH₃OH Combustion. *International Journal of Chemical Kinetics*, 39(3):109–136, 2007.
- [108] H. Feng, J. Zhang, X. Wang, and T. H. Lee. Analysis of auto-ignition characteristics of low-alcohol / iso -octane blends using combined chemical kinetics mechanisms. *Fuel*, 234(April):836–849, 2018.
- [109] K. E. Noorani, B. Akih-kumgeh, and J. M. Bergthorson. Comparative High Temperature Shock Tube Ignition of C₁ - C₄ Primary Alcohols. *Energy Fuels*, 24(8):5834–5843, 2010.

- [110] J. Bian, J. Vandooren, and P. J. Van Tiggelen. Experimental study of the formation of nitrous and nitric oxides in H₂-O₂-Ar flames seeded with NO and/or NH₃. *Symposium (International) on Combustion*, 23(1):379–386, 1991.
- [111] R. P. Lindstedt, F. C. Lockwood, and M. A. Selim. A Detailed Kinetic Study of Ammonia Oxidation. *Combustion Science and Technology*, 108(4-6):231–254, 1995.
- [112] J. A. Miller and P. Glarborg. Modeling the thermal De-NO_x process: Closing in on a final solution. *International Journal of Chemical Kinetics*, 31(11):757–765, 1999.
- [113] Ø. Skreiberg, P. Kilpinen, and P. Glarborg. Ammonia chemistry below 1400 K under fuel-rich conditions in a flow reactor. *Combustion and Flame*, 136(4):501–518, 2004.
- [114] P. Dagaut and A. Nicolle. Experimental and kinetic modeling study of the effect of SO₂ on the reduction of NO by ammonia. *Proceedings of the Combustion Institute*, 30(1):1211–1217, 2005.
- [115] S. J. Klippenstein, L. B. Harding, P. Glarborg, and J. A. Miller. The role of NNH in NO formation and control. *Combustion and Flame*, 158(4):774–789, 2011.
- [116] P. Glarborg, A. D. Jensen, and J. E. Johnsson. Fuel nitrogen conversion in solid fuel fired systems. *Progress in Energy and Combustion Science*, 29(2):89–113, 2003.
- [117] P. Dagaut, P. Glarborg, and M. U. Alzueta. The oxidation of hydrogen cyanide and related chemistry. *Progress in Energy and Combustion Science*, 34(1):1–46, 2008.
- [118] A. A. Konnov and J. De Ruyck. A possible new route for NO formation via N₂H₃. *Combustion Science and Technology*, 168(1):1–46, 2001.
- [119] C. Duynslaegher, F. Contino, J. Vandooren, and H. Jeanmart. Modeling of ammonia combustion at low pressure. *Combustion and Flame*, 159(9):2799–2805, 2012.

- [120] O. Mathieu and E. L. Petersen. Experimental and modeling study on the high-temperature oxidation of Ammonia and related NOx chemistry. *Combustion and Flame*, 162(3):554–570, 2015.
- [121] Y. Song, H. Hashemi, J. M. Christensen, C. Zou, P. Marshall, and P. Glarborg. Ammonia oxidation at high pressure and intermediate temperatures. *Fuel*, 181:358–365, 2016.
- [122] X. He, B. Shu, D. Nascimento, K. Moshhammer, M. Costa, and R. X. Fernandes. Auto-ignition kinetics of ammonia and ammonia / hydrogen mixtures at intermediate temperatures and high pressures. *Combustion*, 206:189–200, 2019.
- [123] B. Shu, S. K. Vallabhuni, X. He, G. Issayev, K. Moshhammer, A. Farooq, and R. X. Fernandes. A shock tube and modeling study on the autoignition properties of ammonia at intermediate temperatures. *Proceedings of the Combustion Institute*, 37:205–211, 2019.
- [124] F. Contino, F. Foucher, C. Mounaïm-Rousselle, and H. Jeanmart. Experimental characterization of ethyl acetate, ethyl propionate, and ethyl butanoate in a homogeneous charge compression ignition engine. *Energy and Fuels*, 25(3):998–1003, 2011.
- [125] J.-B. Masurier. *Experimental study of the HCCI combustion through the use of minor oxidizing chemical species*. PhD thesis, Université d’Orléans, 2016.
- [126] V. E. Kozlov, I. V. Chechet, S. G. Matveev, N. S. Titova, and A. M. Starik. Modeling study of combustion and pollutant formation in HCCI engine operating on hydrogen rich fuel blends. *International Journal of Hydrogen Energy*, 41(5):3689–3700, 2016.
- [127] E. Neshat and R. K. Saray. Effect of different heat transfer models on HCCI engine simulation. *Energy Conversion and Management*, 88:1–14, 2014.
- [128] M. Bissoli, A. Frassoldati, A. Cuoci, E. Ranzi, M. Mehl, and T. Faravelli. A new predictive multi-zone model for HCCI engine combustion. *Applied Energy*, 178:826–843, 2016.

- [129] N. P. Komninou and C. D. Rakopoulos. Heat transfer in hcci phenomenological simulation models: A review. *Applied Energy*, 181:179–209, 2016.
- [130] M. Sjöberg and J. E. Dec. An Investigation of the Relationship Between Measured Intake Temperature, BDC Temperature, and Combustion Phasing for Premixed and DI HCCI Engines. *SAE Technical Paper 2004-01-1900*, 2004.
- [131] F. Contino, P. Dagaut, F. Halter, J. B. Masurier, G. Dayma, C. Mounaïm-Rousselle, and F. Foucher. Screening method for fuels in homogeneous charge compression ignition engines: Application to valeric biofuels. *Energy and Fuels*, 31(1):607–614, 2017.
- [132] N. Bourgeois, S. S. Goldsborough, G. Vanhove, M. Duponcheel, H. Jeanmart, and F. Contino. CFD simulations of Rapid Compression Machines using detailed chemistry: Impact of multi-dimensional effects on the auto-ignition of the iso-octane. *Proceedings of the Combustion Institute*, 36(1):383–391, 2017.
- [133] S. Broekaert, T. D. Cuyper, K. Chana, M. D. Paepe, and S. Verhelst. Assessment of Empirical Heat Transfer Models for a CFR Engine Operated in HCCI Mode. *SAE Technical Paper Series 2015-01-1750*, 2015.
- [134] N. Bourgeois, S. S. Goldsborough, H. Jeanmart, and F. Contino. CFD simulations of Rapid Compression Machines using detailed chemistry: Evaluation of the ‘piston crevice containment’ concept. *Combustion and Flame*, 189:1339–1351, 2018.
- [135] N. Bourgeois. How to ensure the interpretability of experimental data in Rapid Compression Machines ? A method to validate piston crevice designs. *Combustion and Flame*, 198:393–411, 2018.
- [136] S. S. Goldsborough, S. Hochgreb, G. Vanhove, M. S. Wooldridge, H. J. Curran, and C. J. Sung. Advances in rapid compression machine studies of low- and intermediate-temperature autoignition phenomena. *Progress in Energy and Combustion Science*, 63:1–78, 2017.
- [137] N. Bourgeois. *Numerical study of multi-dimensional effects in Rapid Compression Machines*. PhD thesis, UCLouvain, 2017.

- [138] Y. Zhang, O. Mathieu, E. L. Petersen, G. Bourque, and H. J. Curran. Assessing the predictions of a NO_x kinetic mechanism on recent hydrogen and syngas experimental data. *Combustion and Flame*, 182(x):122–141, 2017.
- [139] J. Li, H. Huang, N. Kobayashi, C. Wang, and H. Yuan. Numerical study on laminar burning velocity and ignition delay time of ammonia flame with hydrogen addition. *Energy*, 126(x):796–809, 2017.
- [140] H. Nakamura, S. Hasegawa, and T. Tezuka. Kinetic modeling of ammonia/air weak flames in a micro flow reactor with a controlled temperature profile. *Combustion and Flame*, 185:16–27, 2017.
- [141] P. Glarborg, J. A. Miller, B. Ruscic, and S. J. Klippenstein. Modeling nitrogen chemistry in combustion. *Progress in Energy and Combustion Science*, 67:31–68, 2018.
- [142] S. Gersen, N. B. Anikin, A. V. Mokhov, and H. B. Levinsky. Ignition properties of methane/hydrogen mixtures in a rapid compression machine. *International Journal of Hydrogen Energy*, 33(7):1957–1964, 2008.
- [143] A. Cuoci, A. Frassoldati, T. Faravelli, and E. Ranzi. A computational tool for the detailed kinetic modeling of laminar flames: Application to C₂H₄/CH₄ coflow flames. *Combustion and Flame*, 160(5):870–886, 2013.
- [144] A. Cuoci, A. Frassoldati, T. Faravelli, and E. Ranzi. OpenSMOKE++: An object-oriented framework for the numerical modeling of reactive systems with detailed kinetic mechanisms. *Computer Physics Communications*, 192:237–264, 2015.
- [145] A. M. Dean and J. W. Bozzelli. Combustion Chemistry of Nitrogen. In *Gardiner W.C. Gas-Phase Combustion Chemistry*, chapter 2. New-York, springer edition, 2000.
- [146] P. Glarborg, K. Dam-Johansen, and J. A. Miller. The reaction of ammonia with nitrogen dioxide in a flow reactor: Implications for the NH₂+NO₂ reaction. *International Journal of Chemical Kinetics*, 27(12):1207–1220, 1995.

- [147] S. Xu and M. Li. Kinetics of synthesis of isobutyl propionate over amberlyst-15. *International Journal of Chemical Kinetics*, 41(11):667–677, 2009.
- [148] A. M. Mebel, E. W. G. Diau, M. C. Lin, and K. Morokuma. Theoretical Rate Constants for the $\text{NH}_3 + \text{NO}_x \rightarrow \text{NH}_2 + \text{HNO}_x$ ($x = 1, 2$) Reactions by ab Initio MO/VTST Calculations. *The Journal of Physical Chemistry*, 100(18):7517–7525, 1996.
- [149] G. Harris, R. Atkinson, and J. Pitts. Kinetics of the Reactions of the OH Radical with Hydrazine and Methylhydrazine. *The Journal of Physical Chemistry*, 83(20):2557–2559, 1979.
- [150] P. Glarborg, K. Dam-Johansen, J. A. Miller, R. J. Kee, and M. E. Coltrin. Modeling the thermal DeNO_x process in flow reactors. Surface effects and nitrous-oxide formation. *International Journal of Chemical Kinetics*, 26(4):421–436, 1994.
- [151] J. Otomo, M. Koshi, T. Mitsumori, and H. Iwasaki. ScienceDirect Chemical kinetic modeling of ammonia oxidation with improved reaction mechanism for ammonia / air and ammonia / hydrogen / air combustion. *International Journal of Hydrogen Energy*, 43(5):3004–3014, 2017.
- [152] J. C. Kramlich and W. P. Linak. Nitrous oxide behavior in the atmosphere, and in combustion and industrial systems. *Progress in Energy and Combustion Science*, 20(2):149–202, 1994.
- [153] P. E. Yelvington. *Design of a Viable Homogeneous-Charge Compression-Ignition (HCCI) Engine : A Computational Study with Detailed Chemical Kinetics*. PhD thesis, Massachusetts Institute of Technology, 2004.
- [154] J. A. Eng. Characterization of Pressure Waves in HCCI Combustion. *SAE Technical Paper 2002-01-2859*, 2002.
- [155] N. Seignour, J. Masurier, B. Johansson, G. Dayma, P. Dagaut, and F. Foucher. ScienceDirect Ozone-assisted combustion of hydrogen : A comparison with isooctane. *International Journal of Hydrogen Energy*, (In press), 2019.

- [156] F. Halter, P. Higelin, and P. Dagaut. Experimental and Detailed Kinetic Modeling Study of the Effect of Ozone on the Combustion of Methane. *Energy Fuels*, 25(7):2909–2916, 2011.
- [157] F. Foucher, P. Higelin, C. Mounam-Rousselle, and P. Dagaut. Influence of ozone on the combustion of n-heptane in a HCCI engine. *Proceedings of the Combustion Institute*, 34(2):3005–3012, 2013.
- [158] M. ØStberg and K. I. M. Dam-Johansen. Empirical modeling of the selective non-catalytic reduction of NO: comparison with large-scale experiments and detailed kinetic modeling. *Chemical Engineering Science*, 49(12):1897–1904, 1994.
- [159] E. Pipitone. A New Simple Friction Model for S. I. Engine. *SAE Technical Paper 2009-01-1984*, 2009.
- [160] N. Lam, M. Tuner, P. Tunestal, A. Andersson, S. Lundgren, and B. Johansson. Double Compression Expansion Engine Concepts: A Path to High Efficiency. *SAE International Journal of Engines*, 8(4):2015–01–1260, 2015.
- [161] R. D. Reitz. Reciprocating Internal Combustion Engines. Technical report, 2014.
- [162] S. K. Chen and P. F. Flynn. Development of a Single Cylinder Compression Ignition Research Engine. *SAE paper no 650733*, 1965.
- [163] F. J. Jiménez-Espadafor, M. T. Garcia, J. A. Herrero, and J. A. Villanueva. Effect of turbulence and external exhaust gas recirculation on HCCI combustion mode and exhaust emissions. *Energy and Fuels*, 23(9):4295–4303, 2009.
- [164] T. D. Pedersen and J. Schramm. Reduction of HCCI Combustion Noise Through Piston Crown Design. *SAE Technical Paper 2010-01-1487*, 2010.
- [165] M. Pochet, I. Truedsson, F. Foucher, H. Jeanmart, and F. Continio. Ammonia-Hydrogen Blends in Homogeneous-Charge Compression-Ignition Engine. *SAE Technical Paper 2017-24-0087*, 2017.

- [166] S. Frigo, R. Gentili, and F. De Angelis. Further insight into the possibility to fuel a SI engine with ammonia plus hydrogen. *SAE Technical Papers*, 2014-Novem(Ci), 2014.
- [167] H. M. Hunter, J. W. Makepeace, T. J. Wood, O. S. Mylius, M. G. Kibble, J. B. Nutter, M. O. Jones, and W. I. David. Demonstrating hydrogen production from ammonia using lithium imide â Powering a small proton exchange membrane fuel cell. *Journal of Power Sources*, 329:138–147, 2016.
- [168] R. Stone. *Introduction to Internal Combustion Engines*. Palgrave MacMillan, 4th - 2012 edition, 1985.
- [169] J. officiel de l’Union européenne. DIRECTIVE 2010/75/UE DU PARLEMENT EUROPÉEN ET DU CONSEIL du 24 novembre 2010 relative aux émissions industrielles (prévention et réduction intégrées de la pollution) (refonte). Technical report, 2010.
- [170] P. Mendoza-villafuerte, R. Suarez-bertoa, B. Giechaskiel, F. Riccobono, C. Bulgheroni, C. Astorga, and A. Perujo. Science of the Total Environment NO_x, NH₃, N₂O and PN real driving emissions from a Euro VI heavy-duty vehicle . Impact of regulatory on-road test conditions on emissions. *Science of the Total Environment*, 609(x):546–555, 2017.
- [171] N. Jiang, N. Lu, and K. Shang. High-Efficiency Removal of NO_x From Flue Gas by Multitooth Wheel-Cylinder Corona Discharge Plasma Facilitated Selective Catalytic Reduction Process. *IEEE Transactions on Plasma Science*, 44(11), 2016.
- [172] J. Wang and M. Crocker. N₂O mitigation in a coupled LNT-SCR system N₂O Mitigation in a Coupled LNT â SCR System. *Catalysis Letters*, 142:1167–1174, 2012.
- [173] T. Wittka, B. Holderbaum, and P. Dittmann. Experimental Investigation of Combined LNT + SCR Diesel Exhaust Aftertreatment. *Emission Control Science and Technology*, pages 167–182, 2015.
- [174] J. E. Dec, W. Hwang, and M. Sjöberg. An investigation of thermal stratification in HCCI engines using chemiluminescence imaging. *SAE Technical Paper 2006-01-1518*, 2006.

- [175] M. Sjöberg, J. E. Dec, and N. P. Cernansky. Potential of Thermal Stratification and Combustion Retard for Reducing Pressure-Rise Rates in HCCI Engines , Based on Multi-Zone Modeling and Experiments. *SAE Technical Paper 2005-01-0113*, 2005.
- [176] M. Richter, J. Engström, A. Franke, and M. Aldén. The Influence of Charge Inhomogeneity on the HCCI Combustion Process. *SAE Technical Paper 2000-01-2868*, 2000.
- [177] A. Hultqvist, M. Christensen, B. Johansson, M. Richter, J. Nygren, J. Hult, and M. Aldén. The HCCI Combustion Process in a Single Cycle at Speed Fuel Tracer LIF and Chemiluminescence Imaging. *SAE Technical Paper 2002-01-0424*, 2002.
- [178] C. Li. *Stratification and Combustion in the Transition from HCCI to PPC*. PhD thesis, Lund University Faculty of Engineering, 2018.
- [179] B. Lawler, D. Splitter, J. Szybist, and B. Kaul. Thermally Stratified Compression Ignition: A new advanced low temperature combustion mode with load flexibility. *Applied Energy*, 189:122–132, 2017.
- [180] T. Collette and A. Gatin. Increasing HCCI power density through thermal stratification Impact of water direct injection. Master Thesis. Technical report, UCLouvain, 2019.
- [181] J. Li, H. Huang, N. Kobayashi, Z. He, Y. Osaka, and T. Zeng. Numerical study on effect of oxygen content in combustion air on ammonia combustion. *Energy*, 93:2053–2068, 2015.
- [182] D. Connolly, B. V. Mathiesen, and I. Ridjan. A comparison between renewable transport fuels that can supplement or replace biofuels in a 100 *Energy*, 73:110–125, 2014.
- [183] JCGM 100. JCGM 100:2008 - Evaluation of measurement data - Guide to the expression of uncertainty in measurement. Technical Report September, 2008.
- [184] S. Bhaduri, F. Contino, H. Jeanmart, and E. Breuer. The effects of biomass syngas composition, moisture, tar loading and operating conditions on the combustion of a tar-tolerant HCCI (Homogeneous Charge Compression Ignition) engine. *Energy*, 87:289–302, 2015.

- [185] S. Bhaduri, B. Berger, M. Pochet, H. Jeanmart, and F. Contino. HCCI engine operated with unscrubbed biomass syngas. *Fuel Processing Technology*, 157, 2017.
- [186] G. Petitpas, R. Whitesides, J. Dernotte, and J. Dec. Refining Measurement Uncertainties in HCCI/LTGC Engine Experiments. *SAE Technical Papers*, 2018-April:1–12, 2018.
- [187] K. Liu, Y. B. Xie, and C. L. Gui. A comprehensive study of the friction and dynamic motion of the piston assembly. *Journal of Engineering Tribology*, 212(3):221–226, 1998.
- [188] F. Payri, P. Olmeda, C. Guardiola, and J. Martín. Adaptive determination of cut-off frequencies for filtering the in-cylinder pressure in diesel engines combustion analysis. *Applied Thermal Engineering*, 31(14-15):2869–2876, 2011.
- [189] A. Savitzky and M. J. E. Golay. Smoothing and differentiation of data by simplified least squares procedures. *Analytical Chemistry*, 36(8):1627–1639, 1964.
- [190] S. Butterworth. On the theory of filter amplifiers. *Experimental wireless the wireless engineer*, 7:536–541, 1930.
- [191] S. S. Bhaduri. *Experimental Studies on HCCI Combustion of Biomass Syngas Towards Tar Tolerant Operation*. PhD thesis, UCLouvain, 2015.
- [192] P. Tunestål. *Estimation of the in-cylinder air/fuel ratio of an internal combustion engine by the use of pressure sensors*. PhD thesis, Lund, 2001.
- [193] S. Gopujkar, J. Worm, and D. Robinette. Methods of Pegging Cylinder Pressure to Maximize Data Quality. *SAE Technical Paper 2019-01-0721*, 2019.
- [194] K. Lee, M. Yoon, and M. Sunwoo. A study on pegging methods for noisy cylinder pressure signal. *Control Engineering Practice*, 16(8):922–929, 2008.
- [195] M. Tazerout, O. Le Corre, and S. Rousseau. TDC Determination in IC Engines Based on the Thermodynamic Analysis of the Temperature-Entropy Diagram. *SAE Technical Paper 1999-01-1489*, 1999.

- [196] P. Tunestål. TDC Offset Estimation from Motored Cylinder Pressure Data based on Heat Release Shaping. *Oil & Gas Science and Technology à Rev. IFP Energies nouvelles*, 66(4):705–716, 2011.
- [197] S. Lee, C. Bae, R. Prucka, G. Fernandes, Z. S. Filipi, and D. N. Assanis. Quantification of Thermal Shock in a Piezoelectric Pressure Transducer. *SAE Technical Paper 2005-01-2092*, 2018.
- [198] P. V. Puzinauskas, W. M. Mathis, and M. A. Dzieciuch. Quantification and Modeling the Effects of Thermal Shock on Combustion Pressure Transducers. *SAE Technical Paper 2001-01-3491*, 2018.
- [199] W. L. Brown. Methods for Evaluating Requirements and Errors in Cylinder Pressure Measurement. *SAE Technical Paper 670008*, 1967.
- [200] A. Torregrosa, J. Martin, R. Novella, and K. Thein. Estimation of the in-cylinder residual mass fraction at intake valve closing in a two-stroke high-speed engine. *International Journal of Engine Research*, pages 1–18, 2018.
- [201] A. Irimescu, C. Tornatore, L. Marchitto, and S. S. Merola. Compression ratio and blow-by rates estimation based on motored pressure trace analysis for an optical spark ignition engine. *Applied Thermal Engineering*, 61(2):101–109, 2013.
- [202] R. Miller, S. Russ, C. Weaver, E. Kaiser, C. Newman, G. Davis, and G. Lavoie. Comparison of Analytically and Experimentally Obtained Residual Fractions and NOX Emissions in Spark-Ignited Engines. *SAE Technical Paper 982562*, 2018.
- [203] A. B. Dempsey, S. J. Curran, and R. M. Wagner. A perspective on the range of gasoline compression ignition combustion strategies for high engine efficiency and low NOx and soot emissions : Effects of in-cylinder fuel stratification *. *International Journal of Engine Research*, 17(8):897–917, 2016.
- [204] G. Kalghatgi and R. Head. Combustion Limits and Efficiency in a Homogeneous Charge Compression Ignition Engine. *International Journal of Engine Research*, 7:215–236, 2006.

- [205] S. H. Chan and J. Zhu. Exhaust Emission Based Air-Fuel Ratio Model (I): Literature Reviews and Modelling. *SAE Technical Paper 961020*, 1996.
- [206] A. J. Shahlari, E. Kurtz, C. Hocking, and S. Antonov. Correlation of cylinder pressure-based engine noise metrics to measured microphone data. *International Journal of Engine Research*, pages 1–22, 2014.
- [207] K. Yazdani, E. Amani, and H. Naderan. Multi-objective optimizations of the boot injection strategy for reactivity controlled compression ignition engines. *International Journal of Engine Research*, pages 1–22, 2018.
- [208] R. D. Meininger, C.-b. M. Kweon, M. T. Szedlmayer, K. Q. Dang, N. B. Jackson, C. A. Lindsey, J. A. Gibson, and R. H. Armstrong. Knock criteria for aviation diesel engines. *International Journal of Engine Research*, 18(7):752–762, 2017.
- [209] P. A. Caton and J. T. Pruitt. Homogeneous charge compression ignition of hydrogen in a single-cylinder diesel engine. *International Journal of Engine Research*, 10(1):45–63, 2009.
- [210] S. Broekaert, T. De Cuyper, M. De Paepe, and S. Verhelst. Evaluation of empirical heat transfer models for HCCI combustion in a CFR engine. *Applied Energy*, 205(February):1141–1150, 2017.
- [211] J. Chang, O. Güralp, Z. Filipi, D. N. Assanis, T.-W. Kuo, P. Najt, and R. Rask. New Heat Transfer Correlation for an HCCI Engine Derived from Measurements of Instantaneous Surface Heat Flux. *SAE Technical Paper 2004-01-2996*, 2004.
- [212] S. Hensel, F. Sarikoc, F. Schumann, H. Kubach, and U. Spicher. Investigations on the Heat Transfer in HCCI Gasoline Engines. *SAE International Journal of Engines 2009-01-1804*, 2(1):1601–1616, 2009.
- [213] H. S. Soyhan, H. Yasar, H. Walmsley, B. Head, G. T. Kalghatgi, and C. Sorousbay. Evaluation of heat transfer correlations for HCCI engine modeling. *Applied Thermal Engineering*, 29(2-3):541–549, 2009.

