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Assessment of ammonia ignition as a maritime fuel, using engine experiments and chemical kinetic simulations

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Assessment of Ammonia Ignition as a Maritime Fuel, Using Engine Experiments and Chemical Kinetic Simulations

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Declaration

We certify that all the material in this dissertation that is not our own work has been identified, and that no material is included for which a degree has previously been conferred on us.

The contents of this dissertation reflect our own personal views, and are not necessarily endorsed by the University.

(Signatures): **……………………………….**

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(Date): **…………………………………………………**

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Abstract

Title of Dissertation: **Assessment of Ammonia Ignition as a Maritime Fuel, using Engine Experiments and Chemical Kinetic Simulations**

Degree: **Master of Science**

This study evaluates the environmental impacts of ammonia as a fuel for marine engines using a combination of literature studies of life-cycle assessment of ammonia production, a simplified thermodynamic engine simulation, and real-life engine experiments in the laboratory.

The life cycle of ammonia fuel has been assessed in various publications to identify the problems and quantify its environmental costs and benefits. It was found that it may be possible to produce ammonia with a high conversion efficiency from renewable energy, and that it may be competitive with hydrogen. Ammonia has widely established infrastructures, yet, there exists challenges, for example, its storage, high toxicity, low ignition point, and high compression ratio. Notwithstanding, having been used in the 1940's, no engine manufacturer currently offers an up-to-date ammonia-powered engine off-the-shelf.

Results from the thermodynamic engine simulation of ammonia indicate that direct ignition of ammonia is possible, but also that it requires a pilot fuel injection of diesel fuel at typical compression ratios used in existing diesel engines. This was verified in real engine experiments, where a homogeneous mixture of aqueous ammonia solution and air was ignited using pilot injection of diesel fuel.

KEYWORDS: shipping, environment, sustainability, alternative fuels, decarbonization, ammonia, life cycle assessment, sustainability.

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List of Abbreviations

BDC	Bottom dead centre
BFO	Bunker fuel oil
CCs	Cubic centimes
CI	Compression ignition
CO	Carbone monoxide
CO_2	Carbone dioxide
CR	Compression ratio
ECAs	Emission control areas
EIAPP	Engine International Air Pollution Prevention
EGR	Exhaust gas recirculation
GHG	Greenhouse gas
GWP	Global warming potential
GTL	Gas-to-liquid
H_2	Hydrogen
H_2O_2	Hydrogen peroxide
HC	Hydrocarbon
HCCI	Homogeneous charge compression ignition
HFO	Heavy fuel oil
HSFO	High Sulphur fuel oil
ICCT	International Council on Clean Transportation
IAPP	International Air Pollution Prevention
ICS	International Chamber of Shipping
IEA	International Energy Agency
IMEP	Indicated mean effective pressure
IMO	International Maritime Organisation
IPCC	Intergovernmental Panel on Climate Change

ISO	International standard organization
LCA	Life cycle assessment
LHV	Low heating value
LNG	Liquefied natural gas
LSF	Low Sulphur fuel
MARPOL	International Convention for the Prevention of Marine Pollution from Ships
MDO	Marine diesel oil
Mf	Mass of fuel per cycle
MGO	Marine gas oil
MJ	Mega joule
$NC_{12}H_{26}$	Dodecane
NH_3	Ammonia
NO_x	Nitrogen oxide
OH	Hydroxide
PM	Particulate matter
Q_{HV}	Heating value of fuel
RFO	Residual fuel oil
SCR	Selective catalytic reduction
SI	Spark ignition
SO_x	Sulphur oxide
SSAS	Solid state ammonia synthesis
TDC	Top dead center
UCL	University College London
UN	United Nations
UNCC	United Nations Climate Change
UNCTAD	United Nations Conference on Trade and Development
UNFCCC	United Nations Framework Convention on Climate Change

Wc	Work per cycle
WEF	World Economic Forum
WMO	World Meteorological Organization

1 INTRODUCTION

1.1 Background

The global shipping fleet is expanding amidst unstable energy supplies and stringent environmental regulations (Winebrake, Corbett, & Meyer, 2012; World Energy Council, 2018).“*Shipping is the faithful servant of global trade and a fulcrum of economic growth, facilitating an estimated 90 percent of the global trade volume*” (Kalgora & Christian, 2016). Seaborne trade is the driver of globalization and an enabler of the carriage of goods across the world (UNCTAD, 2016; 2018). The increased demand for maritime transport is driven by growth in world population and industrialization (Bodansky, 2018). However, maritime transport is becoming more efficient and being a key driver of global free trade, it is expected to grow further (ICS, 2019). According to the United Nations Conference on Trade and Development (UNCTAD, 2018), in 2017, the total volume of cargo transported by ships reached 10.7 billion tons. Between the years 2018 and 2023, maritime transport is projected annually at a compounded growth rate of 3.8 percent per annum.

In spite of its enormous benefits to society, shipping and its related activities on the oceans are increasingly creating negative externalities to the environment. From 2007-2012, despite the increase in ship fuel consumption, the total annual CO_2 emissions from shipping reduced drastically by 13 percent. On the other hand, CO_2 emissions from ships increased from 2013-2015, slightly by 2.6 percent, 87 percent of which is attributed to international shipping (See figure 1.3)(CE Delft, 2019 : Olmer, Comer, Roy, Mao, & Rutherford, 2017).

According to the IMO, a collective action to combat climate change is needed because under the “Business As Usual” scenario, shipping emissions could increase between 50 percent (%) and 250 percent (%) by 2050 (IMO, 2015). In the absence of mitigation policies to offset the balance, by 2050, these emissions are expected to increase further and could triple to the 2007 baseline (Chatzinikolaou & Ventikos, 2015). Ship exhaust emission pollution has deleterious impacts on human health and the climate system. The International Maritime Organization (IMO) is aligning its strategy with the United Nations 2030 Agenda for Sustainable Development to mitigate GHG emissions from ships. The IMO is determined to decarbonize international shipping, ensuring a sustainable future for waterborne transport (YubingShi, 2016: Icct, 2017).

In that regard, the IMO has set a climate goal to decarbonise shipping and set a cap on air pollutants from ships (IMO, 2015: 2018; UNCTAD, 2016: 2018). In 2011, the IMO modified MARPOL Annex VI to implement technical and operational measures including energy efficiency design index (EEDI) and ship energy efficient management plan (SEEMP). However, Icct, (2017) reveals that energy efficiency measures alone could not reduce GHG emissions from shipping (Kopela, 2017; IMO, 2018). Still and all, in 2018, the IMO further revised the roadmap based on the 2008 baseline, making it more ambitious to specifically set a minimum of 50 percent reduction in GHG emissions by 2050, and to eventually achieve a 100 percent decarbonisation consistent with the Paris agreement temperature goals (IMO MEPC.304(72), 2018: Walsh, et al., 2019). The IMO is exploring currently thebest low or zero carbon technologies such as alternative fuels to supplement the energy efficiency measures (Gilbert, et al., 2018: Icct, 2017).

The combustion of fossil fuels in large marine engines is contributing significantly to the levels of greenhouse gas (GHG) and the local air pollutants emissions from ships. When released in the atmosphere, carbon dioxide (CO_2) causes climate change and alters the chemical composition of the oceans, whereas nitrogen oxides (NO_x) and sulphur dioxide (SO_2) alter the air quality, affecting human health, contributing to particulates and aerosol formation, causing eutrophication and acidification, among others (EUR-Lex, 2002 : Caron, 2013 : Löö, et al., 2014).

According to Brynolf, Taljegard, Grahn, & Hansson, (2018), a little over 20 percent of the greenhouse gases (GHGs) emitted globally are attributable to the transport sector. The increased global environmental concern to regulate air pollution from ships has been the impetus for the IMO to minimize the impacts of exhaust pollution emissions on human health and the environment (IMO, 2015). Likewise, in his Statement on "Climate Change and Shipping", the former IMO Secretary-General Koji Sekimizu (Clean Shipping Coalition, 2015) elucidated:

> *"The world knows that climate change, and greenhouse gas emissions, simply must be addressed, and this is the mechanism through which world leaders are doing so. Everyone must play a part in this effort-no industry or sector can be excluded, and that applies to shipping, too. As the industry that physically delivers around 90 percent of global trade, and a key driver of the world's economic engine, it is incumbent on shipping to make its own contribution."*

In accordance with the Paris Agreement (PA), the IMO has set an ambitious goal to combat climate change by deploying a roadmap to cut down GHG emissions from ships (UNCTAD, 2018). This historic roadmap includes a number of low cost energy efficiency measures and current best technologies that offer huge economic and environmental incentives (IMO, 2011).

In this regard, the IMO has worked actively over the years to facilitate various discussions on how to confront exhaust gas emissions from ships and improve energy efficiency (Kopela, 2017). Moreover, the IMO is developing a roadmap for the mitigation of exhaust gas emissions from ships. The IMO has an important role in driving the global regulation of airborne emissions. Compliance with these regulations could help reduce the environmental impacts of ship exhaust emissions amidst increasing environmental awareness and growing demand for maritime transport (Clean Shipping Coalition, 2015).

However, Article 2.2 of the Kyoto Protocol under the United Nations Framework Convention on Climate Change (UNFCCC) encouraged Annex I Parties to support the IMO to implement policies and measures that scale down the emissions of GHG from international shipping (United Nations, 1998). Therefore, the IMO has revised and amended MARPOL Annex VI to set up measures for the control of GHG emissions from international shipping (Kopela, 2017 : IMO MEPC (73), 2018). According to the Third IMO GHG Study conducted in 2014, between 2007 and 2012, shipping emissions reduced slightly. On average, shipping accounted for 3.1 percent of CO_2 emissions and about 2.8 percent (%) of GHG based on CO_2 equivalent (CO_2e) of the annual global emissions in 2012. Of this value, 2.6 percent is attributed to international shipping (IMO 3rd GHG Study, 2014). (see Tables 1.1 & 1.2).