A wealth of information creates a poverty of attention.

Herbert Simon



Post-processing and uncertainty analysis of piston engine experimental data
(full version)

This appendix is an extended version of the following publication:

Pochet, M., Jeanmart, H., & Contino, F. (2019). *Uncertainty quantification from raw measurements to post-processed data: a general methodology and its application to an Homogeneous-Charge Compression-Ignition engine*. International Journal of Engine Research, 1-29, <https://doi.org/10.1177/1468087419892697>.

A mathematical methodology to obtain any engine parameter uncertainty is first derived and then used to obtain the uncertainty expressions of the physical quantities of the most generic HCCI research engine (mass-flow induced mixture with $C_uH_yO_xN_zS_w$ fuel). Those expressions are then applied on an existing hydrogen HCCI test bench. This includes the uncertainty propagation chain from sensor specifications, user calibrations, intake control, in-cylinder processes, and post-processing techniques.

Directly measured physical quantities have uncertainties of around 1%, depending on the sensor quality (e.g. pressure, volume, etc.), but indirectly

measured quantities relying on modeled parameters have uncertainties higher than 5% (e.g. wall heat losses, in-cylinder temperature, gross heat release, pressure rise rate, etc.), with a major influence from the selected models. Other findings that such an analysis can bring relate, for example, to the physical quantities driving the uncertainty, and to the ones that can be neglected.

The obtained numeric values serve the general purpose of alerting the experimenter on uncertainty order of magnitudes. The developed methodology shall be used and adapted by the experimenter willing to study the uncertainty propagation in their setup or willing to assess the adequacy of a sensor performance.

This appendix aims at giving a rigorous basis for ICE experimental data post-processing and uncertainty analysis: list of the various elements requiring post-processing, mathematical derivation of uncertainty expressions and application examples. To provide a consistent uncertainty study, this paper is based on the “Guide to the expression of uncertainty in measurement” [183]. The required mathematical tools are first developed and then applied to derive the uncertainty expressions for the most generic research HCCI engine having a mass-flow induced mixture with $C_uH_yO_xN_zS_w$ fuel. The engine inputs and outputs are analysed in a systematic and comprehensive way including influence from bottle impurities, acquisition noise perturbation, detailed air composition, etc. Of course, models must be used to perform post-processing steps or determine some of the required parameters (such as recirculated gases, wall heat losses, effective compression ratio, top dead center offset, blow-by, etc.), yet their related uncertainty is included in the calculations. These models and the choice thereof make the obtained results less general. However the developed methodology can be applied to many other cases that would be of interest to the reader, and requiring more adapted models. Finally the obtained results give qualitative information and orders of magnitude regarding various uncertainty aspects:

- 1 Which are the elements of the propagation chain that induce the highest share of the uncertainty?
- 2 Which are the elements that are negligible?
- 3 How does the uncertainty varies along the engine cycle: where is it critical?
- 4 What are the required sensor characteristics to obtain the engine outputs

in a given desired uncertainty?

- 5 Which are the physical quantities with relative uncertainties below 1%, and above 1%?
- 6 How does the models and post-processing techniques used influence the uncertainties?

This appendix is intended to two kinds of readers. First, all the investigated uncertainties are broken down to highlight the most impacting factors in the uncertainty propagation chain. Then, the required equations to apply the uncertainty analysis techniques are derived in a consistent way to help the reader willing to do so: from the statistical basics, using manufacturer data or through the procedure of sensor calibration, to the final uncertainty.

A.1 The mathematical tools for uncertainty analysis

This section is dedicated to obtaining and illustrating the mathematics of uncertainty analysis for manufacturer and user-calibrated sensors, as well as for any test bench physical quantities.

When a physical quantity is measured (then called a *measurand*), the uncertainty on the measurand comes out two ways: (1) from the statistical methods used to analyse them, that is called *Type A* uncertainty, and (2) from any other method, called *Type B* uncertainty. Often, but not systematically, *Type A* uncertainties represent the stochastic behaviour of the measurand (i.e. its repeatability), and *Type B* uncertainty represent the lack of accuracy of the measurement system, see Figure A.1. The global uncertainty on a measurand is obtained by combining both types of uncertainties as follows:

$$u_{global} = \sqrt{u_{TypeA}^2 + u_{TypeB}^2} . \quad (A.1)$$

A.1.1 Type A uncertainties

Let a physical quantity X be measured through n independent repetitions x_i , having for mean value $\bar{x}$. If $n \rightarrow \infty$, $\bar{x}$ becomes the best estimate of X ,

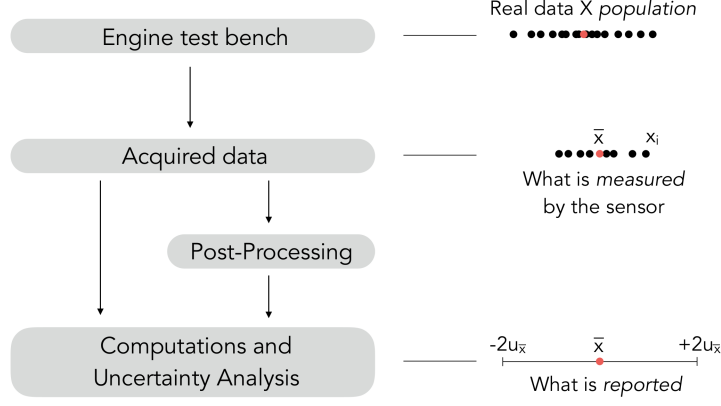


Figure A.1 – Uncertainties and their occurrence within an experimental setup.

which we shall denote $\bar{x}_\infty$. The uncertainty on the measurement of X , $u_{\bar{x}}$, is the region $\bar{x} \pm u_{\bar{x}}$ within which $\bar{x}_\infty$ lies with a given probability. We take the uncertainty on the measurand, or more specifically on $\bar{x}$, as the standard deviation of the **mean**: $u_{\bar{x}} = s_{\bar{x}}$. Indeed, as the standard deviation of the **measure** s_x characterises the probability of having the $n + 1_{th}$ measurement within $\bar{x} \pm s_x$, the standard deviation of the **mean** $s_{\bar{x}} = s_x/\sqrt{n}$ quantifies how well $\bar{x}$ estimates $\bar{x}_\infty$. This is called *Type A* uncertainty:

$$u_{TypeA} = u_{\bar{x}} = s_{\bar{x}} = \sqrt{\frac{1}{n \cdot (n-1)} \sum_{i=1}^n (x_i - \bar{x})^2} . \quad (A.2)$$

For the simplicity of notations, and given that the uncertainty sought for in this paper is always about the true value of a given measurand (i.e. $\bar{x}_\infty$), $u_{\bar{x}}$ will be denoted u_x .

For an assumed normal distribution of X and an infinite sample of measurements, the region $\bar{x} \pm s_{\bar{x}}$ represents a 68.27% probability that $\bar{x}_\infty$ falls in between it. Finally, the notation $U_{P,X}$ denotes the uncertainty on the measurement of X with a $P\%$ probability. For a normally distributed parameter X we have:

$$U_{95,X} = 1.96 \cdot u_{\bar{x}} = 1.96 \cdot s_{\bar{x}} \quad (A.3)$$

Given the considered physics in this research (relatively low temperature and pressure phenomena with generally continuous behaviours), the measur-

ands are all assumed to showcase normal distribution patterns. Therefore if limited repeated measurements of X are made (i.e. a random sample from a population of possible measurements), the *t-Student* distribution theory can be used to compute a representative value for u_X . This is called *Type A* uncertainty.

However, $\bar{x}_\infty$ is by no mean the true value of the physical quantity X , and *Type A* uncertainty is not the complete image of the uncertainty on a measurand. A measurement tool must first be calibrated in all conditions of interest in order to capture a sensible value of a physical quantity. The uncertainty on a measurand is therefore the combination of the uncertainty of the calibration process of the sensor (*Type B*) and the uncertainty of the measure variability (*Type A*). If the measurement tool is calibrated, and that $U_{95,X}$ combines *Type A* and *Type B* uncertainties, there is a 95% probability that X (and not $\bar{x}_\infty$) belongs to the interval $\bar{x} \pm U_{95,X}$.

A.1.2 Type B uncertainties and sensor calibration

The calibration outcome is a mathematical function that links the raw measurement signal (usually a current or a potential difference) of a known reference physical quantity to the actual value of the reference physical quantity itself, see Figure A.2.

Still, calibration procedures and measurement tools suffer from imprecision, which leads to errors that when combined together form the *Type B* uncertainty. For the calibration of a measurement tool with raw signals $x_{i,j}$ (each point n_i of the calibration range is repeated n_j times) and with the reference physical quantity y_i , the following mathematical description of the whole *Type B* uncertainty can be derived and is illustrated in Figure A.2.

Usually the chosen mathematical function is a linear regression which leads to a linearity error ϵ between the output of the linear regression and the reference value:

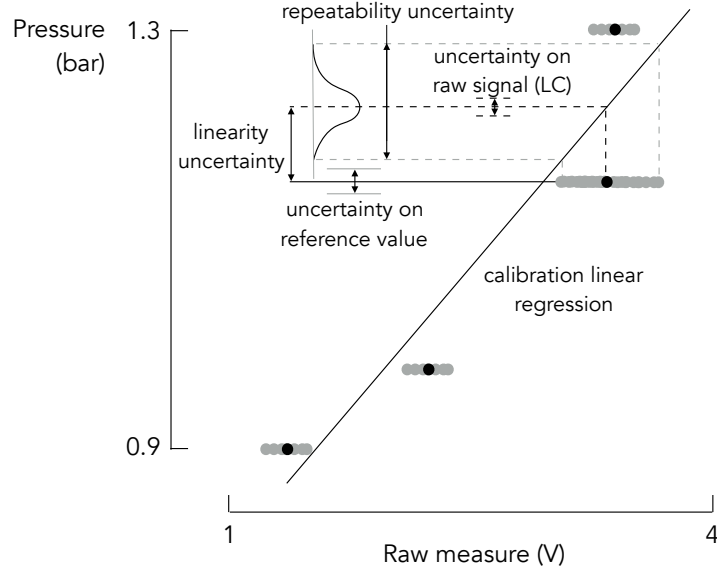


Figure A.2 – Example of hypothetical calibration results for a pressure sensor.

$$\begin{bmatrix} y_1 \\ \vdots \\ y_{n_i} \end{bmatrix} = \begin{bmatrix} \bar{x}_1 & 1 \\ \vdots & \vdots \\ \bar{x}_{n_i} & 1 \end{bmatrix} \cdot \begin{bmatrix} a \\ b \end{bmatrix} + \begin{bmatrix} \epsilon_1 \\ \vdots \\ \epsilon_{n_i} \end{bmatrix}, \quad (\text{A.4})$$

where $\epsilon_i = y_i - \tilde{y}_i = y_i - (a\bar{x}_i + b)$ and (a, b) minimises $\sum_{i=1}^{n_i} \epsilon_i^2$ such that the root mean square of the errors of the linear regression is minimised. Also, $\bar{x}_i$ is the average of the n_j measurements of the reference physical quantity y_i :

$$\bar{x}_i = \frac{1}{n_j} \sum_{j=1}^{n_j} x_{i,j}. \quad (\text{A.5})$$

From this linearity error follows a linearity uncertainty (also called accuracy uncertainty):

$$u_{lin} = \sqrt{\frac{\sum_{i=1}^{n_i} \epsilon_i^2}{n_i - 2}} / \sqrt{n_i - 2}, \quad (\text{A.6})$$

with $n_i - 2$ degrees of freedom due to the linear regression being optimised for (a, b) . The formulation of Equation (A.6) is nothing else than the standard

deviation of the mean of the errors.

Then, repeated measurements of a physical quantity under the same conditions can lead to different measured values, hence repeatability errors. Note that repeatability errors must only be taken into account in *Type B* uncertainty if no measurement repetitions are available under the *Type A* uncertainty. Here, as for *Type A* repeatability uncertainty, the repeatability uncertainty of a set of measurement derives directly from the standard deviation of the mean of the measurand:

$$u_{\text{repeat}} = \sqrt{\max_{i \in n_i} \left\{ \frac{s_{x_i}^2}{n_j} \right\}} , \quad (\text{A.7})$$

where

$$s_{x_i} = \sqrt{\frac{\sum_{j=1}^{n_j} (\bar{x}_i - x_{i,j})^2}{n_j - 1}} . \quad (\text{A.8})$$

Next, the selected calibration points along the calibration range induce a fitting uncertainty that depends on the spacing between the points and eventual repetitions. Indeed, each linearity error must be weighted as a function of the "loneliness" of its measurement point compared to the average "loneliness":

$$u_{\text{fit}} = \sqrt{\frac{\sum_{i=1}^{n_i} \epsilon_i^2}{n_i - 2} \cdot \left(\frac{1}{(n_i - 2)} + \frac{(\bar{\bar{x}} - \bar{x}_i)^2}{S_{sx}} \right)} , \quad (\text{A.9})$$

where

$$S_{sx} = \sum_{i=1}^{n_i} (\bar{\bar{x}} - \bar{x}_i)^2 , \quad (\text{A.10})$$

and

$$\bar{\bar{x}} = \frac{1}{n_i} \sum_{i=1}^{n_i} \bar{x}_i . \quad (\text{A.11})$$

Further, two last points must be considered: the uncertainty on the reference value itself and the smallest variation that can be captured by the measurement tool leading to what is called the *Least Count (LC)* uncertainty:

$$u_{\text{ref}} = \text{from manufacturer ISO standards, often negligible} , \quad (\text{A.12})$$

and

$$u_{LC} = \frac{LC/2}{\sqrt{3}} . \quad (\text{A.13})$$

Consequently, all these uncertainties combine together to form the general *Type B* uncertainty:

$$u_{TypeB} = \sqrt{u_{\text{ref}}^2 + u_{LC}^2 + u_{\text{lin}}^2 + u_{\text{fit}}^2 + \sum u_{\text{drift}}^2 + u_{\text{repeat}}^2} , \quad (\text{A.14})$$

where u_{drift} relates to the uncertainty induced by any perturbation that can lead to a raw signal drift such as temperature, pressure, long-term stability, operator, etc. To be obtained, such influences are captured by performing the calibration process under the various conditions of interest:

$$u_{\text{drift}} = \sqrt{u_{TypeB, \text{perturbed}}^2 - u_{TypeB, \text{without drift term}}^2} . \quad (\text{A.15})$$

Finally, in the event of calibration uncertainties obtained from the manufacturer without any precision on the measurement distribution, the probability distribution of the measurements is assumed to be uniform where the standard uncertainty is therefore $u = U_{\text{given}}/\sqrt{3}$. Unspecified *Type B* sub-uncertainties in manufacturer calibration reports are assumed negligible or taken into account under another sub-uncertainty.

A.1.3 Combined uncertainties

The final case to consider is the one of combined uncertainties, that is the global uncertainty on a physical quantity that is computed from several measurands. In such a case, there is no concept of *Type A* or *Type B* uncertainties since the physical quantity is not directly measured by a sensor. Let us consider the physical quantity Z computed as follows from the measurands W_i :

$$Z = f(W_1, \dots, W_n) \quad (\text{A.16})$$

The uncertainty on Z will be proportional to the global uncertainty (i.e. *Type A* and *Type B*) on W_i by the rate of change of Z with respect to W_i . Given that second order derivative factors can be neglected, and assuming that the W_i are uncorrelated between them, one obtains the uncertainty on Z through the first-order Taylor series approximation of Z :

$$u_Z = \sqrt{\sum_{i=1}^n \left(\frac{\partial f}{\partial W_i} \right)^2 \cdot u_{W_i}^2} \quad (\text{A.17})$$

The proposed methodology for uncertainty derivation can be summarised in a step-by-step procedure to follow. It can be used by the reader willing to derive the uncertainty associated to a specific case not dealt with in this paper.

A - For physical quantities directly measured (i.e. measurands):

- 1) Derive the *Type A* uncertainty (Equation (A.2)) from repeated measurements to assess the statistical uncertainty of a measurand;
- 2) Derive the *Type B* uncertainty associated to the sensor specifications (Equation (A.14)) or by following the calibration procedure detailed in Appendix A.1.2 for missing sensor specifications;
- 3) Derive the overall uncertainty using Equation (A.1);

B - For physical quantities that are not directly measured:

- 1) Develop the expression of the physical quantity until it contains only measurands or physical quantities for which the uncertainty is known;
- 2) Use Equation (A.17) to obtain the uncertainty expression of the physical quantity of interest;
- 3) For an unknown uncertainty within the developed expression, start again at step A or B;

A.2 Experimental setup used for illustration

To illustrate the uncertainties of the engine input and output measurands, the HCCI test bench of UCLouvain is used. This setup has already been described in previous studies [184, 185], but is further detailed here. The engine is a single-cylinder Diesel engine (Yanmar L100V) retrofitted for HCCI operation: the diesel injector has been replaced by a high frequency piezoelectric pressure sensor and the piston bowl has been filled through welding to render a flat piston surface with an effective compression ratio of (22:1). The setup configuration is displayed in Figure A.3 and the engine characteristics are given in Table A.1.

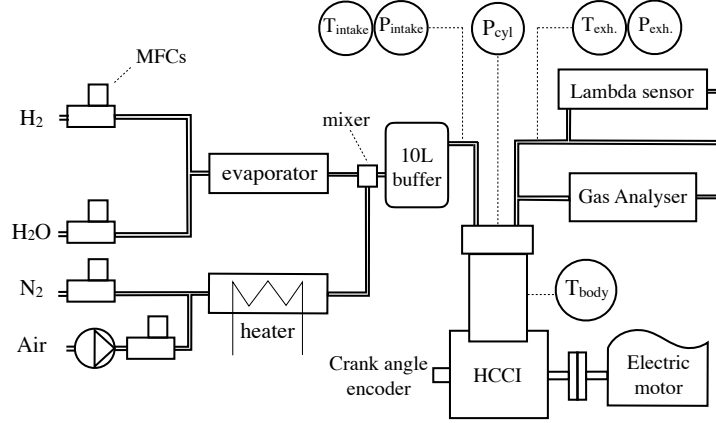


Figure A.3 – Setup for hydrogen combustion and exhaust analysis at various intake temperatures, equivalence ratios and synthetic EGR conditions.

Table A.1 – Engine specifications

YANMAR L100V	Air-cooled
	Single-cylinder
Bore - Stroke	86 - 75 mm
Connecting rod length	145 mm
Geometric compression ratio	23.0:1
Effective compression ratio	21.9:1
Rotational speed	1500 RPM
IVO	340 CAD ATDC
IVC	127 CAD BTDC
EVO	127 CAD ATDC
EVC	380 CAD ATDC
Wall temperature	105°C

All the gaseous inputs are controlled by Brooks Mass Flow Controller (MFC) SLA-585X. The intake water for EGR emulation is controlled by a

Bronkhorst Coriflow M14. The in-cylinder pressure is measured by a relative piezoelectric AVL GH15D transducer and its signal is amplified by a AVL FlexIFEM 2P2E. The crank angle is acquired every 0.1 CAD by a Heidenhain ROD 426 rotary encoder. The intake and exhaust pressures are measured with absolute piezoelectric KISTLER 4260 transducers. The intake, exhaust and cylinder-wall temperature measurements are done by type K thermocouples. The torque sensor is a HBM T40B Torque flange mounted between the HCCI engine and the electric motor. Finally the exhaust oxygen concentration is measured by a BOSCH LSU 4.9 lambda sensor. These sensors and related manufacturer-uncertainties are reported in Table A.3. All the controls and acquisitions were performed by a National Instruments Compact Rio 9022 real-time controller operated with the LabView environment. The uncertainty linked to the acquisition methodology is negligible for NI cards ($U_{95} \leq 0.03\%$) and high precision resistors ($U_{95} \leq 0.005\%$).

The intake temperature has been varied in order to obtain various CA50 (Crank Angle at which 50% of the combustion heat has been released). The raw experimental data were obtained for the following operating conditions:

Table A.2 – *Experimental operating conditions*

Intake temperature	50-130°C
Intake pressure	1 bar
Equivalence ratio	0.1-0.3

The manufacturer specifications and personal calibrations for all the sensors used in the HCCI test bench of UCLouvain are summarised in Table A.3. All the reported uncertainties are uniform distribution (and not U95) if not stated otherwise.

Table A.3 – Equipment uncertainty data summary. *FS* = Full Scale, *PV* = Processed Value (i.e. reading).

MFC (Brooks SLA585X)	Uncertainty
Accuracy	$\pm 0.7\%$ PV
Repeatability	$\pm 0.2\%$ FS
Temperature zero drift	$\pm 0.05\%$ FS/K
Temperature span drift	$\pm 0.05\%$ FS/K
Pressure drift	$\pm 0.429\%$ PV/bar
Bottles (Air Liquide)	Purity
H ₂	99.5%
N ₂	99.999%
H ₂ O	99.999%
Lambda sensor (Bosch LSU 4.9)	Uncertainty
Personal Calibration	0.3 O ₂ % (U95)
Crank Angle Encoder (Heidenhain ROD 426)	Uncertainty
Least Count θ_{LC}	0.1 CAD
TDC manual positioning	± 0.05 CAD
In-cylinder Pressure (AVL GH15D)	Uncertainty
Signal amplifier (AVL FlexIFEM 2P2E)	
Accuracy _{pzt}	$\pm 0.3\%$ FS
Accuracy _{G,pzt}	$\pm 0.11\%$ FS

Tshock _{pzt}	± 0.3 bar
Temperature drift _{pzt}	± 0.5 bar
TSC _{pzt}	$\pm 0.25\%$ FS
Accuracy _{amp}	$\pm 0.01\%$ FS
Accuracy _{G,amp}	$\pm 0.5\%$ (U95)
Δp_{peg}	$u_{P_{in}}$
u_{α}	θ_{LC}
Range	150 bar

Intake & Exhaust Pressure (KISTLER 4260)	Uncertainty
Linearity + Repeatability	$\pm 0.2\%$ FS
Age drift	$\pm 0.1\%$ PV/year
Temperature drift	$\pm 1.5\%$ PV
Range	5 bar
Personal Calibration ($u_{TypeB,p_{in}}$)	± 510 Pa

Torque (HBM T40B)	Uncertainty
Accuracy	$\pm 0.01\%$ FS
Repeatability	$\pm 0.06\%$ FS (U95)
Least Count	0.5 Nm
Temperature drift	$\pm 0.005\%$ PV/K
Temperature zero drift	$\pm 0.005\%$ FS/K
Range	500 Nm

TDC Volume	Uncertainty
Caliper precision	± 0.05 mm

Piston machining ± 0.01 mm

A.3 Uncertainties on the directly measured physical quantities

This section applies the statistical methodology of uncertainty quantification to the measurands of a generic engine, and illustrates each case with the considered hydrogen HCCI engine test bench. In a first step, only the uncertainties of the engine measurands that do not need post-processing techniques to be derived, apart from the effective compression ratio, are investigated. These measurands include every physical quantity unrelated to the engine internal way of working such as intake mole flow rates, crank angle evolution, intake and exhaust pressures, or exhaust gas concentrations, see Figure A.4. The engine input and output uncertainties of interest will be developed here-under in a consistent way: from the measurand definition to its uncertainty formulation and analysis of the influencing factors.