Furthermore, despite being left out from the Paris Agreement, Article 2.2 of the Kyoto Protocol under the UNFCCC mandated the IMO to tackle air pollution from international shipping and urged "parties in Annex I" to support the IMO in implementing policies and measures to scale down the emissions of GHG from international shipping (United Nations, 1998). According to the Third IMO GHG Study conducted in 2014, between 2007-2012, on average, shipping accounted for 3.1 percent of CO_2 emissions and about 2.8 percent (%) of GHG based on CO_2 equivalent (CO_2e) of the annual global emissions in 2012. About 93 percent (2.6%) of the shipping CO_2 emitted in 2014 is attributed to international shipping (IMO 3rd GHG Study, 2014 (see Tables 1.1 & 1.2).

Table 1. 1. Shipping CO_2 emissions compared with global CO_2 emissions (values in million tons of CO_2e)

		Third IMO GHG Study 2014 CO_2			
Year	Global CO_2[1]	Total shipping	% of global	International shipping	% of global
2007	31,409	1,100	3.5%	885	2.8%
2008	32,204	1,135	3.5%	921	2.9%
2009	32,047	978	3.1%	855	2.7%
2010	33,612	915	2.7%	771	2.3%
2011	34,723	1,022	2.9%	850	2.4%
2012	35,640	949	2.7%	796	2.2%
Average	33,273	1,016	3.1%	846	2.6%

Source: (IMO 3rd GHG Study, 2014).

However, a study conducted by Corbett & Winebrake, (2012) indicates that a complete switch from HSFO to LSF reduces global SO_x emissions by 6 percent. For a given alternative, it is prudent to weigh the benefits accrued against the cost to the environment. Some alternatives, especially cleaner low LSFs, are products of energy intensive refining or blending that emit additional GHGs (Corbett & Winebrake, 2012). When deploying an alternative fuel for maritime use, it is important to conduct a full life cycle assessment (LCA), to quantify the environmental loads of alternative marine fuels (Gilbert, et al., 2018). An LCA of alternative fuels over their entire life cycle is necessary to evaluate the various environmental impacts associated with their application in the maritime sector.

Despite the enhancements in energy efficiency through changes in ship design and operational practices, the demand for seaborne transport is growing. Cargo ships constitute the majority of vessels engaged in international shipping and are propelled by highly efficient marine diesel engines that consume approximately 300 million tonnes of heavy fuel oil (HFO) annually (IEA , 2013 : Fridell, 2019). (See figures 1.1 and 1.2). Depending on the "future economic and energy developments", CO_2 emissions from international shipping is predicted to increase substantially in the coming years (IMO, 2015 : Bodansky, 2018). Viana, et al. (Viana, et al., 2014) reveals that:

Residual fuel oil (RFO) is exhaustible and when burned, it emits significant amount of GHG and air pollutants. Still and all, it remains the most dominant choice for marine use. Compared to alternative fuels, it is cheaper, denser and can provide the needed energy supply for the bulk of an oceangoing fleet. Currently, RFO accounts for 77 percent of ship Bunker fuel oil (BFO), consumed mainly by 25 percent of the global fleet (merchant ships) (IEA , 2013 : Fridell, 2019). (See figures 1.1 and 1.2).

Table 1. 2. Shipping GHGs (in CO_2e) compared with global GHGs (values in million tonnes CO_2e)

Year	Global CO_2e^2	Third IMO GHG Study 2014 CO_2e Total shipping	%of global	International shipping	%of global
2007	34,881	1,121	3.2%	903	2.6%
2008	35,677	1,157	3.2%	940	2.6%
2009	35,519	998	2.8%	873	2.5%
2010	37,085	935	2.5%	790	2.1%
2011	38,196	1,045	2.7%	871	2.3%
2012	39,113	972	2.5%	816	2.1%
Average	36,745	1,038	2.8%	866	2.4%

Source: (IMO 3rd GHG Study, 2014).

Table 1. 3. Shipping CO2 emissions compared to global CO2 emissions

	Third IMO GHG Study (million tonnes)						ICCT (million tonnes)		
	2007	2008	2009	2010	2011	2012	2013	2014	2015
Global CO_2 Emissions	31,959	32,133	31,822	33,661	34,726	34,968	35,672	36,084	36,062
International Shipping	881	916	858	773	853	805	801	813	812
Domestic Shipping	133	139	75	83	110	87	73	78	78
Fishing	86	80	44	58	58	51	36	39	42
Total Shipping	1,100	1,135	977	914	1,021	942	910	930	932
% of global	3.5%	3.5%	3.1%	2.7%	2.9%	2.6%	2.5%	2.6%	2.6%

Source: (Olmer, Comer, Roy, Mao, & Rutherford, 2017)

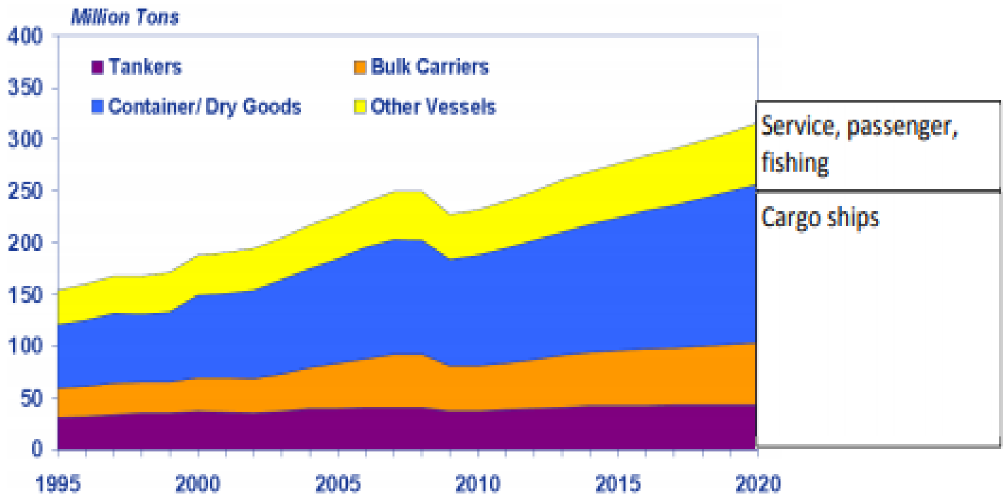

Figure 1. 1: World Bunker Fuel demand. Adapted from (IEA , 2013.)

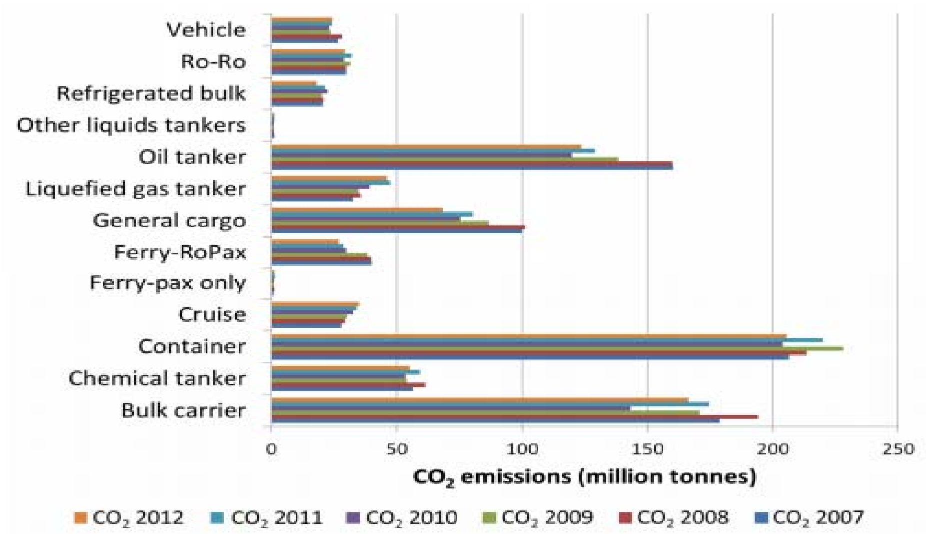

Figure 1. 2 CO_2 emissions by ship type (international shipping only) calculated using the bottom-up. Adapted from (IMO 3rd GHG Study, 2014).

Without a legal and regulatory framework, ship exhaust emissions are expected to grow further by 2050 (AirClim, 2011). Energy efficiency measures alone will never be able to reduce the energy consumption of shipping to zero. Alternative fuels have been proposed and evaluated as viable short and long-term abatement options to mitigate shipping related impacts on human health and the environment (Hanssona, Månsson, Brynolf, & Grahn, 2019) and (Gilbert, et al., 2018). Alternative fuels can deliver significant reduction in total GHG emissions and minimize the impacts of local pollutants in the short term. When deployed as maritime transport fuel, they are optimally suited to comply with existing low emission regulations. Still, to become a feasible option, every alternative fuel is required to "deliver emissions reduction" over its full life-cycle. However, alternative fuels are currently more expensive than fossil fuels, and need to be scalable to deliver emissions reductions across the entire maritime transport fleet. So, the use of alternative fuels for maritime transport vehicles is faced with challenges due to the uncertainties in their economic and environmental performances (Gilbert, et al., 2018).

However, a study conducted by Corbett & Winebrake, (2012) indicates that a complete switch from high sulphur fuel (HSF) to low sulphur fuel (LSF) could deliver a reduced global SO_x emissions by 6 percent, with increased CO_2 emissions by 0.01 percent. For a given alternative, it is prudent to weigh the benefits accrued against the cost to the environment. Some alternative, especially cleaner LSFs, are products of energy intensive refining or blending processes that emit additional GHG (Corbett & Winebrake, 2012). When deploying an alternative fuel for maritime use, it is important to conduct a full life cycle assessment (LCA) because LCA is a tool that helps quantify the environmental loads of alternative marine fuels (Gilbert, et al., 2018). A full life cycle assessment of alternative fuels is necessary to evaluate the various environmental impacts associated with their applications in the maritime sector.