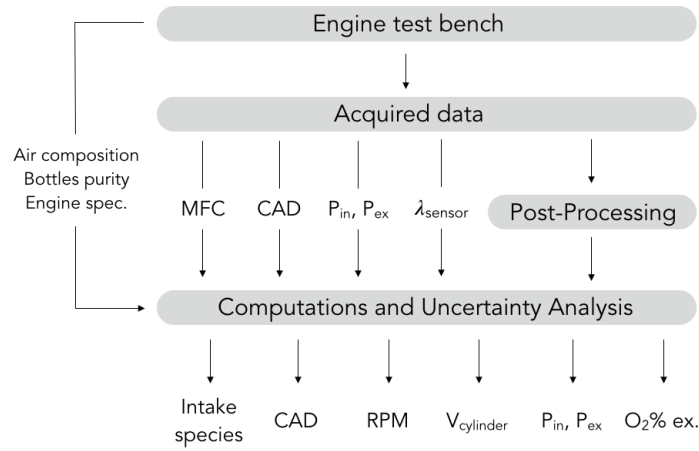


Figure A.4 – Measurand uncertainties that can be directly obtained from the acquired data without post-processing.

A.3.1 Intake species uncertainties

In this test bench configuration, the gases and liquids that enter the engine are controlled by the MFCs. Being the control device of a continuous flow, in addition to a measuring device, a MFC does not offer repeated measurements of the same physical quantity, hence no *Type A* uncertainties are available for them. Therefore each MFC flow uncertainty, $u_{\dot{n},x}$, will be composed of the manufacturer-provided *Type B* uncertainties. In our example test bench, MFCs are manufactured by BROOKS and their uncertainties are: accuracy, repeatability, and temperature-pressure-age drift, as reported in the summary Table A.3. The x^{th} MFC uncertainty is obtained from Equation (A.17):

$$u_{\dot{n},x}^2 = u_{\text{lin}}^2 + u_{\text{drift,p}}^2 + u_{\text{drift,Tspan}}^2 + u_{\text{drift,Tzero}}^2 + u_{\text{repeat}}^2 . \quad (\text{A.18})$$

The total flow entering the engine, and related uncertainty, are obtained from the MFC flows and uncertainties:

$$\dot{n} = \sum_x^{\text{MFCs}} \dot{n}_x \quad (\text{A.19}) \quad \rightarrow \quad u_{\dot{n}} = \sqrt{\sum_x^{\text{MFCs}} u_{\dot{n},x}^2} . \quad (\text{A.20})$$

The respective species flow, $\dot{n}_i$, entering the engine are obtained knowing that a $w_{x,i}$ fraction of the MFC flow is made up of the i^{th} species:

$$\dot{n}_i = \sum_x^{\text{MFCs}} w_{x,i} \cdot \dot{n}_x \quad (\text{A.21}) \quad \rightarrow \quad u_{\dot{n},i} = \sqrt{\sum_x^{\text{MFCs}} (w_{x,i} \cdot u_{\dot{n},x})^2} . \quad (\text{A.22})$$

MFCs being hooked up to bottles or other fluid supply, the uncertainty on the species mass flow rates that enter the engine are not only influenced by the MFC, but as well by the purity and composition of the fluid supply.

Bottle impurities

The purity level of the bottles is never 100%. If a bottled mixture-gas has a i^{th} species fraction of $Pu\%$ purity, it means that its fraction contains at least $Pu\%$ of the prescribed species. Therefore, to translate that in terms of uncertainty, there is a given probability distribution (that we assume to be uniform in case of a lack of precision from the supplier) of the gas purity between $Pu\%$ and

100%. The uncertainty on its real fraction is $u_{w_i} = w_i \cdot (1 - Pu/100/\sqrt{3})$. The uncertainty on the i^{th} species delivered by the MFCs is:

$$u_{\dot{n},i} = \sqrt{\sum_x^{\text{MFCs}} \left[(w_{x,i} \cdot u_{\dot{n},x})^2 + (\dot{n}_x \cdot u_{w_{x,i}})^2 \right]} . \quad (\text{A.23})$$

In the case of our example setup, the bottles purity are reported in the summary Table A.3. For levels of purity as low as the one of hydrogen (99.5%, most common values reaching readily 99.99%) the impact on the species mass flow rate uncertainty U_{95} is minor. Indeed, taking the data for the hydrogen MFC and using Equation (A.18) we obtain $U_{95,\text{MFC}_{\text{H}_2}} = 1.17\%$. Taking into account the bottle purity and using Equation (A.23) we obtain $U_{95,\text{intake},\text{H}_2} = 1.21\%$. Impact of bottle purity on the global species flow uncertainty can be seen in Figure A.5.

Dry air composition

Precise dry air composition is in molar percentages: 78.08 % N₂, 20.95 % O₂, 0.93 % Ar, 0.04 % CO₂, the rest being neglected. Compared to the generally assumed 79% N₂ - 21% O₂, the only difference for oxygen is 0.05% molar. Argon and carbon dioxide being inert it does not induce any combustion-related error to consider them as nitrogen. Let us consider this oxygen 0.05% molar difference as an impurity. Considering a false composition of 79% N₂ - 21% O₂ instead of 79.05% - 20.95% is equivalent as using a 100% purity nitrogen bottle and a 99.52% purity oxygen bottle, as this impurity encloses the possibility of having the real concentration of 79.05% - 20.95%. In such a case, and using at their nominal flow rates the same MFCs as the ones described in the previous section, we obtain that the uncertainty on oxygen flow is $U_{95,\text{intake},\text{O}_2} = 1.24\%$ instead of 1.20% if we had considered 100% purity oxygen bottles. This approximation is minor compared to the inherent uncertainties of the MFCs, and can therefore be used. Impact of dry air composition on the global air flow uncertainty can be seen in Figure A.5.

However, regarding dry air molar mass taking argon into account renders $Mm = 28.96 \text{ g/mol}$, which is the generally accepted value for dry air, instead of $Mm = 28.84 \text{ g/mol}$ for oxygen and nitrogen only. Regarding heat capacity at 20°C, taking argon into accounts renders $C_p = 29.09 \text{ J/molK}$ instead of $C_p = 29.17 \text{ J/molK}$. Carbon dioxide can be neglected in terms of mass and

heat capacity. Therefore we should account for the presence of argon in air through the following composition: 78.1 % N₂, 20.95 % O₂, 0.95 % Ar. This also reduces the uncertainty on the oxygen flow rate since the correct fraction is accounted for.

Air moisture content

The compressed air supply used at the UCLouvain lab is at 7 bar, and it is cooled down to the ambient temperature. Being in Belgium, let us consider a realistic Belgian "worst" case: 100% relative humidity at 20°C. This represents a partial water vapour pressure of 2336 Pa, being equal to the saturation pressure at 20°C. Considering an isothermal compression up to 7 bar (well depicting a polytropic compression followed by an isobaric cooling to the ambient temperature), the partial water vapour pressure ramps up to 16138 Pa, while the saturation pressure stays at 2336 Pa. Consequently, a significant part of the water vapour content condenses (and is purged) and we are left with a partial pressure of 2336 Pa. This represents a 0.33% molar water vapour content in the air. Therefore, if it is taken into account in the uncertainty analysis as an impurity of 0.33%, it changes the uncertainty on a nominal air flow from $U_{95,air} = 1.24\%$ to 1.29%. For such compression and outdoor temperatures, moisture content and related uncertainty is negligible and an over-cooler is non-essential. Impact of air moisture content on the global air flow uncertainty can be seen in Figure A.5.

The relative impact of a 99.5% purity bottle on the intake species uncertainty is reported in Figure A.5, as well as the impact of air moisture content (compressed from 1 atm - 20°C - 100% relative humidity towards 7 bar and chilled to 20°C). Both are found highly negligible next to the MFC uncertainties.

Finally, the actual flow rate being processed has an impact on the relative MFCs uncertainty. Indeed, MFCs have a substantial zero error that was termed previously as "repeatability". In the case of BROOKS MFC the zero uncertainty amounts to $\pm 0.2\%$ of the Full Scale (FS), and the linearity uncertainty amounts to $\pm 0.7\%$ of the Process Value (PV). When the PV is close to the full scale, the zero uncertainty is three times smaller than the linearity

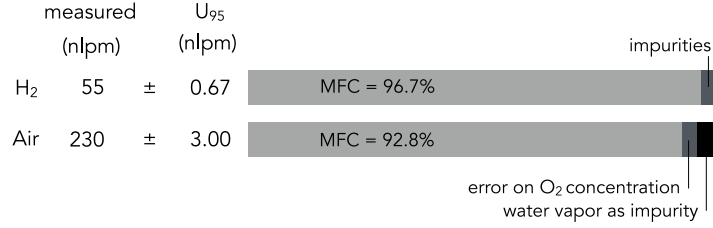


Figure A.5 – Relative impact of MFC, impurities, and air composition uncertainties on the final intake hydrogen and air uncertainties. Performed at 100% of the MFC nominal flow rate, for a hydrogen purity of 99.5% and an air line compressed from 1 atm - 20°C - 100% relative humidity to 7 bar - 20°C.

uncertainty and the global relative U_{95} is around 1%. But when the MFC is used in its lower range, 10% of the FS for example, zero errors grow in relative impact and the global relative U_{95} rises to 6%.

A.3.2 Crank Angle (CA) and RPM uncertainty

The instantaneous CA position and the average engine RPM are both derived from the rotary encoder signal. A proper characterisation of the CA is mandatory as it is conventionally used as the reference for other measurements acquisition. Moreover, many physical quantities are CA-resolved: the HRR, the MPRR, etc. On the other hand, the RPM is only used to compute average physical quantities (e.g. cycle mole content from the MFC flow rates).

If the rotary encoder used has a potential of pulses per revolution higher than what it is asked to send (e.g. 8000 pulses achievable for a CA resolution of 0.1), no uncertainty/overflow can arise from this part. Regarding the CA, the only uncertainty left is the LC uncertainty (i.e. the smallest variation that can be captured by the measurement tool). Since the probability to fall within that smallest variation is 100% and with a uniform distribution, the least count uncertainty is obtained as follows:

$$u_{LC} = \frac{LC/2}{\sqrt{3}} . \quad (A.24)$$

Translating into equations the considerations about the CA count, and using Equations (A.17) and (A.24) for the LC uncertainty and combined uncertainties, we obtain:

$$\theta_{\text{real}} \in [\theta \pm \text{LC}/2] \ ,$$

$$u_{\theta}^2 = u_{\theta, \text{LC}}^2 \ , \quad (\text{A.25})$$

$$U_{95, \theta} = \pm 0.058 \text{ CAD} \ .$$

Another uncertainty exists on the CAD, and arises as this sensor is manually positioned at zero when the piston is manually positioned at TDC. This uncertainty is referred to as *TDC offset* and will be dealt with the pressure uncertainties, see Appendix A.4.2. Indeed, the TDC offset is managed by shifting the pressure signal along the CAD.

Regarding the average engine RPM, it is measured by calculating the time needed to perform 5 complete engine cycles, or 10 revolutions. Since the rotary encoder acquisition card (National Instrument 9411) has a frequency of 300 kHz, and that it is handled in time by the 2.4 MHz National Instrument CompactRio 9022, no error can be made measuring the time taken to complete the 10 revolutions, Δ_{time} . Indeed, for a 1500 RPM engine speed, the 0.1 CAD pulse happen at a frequency of 90 kHz. Therefore the engine RPM uncertainty is only linked to the measurement of 10 revolutions. The associated absolute error being the LC, the uncertainty is:

$$\text{RPM} = \frac{\frac{3600 \pm \text{LC}/2}{360}}{\Delta_{\text{time}}} \cdot 60 \ ,$$

$$u_{\text{RPM}}^2 = \left(\frac{u_{\theta, \text{LC}}}{6 \cdot \Delta_{\text{time}}} \right)^2 \ , \quad (\text{A.26})$$

$$U_{95, \text{RPM}} = \pm 0.024 \text{ RPM} \ .$$

The obtained RPM uncertainty is negligible next to the other uncertainties.

A.3.3 Cylinder volume uncertainty

The instantaneous in-cylinder volume impacts many engine output characteristics such as the heat release, combustion timings, IMEP, etc. It is important to evaluate its uncertainty impact on the engine output uncertainties. The uncertainty on the cylinder volume is derived from its definition:

$$V = \frac{\pi D_b^2 S}{4} \left[\frac{1}{CR-1} + 0.5 \left(\frac{2L}{S} + 1 - \cos(\theta) - \sqrt{\left(\frac{2L}{S} \right)^2 - \sin^2(\theta)} \right) \right] , \quad (\text{A.27})$$

where D_b is the cylinder bore diameter, S the piston stroke, L the connecting rod length, and $CR = V_{\text{BDC}}/V_{\text{TDC}}$ the compression ratio. The bore, stroke and connecting rod dimensions are known up to the machining uncertainty u_{mach} . Finally adding the crank angle θ , the volume counts 5 variables and its uncertainty is obtained from Equation (A.17):

$$\begin{aligned} u_V^2 = & \left(\frac{\partial V}{\partial \theta} u_\theta \right)^2 \\ & + \left(\frac{-\pi D_b^2 S}{4(CR-1)^2} u_{CR} \right)^2 \\ & + \left(\frac{\partial V}{\partial L} u_{\text{mach}} \right)^2 \\ & + \left(\frac{\partial V}{\partial S} u_{\text{mach}} \right)^2 \\ & + \left(\frac{2V}{D_b} u_{\text{mach}} \right)^2 , \end{aligned} \quad (\text{A.28})$$

with the partial derivatives readily obtained from Equation (A.27).

Geometric compression ratio uncertainty

For geometric aspects, the TDC and BDC volumes, and consequently the *geometric* CR, are measured physically. For simple geometries like in our example test bench, a micrometric caliper is sufficient. In the case of more complex piston and firedeck geometries, other techniques such as water weighing can be used with uncertainties depending on the mass measurement uncertainty and operator/repetition/calibration rigor. The uncertainty on the geometric compression ratio is readily obtained from its definition and Equation (A.17):

$$CR_{\text{geom}} = \frac{V_{\text{BDC}}}{V_{\text{TDC}}} , \quad (\text{A.29})$$

$$u_{CR}^2 = \left(\frac{1}{V_{\text{TDC}}} \right)^2 u_{V_{\text{BDC}}}^2 + \left(\frac{-V_{\text{BDC}}}{V_{\text{TDC}}^2} \right)^2 u_{V_{\text{TDC}}}^2 , \quad (\text{A.30})$$

where V_{TDC} and V_{BDC} are the respective chamber volumes at BDC and TDC. The TDC volume determination is a tedious process containing several parts measurements, as displayed on Figure A.6. Most of these parts are measured

using a precision-caliper: bore diameter ' D_b ', piston diameter ' D_p ', crevices height ' cr ', valve seats diameter ' D_v ', valve clearance compared to firedeck ' cl_v ', and cylinder head gasket ' g ' having an uncertainty of u_{cal} . The clearance between the piston and the firedeck is measured in two parts: one with a caliper ' cl_{cal} ' and one being determined by the flat piston surface machining ' cl_{mach} ' having an uncertainty of u_{mach} .

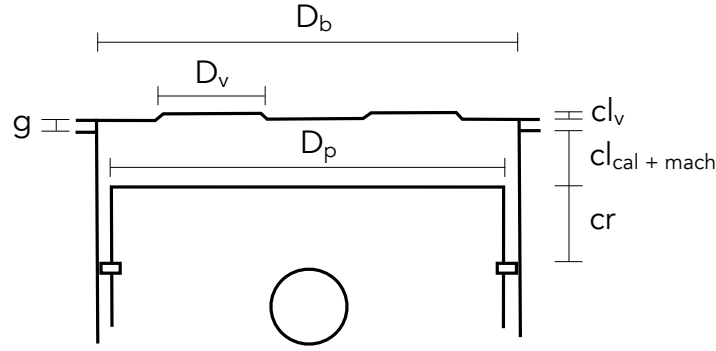


Figure A.6 – Sketch of all the dimensions required for precise TDC volume measurement.

$$V_{TDC} = \frac{\pi D_b^2}{4} (cl_{cal} + cl_{mach} + g) + \frac{\pi(D_b^2 - D_p^2)}{4} cr + \frac{\pi D_v^2}{4} cl_v \quad (A.31)$$

$$V_{BDC} = V_{TDC} + \frac{\pi D_b^2}{4} S, \quad (A.32)$$

where ' S ' is the engine stroke.

Applying Equation (A.17) on the above equations renders their uncertainties and the contribution breakdown of V_{BDC} and V_{TDC} is displayed in Figure A.7 and yields $u_{CR, geometric} = 0.40$. The dimensions impacting the clearance height control 95% of V_{TDC} uncertainty, which itself accounts for 99% of the compression ratio uncertainty.

	$u \text{ (m}^3\text{)}$				
V_{TDC}	$\pm 2.44 \text{ e-}7$	$D_b = 1.7\%$	$D_p + D_v + c_r + c_{lv} = 1.7\%$		
		$Cl_{cal} = 32.3\%$	$Cl_{mach} = 32.3\%$	$g = 32.3\%$	
V_{BDC}	$\pm 5.14 \text{ e-}7$	$D_b = 63.8\%$		$Cl_{cal} = 9.0\%$	$Cl_{mach} = 9.0\%$
				$g = 9.0\%$	$S = 9.0\%$
				$D_p + D_v + c_r + c_{lv} = 0.4\%$	

Figure A.7 – Contribution breakdown of the various parameters influencing the uncertainty of TDC and BDC volumes. Only the cylinder bore diameter and the parameters composing the gross chamber height (cl_{cal} , cl_{mach} , g , S) have a significant impact.

Effective compression ratio uncertainty

Still, once the engine is running, the gas trapped in the cylinder is only affected by the *effective* compression ratio due to delayed IVC, blow-by, or other volumes imperfections that couldn't be measured (e.g. piston ring crevices, valve-seat deflections, etc.). Therefore, for thermodynamic aspects such as the heat release analysis, the compression ratio to be used in Equation (A.27) is the effective one. Knowing the uncertainty on this parameter allows to better grasp the impact it has on in-cylinder pressure variations and therefore to more accurately predict the heat release. Being derived from the heat release, which is itself derived from pressure and volume uncertainties, the uncertainty on the effective compression ratio will need iterations to converge since it is itself required for the volume uncertainty. Two iterations are sufficient for that matter. Several methods exist for estimating the effective compression ratio but all depend on the heat release analysis with the effective compression ratio being the one to minimise the norm of the motoring gross heat release around the TDC. This uncertainty therefore depends on the heat release uncertainties, which are developed in Appendix A.4.12. In our example case, both the methods from Irimescu and Tazerout are used. The uncertainty on the effective compression ratio is obtained by finding the compression ratio that, when inserted into the heat release Equation (A.45), is such that the newly obtained gross heat release norm equals the norm of the measured gross heat release plus the uncertainty on the gross heat release itself. This translates mathematically by:

$$U_{95,CR_e} = |CR_e - CR_{e,U}| \text{ ,} \quad (\text{A.33})$$

with

$$CR_{e,U} \text{ s.t. } \sum |\Delta Q_{\theta, CR_{e,U}}| = \sum |\Delta Q_{\theta, CR_e} \pm u_{\Delta Q_{\theta, CR_e}}|, \quad (\text{A.34})$$

where ΔQ_{θ} is the instantaneous variation in gross heat release. Its uncertainty, $u_{\Delta Q_{\theta}}$, is obtained in Appendix A.4.12. As a final note, as one can either increase or decrease the compression ratio to increase the gross heat release norm, the uncertainty on the compression ratio is therefore taken as the case maximising the gap between CR_e and $CR_{e,U}$. The obtained uncertainty for the effective compression ratio is nearly half of the uncertainty on the geometric compression ratio.

The geometric and effective cylinder volume uncertainties are compared and displayed in Figure A.8.

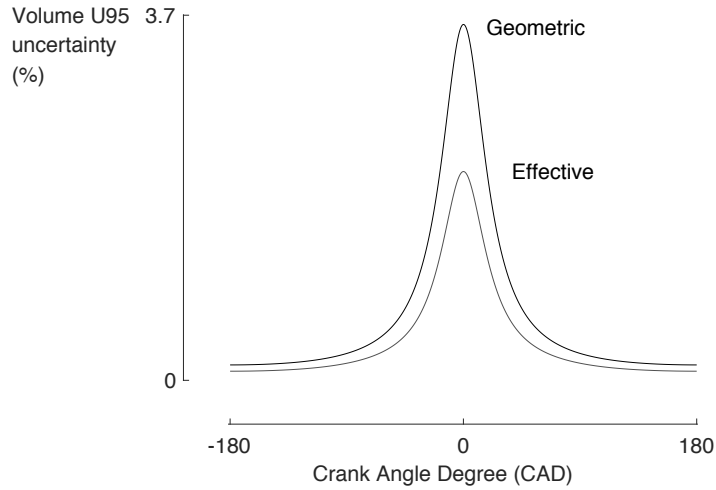


Figure A.8 – Relative chamber volume uncertainty. Geometric and effective uncertainties are close to one another. The example test bench engine using a high compression ratio ($\sim 23:1$), hence a small TDC volume, its related uncertainty is severely impacted.

Their similar order of magnitude is explained by both compression ratio uncertainties being close to each other. Indeed, the uncertainties on the geometric

and effective compression ratio have been estimated to $u_{\text{CR, geometric}} = 0.40$ and $u_{\text{CR, effective}} = 0.24$, which represents 99.9% of the volume uncertainty at TDC, and 84% at peak piston velocity. Finally, considering the impact that volume uncertainties have on in-cylinder temperature and heat release rates, the need for precise engine part dimensions knowledge or quality post-processing for effective compression ratio determination is important.

Rigidity and piston wrist pin offset

The previous in-cylinder volume considerations are imprecise over two aspects: first they assume perfectly rigid engine parts, and second they neglect the offset at the piston wrist pin.

Regarding rigidity, the piston, the connecting rod, the crank shaft, the bearings, and finally the oil layers are all subjected to inertia, pressure, and thermal forces that deform their dimensions and eventually impact the cylinder volume. Petitpas et al. performed a 1D kinetic study of the above-mentioned parts and concluded that the cylinder volume, under a 160 bar combustion cycle, observed an expansion of less than 1% compared to fully rigid parts [186]. The obtained expansion is synced to the in-cylinder pressure. If these deformations were not accounted for in the volume expression, the performed error (+1%) on the cylinder volume would be negligible next to the overall cylinder uncertainties ($\pm 4\%$, see Figure A.8). Therefore they are neglected in Equation (A.27). Moreover, the use of the effective compression ratio for the heat release analysis includes indirectly these deformations.

Regarding the piston wrist pin offset, it can be applied to reduce piston slap and connecting rod stresses, yet it might influence the piston-liner friction and the piston-ring sealing [187]. This offset (usually $\sim 1\text{mm}$ for car engines) leads to a tilt of the piston top surface and changes the slider-crank system by adding an additional bar to the mechanism. The tilt of the surface is around 0.1 degree for a 1 mm offset, or a change of 0.015% of the V_{TDC} , whose influence on the piston volume and compression ratio is negligible since the error is several orders of magnitude smaller than the uncertainty due to the dimensions knowledge. On the other hand, the modified slider-crank mechanism induces an offset of the CA at which the minimum cylinder volume is reached. However, since the influence of the piston wrist pin offset on the cylinder volume and piston ring sealing is indirectly taken into account in the effective compression ratio, and that the influence on the minimum volume CA timing is indirectly taken into

account in the TDC offset calculations (see Appendix A.4.2), the piston wrist pin offset is not accounted for in Equation (A.27).

A.3.4 Intake and exhaust pressures

Intake and exhaust pressures are most of the time measured using absolute pressure sensors. In our example test bench, KISTLER piezoelectric pressure sensors are used, with characteristics common to most of the engine test benches: their rated measurement range, or FS, is from 0 to 5 bar; they have a high accuracy of $\pm 0.2\%$ of their FS; and they possess a $\pm 0.1\%$ of FS deviation per year. The repeatability uncertainty being unspecified by the manufacturer, a 12 points calibration performed on the 1-1.3 bar range following the prescriptions of Appendix A.1.2 revealed it to be $\pm 0.02\%$ of the FS, negligible compared to accuracy errors. Applying Equation (A.14) for the obtained and remaining manufacturer specified uncertainties, and applying Equation (A.2) for 100 consecutive cycles registered, the global uncertainty is displayed in Figure A.9.

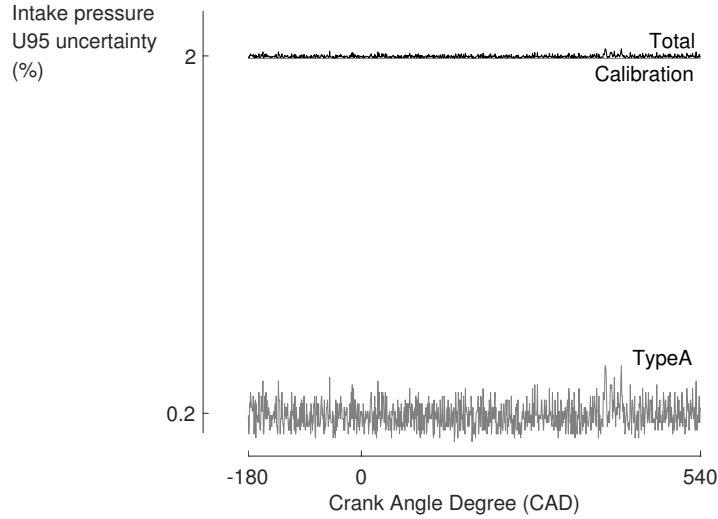


Figure A.9 – U95 uncertainty on the intake pressure from Type A (100 consecutive cycles) and Type B (i.e. calibration) uncertainties.

Plotting the evolution of intake pressure *Type A* uncertainty as a function of the CA can be very informant of a test bench variability of operation. For our example test bench the following observations can be made: the cycle-to-cycle variations in intake pressure (*Type A* of $\sim 0.2\%$, see Figure A.9) being much greater than the repeatability uncertainty of the sensor ($\sim 0.02\%$), these are physical and significant intake variations of the test bench that must be taken into account. If only one cycle had been recorded, *Type A* uncertainties would be about $\sim 3\%$. However, for a conventional number of consecutive cycles recorded, *Type A* uncertainties are negligible compared to *Type B* uncertainties.

The impact of intake pressure variations and number of consecutive cycles recorded on other engine measurands will be reported later, yet a clarification must be made. To use *Type A* uncertainties, the experiment must be perfectly repeatable: everything occurs under the exact same conditions every time. However it is not the case with an engine setup due to variations in intake pressure, hot spots, etc. Nonetheless, such variations occur randomly given that the average intake pressure is not oscillating with time (i.e. low coefficient of variation). Therefore, by using such *Type A* uncertainties we characterise the uncertainty on the experimentally measured average intake pressure compared to the average of the physical intake pressure (with inherent variations) but not compared to the physical pressure there would be if no variations were present. The test bench variations become part of the measuring device. Finally if we wanted to characterise each cycle individually, without influencing them with the test bench imperfections, only *Type B*, pegging, and TDC offset uncertainties must be used.

A.3.5 Exhaust gases: oxygen fraction through lambda sensors

Measuring the exhaust oxygen concentration can be of great help when willing to estimate the combustion efficiency, or gain insight in the combustion performance. In this section the related uncertainties with wet exhaust oxygen concentration measurement is investigated, and more specifically through the use of a lambda sensor. Lambda sensors are considerably cheaper and easier to integrate in a test bench compared to gas analyser systems, and can provide accurate and repeatable measurements as shall be seen below. More-

over, the process/methodology required to obtain lambda sensor uncertainties (equations, calibration, interference) can be quite similar to other gas analyser systems and is therefore an indicated illustration case.

In our example test bench, the oxygen fraction is obtained from a 4.9 LSU BOSCH lambda sensor. Yet it only provides an uncertainty for the equivalence ratio measurement based on a hydrocarbon fuel, and down to 0.6 of equivalence ratios only. Therefore I performed a calibration for O_2 concentrations between 20.95 $O_2\%$ and 0 $O_2\%$, following the procedure in Appendix A.1.2. It takes accuracy, repeatability, fit, least count, and reference errors into account. The reference O_2 concentration is obtained from controlled air and nitrogen MFC inputs. For low oxygen concentrations the MFC used for air input was either a 250 or a 55 nlpm range. The raw output measured is an average value over 10 seconds and the LC uncertainty is $u_{LC} = 0.005V$.

As the lambda sensor measures oxygen molar concentrations in the exhaust stream, its uncertainty is directly applicable to the exhaust oxygen concentration. The calibration data is used to obtain the lambda sensor uncertainty as displayed in Figure A.10. Using the linear regression over the whole oxygen range renders U_{95} around 0.25 $O_2\%$.

A.3.6 Combustion efficiency and lambda sensor interference

The uncertainty of combustion efficiency estimation is often overlooked. Two main methods exist to compute the combustion efficiency: the deduction from the input energy and energy closure of the heat release analysis, or the deduction from the direct measure of exhaust species concentrations. The energy closure method can be highly uncertain, or even inadequate, and is dealt with in Appendix A.4.12. The estimation from exhaust gas measurements can lead to U_{95} uncertainties ranging from less than 1% to more than 10% depending on the measurement device, the range of concentrations considered, the presence of interference, and the use or not of the combustion equation if one species measurement is missing (therefore bringing the reactant and Residual Gas Fraction (RGF) uncertainties into play). In our hydrogen HCCI example test bench, knowing the exhaust oxygen concentration gives us the unburned

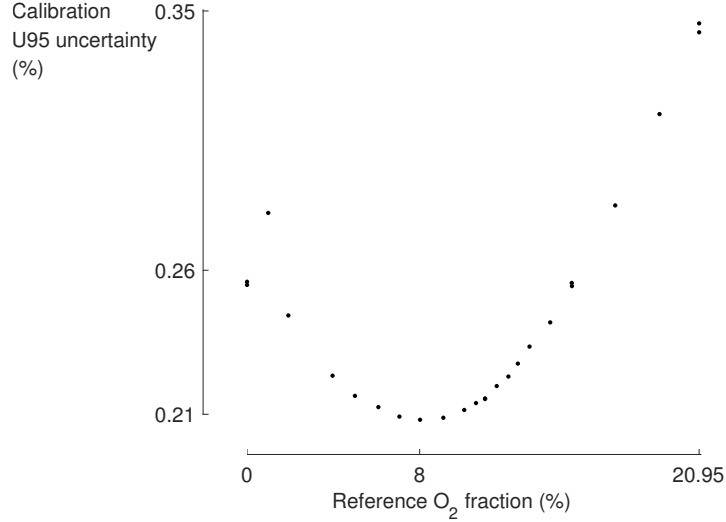


Figure A.10 – The global lambda sensor U95 obtained following the calibration is about 0.25 O₂%. The uncertainty increases non-linearly at the O₂% extremes due to the air and nitrogen MFC being used in their lower range. The lower uncertainty at 0 O₂% is obtained since only the nitrogen MFC is used in its high range to create the mixture.

hydrogen from the combustion equation, therefore higher uncertainties are to be expected. In the case where hydrogen could have been directly measured, therefore eliminating the interference issue and the need for the combustion equation, the U95 uncertainty on the combustion efficiency would be reduced to about 1%. State-of-the-art measurement systems (FTIR, UV spectrometers, etc.) can achieve U95 uncertainties lower than 0.1% if used within their calibrated range, and typical MFC achieve U95 at around 1.2%, see Figure A.5.

The uncertainty for our example test bench is derived here-under. The hydrogen intermediate species (H, OH) at the exhaust can be neglected being either too reactive to be left unburned or in too small concentrations next to the oxygen uncertainty. Since the exhaust unburned hydrogen produces an interference on the lambda sensor signal, and that the lambda sensor signal is used to compute the combustion efficiency, both concepts of combustion efficiency and lambda sensor interference are dealt with together in this section. The initial lambda sensor calibration only contained oxygen and nitrogen in the exhaust stream, although real exhaust contains water vapor and unburned fuel,

hydrogen in our example test bench. I further calibrated the lambda sensor with water vapor concentrations from 0% to 30%vol., and hydrogen concentrations from 0% to 2%vol., corresponding to a 90% combustion efficiency in the case of a 0.3 equivalence ratio run, see Figure A.11. The water vapor had no significant impact on the sensor output signal which was randomly spread around the reference value (i.e. sensor repeatability). On the other hand, the hydrogen had a significant impact on the sensor output signal. Regardless of the oxygen concentration, the obtained interference was 0.13 mV/H₂%, or 0.23 O₂%/H₂%.

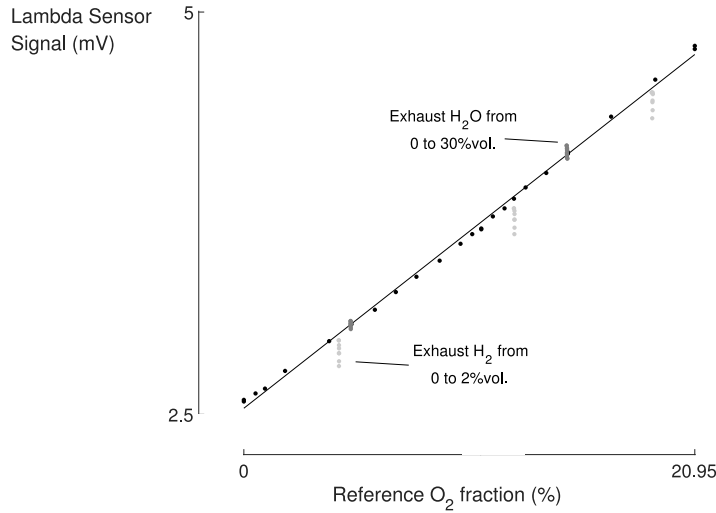


Figure A.11 – Water vapor does not interfere with the lambda sensor raw measurement, but hydrogen induces a concentration drift at a rate of 0.13 mV/H₂%. Water vapor in addition to hydrogen had no further influence.

To integrate that hydrogen-induced drift into the exhaust O₂% uncertainty, the exhaust unburned hydrogen uncertainty must be accounted for. However iterations are needed since the unburned hydrogen fraction is extracted from the lambda sensor measurement itself. The measured O₂% value must be increased (compensating the interference) until the deduced combustion efficiency matches the interference. Three iterations are enough to reach convergence.

To convert the measured oxygen concentrations into combustion efficiencies, unburned hydrogen concentration and induced oxygen interference, the following set of equations is used. To simplify the notations, let us define β the number of oxygen moles required to ensure the complete combustion of one mole of $C_uH_yO_xN_zS_w$:

$$\beta = \frac{2u + y/2 - x + 2w}{2} . \quad (A.35)$$

The formulation of the combustion efficiency making use of the exhaust oxygen concentration is as follows:

$$\begin{aligned} \eta_{\text{comb}} &= 1 - \frac{n_{\text{H}_2, \text{ex}}}{n_{\text{H}_2, \text{in}}} \\ &= 1 - \frac{\beta \cdot (n_{\text{H}_2, \text{in}} - n_{\text{H}_2, \text{burned}})}{\beta \cdot n_{\text{H}_2, \text{in}}} \\ &= 1 - \frac{\beta \cdot n_{\text{H}_2, \text{in}} - (n_{\text{O}_2, \text{in}} - n_{\text{O}_2, \text{ex}})}{\beta \cdot n_{\text{H}_2, \text{in}}} \\ &= 1 - \frac{\beta \cdot n_{\text{H}_2, \text{in}} - (n_{\text{O}_2, \text{in}} - \frac{\text{O}_2\%}{100} \cdot n_{\text{ex}})}{\beta \cdot n_{\text{H}_2, \text{in}}} . \end{aligned} \quad (A.36)$$

The exhaust hydrogen concentration, $\text{H}_2\%$, is obtained from the combustion efficiency as follows:

$$\text{H}_2\% = \frac{(1 - \eta_{\text{comb}}) \cdot n_{\text{H}_2, \text{in}}}{n_{\text{ex}}} \quad (A.37)$$

Finally the induced interference on the lambda sensor, expressed in $\text{O}_2\%$, is obtained from the exhaust hydrogen concentration:

$$\text{O}_2\%_{\text{interference}} = 0.23 \cdot \text{H}_2\% . \quad (A.38)$$

The uncertainties on the combustion efficiency and exhaust oxygen concentration can be derived from their definitions given right above and using Equation (A.17):

$$u_{\text{O}_2, \text{final}}^2 = u_{\text{O}_2, \text{measured}}^2 + u_{\text{O}_2, \text{interference}}^2 , \quad (A.39)$$

$$\begin{aligned} u_{\text{O}_2, \text{interference}}^2 &= \left(\frac{0.13 \cdot (1 - \eta_{\text{comb}})}{n_{\text{ex}}} u_{n_{\text{H}_2, \text{in}}} \right)^2 \\ &+ \left(\frac{0.13 \cdot n_{\text{H}_2, \text{in}}}{n_{\text{ex}}} u_{\eta_{\text{comb}}} \right)^2 \\ &+ \left(\frac{0.13 \cdot (1 - \eta_{\text{comb}}) \cdot n_{\text{H}_2, \text{in}}}{n_{\text{ex}}^2} u_{n, \text{ex}} \right)^2 , \end{aligned} \quad (A.40)$$

$$\begin{aligned}
u_{\eta_{\text{comb}}}^2 = & \left(\frac{1}{\beta \cdot n_{\text{H}_2, \text{in}}} u_{n_{\text{O}_2, \text{in}}} \right)^2 \\
& + \left(\frac{\text{O}_2\%}{100 \cdot \beta \cdot n_{\text{H}_2, \text{in}}} u_{n, \text{ex}} \right)^2 \\
& + \left(\frac{n_{\text{ex}}}{100 \cdot \beta \cdot n_{\text{H}_2, \text{in}}} u_{\text{O}_2\%} \right)^2 \\
& + \left(\frac{\text{O}_2\% \cdot n_{\text{ex}}}{100 \cdot \beta \cdot n_{\text{H}_2, \text{in}}^2} u_{n_{\text{H}_2, \text{in}}} \right)^2 .
\end{aligned} \tag{A.41}$$

For the reference case using hydrogen at an equivalence ratio of 0.26 and without EGR, we obtain $\eta_{\text{comb}} \pm U_{95} = 97.0 \pm 12.8\%$, and $\text{O}_{2, \text{final}}\% \pm U_{95} = 14.65 \pm 0.27\%$. Such a high uncertainty in combustion efficiency comes partly from the need of the combustion equation to obtain the unburned hydrogen, and partly from the uncertainty on the lambda sensor, each inducing half of the global uncertainty. As will be explained in Appendices A.4.4 and A.4.4, the residual gas fractions taken into account in the combustion equation are highly uncertain and therefore impacts the uncertainty on the intake fuel quantity, intake oxygen, and hence combustion efficiency.

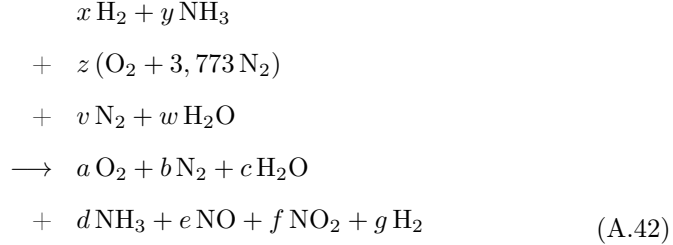
The same procedure can be performed for any other fuel, on the condition that other emissions than unburned fuel can be neglected. If exhaust emissions contain partially oxidized fuel, they must then be measured individually in order to take advantage of the combustion equation. In order to avoid the high uncertainty linked to the use of the combustion equation, each exhaust species must be measured individually.

A.3.7 Calibration and uncertainty of a UV spectrometer

Although this appendix only considers an hydrogen HCCI engine as an illustration, since the ammonia-hydrogen case has been considered in this thesis, I have to investigate the case of more than one unburned compound where we are forced resorting to the use of an additional exhaust gas analyser. In this subsection, I investigate the uncertainty performances of a gas analyser that is calibrated in-house, and the impact on the overall exhaust gases uncertainties.

For the exhaust gases measurement of ammonia-hydrogen HCCI combustion, two devices are used. The TETHYS EXM400 UV spectroscopy analyser measures NH_3 , NO , and NO_2 molar concentrations and the BOSCH 4.9 LSU lambda sensor measures exhaust oxygen concentration. Argon being inert in terms of pollutants formation and moles count, let us account it here as nitrogen for the sake of conciseness. Finally assuming that no other pollutant

is formed, these two devices give sufficient information to solve the following combustion equation:



Indeed, having three different atoms (oxygen, nitrogen, hydrogen), doing the balance on them gives us 3 equations for 3 unknowns ('b, c, g'), since the other molar coefficients are controlled by the MFCs. Solving for the unknowns renders:

$$\begin{aligned}
 c &= 2z + w - 2a - e - 2f \\
 b &= (x + 7,546z + 2s - d - e - f)/2 \\
 g &= (2y + 3x + 2w - 2c - 3d)/2
 \end{aligned} \tag{A.43}$$

The 'v-z' molar values are the respective moles per cycle of each specie present in the cylinder. They combine the flow sent by the MFCs and the residual gas fraction containing burned and unburned species. The uncertainty on the 'a' parameter is obtained from the 4.9 LSU BOSCH lambda sensor, see Appendices A.3.5 and A.3.6.

The uncertainty on the measurement of the nitrogen exhaust species (except N_2) is obtained from the TETHYS EXM 400 UV spectrometer calibration. The UV sensor renders the three molecules concentrations (in ppm) in the exhaust gas. To do so, the analyser uses the Beer-Lambert law to convert the measured light intensity at the user-prescribed wavelength, where the gases of interest are known to absorb, into concentrations. However, as the analyser band-pass resolution is not infinitesimal, the output of the Beer-Lambert law behave non-linearly with an increasing absorbance (i.e. increasing concentrations of gases absorbing in the prescribed band-pass), see Figure A.12. Therefore, the analyzer non-linearity has to be assessed through a calibration process. The calibration is performed using three standard gas bottle from which mole flows are drawn by MFCs. Used bottles are 1.263%mol. NH_3 , 1.008%mol. NO and 0.502%mol. NO_2 , but lower concentrations are achievable through dilution

with air. Figures A.12 to A.14 display the analyser raw measurements, and associated uncertainties, as a function of the injected gas concentration. The mixture reference uncertainty is obtained from the MFC uncertainties and bottle purity. The repeatability/variability errors of the analyser are finally taken into account.

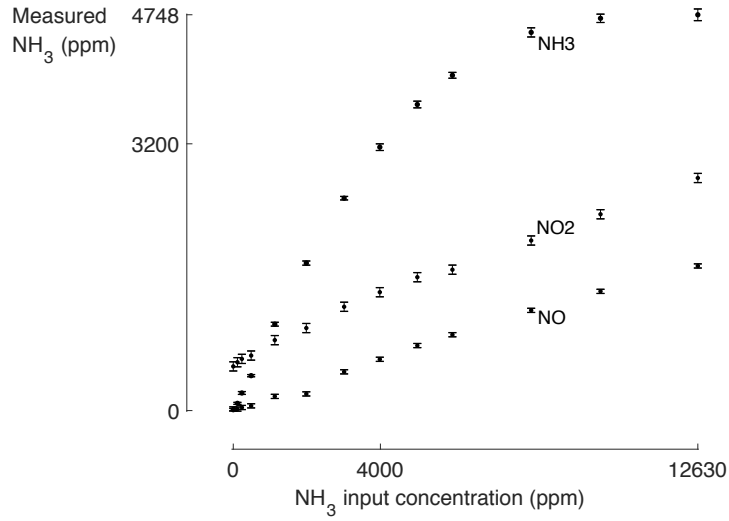


Figure A.12 – NH_3 raw measurement, and associated uncertainty at a 95% confidence level, as a function of the input NH_3 concentration. The raw measurement can be seen saturating for input concentrations above 4000 ppm. Ghost measurements of NO and NO_2 can be seen and are linearly correlated to the NH_3 input concentration. This interference is due to the NH_3 molecule that is absorbing at the specific lookup wavelengths chosen for NO and NO_2 .

The fact that NO_2 measurements start at around 550 ppm is due to a different measurement method: the measurements done at the specified wavelengths are compared to a reference wavelength where NO_2 is known to absorb the least. The specified lookup wavelengths are: 207-213 nm for NH_3 , 214-216 nm for NO , and 219-223 nm compared to 278-282 nm for NO_2 . These wavelengths have been chosen to minimise the mutual interference, while minimising measurement saturation in the concentration range of interest.

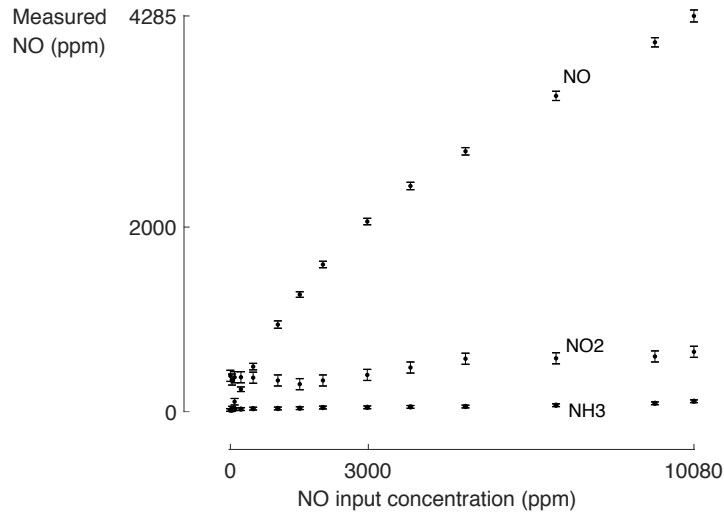


Figure A.13 – NO raw measurement, and associated uncertainty at a 95% confidence level, as a function of the input NO concentration. The raw measurement can be seen changing slope for input concentrations above 3000 ppm. Still the response stays linear and no pure saturation is observed for the range of interest. Finally NO is barely interfering with NH₃ and NO₂ measurements: an additional 100 ppm is obtained for both going from zero to maximum NO input concentration.

Before obtaining the final post-treated measurement, the linearisation and interference must be taken into account. For each species, a conversion factor (depending on the input species concentration) is computed to linearise the measurements. This conversion factor can have a huge impact on the uncertainties, as can be seen in Figure A.15, especially if the measurement is saturated. Indeed, when saturating the repeatability of the measurement becomes of the same order of magnitude as the change in measurement. The interference is linearised in the same way. To finally account for interference, an iteration until convergence is performed where the retained value for a given species is the post-processed value to which the obtained interference from both other species is subtracted. During the convergence, the retained value for each species at each step will give a smaller and smaller interference with the two other species, until convergence.