1.1.1 Regulating exhaust gas emissions from shipping

Generally, emitted exhaust gases from ship engines fall in two categories, based on their direct impact on air quality and global warming potential. "The marine shipping industry is facing challenges to reduce exhaust emissions and GHGs in particular, CO_2 and methane (CH_4) from ships" (IEA , 2013 : Goldsworthy, 2010). The sector has been slow in developing policies and deploying measures to reduce emissions from ships. So, in accordance with the Kyoto Protocol, a sectoral approach is necessary in addressing shipping impacts on the climate system (United Nations, 1998 : Gilbert & Bows, 2012).

However, (Kopela, 2017) reveals that:

> *"Adopting such a regulatory framework has been challenging due to the cost implications for the shipping industry, the competitiveness of the maritime transport vis-à-vis other means of transport, and potential impacts on trade. The International Maritime Organization (IMO) has been actively engaged in discussions on how to tackle air pollution from ships, enhance energy efficiency and ensure sustainable maritime transport for the future."*

The upswing in maritime transport demands coupled with the urgent need to control airborne emissions from ships have accelerated efforts to develop a robust legal framework, because "maritime transport and shipping concern global commons, an international regulatory framework is required to ensure an effective solution to the problem" (UNCTAD, 2018 : Kopela, 2017).

According to (AirClim, 2011), "this air pollution must be reduced drastically to protect human health and the environment and to make shipping a more sustainable form of transport". Hence, a sustainable maritime transport can be achieved without causing much damage to the environment (UN, 2012). In this regard, the IMO has proposed the deployment of a number of emission reduction measures and technologies. In addition, the IMO is overseeing the drafting of mitigation policies to attract the use of low cost technical and operational measures amidst stringent regulations (S.Seddiek & M.Elgohary, 2014 : ICCT, 2015).

In 1997, the United Nations Framework Convention on Climate Change (UNFCCC) mandated international shipping to de-carbonize under the Kyoto Protocol (United Nations, 1998) to the IMO, thereby proposing the use of energy efficiency measures as well as the development of alternative marine fuel technologies in lieu of fossil fuels (United Nations, 1998). In accordance with the Kyoto Protocol under the (United Nations, 1998) explicitly stated that:

> *"The parties included in Annex I shall pursue limitation or reduction of emissions of greenhouse gases not controlled by Montreal Protocol from aviation and marine bunker fuels, working through the International Civil Aviation and the International Maritime Organization, respectively."*

Hence, the Kyoto Protocol encouraged developed countries to? otherwise "Annex I parties" to make commitments in order to support the work of the IMO to holistically cut down the GHG emissions from international shipping (ICCT, 2015 : United Nations, 1998). However, the IMO was not included under the Paris Agreement that seeks to achieve a key climate goal by maintaining the global average mean temperature of 2ºC or further below, such as 1.5ºC. To decarbonize the maritime sector, the IMO is shouldered with responsibility to regulate air pollution from shipping (UNCC, 2017).

As a result, the IMO has deployed a roadmap as an ambitious target to reduce the total annual GHG emissions by 50 percent (%) by 2050, against the 2008 baseline (IMO MEPC.304(72), 2018). This can be partly achieved through energy efficiency measures to reduce air pollutants and particulate matters. The IMO is planning to reduce the carbon intensity of shipping by 40 percent by the year 2030 and 70 percent by the year 2050, against the 2008 benchmark (Hanssona, Månsson, Brynolf, & Grahn, 2019). (See figure 1.3).

In 1997, the IMO adopted Annex VI to its MARPOL Convention to address air pollutant emissions from ships (IMO MEPC (70), 2016). A study conducted by IMO on ship GHG emissions revealed that 1.8 percent of the total global CO2 emissions in 2000 were attributed to ships (Ölçer, Kitada, Dalaklis, & Ballini, 2018). The IMO adopted an amendment to MARPOL Annex VI to include an initial strategy to GHG emissions from ships through the implementation of various technical and operational requirements as well as the deployment of alternative fuels, amongst others (IMO MEPC (70), 2016: IEA , 2013 : IMO MEPC (73), 2018). The deployment of these technical measures can drastically reduce shipping impacts on air quality by 80-90 percent (AirClim, 2011).

Despite the different measures already being mature and widely available, their full implementation across the sector is impeded due to underlying economic, social and administrative barriers (Ölçer, Kitada, Dalaklis, & Ballini, 2018). In this regard, a holistic approach comprising of the aforementioned measures will be apposite to reach the IMO ambitious target to reduce the emissions of air pollutants and GHG from international shipping (IEA, 2019). (See 1.3).

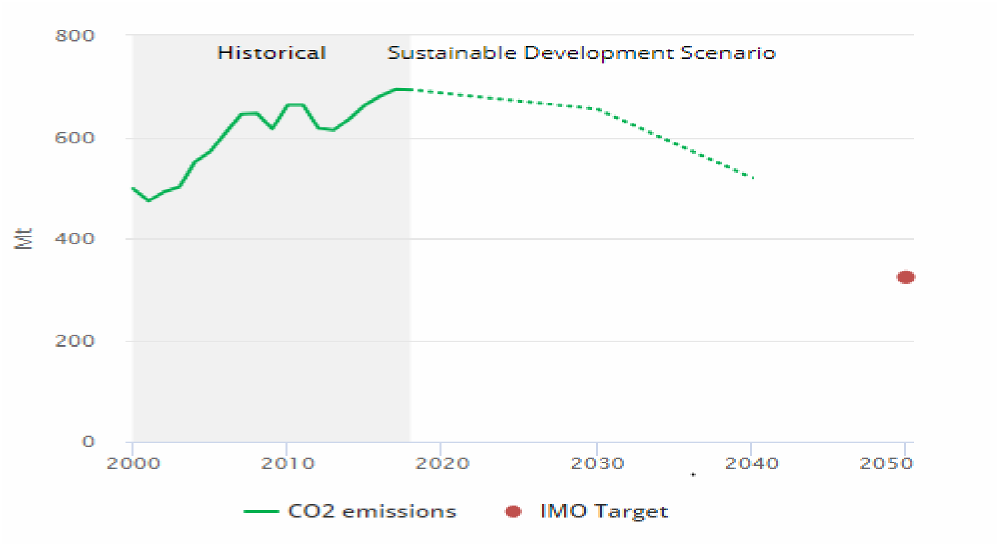

Figure 1. 3 CO2 emissions from international shipping. Adapted from (IEA, 2019).

As of now, the shipping industry is facing challenges due to fluctuating marine fuel prices and stringent environmental regulations (Ölcer & Ballini, 2015). Therefore, the use of alternative fuels as maritime transport to replace heavy bunker fuel oil comes with a number of incentives to overcome the challenges (IEA , 2013). Already, some studies have revealed that alternative fuels are suitable for marine use.

However, their efficient use and impacts on the environment are not yet fully established. However, a full life cycle of the marine fuel has been assessed to distinguish the sources of pollution (Winebrake, Corbett, & Meyer, 2012).

1.1.3 Legislation for NO_x, SO_x and PM emissions from ships

"Compression ignition (CI) engines which are the dominant shipboard propulsion system are major source of urban air pollution" (Heywood, 1988; 2008 : Eyring, Ko¨hler, Lauer, & Lemper, 2005). A bulk of oceangoing ships are reliant on RFO due to its low cost and high viscosity. RFO contains high sulphur content, which when burned in the ship engines produces predominantly SO_x (JerzyKowalski, 2014). Emissions of SO_x from ships have adverse effects on the environment and increases the risks to human health. SO_x emission is also a source of particulate matters (PMs) that pose major health threats (Burnett, et al., 2018 : ICCT, 2019).

In compression ignition engines, the sulphur content of the fuel is strongly correlated with the total particulate matters emitted (Saiyasitpanich, Lu, Keener, & Khang, 2005). In CI engines, fuel is injected into air at high temperature and pressure. Combustion takes place at an equivalence ratio of unity, as the fuel mixes with the surrounding air, yielding high combustion temperatures. So, the formation of NO_x in CI engines is typically higher than NO_x produced in gas turbines or boilers. Also, when operating diesel engines, the efficiency can reduce over time, depending on the condition of the engines, and can increase emissions of NO_x. For instance, in 2011, over 50 percent of the global fleet were found to be older than 15 years (JerzyKowalski, 2014).

Of the total transport emissions, 60 percent of SO_x and 40 percent of NO_x emissions are attributed to shipping. The effects of air pollutants from ships are widespread in urban areas that are closest to ship traffics. In his study on ship emissions, Tzannatos (2010) evaluated global PM from shipping and its annual cost to society. He revealed that a 60,000 death toll per annum costs the US $300 billion loss. As a result, some countries and regions such as the United States and the European Union, have instituted some stringent measures to regulate these shipboard air pollutants (Eyring, Ko¨hler, Lauer, & Lemper, 2005). In addition, the IMO has set up emission limits in MARPOL Annex VI (see figures 5) to control local pollutants from ships despite the lack of international legislations to regulate black carbon and the PM emissions from ships (IMO, 2016 : Goldsworthy, 2010 : Eyring, Ko¨hler, Lauer, & Lemper, 2005). The following sources have extensively discussed the modifications of MARPOL Annex VI, Regulations 13 and 14 as summarized from (IMO, 2019 : ABS, 2019 : IMO, 2019 : EU, 2019 : IMO, 2019):

The IMO has also modified MARPOL Annex VI to include Regulations 13 and 14 to set strict limits on NO_x and SO_x emissions from marine engines. To meet up these requirements, marine diesel engines must be certified. Therefore, MARPOL Annex IV is applicable to all vessels, drilling rigs and other platforms above 400 gross tonnage (GT). Under MARPOL Annex IV, the IMO has made it compulsory for the international air pollution prevention (IAPP) certificate or its equivalent to be available on all vessels trading globally. It is also mandatory for engines to have engine international air pollution prevention (EIAPP) certificates.