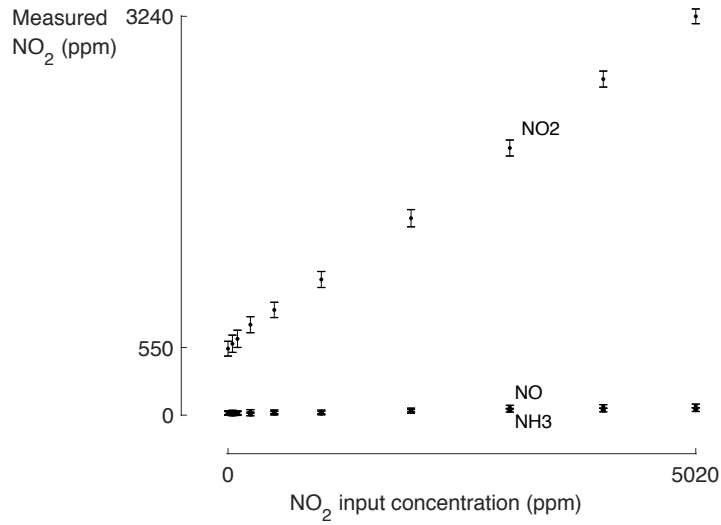


Figure A.14 – NO_2 raw measurement, and associated uncertainty at a 95% confidence level, as a function of the input NO_2 concentration. The raw measurement is not saturating for the input range of interest and stays linear. Finally NO_2 is not interfering with NH_3 and NO measurements.

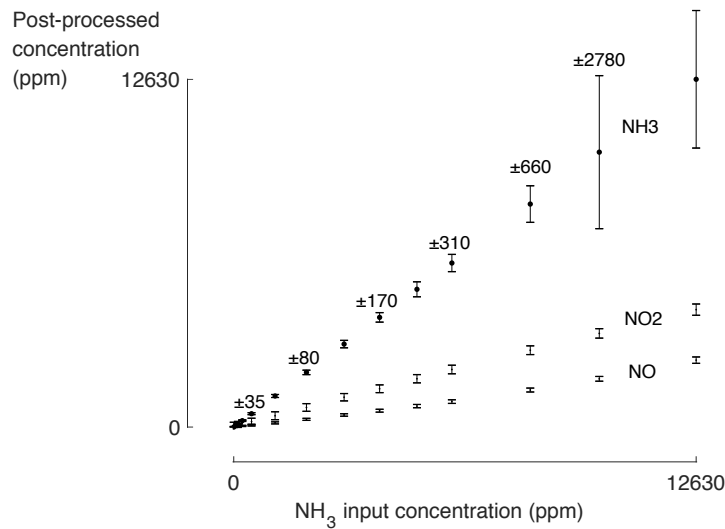


Figure A.15 – NH_3 post-processed measurement, and associated uncertainty at a 95% confidence level, as a function of the input NH_3 concentration. The uncertainty is greatly impacted by the conversion factor when measurement is saturated.

A.4 Uncertainties on the physical quantities requiring a data post-processing

In this section, the uncertainty quantification methodology is applied to the engine measurands that cannot be used directly, but that require post-processing techniques, see Figure A.16. Indeed, these measurands need unknown intermediate physical quantities to be derived (such as the effective compression ratio, or the wall heat loss fluxes for example). These unknown physical quantities are first modelled, which includes further uncertainty. The engine input and output uncertainties will be developed here-under in a consistent way: from the measurand definition to its uncertainty formulation and influencing factors analysis. Finally, each measurand uncertainty will be illustrated thanks to the hydrogen HCCI engine test bench considered.

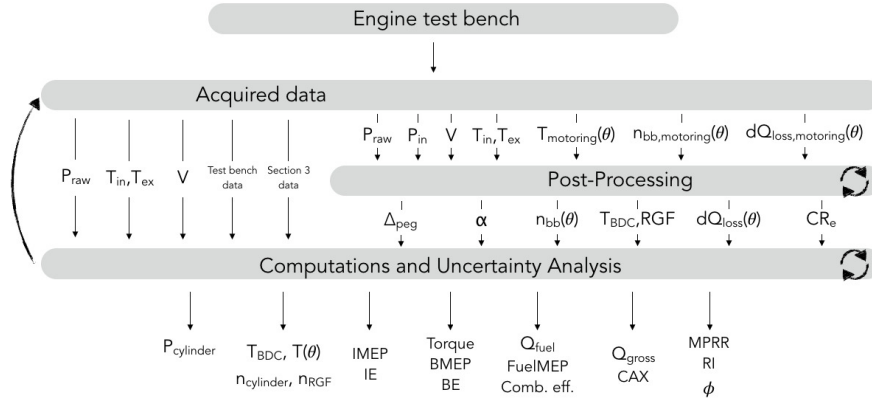


Figure A.16 – Graphical visualisation of the measurand uncertainties that need post-processing to be obtained from the acquired data.

A.4.1 Post-processing methodology

The methods used to post-process the raw measurands are described in this section, as the procedure itself induces uncertainty. These methods cover, respectively, in-cylinder pressure filtering and pegging, effective compression

ratio, TDC offset, pressure transducer thermal shock, effective intake/BDC temperature, blow-by, and wall heat losses. Let us mention that an iteration on the methodologies is necessary as each quantity determination requires the use of the other ones. In overall, 3 iterations are required in order to reach convergence (by 0.1%) on all the post-processed quantities.

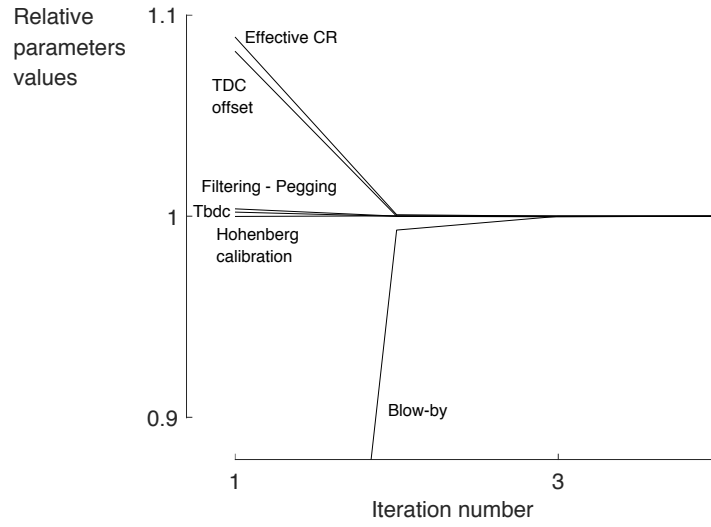


Figure A.17 – Convergence for the various parameters of the post processing methodology

In-cylinder system governing equations

The piston engine system can be represented through the first law of thermodynamics and the ideal gas assumption. For a system of internal energy U that is proceeding to exchanges with its surroundings (heat Q , work W , and *blow-by* mass m of specific enthalpy h), the differential form of the first law of thermodynamics for an open system can be written as:

$$dU = \delta Q + dW + h \cdot dm \quad . \quad (\text{A.44})$$

The heat/energy loss of the system through mass exchange is therefore differentiated from the other heat exchanges Q . This mass exchange, called

blow-by, occurs through the imperfect sealing of the piston segments. This is why a piston engine must be studied through an open system approach. In the case of an ideal gas, the system pressure p , volume V , temperature T , and mole quantity n are related to the universal gas constant R by the equation: $pV = nRT$. With the Mayer relation $R = c_p - c_v$ and defining $\gamma = \frac{c_p}{c_v}$ the ratio of the specific heat capacities of the cylinder mixture, one obtains:

$$dQ_{net} = \frac{\gamma}{\gamma - 1} \cdot p \cdot dV + \frac{1}{\gamma - 1} \cdot V \cdot dp - \frac{\gamma}{\gamma - 1} \cdot p \cdot V \cdot \frac{dm}{m}, \quad (\text{A.45})$$

where dQ_{net} is the infinitesimal change in net, or global, heat exchange to the surroundings. This heat exchange is to be differentiated from the gross heat released by the combustion and the heat lost to the system boundaries, all linked by the following equation:

$$dQ_{gross} = dQ_{net} + dQ_{loss} . \quad (\text{A.46})$$

To obtain the temperature-entropy form, Equation (A.44) is used together with the same ideal gas assumptions and the formal definition of entropy $dS = \delta Q/T$ to obtain:

$$dS = nR \left(\frac{\gamma}{\gamma - 1} \frac{dV}{V} + \frac{1}{\gamma - 1} \frac{dp}{p} - \frac{\gamma}{\gamma - 1} \frac{dm}{m} \right), \quad (\text{A.47})$$

A.4.2 In-cylinder pressure

Properly measuring the in-cylinder pressure is a challenge. It spans from the atmosphere to more than a hundred bar and varies quite dynamically. Piezo-electric sensors are able of such acquisition, but at a certain cost. First, the measured signal is quite noisy, especially when the dynamic changes in pressure are low (e.g. during the gas exchange process). Second, they only capture variations in pressure, meaning they are relative pressure sensors. The management of the noise is performed through the use of a double Butterworth low-pass developed by Payri et al. [188] and is assumed not to add any spurious information and not to remove physical one. The relativity of the pressure signal is compensated through the so-called *pegging* process. Finally, pressure transducers are subject to progressive drift and it is the responsibility of the operator to make sure the recorded data are valid. There is no practical way of

noticing such deviation unless a reference motoring run is being performed and assessed regularly within the exact same conditions, or a factory calibration.

Pressure filtering

An easy approach would be to simply average the consecutive cycles that have been recorded. Although acceptable as a first approximation, the result is incorrect as it assumes that all the cycles started with the exact same intake pressure, encounter the same combustion, and finally doing so produces a loss of information. On the other hand, filtering allows to remove the non-physical information from the signal of each cycle, independently. With time, more and more elaborated filters have been developed, from the least squares method from [189] to the low-pass filter from [190], with the aim of maintaining ever more physical information. The method used in this paper is the one developed by [188], which consist of a simple Butterworth low-pass filter but with a thoughtfully determined cut-off frequency. The method is fully described in [188, 191] but can be summarised as follows: first, all the pressure cycles are inserted consecutively in a single vector which is converted to the frequency domain using a Discrete Fourier Transform (DFT); then, the frequency signal is separated between the amplitudes obtained at frequencies that are natural multipliers of the engine rotation frequency (i.e. signal harmonics) and the amplitudes obtained at other frequencies (i.e. non-signal, or noise, harmonics); finally, the cut-off frequency is the one at which the amplitudes of the signal and non-signal harmonics become indistinguishable with a statistical probability of $p = 1 - \alpha = 0.98$. This allows to effectively filter in-cylinder pressure curves separately, while conserving combustion information such as ignition timing, see Figure A.18.

Pressure pegging

The pegging shift is constant within each cycle but may vary between consecutive cycles [191, 192]. Two ways can be used to compute this pegging offset, termed Δ_{peg} , each one having different requirements and output uncertainties.

An absolute pressure sensor placed at the engine intake can be used as a reference. Gopujkar et al. compared various positions for the insertion of the ref-

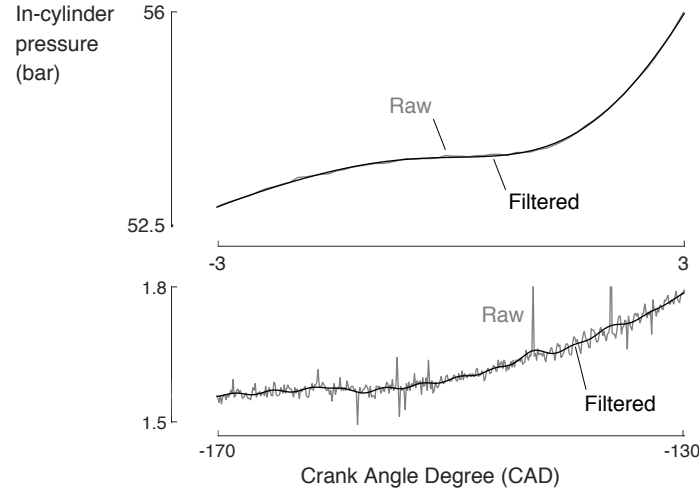


Figure A.18 – From raw pressure signal to filtered signal at intake and around combustion onset (i.e. CA10).

erence pressure sensor (intake manifold, intake/exhaust runner, intake/exhaust valve) and concluded that the intake runner was leading to the smallest fluctuations between cycles [193]. The in-cylinder pressure signal is shifted to the intake manifold pressure signal when the intake valve is open, therefore connecting both sensors, and at BDC when the gas dynamics are the smallest. This can also be performed on the exhaust manifold pressure sensor, at the BDC after the expansion. It requires a high precision and frequency pressure signal as the shift must be performed for measurements performed precisely around BDC. However, intake pressure sensors measurements can be flawed by pressure oscillations occurring in the intake pipes due to the valves and piston cyclic motion, see Figure A.19. This is why a range of 10 CAD measurements has to be used to compute the reference pressure, and imperatively at BDC where pressure oscillations are consistently cancelled. In our example test bench, intake and exhaust pressures are recorded every 0.7 CAD to improve the estimation of the pressure over the CA span of interest. Finally, as the pegging might vary between cycles, the intake pressure acquisition has to be done for every cycle. The related uncertainty to this method is the uncertainty on the pegging value, Δ_{peg} , being the uncertainty of the intake pressure itself, plus any systematic error.

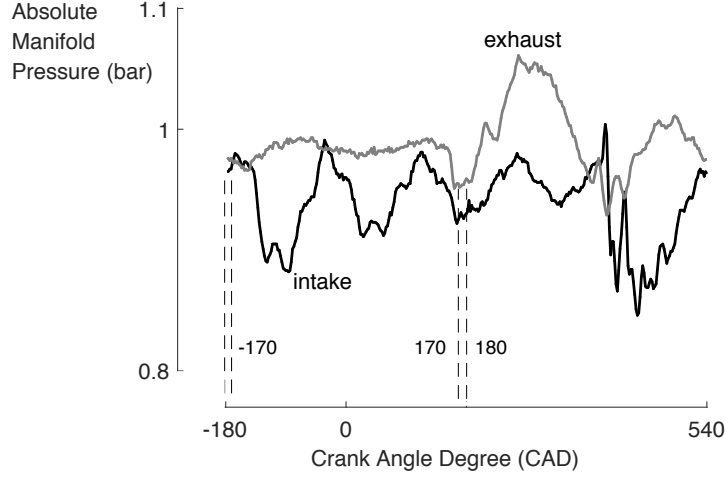


Figure A.19 – From raw pressure signal to filtered signal at intake and around combustion onset (i.e. CA10).

The second method, developed by Tunestål [192], is briefly introduced here but readers should refer to its original publication for further information about the resolution and derivation of Δ_{peg} . Variations of that method for slightly improved results have been published afterwards [194], yet they do not overcome the issues I shall be relating here. Tunestål base point is that the real in-cylinder pressure follows a polytropic compression ($pV^n = C$) and therefore:

$$p_i = CV_i^{-n} = p_{i,\text{measured}} + \Delta_{\text{peg}} \quad , \quad (\text{A.48})$$

where i represents the i^{th} measurement point. Yet Equation (A.48) is only to be solved for the points where the polytropic assumption is acceptable: after IVC (i.e. closed system) and before the Start Of Combustion (SOC). Tunestål then makes the hypothesis that the polytropic coefficient will be constant through the whole polytropic span. We therefore have a set of equations (one for each measurement point between IVC and SOC) with two unknowns: n and Δ_{peg} . First assuming that n is known, the selected Δ_{peg} will be the one that minimizes the least square errors of the system. To obtain n , we iterate on the previous system so that the newly-found n renders a smaller least square error for the best Δ_{peg} .

This method, as developed by Tunestål, converges in less than 5 iterations

and is robust to user-inserted random offsets [191]. Still, Tunestål fixes the cycles bounds of the study at [IVC ; -40 CAD], without giving any information on that decision. Taking the IVC as a starting point seems fair to us as the hypothesis of polytropic compression is acceptable for the closed part of the cycle of a piston engine, yet the choice for an ending point should be motivated as when getting closer to the TDC the hypothesis of polytropic compression is getting too rough. Indeed, Figure A.20 displays the evolution of the optimal Δ_{peg} found by the Tunestål method for varying ending points of the study span. We can see that the method output is highly sensitive to the ending point, with a 3800 Pa difference for a 4CAD difference in ending point. For two consecutive runs of the same operating conditions (50 consecutive cycles each), the Δ_{peg} suggested by the method for an ending point at -40 CAD differ by 2600 Pa.

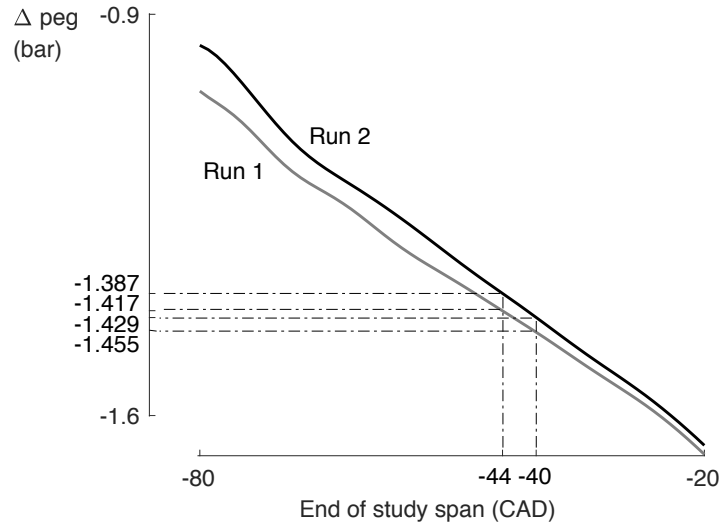


Figure A.20 – Evolution of the predicted Δ_{peg} by the Tunestål method for varying ending points of the study span and for two sets of runs of the same operating conditions. For a randomly chosen ending point, the variability on the predicted Δ_{peg} is at least in the range of ± 2000 Pa

To avoid a random choice of the ending point of the study cycle span, I

suggest the following approach. Since the original Tunestål method consist of selecting the polytropic exponent and Δ_{peg} that minimises the least square errors of the system composed of Equation (A.48), the optimal ending point should be the one that minimises the least square error of all the respective cases. The evolution of the least square error between the experimental pressure curve pegged accordingly to Tunestål and the polytropic compression (using the optimal polytropic exponent and Δ_{peg} of each case) as a function of the ending point of the study range is displayed in Figure A.21. An optimum can be observed around -40 CAD, as the points closer to TDC do not respond to the polytropic compression approximation. For the two runs studied above, the predicted Δ_{peg} by the suggested method now differ only by 1200Pa. Still, this shows that the variability of the Tunestål method is higher than the one of the intake manifold measurements. Therefore, I decided to use the first method (comparison with intake manifold pressure measurement).

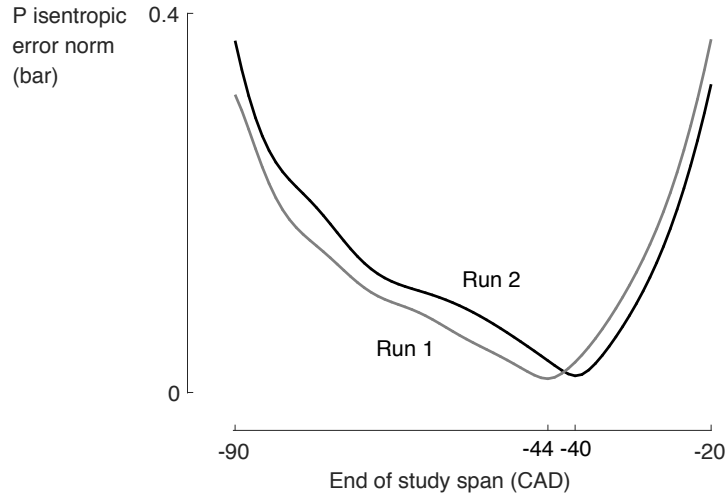


Figure A.21 – Evolution of the least square error between the experimental pressure curve pegged accordingly to Tunestål and the optimised polytropic compression as a function of the ending point of the Tunestål study range. The optimal ending point is close to -40 CAD but differs between different runs of the same operating conditions.

In-cylinder pressure uncertainty derivation

The in-cylinder pressure is transformed into a current by the piezoelectric sensor, which in turn is amplified by the charge amplifier and sent to the recording system. The value recorded is finally pegged during the post-processing by the offset Δp_{peg} , to convert it from relative to absolute pressure. Therefore we use the following:

$$P_{\text{cylinder}} = P_{\text{meas.,relative}} \frac{G_{\text{pzt}}}{G_{\text{amp}}} + \Delta p_{\text{peg}} , \quad (\text{A.49})$$

where $G_{\text{pzt}} = G_{\text{amp}} = 19.27 \text{ pC/bar}$ are the gain of the piezoelectric sensor and of the charge amplifier.

Using once again Equation (A.17), and knowing the sensor and amplifier characteristics (see Table A.3), the uncertainty on the measured pressure is obtained:

$$\begin{aligned} u_{p,\text{cylinder}}^2 = & u_{\text{lin},\text{pzt}}^2 + u_{\text{lin},\text{amp}}^2 \\ & + u_{\text{T,drift,pzt}}^2 + u_{\text{T,shock,pzt}}^2 \\ & + \left(\frac{P_{\text{pzt}}}{G_{\text{pzt}}} \right)^2 (u_{\text{TSC,pzt}}^2 + u_{\text{lin,G,pzt}}^2 + u_{\text{lin,G,amp}}^2) \\ & + u_{\Delta p,\text{peg}}^2 , \end{aligned} \quad (\text{A.50})$$

where P_{pzt} is the pressure signal send by the sensor, and $u_{\text{lin,G,pzt}}$ and $u_{\text{lin,G,amp}}$ the uncertainties on the sensor and amplifier gains. The amplifier only possesses linearity uncertainties $u_{\text{lin,amp}}$. The piezoelectric sensor has linearity uncertainties $u_{\text{lin,pzt}}$ (usually including hysteresis, if not an additional term in Equation (A.50) must be added), temperature cyclic drift uncertainties $u_{\text{T,drift,pzt}}$, Thermal Sensitivity Changes (TSC) uncertainties due to the temperature at the sensing element $u_{\text{TSC,pzt}}$, and dynamic temperature shock uncertainties due to the sharp rises in temperature $u_{\text{T,shock,pzt}}$.

The final factor regarding the *Type B* uncertainty of the in-cylinder pressure is the accuracy with which the pressure curve is synced with the real piston position. Indeed, as the crank encoder is mounted onto the crankshaft, it must be set at the same exact position that the piston is. The crank encoder is set at 0.0 CAD and the piston is manually positioned at TDC, which encompasses some imprecision called TDC offset, or τ . Many methods exist for TDC offset estimation, all giving comparable results and variabilities, see for example

Tazerout et al. [195] or Tunestål [192, 196]. The uncertainty linked to it is directly proportional to the rate of change of the pressure with the τ value, multiplied by the uncertainty on the value itself, which is the LC error of the rotary encoder:

$$u_{p,TypeB} = \sqrt{u_{p,\text{measured}}^2 + \left(\frac{\partial p}{\partial \tau} u_\tau\right)^2} . \quad (\text{A.51})$$

The final uncertainty on the pressure measurement is found by adding the *Type A* uncertainty linked to our n consecutive cycles recorded, see Equation (A.52). Again, as for the intake pressure, this uncertainty is characterising the average experimental measure within the test bench. However if one wants to characterise a single cycle, only classical *Type B*, pegging and TDC offset uncertainties must be used.

$$u_p = \sqrt{u_{p,TypeB}^2 + u_{p,TypeA}^2} = \sqrt{u_{p,TypeB}^2 + \frac{\sum (p_i - \bar{p})^2}{n(n-1)}} . \quad (\text{A.52})$$

By applying the newly obtained cylinder pressure uncertainty expression to our example hydrogen HCCI test bench, I obtain a roughly constant uncertainty of 1 bar through the whole engine cycle, see Figure A.22. During the breathing phase the relative uncertainty on the pressure is close to 50% since the pressure is not evolving dynamically and that the sensor is designed for relative dynamic variations. Therefore the driving uncertainty factor during the breathing phase is the *Type B* uncertainty. During the combustion phase both the *Type A* and *Type B* uncertainties matter. Whatever the cycle position, the pegging related uncertainty is negligible. On the other hand, the TDC offset uncertainty is quite significant during the combustion phase. Therefore sensors with perfect accuracy could only reduce the total U_{95} uncertainty by half in our example case.

To better grasp the relative pressure uncertainty evolution throughout the cycle, it is displayed for both 50 and 150 consecutive cycles recorded under a *non-ideal* case for stability: 3.7% CoV_{IMEP} (see Figure A.23). For 150 consecutive cycles recorded, the *Type A* uncertainties encompasses 45% of the overall

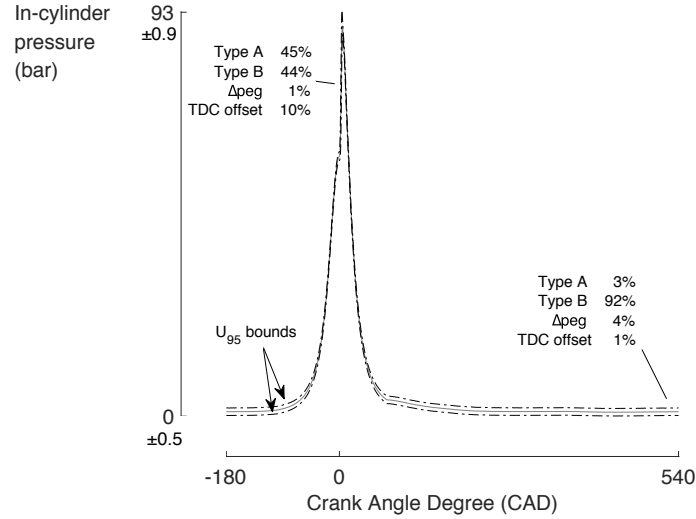


Figure A.22 – The in-cylinder pressure absolute uncertainty stays nearly constant throughout the cycle, although its relative impact and its composition vary significantly. Overall, cycle-to-cycle variabilities impact drastically the pressure uncertainty around the combustion time although the CoV_{IMEP} is only 1.24%.

uncertainty during the combustion, against 44% when only 50 consecutive cycles are recorded. Cycle-to-cycle variabilities are a stochastic phenomenon for which 50 consecutive cycles is sufficient to capture all the meaningful pressure information, even at high CoV_{IMEP} .

The temperature induced uncertainties of the piezoelectric sensor (thermal shock and temperature cyclic drift) deserve extended explanations. The temperature to which the sensor is subjected is varying within the cycle (due to the compression-combustion-expansion), hence inducing sensor diaphragm compression and expansion not related to pressure. Great efforts have been dedicated to understand these phenomena, quantify them and suggest mathematical corrective measures [197–199]. However to apply these corrective methods, a firedeck dynamic temperature sensor is required (which is often not available on engine setups) as well as a prior sensor calibration to obtain the temperature

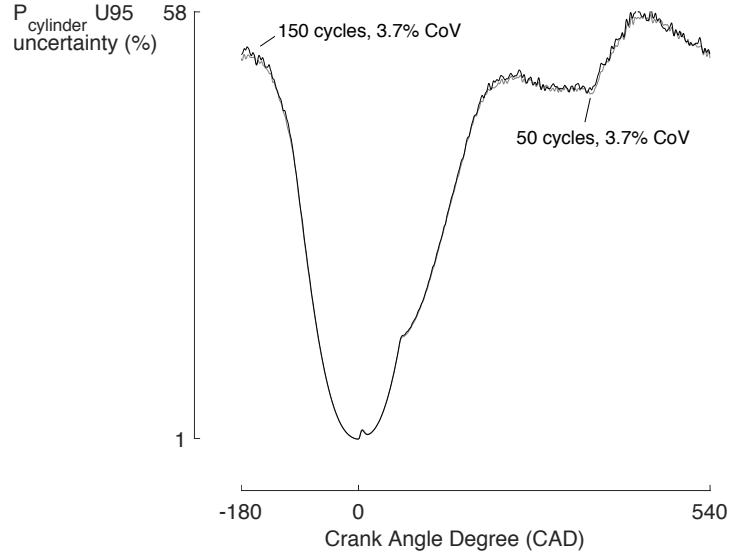


Figure A.23 – In-cylinder pressure uncertainties are not affected by the number of consecutive cycles recorded, Type A uncertainties being minor.

response gain of the pressure sensor. To know whether neglecting the thermal effects will impact the results, the uncertainty analysis tool can be used. Thermal shock and drift can be accounted for in the uncertainties since an error is made. Most manufacturers (as suggested in Equation (A.50)) use a random uncertainty to characterise them although their peak value is only reached a few CAD after the cycle peak pressure and then decays gradually during the expansion. This induces an uncertainty overestimation during the breathing phase and early compression, yet this part of the cycle is of much lesser importance and already impacted by the sensor linearity errors. In the example test bench considered, the peak U95 uncertainty induced from thermal shock and cycle drift aspects is ± 0.3 bar and ± 0.5 bar, respectively, see Table A.3. During the combustion and expansion phases they are taken into account and represent less than 15% of the overall uncertainty, see Figure A.22. During the breathing and early compression phases they induce an overestimation of only one third of the overall uncertainty, given the high linearity uncertainty of the sensor itself at low pressures. Therefore, their impact on pressure measurement errors is minor next to other *Type B* uncertainties and simply including them in the uncertainty analysis is a satisfactory measure when a firedeck dynamic

temperature sensor is not available.

A.4.3 A conservative (i.e. lower bound) estimate of the in-cylinder pressure uncertainty

The in-cylinder pressure uncertainty obtained in the previous section may seem non-logical for the breathing phase. Indeed, the uncertainty obtained for the in-cylinder pressure around IVC is about 1 bar even though the pressure itself is at 1 bar. Moreover the in-cylinder pressure signal has been shifted to the value of the intake pressure sensor, which has an uncertainty nearly two orders of magnitude lower: ± 4000 Pa. The high uncertainty of the in-cylinder pressure during the breathing phase and early compression and late expansion is due at 80% (see Figure A.22) to the sensor being used in its extreme low range (constant pressure around 1 bar, although dimensioned for dynamic variations up to 150 bar). The issue faced is that the pressure uncertainty for the breathing phase, early compression and late expansion (that will have a huge impact on temperature and RGF, see Appendix A.4.4) is not representative of the reality. Therefore it is desirable to develop another approach of the in-cylinder pressure uncertainty for the breathing phase, early compression, and late expansion that is physically sensible and uses the intake pressure sensor as a base point. This new in-cylinder uncertainty approach shall be called *lower bound*, against the one developed in Appendix A.4.2 that I shall refer to as *upper bound*.

Based on the polytropic assumption, one can represent the in-cylinder pressure in two parts, one for the compression and one for the expansion, using two different polytropic coefficients k_1 and k_2 :

$$p_{\text{comp}} = p_{\text{in}} \left(\frac{V_{\text{IVC, eff}}}{V} \right)^{k_1}, \quad (\text{A.53})$$

$$p_{\text{exp}} = p_{\text{EVO}} \left(\frac{V_{\text{EVO}}}{V} \right)^{k_2}. \quad (\text{A.54})$$

Then, neglecting the uncertainty on the polytropic coefficients k_1 and k_2 , the lower bound uncertainty of the in-cylinder pressure is obtained through Equations (A.17) and (A.53) (only shown here for the compression part):

$$\begin{aligned}
u_{p, \text{comp, low}}^2 = & \left(\left(\frac{V_{\text{IVC, eff}}}{V} \right)^{k_1} \right)^2 u_{p, \text{IVC, eff}}^2 \\
& + \left(k_1 \frac{p_{\text{IVC, eff}}}{V_{\text{IVC, eff}}} \left(\frac{V_{\text{IVC, eff}}}{V} \right)^{(k_1-1)} \right)^2 u_{V, \text{IVC, eff}}^2 \\
& + \left(k_1 \frac{p_{\text{IVC, eff}}}{V} \left(\frac{V_{\text{IVC, eff}}}{V} \right)^{(k_1-1)} \right)^2 u_V^2,
\end{aligned} \tag{A.55}$$

Compared to the upper bound uncertainty, the lower bound uncertainty follows the volume uncertainty shape throughout the cycle, with the intake pressure uncertainty as a base point. At the intake it is 30 times smaller than the upper bound (since the intake pressure sensor is made for low pressure measurements) and the same order of magnitude close to TDC due to a combination of intake pressure and volume uncertainties. Figure A.24 displays such comparison between high and low bound uncertainty for the in-cylinder pressure, and as a function of the number of consecutive cycles recorded and CoV_{IMEP} . The CoV and recorded cycle numbers are shown to have no influence.

A.4.4 Effective BDC, RGF, and cycle temperatures

Obtaining the effective temperature at BDC and the RGF allows to compute the effective in-cylinder temperature. Yet their derivation is tedious and therefore being able to compute their related uncertainties is of interest. This section relates the computation of the effective BDC and in-cylinder temperatures and related uncertainties based on the model from Sjöberg et al. [130] for RGF determination which I have further developed. The model from Sjöberg et al. is initially intended for premixed and Direct Injection (DI) HCCI engines, yet the assumptions made can be adapted to other combustion modes. For two-stroke engines however, the recirculation process being different, I suggest the readers to refer to the recent comprehensive work on that matter from Torregrosa et al. [200]. The derived uncertainty expressions are therefore not general solutions since based on a specific model, yet they provide reference figures as I apply them to our example hydrogen HCCI test bench.

Although the intake temperature thermocouple is placed only 5 cm away from the intake valve, the mixture has yet to encounter wall heating/cooling,

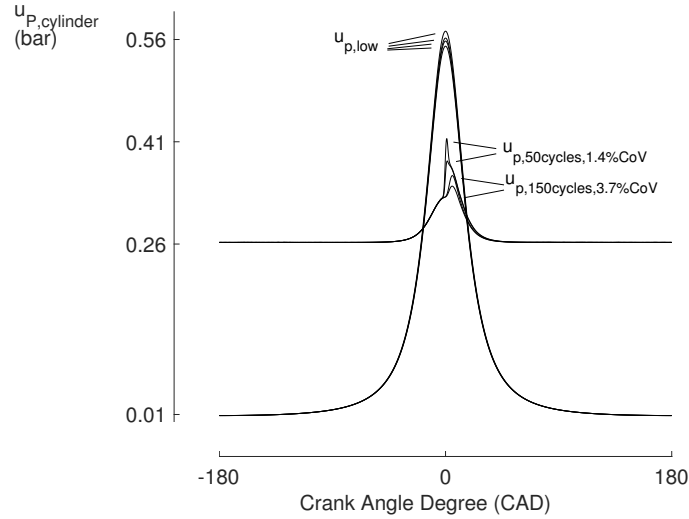


Figure A.24 – The lower bound for the in-cylinder pressure uncertainty is shaped as the volume uncertainty. Compared to the upper bound uncertainty, it has the same order of magnitude during the combustion but it is negligible during most of the compression and expansion. For the example test bench, the number of recorded cycles or the cycle-to-cycle variability has no influence on both of the pressure uncertainties.

mixing with residual gases and gas dynamic effects. Therefore the intake manifold thermocouple is not a precise measurement of the mixture temperature at the start of compression. The wall heating, dynamic effects, and the temperature of the residual gases are indirectly given to us through the MFCs and the intake pressure sensor: since the mole quantity that enters the engine and the pressure are known, the mixture temperature is deductible from the ideal gas law. Yet for a correct estimation of the in-cylinder temperature, the quantity of residual gases present during the intake stroke must be accounted for as they fill part of the cylinder volume. This is an iterative process as the BDC temperature is required to obtain the residual gases temperature, and *vice-versa*, as shown in Figure A.25. The needed equations and their related uncertainties are developed below.

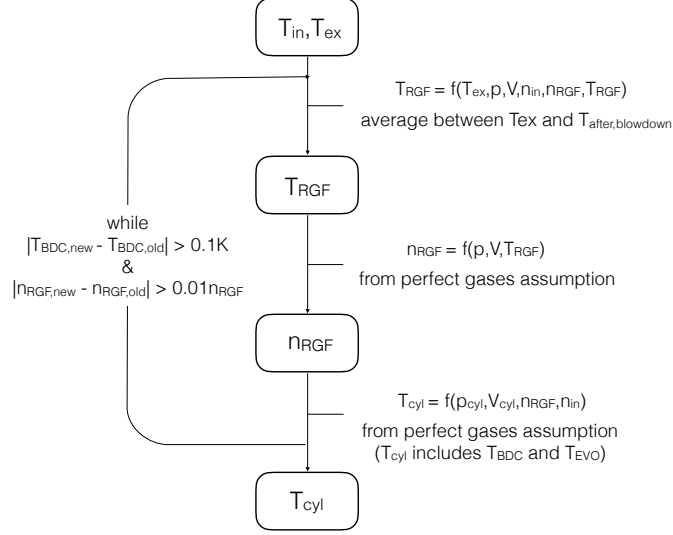


Figure A.25 – Description of the methodology for both BDC temperature and RGF moles and temperature. Three iterations are sufficient to reach convergence.

RGF temperature and mole quantity uncertainties

According to the work of Sjöberg et al. [130], which used combined experiments and numerical investigations, the RGF temperature is best estimated through an average of the exhaust manifold temperature T_{ex} and the in-cylinder temperature after the blowdown process:

$$T_{\text{RGF}} = \frac{T_{\text{ex}} + T_{\text{EVO}} \left(\frac{p_{\text{ex}}}{p_{\text{EVO}}} \right)^{\frac{\bar{\gamma}-1}{\bar{\gamma}}}}{2}, \quad (\text{A.56})$$

where the second term represents the temperature after the blowdown process if one assumes an isentropic expansion of the gases during it, as they reversibly expand against the decreasing in-cylinder pressure. Then, $\bar{\gamma}$ is the mean specific heat ratio over the whole blowdown process, p_{ex} the exhaust manifold pressure at TDC, and T_{EVO} and p_{EVO} the in-cylinder temperature and pressure at EVO. Although Sjöberg et al. model has provided good agreements between simulations and experimental measurements, I must inform the reader that the position of the exhaust temperature sensor is of crucial importance: the thermocouple junction is at the center of the flow, 255 mm away from the valve seat. The uncertainty on the RGF temperature is obtained using

Equation (A.17):

$$\begin{aligned}
u_{T_{\text{RGF}}}^2 &= \left(\frac{u_T}{2}\right)^2 \\
&+ \left(\left(\frac{p_{\text{TDC, ex}}}{p_{\text{EVO}}}\right)^{\frac{\bar{\gamma}-1}{\bar{\gamma}}}\right)^2 \left(\frac{u_{T_{\text{EVO}}}}{2}\right)^2 \\
&+ \left(\frac{(\bar{\gamma}-1)T_{\text{EVO}}\left(\frac{p_{\text{TDC, ex}}}{p_{\text{EVO}}}\right)^{\frac{-1}{\bar{\gamma}}}}{p_{\text{EVO}}\bar{\gamma}}\right)^2 \left(\frac{u_{p_{\text{TDC, ex}}}}{2}\right)^2 \\
&+ \left(\frac{p_{\text{TDC, ex}}(\bar{\gamma}-1)T_{\text{EVO}}\left(\frac{p_{\text{TDC, ex}}}{p_{\text{EVO}}}\right)^{\frac{-1}{\bar{\gamma}}}}{p_{\text{EVO}}^2\bar{\gamma}}\right)^2 \left(\frac{u_{p_{\text{EVO}}}}{2}\right)^2 \\
&+ \left(\frac{T_{\text{EVO}}\left(\frac{p_{\text{TDC, ex}}}{p_{\text{EVO}}}\right)^{\frac{\bar{\gamma}-1}{\bar{\gamma}}}\log\left(\frac{p_{\text{TDC, ex}}}{p_{\text{EVO}}}\right)}{\bar{\gamma}^2}\right)^2 \left(\frac{u_{\bar{\gamma}}}{2}\right)^2 .
\end{aligned} \tag{A.57}$$

The temperature at EVO is obtained using the ideal gas equation:

$$T_{\text{EVO}} = \frac{p_{\text{EVO}}V_{\text{EVO}}}{R \cdot n_{\text{cyl}}} , \tag{A.58}$$

with

$$n_{\text{cyl}} = n_{\text{in}} + n_{\text{RGF}} - n_{\text{bb}} , \tag{A.59}$$

n_{cyl} being the in-cylinder number of moles, at EVO in this case. As n_{in} refers to the number of moles per cycle sent by the MFCs and n_{RGF} the quantity kept in the cylinder through RGF, n_{bb} refers to the number of moles lost due to the *blow-by* phenomenon: the mass lost during the compression due to the piston segments imperfect sealing. The blow-by, accounting for less than 1% of the total mole quantity, is obtained following the methodology of Irimescu et al. [201], and its related uncertainty is obtained in Appendix A.4.12. The uncertainty of the EVO temperature is finally obtained as:

$$\begin{aligned}
u_{T_{\text{EVO}}}^2 &= \left(\frac{V_{\text{EVO}}}{R \cdot n_{\text{cyl}}} u_{p, \text{EVO}}\right)^2 \\
&+ \left(\frac{p_{\text{EVO}}}{R \cdot n_{\text{cyl}}} u_{V, \text{EVO}}\right)^2 \\
&+ \left(\frac{-p_{\text{EVO}}V_{\text{EVO}}}{R \cdot n_{\text{cyl}}^2}\right)^2 \cdot \left(u_{n, \text{in}}^2 + u_{n, \text{RGF}}^2 + u_{n, \text{bb}}^2\right) .
\end{aligned} \tag{A.60}$$

The following uncertainty to obtain is the one of n_{RGF} . Using the ideal gas law we obtain:

$$n_{\text{RGF}} = \frac{p_{\text{TDC,ex}} V_{\text{TDC}}}{R \cdot T_{\text{RGF}}} , \quad (\text{A.61})$$

where $p_{\text{TDC,ex}}$ is the in-cylinder pressure at the TDC happening during the exhaust process. Its uncertainty is readily derived:

$$\begin{aligned} u_{n_{\text{RGF}}}^2 &= \left(\frac{V_{\text{TDC}}}{R \cdot T_{\text{RGF}}} u_{p_{\text{TDC,ex}}} \right)^2 \\ &+ \left(\frac{p_{\text{TDC,ex}}}{R \cdot T_{\text{RGF}}} u_{V_{\text{TDC}}} \right)^2 \\ &+ \left(\frac{-p_{\text{TDC,ex}} V_{\text{TDC}}}{R \cdot T_{\text{RGF}}^2} u_{T_{\text{RGF}}} \right)^2 . \end{aligned} \quad (\text{A.62})$$

Finally, the uncertainty on the moles lost to the blow-by phenomenon can be derived, neglecting the uncertainty on the molar masses, as follows:

$$n_{\text{bb}} = \frac{m_{\text{bb}}}{M_{m,\text{bb}}} = \frac{\int dm_{\text{bb}}}{M_{m,\text{bb}}} , \quad (\text{A.63})$$

$$u_{n,\text{bb}}^2 = \sum u_{\Delta m,\text{bb}}^2 , \quad (\text{A.64})$$

with the uncertainty on the rate of mass exchange due to blow-by being obtained by assuming that its most impacting component is the crank angle:

$$u_{\Delta m,\text{bb}}^2 = \left(\frac{\partial \Delta_{m,\text{bb}}}{\partial \theta} u_{\theta} \right)^2 . \quad (\text{A.65})$$

Using the developed uncertainty expressions on the hydrogen test bench, we obtain that $U_{95,n,\text{cylinder}} = 1.6\%$. Its composition breakdown, given in Figure A.26, shows that the RGF uncertainty accounts for 31% of the cylinder mole uncertainty although RGF accounts for a mere 3% of the total mole quantity. Similar figures for RGF have been obtained experimentally by Miller et al. for a wide open throttle SI engine [202]. Four times more accurate MFC will only make the total relative $U_{95,n,\text{cylinder}}$ drop to 0.5%.

BDC and cycle temperatures

The BDC temperature can be obtained from the ideal gas law:

$$T_{\text{BDC}} = \frac{p_{\text{BDC}} V_{\text{BDC}}}{n_{\text{cyl}} R} , \quad (\text{A.66})$$

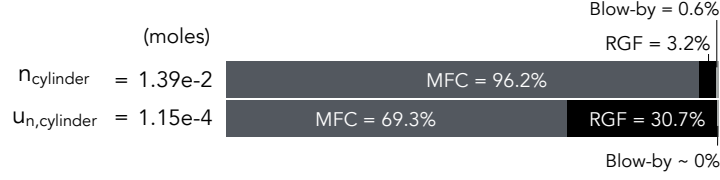


Figure A.26 – In-cylinder mole quantity and mole uncertainty breakdown for typical firing cases. Although RGF accounts for a mere 3% of the total mole quantity, its related uncertainty reaches 31%.

The difference between the measured intake temperature and the effective BDC temperature can be quite significant, especially when the RGF are hot, see Figure A.27. The displayed linear relation between T_{in} and T_{BDC} are for motoring and firing (H_2 with $\phi = 0.2$) runs with intake temperature ranging between 50°C and 120°C. The uncertainty of the BDC temperature is readily obtained from Equation (A.17), yet the need for an iterative process is clear: $u_{T_{\text{RGF}}}$ requires to know the in-cylinder temperature uncertainty (at EVO), which is based on the in-cylinder moles quantity uncertainty, itself based on $u_{T_{\text{RGF}}}$, both of which needing T_{BDC} to know the in-cylinder temperature. Convergence at 0.1 K is generally obtained after two-three iterations.

The uncertainty on the in-cylinder temperature is obtained from the ideal gas law using the previously-obtained T_{BDC} , and is displayed in Figure A.28 for the 0.26 equivalence ratio hydrogen fired case. Although these uncertainties are significant (around 3% of relative U_{95}), they are often used to study the formation of pollutants [203] or the fuel properties: the temperature at BDC and near TDC can be used as benchmarks to characterise a fuel [131, 204]. Therefore caution should be taken when using the in-cylinder temperature to characterise a fundamental phenomenon or property.