To reduce NO_x emissions from marine diesel engines, the NO_x standards are applicable to all new engines, existing ones, and those that have been modified. The exceptions are marine engines used for emergency purposes. The NO_x emission limits for marine diesel engines are set based on the rated crankshaft speed (n), the power output per cylinder cycle (g/kWh) and effective from the date the vessel keel was laid. Furthermore, new marine engines are required to meet the three tier structures. Tier I, represents existing technologies and engines built before 2011. Tier II reflects newer technologies with a 25 percent reduction in emissions. This category applies to two types of vessels: vessels built from 2011-2015 and those built from January 1, 2016, that are operating beyond the designated emission control areas

(ECAs). Tier III reflects future technologies and engines installed after January 1, 2016, operating within ECAs. (See Table 1.4 & Figures 1.4 & 1.5).

Table 1. 4 NO_x limits under MARPOL Annex VI

Tier	Ship construction date on or after	Total weighted cycle emission limit (g/kWh) n = engine's rated speed (rpm)		
		n < 130	n = 130 - 1999	n ≥ 2000
I	1 January 2000	17.0	$45 \cdot n^{(-0.2)}$ e.g., 720 rpm – 12.1	9.8
II	1 January 2011	14.4	$44 \cdot n^{(-0.23)}$ e.g., 720 rpm – 9.7	7.7
III	1 January 2016	3.4	$9 \cdot n^{(-0.2)}$ e.g., 720 rpm – 2.4	2.0

Source: (IMO, 2019)

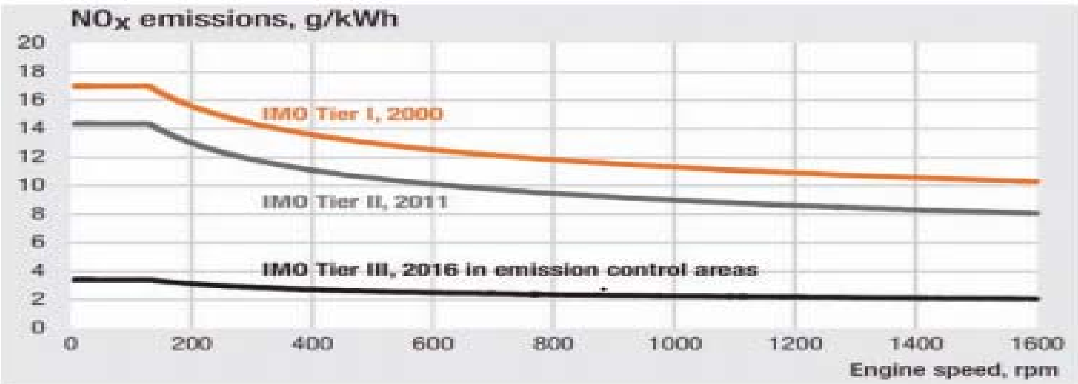

Figure 1. 4 MARPOL Annex VI NO_x emissions requirements. Adapted from (Herdzik, 2011).

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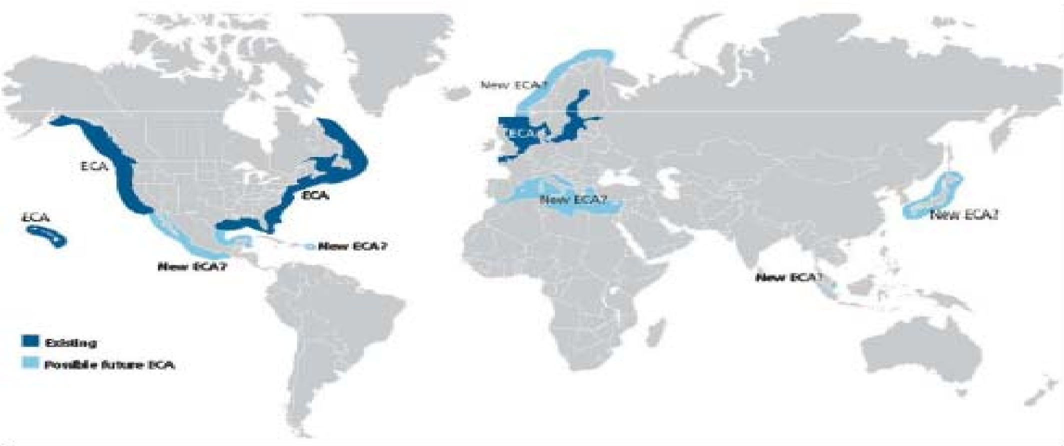

Figure 1. 5 Current and Possible Future ECAs. Adapted from (IEA, 2013).

MARPOL Annex VI sets limits on sulphur content in marine fuels for vessels operating in sulphur emissions control areas (SECAs). By and large, MARPOL Annex VI ?has been modified to limit sulphur content as seen in Table 1.4,to 1.5 % parts per million (ppm) before July, 2010, 1% ppm from 2010-2015, and 0.1% ppm after January 1, 2015. From January 2020, the Global Sulphur Cap will be enforced to limit sulphur content to 0.5% ppm for vessels operating internationally.

Table 1. 5 MARPOL Annex VI ship emissions reduction areas with sulphur limits

	Year	Fuel Sulfur (ppm)	Fuel Sulfur (%)
European SECAs			
North Sea, English Channel	Current Limits	10,000	1
	2015	1,000	0.1
Baltic Sea	Current Limits	10,000	1
	2015	1,000	0.1
North American ECAs			
United States, Canada	2012	10,000	1
	2015	1,000	0.1
Global	2012	35,000	3.5
	2020[a]	5,000	0.5

[a] Alternative date is 2025, to be decided by a review in 2018.

Source: (IEA , 2013)

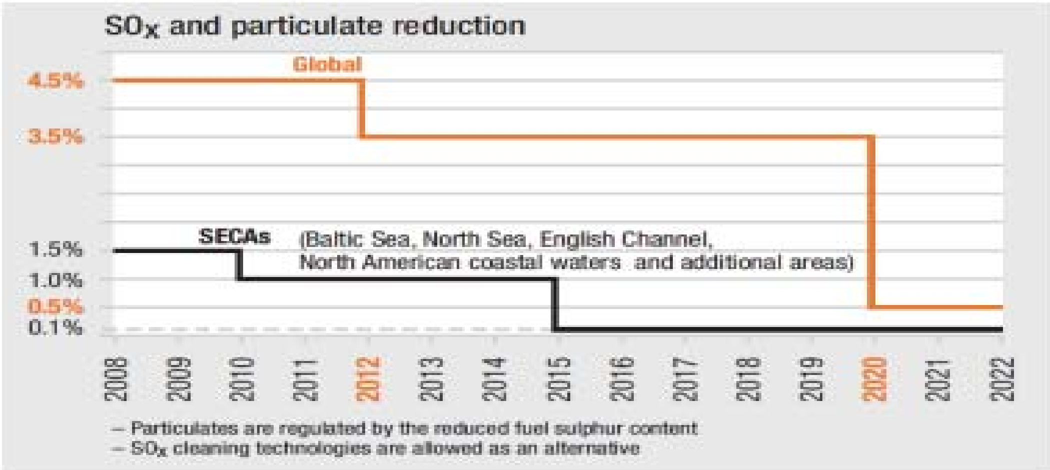

Figure 1. 6 MARPOL Annex VI requirements for SO_x and PMs reduction. Adapted from Herdzik, (2011).

To comply with the regulations, the shipping companies in collaboration with the engine makers adopt the available technologies (see figure 1.7) while continuing to search for further improvements such as alternative fuels. Among the technologies able to address NO_x emissions, we can cite selective catalytic reduction (SCR) which is the most adopted method with most of the container ship retrofitted in these last year instalments?. The most important part of the SCR is the catalyst. The installation of SCR combined with HFO or MDO used? as fuel allows the ship to meet NO_x Tier III standard independently. In addition, the exhaust gas recirculation (EGR) is also one of the solutions used to reduce NO_x emissions.

EGR reduces the maximum combustion temperature by recirculating the exhaust gas mixed with air to the engine. Around 20 percent (%) of the exhaust gas recirculated reduces NO_x production by up to 50 percent (%) (Guo, et al., 2015). However, to reduce the negative effect of the EGR in the combustion efficiency, the system should be integrated in the design phase such as increasing the firing pressure rather than be used as a retrofit solution (Lindgren, et al., 2016 : Eyring, Ko¨hler, Lauer, & Lemper, 2005).

Another method of reducing NO_x emissions from engines is to use fuel-air premixing prior to ignition, as is the case for Otto-cycle engines using lean operation. This has been practically implemented using the gaseous fuel natural gas (from LNG), but has the possible disadvantage of increasing methane emissions, which can result in total GHG emissions becoming worse than those of HFO or MDO (IMO 3rd GHG study, 2014).

1.2 Problem Statement

The maritime sector is facing challenges due to energy scarcity, energy security and the recent IMO regulation to set a cap on the sulphur content in marine fuel oil. For over a decade, engine manufacturers have focused on improving existing diesel engines to reduce pollutants emitted from ship exhaust gas. Diesel engines which are the commonly used propulsion systems in merchant shipping are not likely to be substituted soon due to the superior advantages they offer in terms of cost, longevity and flexibility in fuel choice (Eyring, Ko¨hler, Lauer, & Lemper, 2005).

Moreover, Brynolf, Taljegard, Grahn, & Hansson (2018) reveal that by lowering the carbon content in fossil fuels, GHG emissions from the transport sector could be substantially reduced. This can be achieved with the deployment of alternative fuels, especially those with energy carrying potential such as hydrogen and ammonia. Alternative fuels such as methanol and hydrogen are gaining momentum in the energy system due to their increased market share. Compliances with these stringent regulations are proving to be an incentive for many ship owners to consider the different alternative fuels as a solution (IEA , 2013).

In contrast, the DNV GL (see figure 1.7) asserts that reducing the GHG to meet the IMO target would be difficult unless new ship designs are more innovative to be powered by ammonia as maritime fuel . In its 2019 Energy Transition Outlook, the DNVGL analysed the shipping industry and projected that depending on the development of regulation for new ships, ammonia could likely substitute 25 percent of maritime fuel by the year 2050 (DNV-GL, 2019).