Such temperature uncertainties are achievable only when considering the lower bound for the in-cylinder pressure. When using the upper bound for the

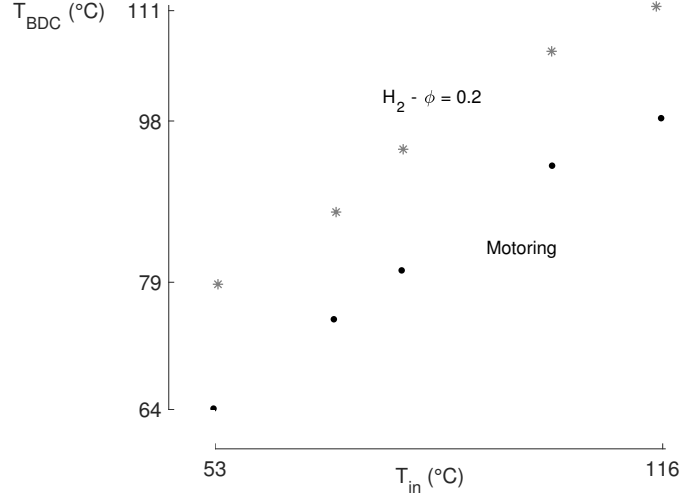


Figure A.27 – Computed effective temperature at BDC as a function of the measured intake temperature for motoring and firing (H_2 with $\phi = 0.2$) conditions. The observed relations are only valid for these specific conditions. The major impact of the RGF temperature on the BDC temperature can be observed, as it is the main difference between motoring and firing conditions.

in-cylinder pressure, the BDC and EVO temperature uncertainties are higher than 100 K, which makes no physical sense. Moreover let us recall that the chamber spatial gradients are not being account for. Finally the current loop is not complete as the heat capacity ratio γ and the specific heat capacity c_p are themselves a function of the in-cylinder temperature, and their uncertainties should be accounted for.

Heat capacity ratio and specific heat capacity uncertainties

The heat capacity ratio γ and the specific heat capacity c_p are themselves a function of the in-cylinder temperature, and their uncertainties should be accounted for in the Sjöberg method [130]. Since I am using the JANAF tables for heat capacity computation, the uncertainty on γ and c_p must be inserted into the iteration loop and can be obtained as follows:

$$\gamma = \frac{\sum_i \gamma_i \cdot n_i}{\sum_i n_i} \quad (\text{A.67})$$

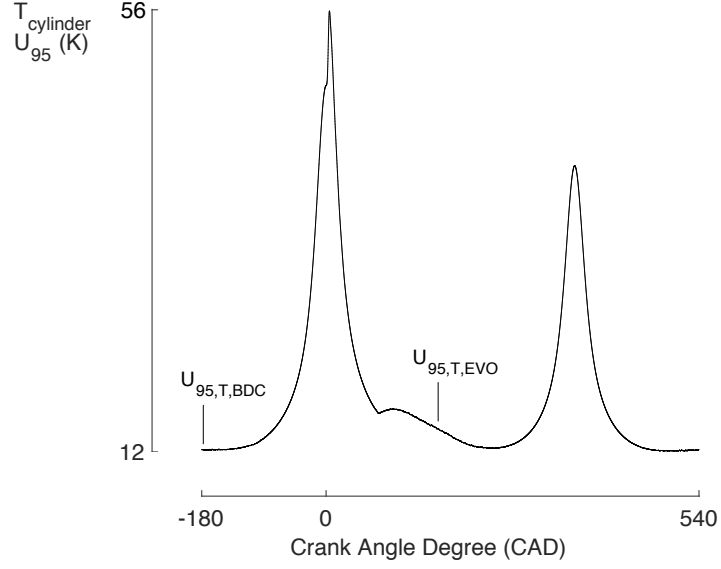


Figure A.28 – In-cylinder temperature U_{95} . For BDC and EVO temperatures, the uncertainty is around 12 K, and 56 K at peak pressure. In other words, the in-cylinder temperature relative U_{95} is between 1% and 3% throughout the entire engine cycle.

$$\gamma_i = \frac{C_{p,i}}{C_{p,i} - R} \quad (\text{A.68})$$

$$u_{\gamma_i}^2 = \left(\frac{-1}{(C_{p,i} - R)^2} \right)^2 u_{C_{p,i}}^2 \quad (\text{A.69})$$

$$u_{C_{p,i}} = R \cdot (a_{1,i} + 2a_{2,i}T + 3a_{3,i}T^2 + 4a_{4,i}T^3)u_{T_{\text{cyl}}} \quad (\text{A.70})$$

The relative U_{95} is found below 0.05% throughout the cycle, see Figure A.29. Repeatability uncertainties are not taken into account since already included into the pressure (hence temperature) signal.

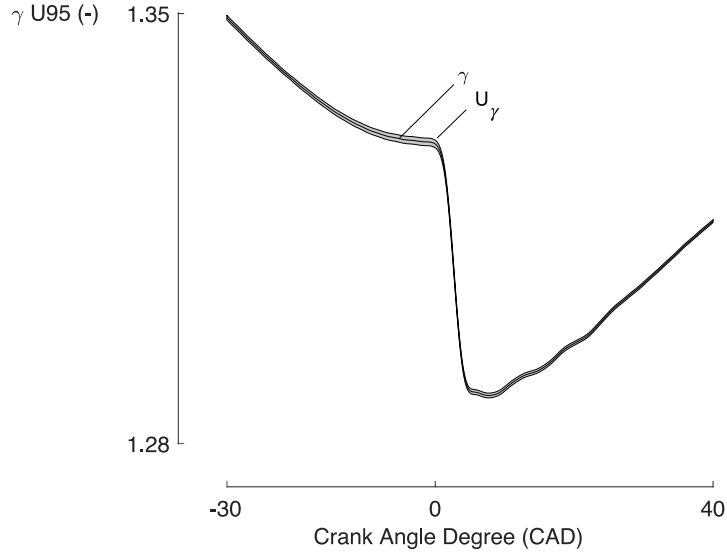


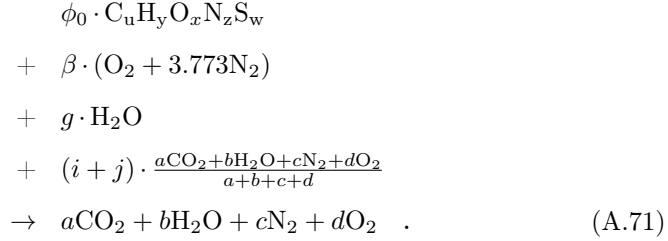
Figure A.29 – The relative U_{95} on the heat capacity ratio is found below 0.05% throughout the cycle.

A.4.5 Equivalence ratio

The equivalence ratio is often used as an indicator to represent the engine operating mode, or to represent engine performance trends. It is therefore interesting obtaining its related uncertainty and observing the driving parameters. Two main methods exist to compute the equivalence ratio: from the intake species concentrations, or from the exhaust species concentrations. The derivation from intake species is detailed here as it is more often used, yet the derivation from exhaust concentrations is fairly similar and reviewed in [205]. The uncertainty on the equivalence ratio is finally obtained using the developed methodology and further analysed.

To obtain the uncertainty on the equivalence ratio, one must first write down the most general combustion equation for piston engine combustion. The considered case is the complete combustion of an hydrocarbon containing oxygen, nitrogen and sulfur atoms, using EGR and taking the RGF into account, with the possibility of water addition or air moisture content. Unburned species that might be recirculated are therefore neglected since the equivalence ratio is always computed considering the injected/admitted fuel. The initial equivalence ratio which does not consider the oxygen recirculated by the EGR or

RGF is termed ϕ_0 . The complete combustion equation is therefore:



With β the number oxygen moles required to ensure the complete combustion of one mole of $C_u H_y O_x N_z S_w$:

$$\beta = \frac{2u + y/2 - x + 2w}{2} \quad . \tag{A.72}$$

The coefficient i represents the EGR and is linked to the number of recirculated moles:

$$i = \text{EGR} \cdot (a + b + c + d) \quad . \tag{A.73}$$

The coefficient j represents the RGF and is linked to the number of residual exhaust moles:

$$j = \text{RGF} \cdot (a + b + c + d) \quad . \tag{A.74}$$

Following the definition of the equivalence ratio, one obtains:

$$\begin{aligned}
 \phi &= \frac{n_{\text{fuel}}}{n_{O_2}} \bigg|_{\text{cyl}} \cdot \frac{n_{O_2}}{n_{\text{fuel}}} \bigg|_{\text{stoic}} \\
 &= \frac{\phi_0}{\beta + (i + j) \cdot d} \cdot \frac{\beta}{1} \\
 &= \frac{n_{\text{in, fuel}}}{n_{\text{in, O}_2} + n_{O_2, ex} \cdot [n_{\text{EGR}} + n_{\text{RGF}}]} \cdot \beta
 \end{aligned} \tag{A.75}$$

where n_{RGF} has been obtained in the previous section, n_{EGR} is either known from the process or from the MFC if it is simulated, and the various intake mole flow rates have been obtained in Appendix A.3.1.

The remaining uncertainties from Equation (A.75) is the exhaust oxygen mole quantity. It can be obtained from molecule sensitive gas analysers such as Non Dispersive Infrared Sensor (NDIR), Fourier-Transform Infra-Red spectroscopy (FTIR), or UV spectroscopy. These systems can achieve high precision measurements but are extremely expensive. Lambda sensors, on the other

hand, are low cost and can be used for oxygen concentration measurement with U_{95} uncertainties below 0.25 O₂%, as obtained in Appendix A.3.5. This section was performed for wet exhaust gas measurements, yet it can be done for dry measurements as well with a similar procedure, see [205].

The uncertainty on the equivalence ratio is consequently obtained from Equations (A.17), (A.18) and (A.75):

$$\begin{aligned}
 u_{\phi}^2 = & \left(\frac{\partial \phi}{\partial n_{\text{in, fuel}}} \right)^2 \cdot u_{n, \text{in, fuel}}^2 \\
 & + \left(\frac{\partial \phi}{\partial n_{\text{in, O}_2}} \right)^2 \cdot u_{n, \text{in, O}_2}^2 \\
 & + \left(\frac{\partial \phi}{\partial n_{\text{O}_2, \text{ex}}} \right)^2 \cdot u_{n, \text{O}_2, \text{ex}}^2 \\
 & + \left(\frac{\partial \phi}{\partial n_{\text{EGR}}} \right)^2 \cdot u_{n, \text{EGR}}^2 \\
 & + \left(\frac{\partial \phi}{\partial n_{\text{RGF}}} \right)^2 \cdot u_{n, \text{RGF}}^2,
 \end{aligned} \tag{A.76}$$

with the partial derivatives obtained from Equation (A.75).

For the example case with an equivalence ratio of 0.18, the composition of the equivalence ratio uncertainty is given for the most generic case (no EGR) in Figure A.30. The main uncertainty driver is the uncertainty on the fuel quantity given that the fuel MFC is being used quite low in its range in this case. The overall U95 uncertainty is about 2.6%. Interestingly, the RGF and EGR do not impact significantly the equivalence ratio uncertainty. This ought to the unburned emissions not being considered in this section.



Figure A.30 – Equivalence ratio uncertainty breakdown for a low equivalence ratio run, without EGR, and with a combustion efficiency of 99.2%. The most impacting component is the fuel uncertainty itself, and the RGF is not impacting given that the unburned molecules are neglected for the computation of the equivalence ratio.

A.4.6 Maximum Pressure Rise Rate (MPRR)

Given that pressure and CA are discrete data experimentally acquired, the MPRR can be expressed in discrete change terms (Δ) from its definition:

$$\text{MPRR} = \max \left(\frac{dp}{d\theta} \right) \cong \max \left(\frac{\Delta p}{\Delta \theta} \right) . \quad (\text{A.77})$$

If one uses Equation (A.17) on this particular case, the obtained uncertainty would have no physical sense and render relative uncertainties higher than 100%: the differentiation on the crank angle and on the pressure would add further uncertainty. For example, as the uncertainty on the crank angle is the LC, the uncertainty on $\Delta\theta$ would be twice the LC. Following that mindset, the uncertainty on the pressure being close to 1 bar, the uncertainty on the MPRR would be around $\frac{2\text{bar}}{0.2 \text{ CAD}} = 10 \text{ bar/CAD}$.

However the physical continuity of the compression and combustion phenomenon tells us that if the measured value at time θ_i has some offset/error compared to the real value, the same offset would be obtained at time θ_{i+1} . The MPRR being the maximum rate at which the pressure rises in time, its uncertainty is rather linked to the maximal variation in pressure-rise with time:

$$u_{\text{MPRR}}^2 = \max \left(\frac{\partial \text{MPRR}}{\partial \theta} u_{\theta} \right)^2 , \quad (\text{A.78})$$

The U_{95} relative uncertainty on the MPRR is around 4% of the MPRR itself, see Figure A.31. Indeed, the continuity of the pressure curve helps keeping the MPRR uncertainty low, even though the pressure rise is peaking.

A.4.7 Combustion noise: the case of Ringing Intensity (RI)

The combustion noise is a critical point of attention for engine combustion research given the possible related engine damage. Different metrics exist to quantify combustion noise, from the HCCI-suited RI (MW/m^2) indicating the power flux delivered by the pressure waves [154], to the *Noise* (dB) indicating the perceived noise outside of the engine (more indicated for conventional engine modes [206]). Given that the RI metric has been specifically developed

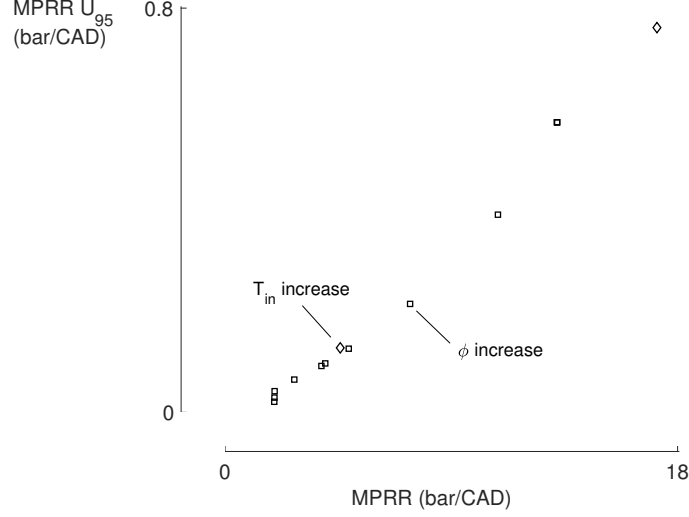


Figure A.31 – The relative U_{95} uncertainty on the MPRR is linearly correlated to the MPRR itself, and below 4% of the MPRR itself.

for HCCI engines and is still being used today (see for example [207, 208]), this metric uncertainty will be developed here-under. However the uncertainty related to any other metric can be obtained following the general methodology developed in this paper.

In HCCI engines, as the ringing results in resonating in-cylinder pressure waves due to high intensity local auto-ignitions, the ringing is defined as the energy content of such pressure waves and the following expression is used [154]:

$$RI = \frac{1}{2\gamma} \frac{(\Delta P)^2}{P_{\max}} \sqrt{\gamma RT} . \quad (\text{A.79})$$

Ringing is mainly linked to ΔP , the ringing amplitude of a combustion cycle. It is defined as the average over 100 consecutive cycles of the maximal amplitude of the pressure signal filtered between 4 kHz and 25 kHz [154]. Recalling that for any measurand X for which we seek the uncertainty of its variation ΔX along the crank angle evolution one has:

$$u_{\Delta X} = \frac{\partial \Delta X}{\partial \theta} u_{\theta} , \quad (\text{A.80})$$

the uncertainty on the RI is obtained using Equations (A.17) and (A.79).

This uncertainty result is general as far as the RI metric is concerned, yet it does not include the influence of the pressure filtering. Although the obtained RI is highly dependant on the pressure filter, the exact same cut-off frequencies are always used for engines having a bore of about 86mm [154], a standard for small size and automotive engines.

Using our example hydrogen HCCI engine test bench, the RI and related uncertainties are plotted against the MPRR for several firing runs in Figure A.32. Ringing seems to appear in the hydrogen HCCI test bench at around 11 bar/CAD of MPRR. The RI has a low uncertainty, even when it is intense and damaging to the engine (i.e. higher than 2 MW/m²).

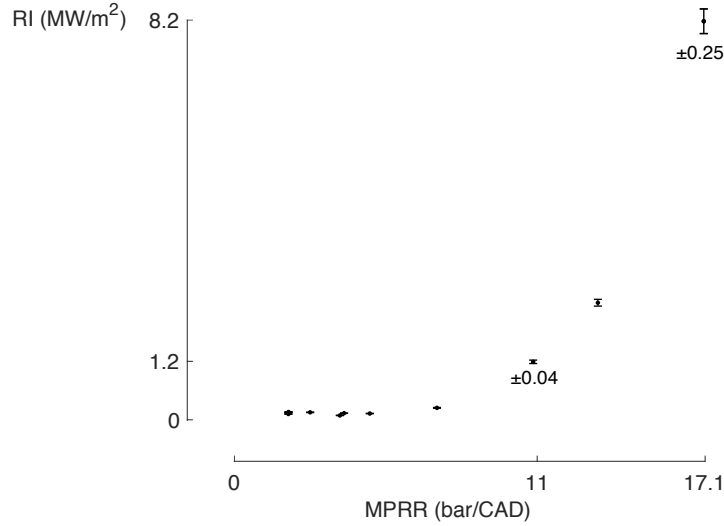


Figure A.32 – An MPRR of 11 ± 0.39 bar/CAD is required to trigger the ringing phenomenon, and 14 bar/CAD are required to reach the generally accepted threshold for damaging ringing: 2 MW/m². The relative U_{95} on the RI is low and about 3%.

Achieving a moderate ringing intensity even with high MPRR is explained by the high pressures at the combustion onset due to the high engine compression ratio, hence decreasing the energy content of the oscillating pressure waves. This similar effect has already been observed when increasing the intake pressure of the engine to reduce the ringing intensity [165].

A.4.8 Q_{fuel} and FuelMEP

Given that any fuel LHV can be known precisely (with negligible uncertainty compared to MFC uncertainties), the LHV uncertainty is neglected and the contained cycle fuel energy (Q_{fuel}) uncertainty is obtained using Equation (A.17) and the definition of Q_{fuel} :

$$Q_{\text{fuel}} = \text{LHV}_{\text{H}_2} \cdot n_{\text{in, H}_2} \cdot (1 + (1 - \eta_{\text{comb}}) \cdot \text{RGF}) \quad (\text{A.81})$$

where all the necessary uncertainties have been obtained previously.

The Fuel Mean Effective Pressure (FuelMEP) and its uncertainty are derived from Equation (A.17) as follows:

$$\text{FuelMEP} = \frac{Q_{\text{fuel}}}{V_c} \quad , \quad (\text{A.82})$$

$$u_{\text{FuelMEP}}^2 = \frac{u_{Q_{\text{fuel}}}^2}{V_c^2} + \frac{Q_{\text{fuel}}^2 u_{V_c}^2}{V_c^4} \quad . \quad (\text{A.83})$$

For the reference case using hydrogen at an equivalence ratio of 0.26 and without EGR, we obtain $Q_{\text{fuel}} \pm U_{95} = 366.7 \pm 5.4 \text{ J}$ (1.5%), with $\text{FuelMEP} \pm U_{95} = 8.45 \pm 0.12 \text{ bar}$.

A.4.9 Indicated efficiency and IMEP

The IE and IMEP are solely obtained from the pressure, volume, and Q_{fuel} data. Given that pressure and volume are discrete data, their derivatives can be expressed in terms of discrete change (Δ). Following the net IE and IMEP definitions, and using Equation (A.17), their uncertainties are as follows:

$$u_{\text{IMEP}} = \sqrt{\sum_{\theta=-180}^{180} \cdot \cdot} \quad , \quad (\text{A.84})$$

$$u_{\text{IE}} = 100 \sqrt{\sum_{\theta=-180}^{180} \cdot \cdot} \quad , \quad (\text{A.85})$$

$$\cdot \cdot = \left(\frac{\Delta V_{\theta}}{M} u_{p_{\theta}} \right)^2 + \left(\frac{p_{\theta}}{M} u_{\Delta V_{\theta}} \right)^2 + \left(\frac{-p_{\theta} V_{\theta}}{M^2} u_M \right)^2 \quad , \quad (\text{A.86})$$

with M being $V_{\text{displacement}}$ for the IMEP and Q_{fuel} for the IE.

The in-cylinder pressure uncertainty to use (whether overall or only *Type*

B , pegging, and TDC offset) will depend on the IMEP that is being considered: of a particular cycle, or of the average cycle.

Still, the lower or upper bound for the pressure uncertainty can be used. For the considered example test bench, the IMEP U_{95} computed with the lower bound on the pressure uncertainty is three times smaller than with the upper bound, see Figure A.33. From the cumulative build-up of the IMEP uncertainty it can be seen that both approaches do not accumulate the uncertainty in the same way along the combustion cycle. The higher uncertainty of the upper bound pressure during the breathing phase is responsible for the factor three difference in uncertainty from both approaches.

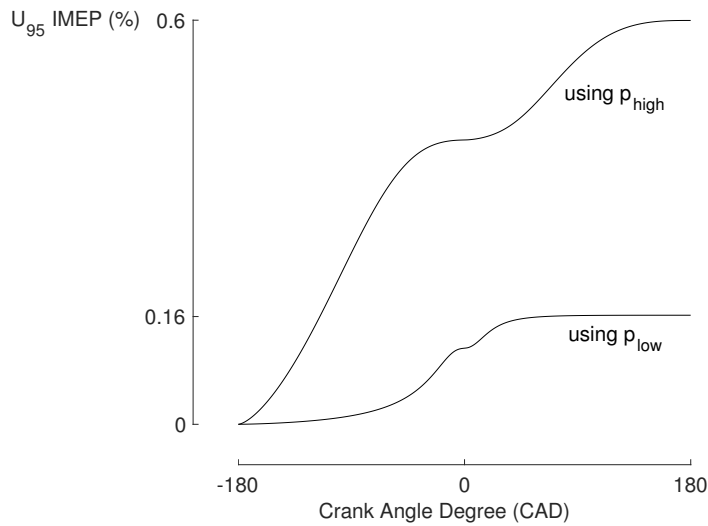


Figure A.33 – The U_{95} of the IMEP is three times higher when computed using the upper bound of the pressure uncertainty. This difference results from the high uncertainty during the breathing phase as seen from the cumulative build-up of the uncertainty.

Whichever the lower or upper bound in-cylinder pressure uncertainty being used, the relative U_{95} uncertainty on the IMEP stays below 1% regardless of the number of consecutive recorded cycles and CoV_{IMEP} , see Figure A.34. This

tells us that the cycle-to-cycle variations of the considered example test bench are randomly occurring from one cycle to another instead of gradually evolving from one state to another. Such variations are stochastic and linked to the test bench, not to the sensor repeatability errors. However they are part of the uncertainty analysis: they are included in the in-cylinder pressure uncertainty through *Type A* uncertainties.

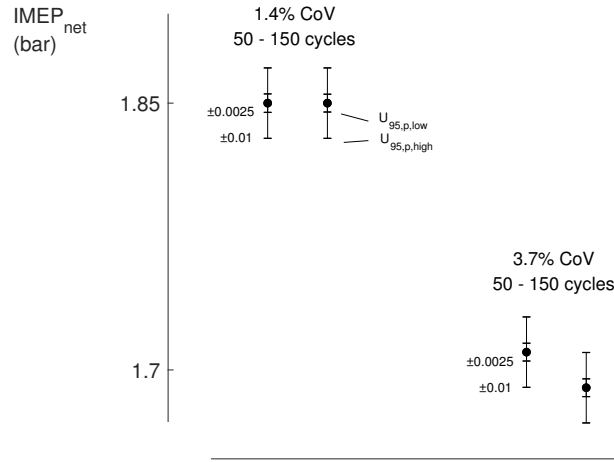


Figure A.34 – Mean IMEP and related U_{95} when considering low and high CoV, lower or upper bound of the in-cylinder pressure uncertainty, and 50 or 150 consecutive cycles recorded. Whichever the CoV case considered, the number of consecutive cycles recorded and the in-cylinder pressure uncertainty used have no substantial influence on the IMEP uncertainties.