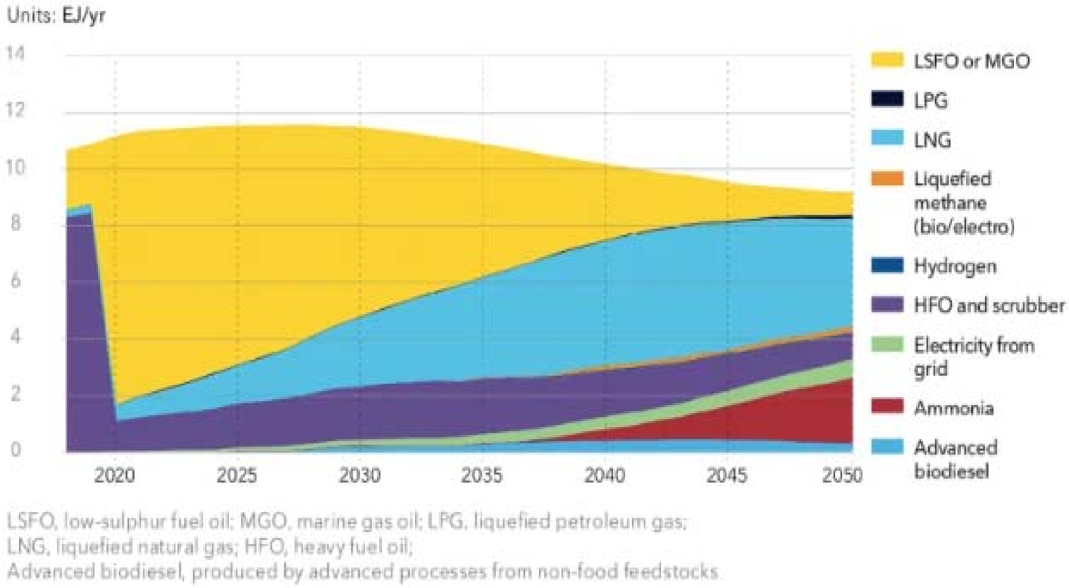

Figure 1. 7 Energy use and projected fuel mix 2018-2050 for the simulated IMO ambitions pathway with main focus on design requirements (DNV-GL, 2019).

Furthermore, alternative fuels have proved to be viable pathways for the decarbonization of the shipping industry, despite lowering the high cost to increase uptakes of the energy remains a challenge (World Energy Council, 2018 : Bouman, Lindstad, Rialland, & H.Strømman, 2017 : Rehmatulla, Parker, Smith, & VictoriaStulgis, 2017 : IPCC, 2014). Notwithstanding, ammonia is a clean energy, which is a cheap and a safe medium for the storage and carriage of renewable energy. NH3 is flexible with high energy density and a widely established distribution network (World Energy Council, 2018 : AValera-Medina, Xiao, Owen-Jones, W.I.F.David, & P.J.Bowen, 2018 : Fertilizers Europe, 2018).

1.3 Research objectives

The purpose of this study is to identify whether it is feasible from a technical concept and environmental perspectives to use ammonia as marine fuel instead of traditional fossil fuels.

Hence, the study will specifically be looking:

I. To evaluate the environmental impact of exhaust emissions from oceangoing ships.
II. To identify opportunities and barriers to decarbonization of seaborne trade.
III. To outline the technological overview of ammonia production, future prospects, possible challenges and limitations as marine fuel.
IV. To assess ammonia in terms of its GHG life-cycle performance.
V. To study the conditions necessary to ignite ammonia in marine engines.
VI. To study the viability of using aqueous solutions of ammonia in marine engines.
VII. To identify alternative ways of making ammonia ignitable in marine engines.

1.4 Research questions

To achieve the objectives of this study the following questions must be answered.

I. What are the environmental impacts of air pollution from maritime transport?
II. How and why have the regulation(s) of air emissions from ships/shipping evolved over the years?
III. What are "the most important" environmental effects of maritime transport and why are they?
IV. What are the prospects and challenges for low emission shipping?
V. How and why is ammonia considered a "viable pathway" for decarbonization of maritime transport? Where is the available literature on previous studies of ammonia as a transport fuel?

VI. What is the life-cycle performance of ammonia in terms of its GHG emissions?

VII. Is ammonia technically viable for marine engines, and how could it be stored and injected?

VIII. How do the LCA results from reviewed literatures and engine simulation of ammonia fuel affect the decision making of policymakers and regulators of the maritime industry?

1.5 Scope

This research focuses on why ammonia produced from renewable energy could be an alternative to substitute fossil fuel for marine use. To demonstrate how ammonia produced from renewable sources is the best choice that meets the IMO low emission regulation, previous life cycle assessment studies of ammonia were reviewed to evaluate its environmental loads from well-to-tank. In addition, ignition of NH_3, hydrogen and marine diesel oil (MDO) were simulated in a thermodynamic and chemical kinetic engine model based on two-stroke compression ignition (CI) and homogeneous charge compression ignition (HCCI) engines to compare their ignition time, chemical kinetics and thermodynamic performance.

In this study, the LCA was based on previous publications available in the open literature. However, the engine simulations were conducted using a pre-coded basic program in Python, which adapted and developed further for the purpose of the engine simulations used herein. In addition to this, engine tests were carried out the University College London (UCL) engine laboratory, to obtain some practical experience [and validation] of the simulations.

1.6 Research methods

This dissertation utilises three research methods to assess ammonia as a marine fuel. First, a literature review of existing life-cycle assessments on ammonia was conducted. Second, thermodynamic and chemical kinetic simulations of ammonia, aqueous ammonia solution, hydrogen and diesel fuel (represented by n-dodecane) were conducted to assess the technical viability of ammonia as a marine fuel. Third, engine tests were conducted at the UCL engine laboratory, to gain practical experience and the validation of ammonia ignition strategies in a compression ignition engine. Data for the LCA analyses consists of previous case studies of LCA available in annual reports, textbooks, journals, articles, magazines, conference reports, recommended websites such as IMO, shipping and energy companies, refineries,et al.. To assess the environmental footprint of ammonia, results from previous studies were reviewed, and critically analysed. The engine simulations were conducted using an existing simulation model (Schönborn, 2018) which was further developed and adapted to compare the kinetic and thermodynamic performance of NH_3, hydrogen and MDO modelled according to the working principles of the diesel and HCCI engines.

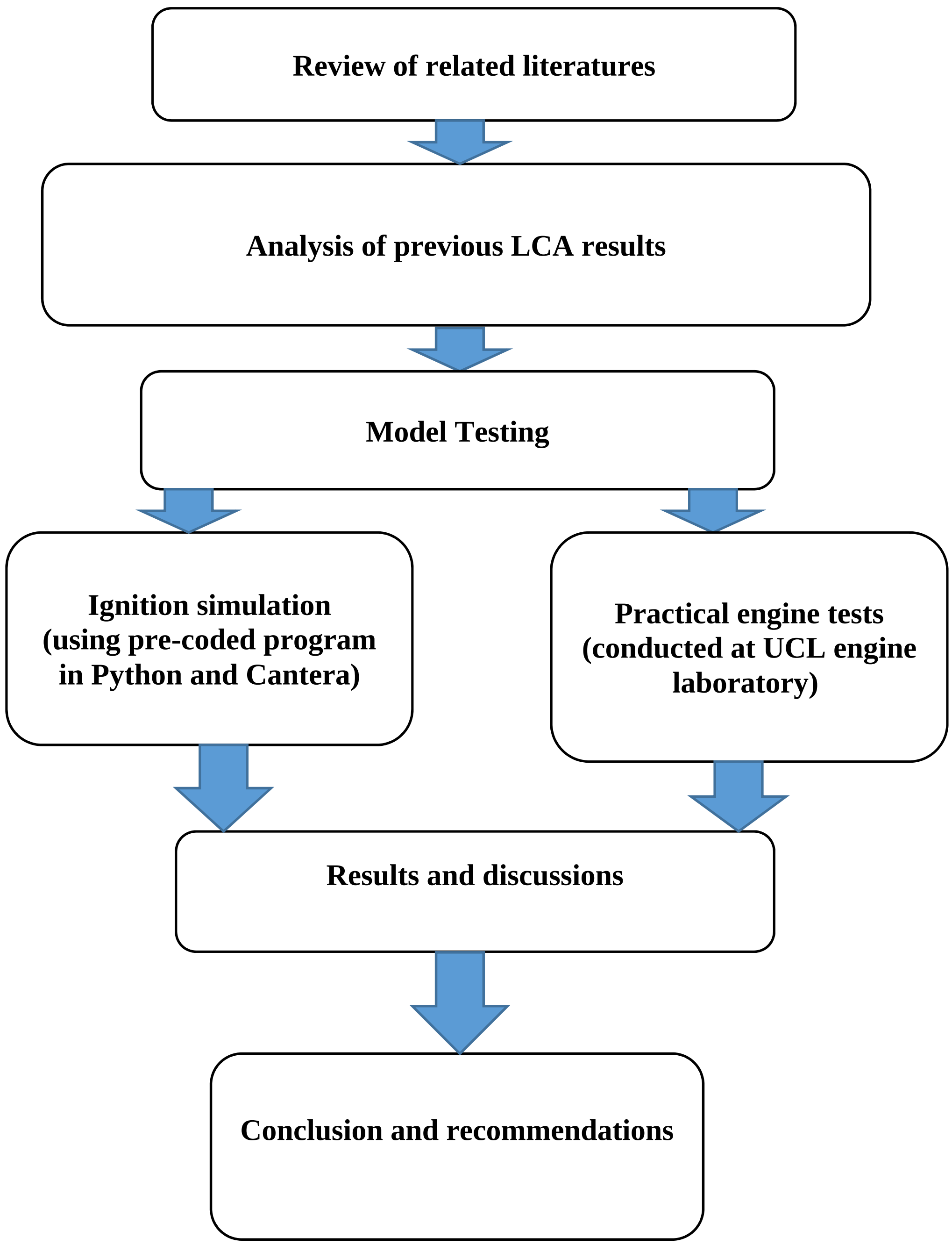

Figure 1. 8 A flow diagram of research methods

1.7 Significance of the study

The motive behind this study is to examine from environmental and technical concept perspectives whether ammonia is optimally viable to substitute traditional fossil fuel and whether it meets all requirements of the current IMO low emission regulations. The results and outcome of this study may be relevant to policy makers in advancing the overall agenda of the IMO low emissions and sustainable shipping. The study seeks to establish how ammonia produced from renewable sources can become an energy carrier for renewable energy, and eventually a replacement for fossil fuels.

1.8 Thesis outline and organization

This research consists of five chapters, structured as follows; Chapter One is the introductory chapter that gives a background to the dissertation topic, defines the problem statement, research objective, scope, questions, and significance. Chapter Two gives a thorough review of existing literature related to the research topic, whereas approaches and methodologies applied in previous studies were discussed. In Chapter Three, the research methodology is illustrated in a flowchart and the different approaches are discussed in depth. In Chapter Four, the engine simulations and experimental tests are carried out as displayed in various graphs. The results from the engine simulations and experimental tests are analysed and discussed. In Chapter Five, a conclusion was made, followed by a list of recommendations for future research.

2 Literature review

2.1Choice of alternative marine fuels

There is a growing interest for the use of alternative fuels for maritime transport (Hanssona, Månsson, Brynolf, & Grahn, 2019). Alternative fuels have proved to be compliant with existing regulations, reduction in local air pollutants and GHG emissions, as well as the mitigation of climate change, among others. Of the overall global GHG emitted annually, shipping contributes relatively about 3 percent (IMO 3rd GHG study, 2014). Hence, the deployment of alternatives for maritime transport is both a viable short and long-term abatement option to mitigate the impacts of climate change. Despite the promises of low emissions feature, findings from Gilbert, et al., (2018) have revealed that there is no single universally available alternative fuel that satisfies and can completely offset the GHG emissions from ships and in tandem, comply with the existing regulations. This is due to the he barriers to decarbonize or reduce the impacts of emissions from the input energy and feedstocks. Albeit the key requirement for an alternative fuel to become a feasible option for marine use is its ability to reduce emissions throughout its entire life cycle (Gilbert, et al., 2018). In this study, using MDO as a reference fuel, ammonia and hydrogen fuels will be discussed in depth, for justification.

2.1.1 Ammonia as renewable energy medium

Ammonia is identified not only as second the most widely used chemical feedstock but also a sustainable energy carrier. Hydrogen (H_2) is considered a potential driver of the “low carbon economy”, however, its full implementation is impeded by a number of barriers underpinned by the infrastructural challenge for its storage and distribution. Being that “NH_3 is H_2 in another form”, ammonia has been proposed as a practical solution to overcome these barriers (AValera-Medina, Xiao, Owen-Jones, W.I.F.David, & P.J.Bowen, 2018). Compared to hydrogen, ammonia is a hydrogen-rich compound that is highly flexible with reasonably high energy density, and a well-established distribution network. So NH_3 is a feasible medium for the storage and carriage of renewable energy. NH_3 fuel is less costly, safer and easier to transport than hydrogen.

In this regard, NH_3 is a promising pathway for driving a sustainable energy transition in the future. A Fertilizers Europe report “Feeding Life 2030” published in 2018 reveals that by increasing green ammonia production capacity it is possible to produce 10 percent of European ammonia by 2020 when using novel technologies such as solid-state processes and electrochemical syntheses. Therefore, it describes ammonia as “the crossroads of energy and nutrition” and recognizes it as a driver of energy transformation (Fertilizers Europe, 2018 : AValera-Medina, Xiao, Owen-Jones, W.I.F.David, & P.J.Bowen, 2018 : ISPT, 2018 : Lehigh University, 2018 : University of central Florida, 2018 : USA Patent No. US 2010/0019506 A1, 2010).

Ammonia can be synthesized using both conventional and novel technologies, and the electricity required for the process can be utilized from either fossil fuels or renewable energy resources (Chena, et al., 2018 : Giddey, Badwal, & A.Kulkarni, 2013 : Bicer, Dincer, Zamfirescu, Vezina, & Razo, 2016).(See figures 2.1, 2.2 & 2.3). Besides, ammonia is a carbon neutral fuel with a potential to substitute traditional fossil fuel, because if it can be burned completely, it has potentially zero GHG emissions and produces nitrogen and water as by-products (Guo, Ran, Vasileffa, & Qiao, 2018) (Hofstrand, 2009). At atmospheric pressure and ambient temperature, NH_3 can be easily stored and transported in liquid form and can be directly or indirectly used in ammonia and hydrogen fuel cells (See figures 2.1, 2.2 & 2.3) (Nazemi, Panikkanvalappila, & A.El-Sayed, 2018) and (Giddey, Badwal, & A.Kulkarni, 2013) and (AValera-Medina, Xiao, Owen-Jones, W.I.F.David, & P.J.Bowen, 2018).

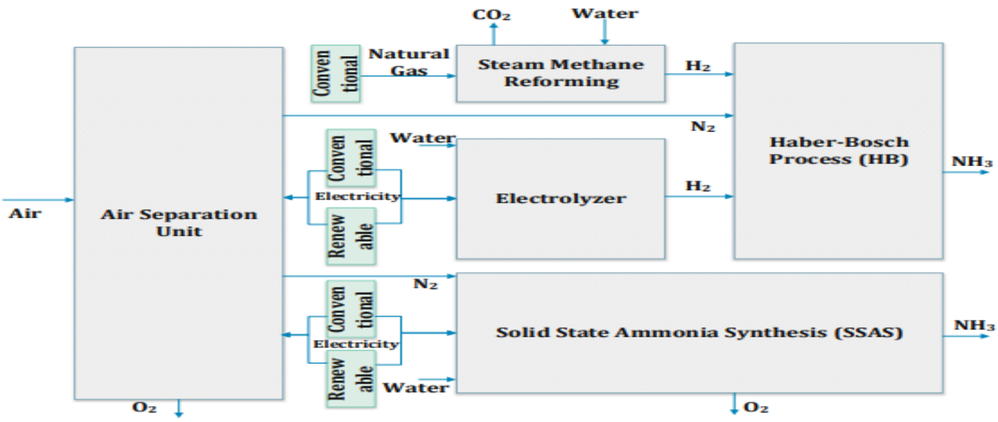

Figure 2. 1 Main NH_3 production pathways via conventional and renewable energy resources. Adapted from (Bicer, 2017).

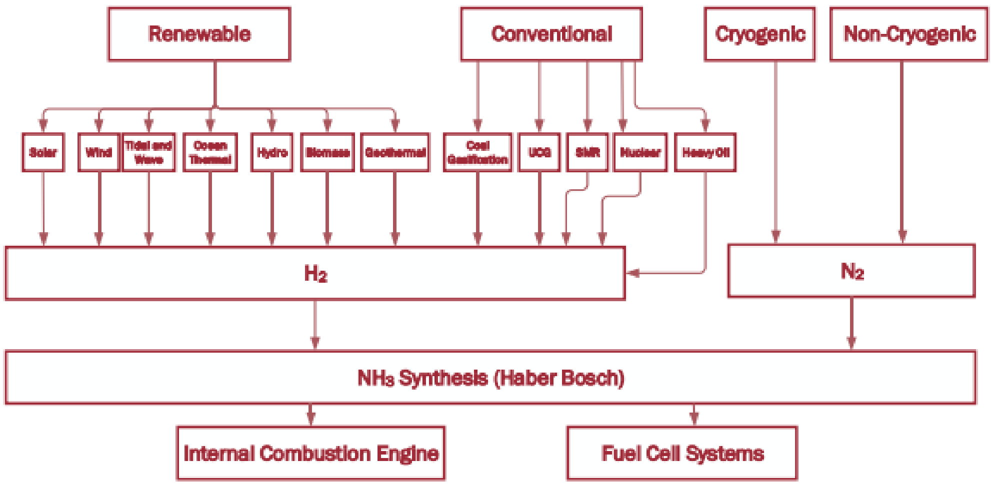

Figure 2. 2 Main NH_3 production and utilization pathways using Haber-Bosch synthesis. Adapted from (Bicer, 2017).

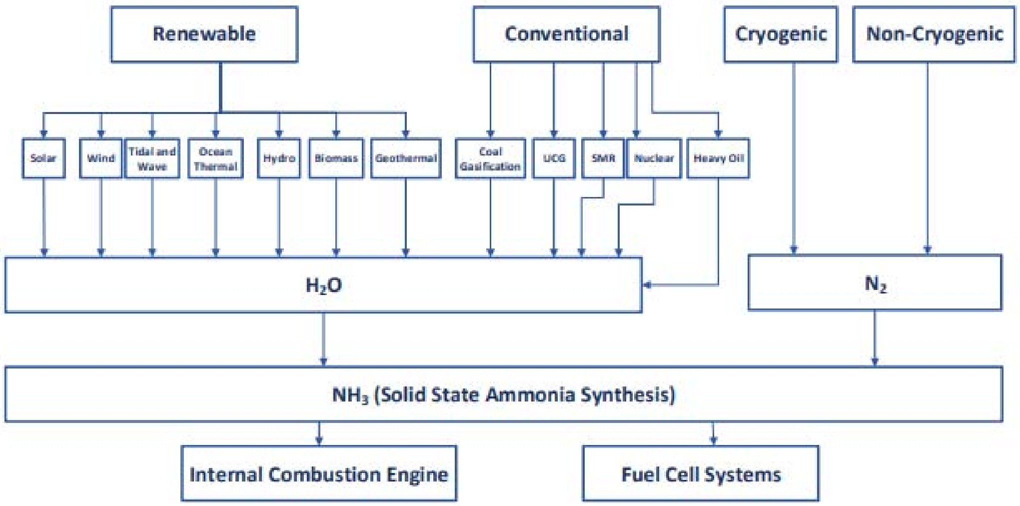

Figure 2.3 Main NH_3 production and utilization pathways using SSAS synthesis. Adapted from (Bicer, 2017).