For the reference case using hydrogen at an equivalence ratio of 0.26 and without EGR, we obtain $IE \pm U_{95} = 37.1 \pm 0.3\%$, with $IMEP \pm U_{95} = 3.13 \pm 0.02$ bar. Finally, the IMEP is composed at more than 99% by the in-cylinder pressure *Type B*, pegging, and TDC offset uncertainties, see Figure A.35, given that at the times where the *Type A* in-cylinder pressure is substantial, dV is close to zero.



Figure A.35 – Breakdown composition of the IMEP uncertainty. The Type B, pegging, and TDC offset in-cylinder pressure uncertainty is the main contributor by far.

A.4.10 Torque, Brake Efficiency and BMEP

The output torque is measured every 0.7 CAD and for the same number of consecutive cycles as for the in-cylinder pressure. The torque sensor specifications are given in Table A.3 and the torque uncertainty is obtained following once again Equation (A.14). *Type B* uncertainty is $U_{95,TypeB} = \pm 0.36 \text{ Nm}$ and *Type A* uncertainty is $U_{95,TypeA} = \pm 0.26 \text{ Nm}$. Given that the torque is a measurand and not a combined uncertainty of other measurands (as for the IMEP), its global uncertainty encompasses *Type A* and *Type B* uncertainties, even though it includes the cycle-to-cycle variabilities inherent to the test bench, a physical and valuable information as demonstrated in Appendix A.4.9.

The BE and its uncertainty are derived from Equation (A.17) as follows:

$$\text{BE} = \frac{\text{BMEP}}{\text{FuelMEP}} = \frac{\frac{C \cdot \omega \cdot 2.60}{\text{rpm}}}{Q_{\text{fuel}}} = 4\pi \frac{C}{Q_{\text{fuel}}} , \quad (\text{A.87})$$

$$u_{\text{BE}}^2 = 4\pi \left(\frac{u_C^2}{Q_{\text{fuel}}^2} + \frac{C^2 u_{Q_{\text{fuel}}}^2}{Q_{\text{fuel}}^4} \right) , \quad (\text{A.88})$$

where C is the average torque over a complete cycle expressed in (Nm), and ω is the angular velocity of the crank expressed in (rad/s).

The BMEP and its uncertainty are obtained from Equation (A.17) as follows:

$$\text{BMEP} = \text{BE} \cdot \text{FuelMEP} \quad (\text{A.89})$$

$$u_{\text{BMEP}}^2 = \text{FuelMEP}^2 \cdot u_{\text{BE}}^2 + \text{BE}^2 \cdot u_{\text{FuelMEP}}^2 \quad (\text{A.90})$$

For the reference case using hydrogen at an equivalence ratio of 0.26 and without EGR, we obtain $BE \pm U_{95} = 27.1 \pm 0.4\%$, with $BMEP \pm U_{95} = 2.25 \pm 0.02$ bar. The relatively low BE is explained by the low power density, single cylinder configuration, and engine small stroke-to-bore ratio inducing a pancake combustion chamber that maximises the heat exchange area, as obtained by Caton et al. [209] in a similar stroke-to-bore ratio HCCI engine. Indeed the engine stroke was initially designed for piston-bowl Diesel injection where the chamber would have a much lower surface-to-volume ratio.

A.4.11 Engine wall heat losses

Engine walls heat transfer calculations is, in many ways, a crucial part of the HCCI motoring and combustion raw data post-processing. It impacts the heat release analysis (and therefore all the combustion timings) and, of course, all the calibrations studies undergone in this section. In this subsection, the description of a HCCI-suited heat loss model is first performed, followed by the determination of its associated errors/uncertainties. The calibration process for motoring and fired conditions is explained in the second part of this subsection.

Heat transfer model and calibration

Equipping research engine walls with heat flux sensors is a tedious process, that asks for a lot of maintenance and fine tuning [133, 210–212]. Having such a heat-flux sensor on a test bench being rare (being a research field in its own), I investigated the performances and related errors of the heat transfer correlations that are used in the vast majority of experimental and numerical studies.

All existing heat flux models assume an overall convective heat transfer through Newton’s convective cooling/heating law:

$$dQ_{\text{loss}} = h \cdot A \cdot (T - T_{\text{wall}})dt \quad , \quad (\text{A.91})$$

where A is the total mixture-wall exchange surface area (m^2) and h is the convection coefficient ($\text{W}/\text{m}^2/\text{K}$). All models develop their own correlation for the convection coefficient, every time based on the convective heat transfer on a flat plate using the boundary layer theory. Among the existing SI and CI engine convective coefficient correlations that have been tested against HCCI experiments are the ones from Hohenberg, Annand, Woschni, and Bargende

[210, 213]. Without any modification to their original correlations except for the scaling factor, these two independent studies found Hohenberg and Bargende to best fit HCCI conditions. Yet, Hohenberg correlation is by far the easiest to use, readily from the other post-processing parameters:

$$h_{\text{Hohenberg}} = \alpha_{\text{scaling}} \cdot L^{-0.06} \cdot p^{0.8} \cdot T^{-0.4} \cdot (S_p + 1.4)^{0.8} , \quad (\text{A.92})$$

where p is the instantaneous in-cylinder pressure expressed in bar, L is a characteristic length, T the instantaneous in-cylinder temperature, and finally S_p the mean piston speed with $S_p = 2 \cdot \text{stroke} \cdot \text{RPM}/60$. The original Hohenberg scaling factor for SI and CI engines is $\alpha_{\text{scaling}} = 130$. The commonly used characteristic length in the literature for Hohenberg correlation is the instantaneous cylinder volume itself. Still, the original Hohenberg correlation considers the cubic root of the instantaneous cylinder volume instead, as reported by [133, 210].

Even with calibration, Hohenberg and Bargende cannot match perfectly HCCI wall heat fluxes shape over a whole cycle. To cope with this issue, [211] and [212] have modified existing correlations to better fit HCCI characteristics. Chang et al. modified the original Woschni correlation by changing the cylinder bore to the instantaneous piston stroke, as the characteristic length, to match HCCI operation. Still, due to the ill-suited Woschni base in the way it accounts for combustion, Chang model has been shown less effective than Hohenberg by two independent experimental HCCI studies [191, 213]. Hensel et al. modified Annand correlation by using Hohenberg characteristic length and by deciding to take a combination of the engine velocity and charge velocity as characteristic velocity for the correlation. Still Hensel correlation is relatively inconvenient to use as it requires new parameters such as the valve lift profile, mixture dynamic viscosity and mixture heat conductivity throughout the cycle.

Broekaert et al. [210] recently performed a comparative study on the most used correlations: Hohenberg, Annand, Woschni, Bargende, Chang, and Hensel. They showed that none of the correlations could be used directly, but rather needed their scaling factors to be re-calibrated against wall heat flux sensors for any change in operating condition (e.g. intake temperature, equivalence ratio, engine speed, fuel, etc.). In addition, they showed that all the correlations are effective in capturing compression ratio and engine speed influence and

that taking the mixture gas properties into account (Annand, Bargende, and Hensel) has a negligible impact on the wall heat flux prediction.

Given its comparable performances to other correlations, and ease of use, the convection coefficient correlation chosen for this study is the one from Hohenberg. Four experimental heat flux curves from the previous review studies are analysed hereafter to showcase how the Hohenberg correlation performs and to extract the uncertainty on the wall heat loss correlations. Figure A.36 displays the estimation error on the experimental heat flux using the original Hohenberg correlation with the cubic root of the chamber volume as the characteristic length. The calibration has been performed on the scaling factor of Hohenberg so that the estimated heat lost through the engine walls equals the experimental one.

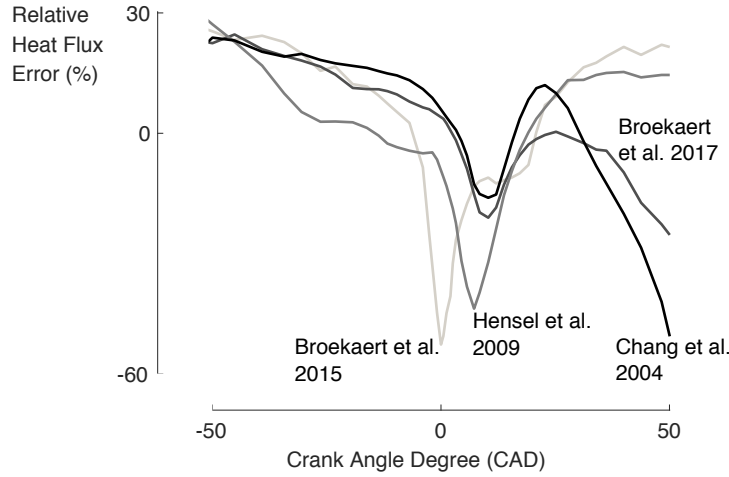


Figure A.36 – Relative errors made by the calibrated Hohenberg model on the four studied experimental heat fluxes [133, 210–212]. A clear error pattern is observed, the error intensity seems proportional to the combustion timing.

Looking at the relative errors performed by Hohenberg, two comments need to be made. First, the error intensity seems to be proportional to the combustion timing. The peak error occurring at the time of combustion, the maximal error is observed to decrease when the combustion is delayed. Secondly, a clear

trend in the performed error is observable up to the end of combustion. I believe this error (plus a time shift) to be related to the difference between the mean piston speed and its actual speed. This joins the idea of Bargende and Hensel of introducing the mixture kinetic energy in the characteristic velocity term, since the piston motion induces gas kinetics with some delay. Yet this idea is out of the scope of this study to be investigated and only Hohenberg calibrated correlation is considered given the above study.

To conclude on the heat loss correlation part, the associated uncertainty has to be extracted. Given the error intensities observed in Figure A.36, and assuming that the uncertainty of the experimental heat flux itself is at least one order of magnitude lower, the relative U_{95} uncertainty on the heat losses is assumed to be $\pm 50\%$ throughout the whole combustion cycle.

Wall heat loss model calibration

In order to be sensible to the physical reality, the heat losses estimated from the correlation must be such that the tail and head of the gross heat release are flat, i.e. no heat is being released before or after the combustion. However, given the inappropriate behavior of the wall heat loss correlations for HCCI engines, forcing the flatness of the gross heat release may not render the correct amount of dissipated heat through the walls hence flawing the energy closure. Yet the calibration of the convection correlation scaling factor to flatten the tail and head of the cumulative gross heat release is crucial to obtain representative combustion timings. Therefore I choose to always optimise the flatness or their gross heat release 10 CAD away from their CA10 and CA90 to obtain representative combustion timings.

A.4.12 Heat release and combustion timings

The gross heat release uncertainty and related combustion timing uncertainties (i.e CAX) are at the far end of the uncertainty propagation chain. They will depend on the in-cylinder pressure, pressure gradient, volume, crank angle, wall heat losses, blow-by, specific heat ratio, and therefore temperature. Indeed, the piston engine system can be represented through the first law of thermodynamics and the ideal gas assumption. For a system of internal energy U that is proceeding to exchanges with its surroundings (heat Q , work W , and *blow-by* mass m of specific enthalpy h), the differential form of the first law

of thermodynamics for an open system was obtained in Equation (A.45). The term dQ_{net} is the infinitesimal change in net, or global, heat available for the gas from the combustion. This available heat is to be differentiated from the gross heat released by the combustion, from which a part is lost to the system boundaries, all linked by the following equation:

$$dQ_{gross} = dQ_{net} + dQ_{loss} . \quad (\text{A.93})$$

Combining equations Equations (A.45) and (A.93), one obtains:

$$\begin{aligned} dQ_{gross} &= \frac{\gamma}{\gamma-1} \cdot p \cdot dV + \frac{1}{\gamma-1} \cdot V \cdot dp \\ &\quad - \frac{\gamma}{\gamma-1} \cdot \frac{RT}{Mm} \cdot dm + dQ_{loss} . \end{aligned} \quad (\text{A.94})$$

Being interested in the uncertainty of the cumulative gross heat release, and using discrete change terms (Δ) to represent derivatives of discrete data, one can write:

$$u_{Q_{gross},\theta}^2 = \sum_{\theta=-30 \text{ CAD}}^{40 \text{ CAD}} u_{\Delta Q_{gross},\theta}^2 . \quad (\text{A.95})$$

Finally, applying Equation (A.17) to Equation (A.94) given that the heat release is a combination of measurands but not a measurand itself, one obtains:

$$\begin{aligned} u_{\Delta Q_{gross},\theta}^2 &= \left(\frac{1}{\gamma_\theta-1} u_{\Delta(p_\theta V_\theta)} \right)^2 + (p_\theta \cdot u_{\Delta V_\theta})^2 \\ &\quad + (\Delta V_\theta \cdot u_{p,\theta})^2 + \left(\frac{\frac{RT_\theta}{Mm_\theta} \Delta m_\theta - \Delta(p_\theta V_\theta)}{(\gamma_\theta-1)^2} u_{\gamma,\theta} \right)^2 \\ &\quad + \frac{\gamma_\theta}{\gamma_\theta-1} \frac{RT_\theta}{Mm_\theta} u_{\Delta m,\theta} + \frac{\gamma_\theta}{\gamma_\theta-1} \frac{R \Delta m_\theta}{Mm} u_{T,\theta} \\ &\quad + u_{\Delta Q_{loss},\theta} , \end{aligned} \quad (\text{A.96})$$

where

$$u_{\Delta(p_\theta V_\theta)}^2 = \Delta V_\theta \cdot u_{p,\theta} + p_\theta \cdot u_{\Delta V_\theta} + V_\theta \cdot u_{\Delta p,\theta} + \Delta p_\theta \cdot u_{V,\theta} . \quad (\text{A.97})$$

The gross heat release must always be computed for individual cycles and therefore only the *Type B*, pegging, and TDC offset uncertainties of the in-cylinder pressure have to be used. Indeed, an average cycle will have longer combustion duration than any individual cycle and would therefore not be

representative for the heat release analysis.

Using Equation (A.17) implies that the hypothesis of independent variables is verified for the equation of the derivative of the gross heat release. Still it is not the case as the in-cylinder mass, temperature, blow-by and heat losses are all correlated to the in-cylinder pressure and volume. However, accounting for those would be done by computing co-variances in the form of second derivatives and would therefore be negligible compared to the first derivatives of the other terms.

The uncertainty on the cumulative gross heat release is reported in Figure A.37. Prior to the TDC and CA10, it is rather low since the uncertainties on all the components are low. Yet as soon as the combustion starts, and since it is a cumulative value, the uncertainties on Q_{gross} start to add up and end at a substantial relative value: $U_{95,Q,\text{gross}} = \pm 6.8\%$. Performing an energy closure on the gross heat release by comparing it to the input fuel energy is quite imprecise for HCCI engines due to the high uncertainty on the wall heat loss models. Moreover, if the wall heat losses are tuned for any new operating conditions to allow a flat curve (at the start and end) of the cumulative gross heat release energy, they cannot represent the correct amount of dissipated energy anymore, hence a flawed energy closure. This consideration is further developed in Appendix A.4.11 and in [191]. Therefore the authors discourage the use of energy closure for HCCI engines, yet it could be considered in the case the heat loss model calibrated for correct estimation of dissipated energy would also provide a flat start and end for the cumulative gross heat release curve.

The uncertainty on the wall heat losses accounts for more than 85% of the total uncertainty, see the breakdown in Figure A.38. Next to the wall heat losses, only $\Delta(pV)$ is observed to have a significant impact on the gross heat release uncertainty.

Based on the uncertainty on the cumulative gross heat release, one can obtain the uncertainty on CAX considering that it represents the crank angle difference between the timing of $Q_{X\%}$ and $Q_{X\%} \pm U_{95,Q,X\%}$:

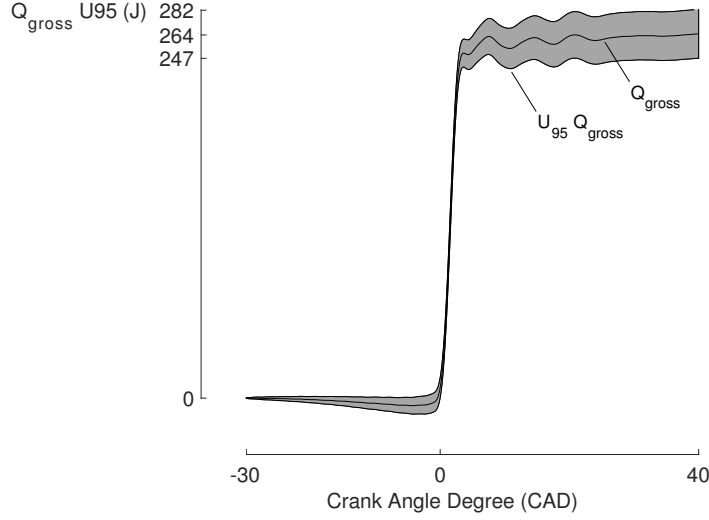


Figure A.37 – Cumulative gross heat release and related U_{95} . Since it is a cumulative value, the uncertainties add up and end at a substantial relative value of $U_{95, Q, \text{gross}} = \pm 6.8\%$

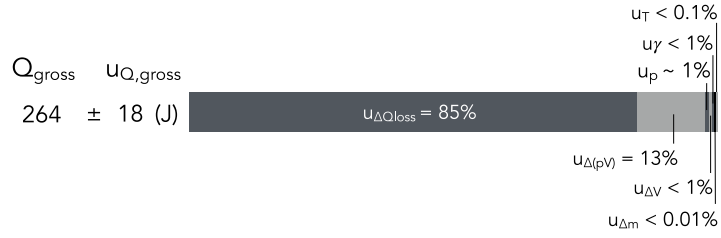


Figure A.38 – Decomposition of the impacting uncertainties on the gross heat release uncertainty. Two contributions account for more than 98% of the total: the uncertainty on the heat losses (85%) and on the derivative of the pressure-volume factor (13%).

$$u_{\text{CAX}} = \text{CA}_{QX+u_{QX}} - \text{CA}_{QX} \quad , \quad (\text{A.98})$$

$$u_{QX}^2 = \left(\frac{X}{100} \right)^2 (u_{Q_{\text{max}}}^2 + u_{Q_{\text{min}}}^2) \quad . \quad (\text{A.99})$$

Given the shape of $U_{95, Q, \text{gross}}$, the uncertainty on CA10 is always smaller

than that of CA50, which is always smaller than that of CA90, see Figure A.39. As the uncertainty on CA10 is always close to zero, the uncertainty on CA50 and CA90 are increasing with the actual timing. This implies an increasing uncertainty on the combustion duration as it increases. Let us finally stress the importance of calibrating the heat losses to maximise the flatness of the gross heat release before and after the combustion to obtain representative and precise combustion timings, see Appendix A.4.11.

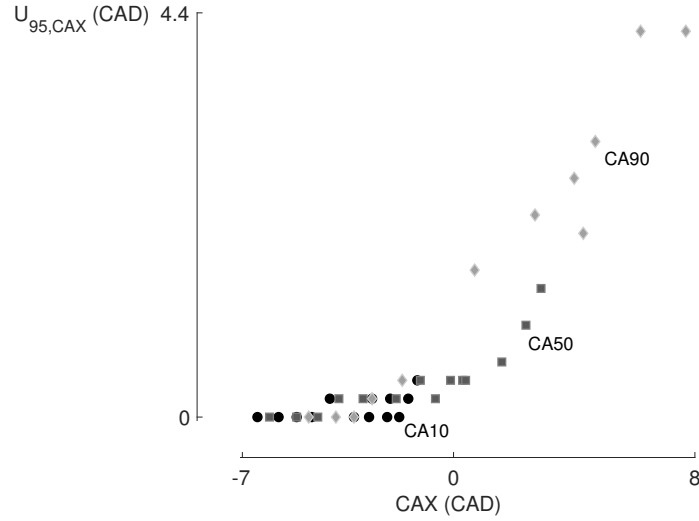


Figure A.39 – *Uncertainties on the combustion timings as a function of the combustion timings themselves, for the entire set of runs with varying equivalence ratios and intake temperatures. Given the shape of $U_{95,Q_{\text{gross}}}$, the uncertainties on CA10 are negligible compared to the ones of CA50 and CA90. For later CAD, the uncertainties on CA50 and CA90 are increasing.*

A.5 Conclusions: findings based on the obtained uncertainties

In this appendix, I detailed a methodology that allows to derive the uncertainty expression for any engine physical quantity, as well as to calibrate sensors. The

methodology is then applied to the most generic HCCI research test bench (mass flow induced mixture with $C_uH_yO_xN_zS_w$ fuel), and the obtained expressions are illustrated using an hydrogen HCCI test bench.

The physical quantities that directly derive from sensor measurements have the lowest uncertainties: intake species concentrations, intake and exhaust pressures, in-cylinder pressure and volume, equivalence ratio, IMEP, FuelMEP, BMEP, fuel intake energy, torque, etc. Relative U95 uncertainties of about 1% were obtained for these physical quantities for the example test bench using the sensors reported in Table A.3.

For physical quantities depending on models, that are not directly measured, or that depend on derivatives, much higher uncertainties have been found. Relative U95 uncertainties varying between 5% and 15% have been obtained for: the in-cylinder temperature (depending on Sjöberg RGF model); the gross heat release (depending on Hohenberg correlation for convective wall heat transfers); the maximum pressure rise rate and ringing intensity; and the combustion efficiency (when relying on the use of the combustion equation to compensate for a missing unburned gas measurement). Such a result stresses the claim that any publication relating experimental engine measurements must specify the sensors and post-processing techniques used as well as the related uncertainties.

For the considered example test bench, thanks to the uncertainty analysis, I showed the following factors to be negligible next to the main sensor uncertainties: engine blow-by, piston wrist pin offset, piston-crank assembly deformations, bottle purity, air moisture content, and dry air composition. These results are believed to stay valid for test benches using MFC with accuracy uncertainties lower than 1%, bottle purities higher than 99.5%, and air compressors with about 7 bar compression and maintained temperature.

For HCCI engines, the physical quantities found to drive the uncertainty for the main engine output performances (IMEP, combustion timings, etc.) are the residual gas fraction, the in-cylinder pressure, the in-cylinder volume (through the compression ratio), and the wall heat losses. On a general basis, I believe that the uncertainties on the wall heat losses and the residual gas fraction themselves cannot be neglected, in any calculations.

To conclude on the findings, here is a selection of the most significant observations made using the uncertainty methodology on the example hydrogen HCCI test bench. As the CA10 and CA50 combustion timings have negligible

uncertainties, the uncertainty on the CA90 is significant and scales up with late combustion (up to 4CAD of U95). The classical representation for the in-cylinder pressure uncertainty is ill-suited for the breathing phase and early compression, which flaws the uncertainty estimation of the in-cylinder temperature, and the developed alternative of lower bound uncertainty should be preferred to it. For the considered test bench, the uncertainty analysis allowed to demonstrate the strictly random behaviour of cycle-to-cycle variations (i.e. uniformly distributed) by comparing the observed in-cylinder pressure and IMEP variability to the sensor repeatability uncertainty. Finally, I want to stress the unavoidable need of data post-processing to take into account the engine wall heat losses, TDC error, intake temperature error, compression ratio error, and raw pressure signal noise and relativity, and related uncertainties.

As a final note, although most of the obtained numeric results are specific to HCCI engines (or even specific to the particular test bench considered), the developed methodology can be adapted to any engine mode and test bench. This methodology and the uncertainty analysis in general can help the experimenter to answer the following needs: assess the adequacy of a sensor for a desired end-result precision; detect the factors that can be neglected; detect the significant trends from the experimental noise; and finally assess the quality of publishable results. From the figures and orders of magnitude related in this research, it is obvious that experimental results publication goes along uncertainty quantification.