2.1.1.1 Ammonia production methods and technology overview

Ammonia production today is a form of energy that can be synthesized from diverse primary energy sources including conventional and renewable energy resources (see figures 2.6, 2.7 & 2.8) and, can be synthesized by different production routes. Conventionally, ammonia can be produced through a high temperature and high pressure Haber-Bosch process, where iron oxide catalyzes the reaction of hydrogen with nitrogen at high temperature and pressure (See figures 2.1, 2.2 & 2.3) (Giddey, Badwal, & A.Kulkarni, 2013 : Bicer, Dincer, Zamfirescu, Vezina, & Razo, 2016). This process requires a "large" infrastructure for the mass production of ammonia, thus making it energy intensive and highly exothermic due to the reaction of N_2 and NH_3 (Nazemi, Panikkanvalappila, & A.El-Sayed, 2018). Also, using this route, NH_3 can be synthesized by desulfurization of (mostly natural gas) through "methane steam reforming" to extract hydrogen, "followed by a "water gas shift" reaction to convert CO to hydrogen and CO_2. The residual CO is then removed by methanation and the CO_2 is removed by a pressure swing adsorption process" (See figures 2.2, 2.4)

Giddey, Badwal, & A.Kulkarni, 2013 : Holladay, Hu, King, & Wang, 2009 : Shipman & D.Symes, 2017 : ISPT, 2018 : ISPT, 2018 : Bicer, Dincer, Zamfirescu, Vezina, & Razo, 2016). Globally, about 150 million tons of ammonia are produced annually via a Haber-Bosch process (Guo, Ran, Vasileffa, & Qiao, 2018).

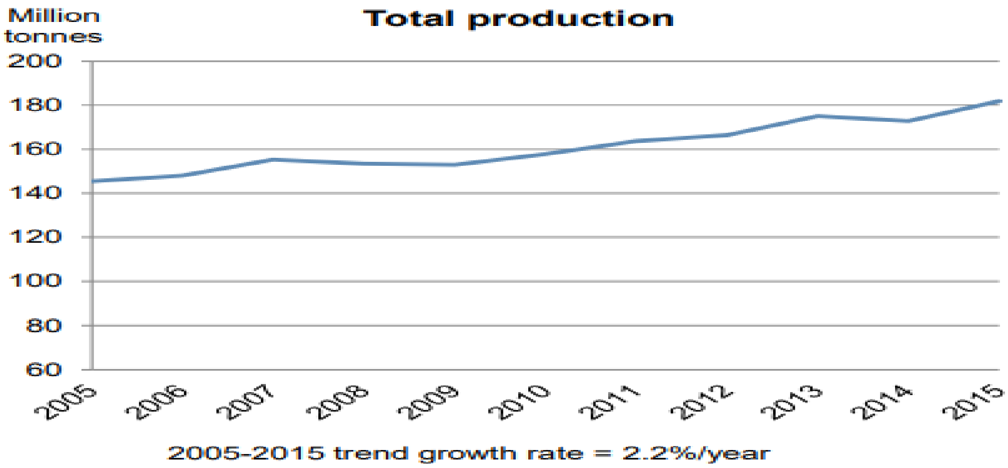

Figure 2. 4 Global NH3 production. Adapted from (YARA, 2017).

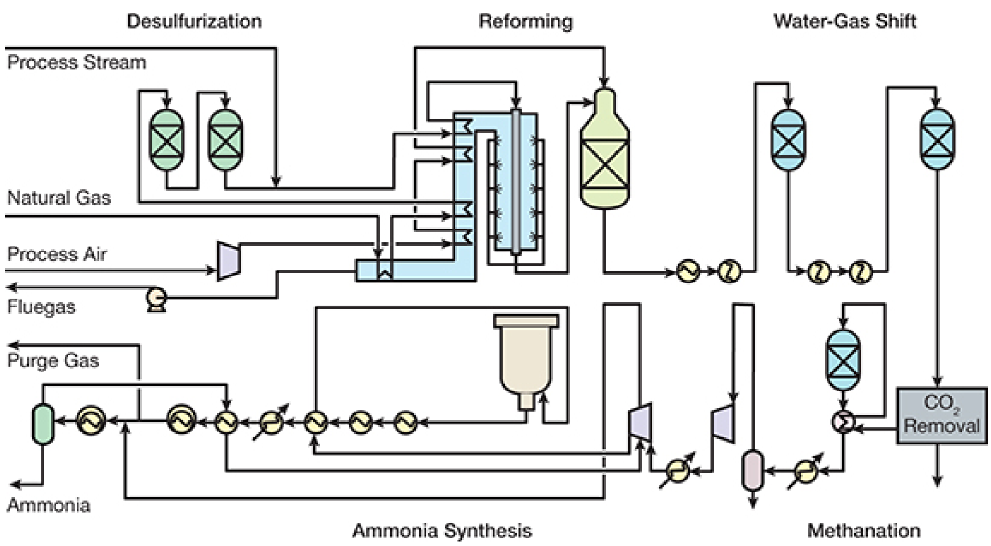

Figure 2.5 NH_3 production route via Haber-Bosch synthesis. Adapted from (Pattabathula & Richardson, 2016).

Notwithstanding, this traditional method of ammonia production is energy intensive, since it is heavily dependent on fossil fuel that has a deleterious effect on the environment. In fact, 1 percent of the overall GHG emissions is attributed to the ammonia manufacturing industry and for every one ton of ammonia produced, 1.5 tons of CO_2 are emitted. Hence, the production of ammonia from renewable energy sources can substantially decarbonize the production process (Bicer, Dincer, Zamfirescu, Vezina, & Razo, 2016 : Makhlouf, Serradj, & Cheniti, 2015 : Kobayashi, Hayakawa, A.Somarathne, & C.Okafor, 2019).

Ammonia has been used for over two centuries and the technology for ammonia production has evolved over the years. The first known ammonia production route was when N_2 could be fixed by calcium carbide to yield calcium cyanimide, which was then hydrolyzed with water to form ammonia (Pattabathula & Richardson, 2016 : ISPT, 2018).

$CaO + 3C \leftrightarrow CaC_2 + CO$

$CaC_2 + N_2 \leftrightarrow CaCN_2 + C$

$CaCN_2 + 3H_2O \leftrightarrow CaCO_3 + 2NH_{30}$

However, this process was limited due to the high energy consumption and could not produce large amounts of ammonia, while meanwhile, it was impossible at that time to produce large equipment that could operate at high pressure. Unlike the previous routes, the invention of the Haber Bosch process of ammonia production route marks a monumental breakthrough, where, for the first time a commercial quantity of ammonia was produced at high pressure (Pattabathula & Richardson, 2016).

Notwithstanding, ammonia can be synthesized in a sustainable way from renewable energy sources such as solar and wind power, through an electrochemical synthesis. Compared to Haber-Bosch synthesis, this method comprises a simple technology that requires smaller devices that enable the production and consumption of ammonia to meet different levels of demands *"it is possible to envisage electro synthetic cells where water could be oxidized to produce protons and electrons at the node then be used to reduce and protonate nitrogen to give ammonia at the cathode. If this nitrogen were sourced from the air, then the only required infrastructure for this process would be supplies of water, air and electricity, the latter of which could be provided by renewables. Thus, an electro synthetic cell for ammonia production could allow NH3 to be generated sustainably in small, low-cost devices requiring only minimal facilities."*(Shipman & D.Symes, 2017 : Nazemi, Panikkanvalappila, & A.El-Sayed, 2018).

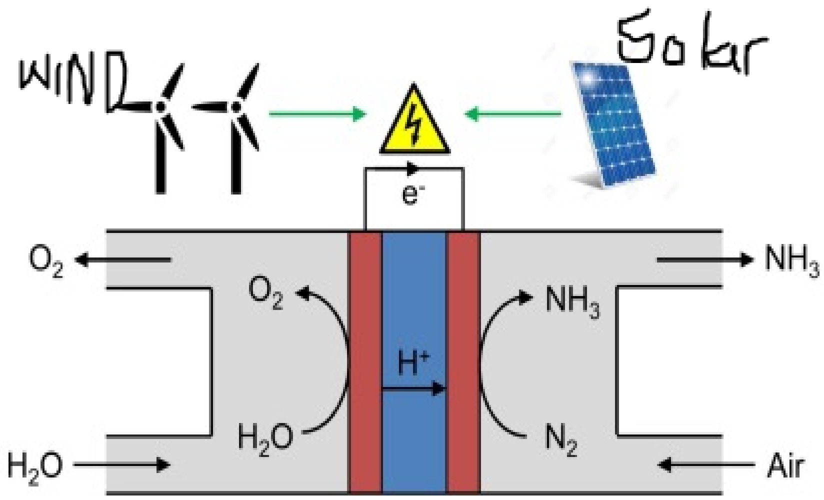

Figure 2. 6 A Flow diagram of green ammonia production from solar and wind energy. Adapted from (Shipman & D.Symes, 2017).

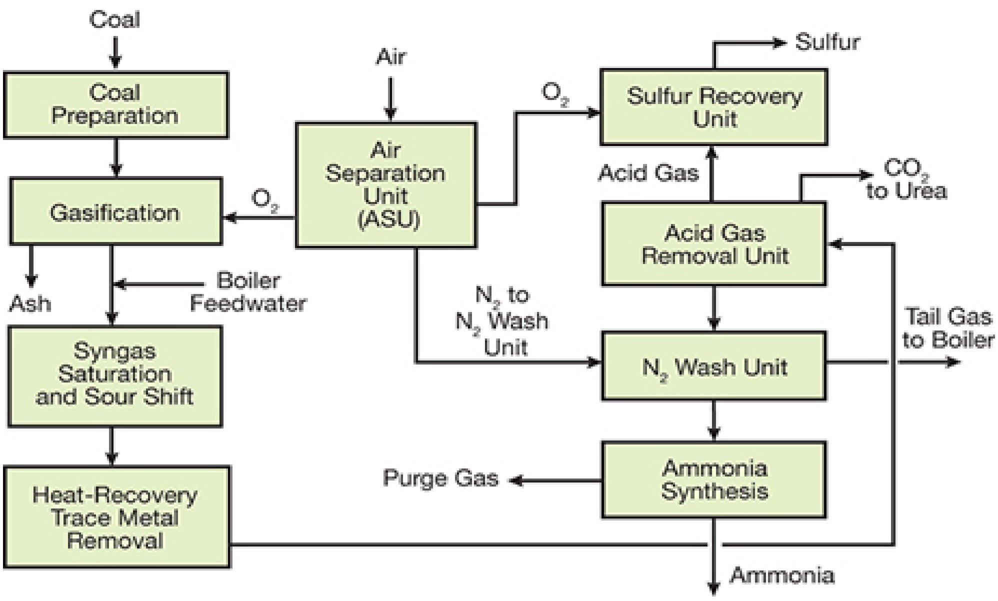

Figure 2.7 Flow diagram of ammonia production from coal. Adapted from (Pattabathula & Richardson, 2016).

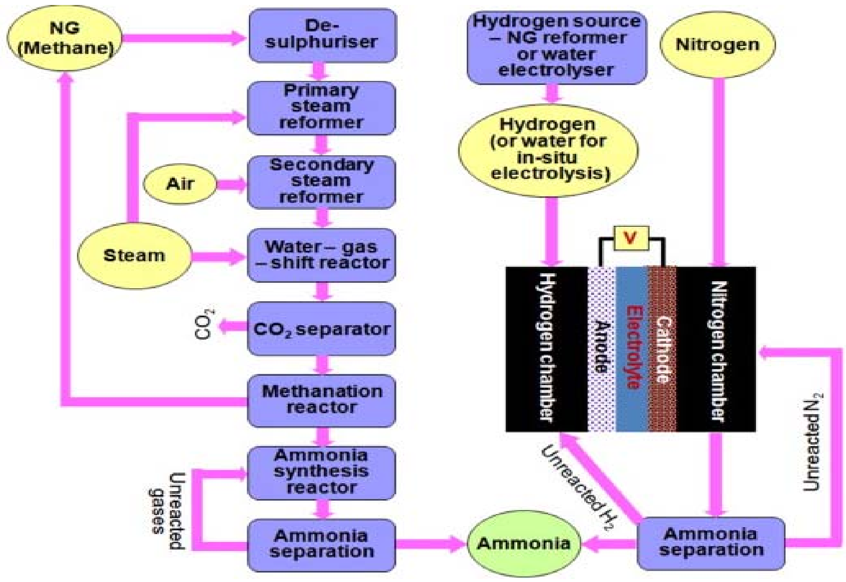

Figure 2.8 Flow diagram comparing the standard Haber-Bosch process (left) with electrochemical route for NH3 synthesis (right). Adapted from (Giddey, Badwal, & A. Kulkarni, 2013).

2.1.1.2 Challenges and limitations

The use of electrochemical technology to generate nitrogen from its element is environmentally benign since it requires smaller devices that are less costly and consumes minimum electricity. Compared to the Haber Bosch process, it is limited in terms of mass production of ammonia and it suffers a major drawback as it relates to the reduction of nitrogen in the presence of water. Notwithstanding, a number of studies have indicated some technological breakthroughs to enhance the pathways for the electrochemical synthesis of ammonia from its elements, including nitrogen fixation to ammonia via hydrogenation using special enzymes that may be possible to use. Likewise, an electrochemical technology that reduces nitrogen to ammonia by oxidizing water in order to extract protons and electrons and subsequent reduction of nitrogen, electrolytes of molten salts, could be used; among others (Shipman & D.Symes, 2017 : Nazemi, Panikkanvalappila, & A.El-Sayed, 2018 : ISPT, 2018).

2.1.1.3 Political stance

"*Ammonia is the nexus between food production and power generation and is believed that its future economy will be heavily influenced by the politics likely to affect the agriculture and the energy sectors in the coming years*" (Fertilizers Europe, 2018). The heightened global consciousness to decarbonize energy generation to reduce the carbon footprint of combustion has made green ammonia to be attractive for many industrialized countries. Some developed countries have aligned themselves to the Paris Agreement target to substantially decarbonize energy generation routes. They have invested in some best current low or zero carbon technologies. Already, the ammonia industry is available and mature, with well-established transportation and storage infrastructures. To meet its target for GHG reduction, the Government of Japan has cut down its reliance on fossil fuels, thereby investing in renewable and zero carbon energy resources. By setting a well-defined goal for decarbonization, it intends to further reduce GHG emissions by 80 percent by the year 2050 (Kobayashi, Hayakawa, A.Somarathne, & C.Okafor, 2019).

Moreover, the United States Government has a huge interest in decarbonizing ammonia production and is developing it both for military and civilian purposes including fuel for military vehicles (Harz, 2014). Due to the carbon neutrality of green ammonia it is a topic of interest for many energy research institutes presently exploring the current most environmentally benign clean energy sources. For instance, the International Energy Association report in 2019 identifies ammonia as "one of the most aatractive energy carriers with economic advantages" (Kobayashi, Hayakawa, A.Somarathne, & C.Okafor, 2019). In addition, a joint research team led by British academics from University College London and the University of Oxford considerd ammonia as a "genuine contender, and perhaps the contender for carbon-free energy that competes with fossil fuels." In this respect, green ammonia has a promising feature just as solar and wind power. Ammonia is a breakthrough that facilitates the storage and distribution of hydrogen generated from wind and solar power in a safe and cheap way. Compared to hydrogen, ammonia has a higher volumetric density and is a potential carrier and storage medium for renewable energy resources (Brown, 2015).

2.2.1.4 Environmental impacts of ammonia

Assessing the impacts of non-conventional methods of ammonia production such as solid state syntheses and electrochemical processes, on human health, the environment, and associated energy efficiencies throughout the entire life cycle of an alternative fuel, is a significant criterion (Bicer, Dincer, Zamfirescu, Vezina, & Razo, 2016). The Haber Bosch process is the most dominant method of producing ammonia. (See figures 2.1, 2.2 & 2.5). This method of ammonia synthesis produces a high carbon footprint because it is using current practices heavily reliant on natural gas (about 2-3 percent), making it to emit about 450 million metric tons of CO_2 annually (Nazemi, Panikkanvalappila, & A.El-Sayed, 2018) and in which for every tonne of ammonia produced, about 1.5 tonnes of CO_2 is emitted to the environment (Bicer, Dincer, Zamfirescu, Vezina, & Razo, 2016). Ammonia produced from renewable sources is potentially suited to reduce the carbon footprint of shipping because it contains zero carbon and is a vehicle for the storage renewable hydrogen (Kobayashi, Hayakawa, A.Somarathne, & C.Okafor, 2019). (See figures 2.1, 2.3 & 2.6).

2.2.1.5 Feasibility of ammonia as a marine fuel

According to Reiter & Kong, (2008), ammonia has a high ignition temperature and when burned in engines it produces less NO_x. However, the use of ammonia as direct fuel in an engine offers some drawbacks due to its low flame propagation and "low radiation intensity" (Jerzy Kowalski, 2014: Kobayashi, Hayakawa, A.Somarathne, & C.Okafor, 2019). Besides, by modifying the shape of the combustion chamber or designing a new engine that operates on ammonia only could enhance the combustion of ammonia (USA Patent No. US 2010/0019506 A1, 2010). Per liquid volume, ammonia can store more than 30 times the same amount of energy as liquid hydroegen (Brown, 2015).

2.2.2 Hydrogen

Hydrogen is a versatile chemical substance that could be produced by the electrolysis of water. Hydrogen is a potential energy carrier (energy vector) and could become an enabler of decarbonization and electrification. The use of hydrogen as a transport fuel is not a new practice but, its re-emergence in recent years have been driven by the quest for energy scarcity and energy security as well as the increasing level of GHG gases present in the atmosphere. Hydrogen is gaining more importance in the global energy system because it is a clean and feasible carrier to drive a "low carbon economy". Hydrogen can be synthesized through a number of conventional and novel technologies such as Haber Bosch and solid-state syntheses, whereas the energy required for the process can be utilized from primary energy resources that include traditional fossil fuels and renewable energy resources. The use of hydrogen produced from renewable energy sources typically has much lower GHG emissions than fossil fuels, even though the plan to build a hydrogen economy generally suffers from the limitations in existing technologies for mass production, storage, utilization, and the lack of a simple means of transportation. As a result, a number of storage media are currently being considered for hydrogen storage, including ammonia, owing to its "higher energy density" and widely available transport infrastructure. Furthermore, the implementation of hydrogen related policies could help remove barriers, drive market competition and innovation to enhance the performance of existing technologies and infrastructure, boost hydrogen production and availability in different places, as well as dropping the price of hydrogen fuel continuously (A Valera-Medina, Xiao, Owen-Jones, W.I.F. David: P. J.Bowen, 2018 : Cheng, Vo, & Ideris, 2018: Christopher & Dimitrios, 2012: IEA, 2019).

2.3 Results from previous LCA studies, methodologies, uncertainties and limitations

A clear understanding of the LCA and a review of the different LCA studies on fuel used in the maritime transport is necessary in assessing the environmental performance of a fuel. A Life cycle assessment is a standard method used to analyze the life of a product from design to waste and its impact in the environment. However, ammonia is widely used as feedstock in many industrial processes, but the application of ammonia as maritime transport fuel has not been well researched in the open literatures. However, different studies have used the LCA method to determine the impacts of introducing a product in maritime transport, particularly the deployment of new fuel types such as hydrogen and methanol, to comply with the evolutionary regulations (Gasparotti & Rusu, 2012: Chatzinikolaou & Ventikos, 2013: Bengtsson,S, Anderson, K, Fridell, E, 2011: Klöpffer & Grahl, 2014).

According to the International organization for Standardization, the ISO 14040 (1997) defines the life cycle assessment as follows:

> *"LCA is a technique for assessing the environmental aspects and potential impacts associated with a product….;LCA studies the environmental aspects and potential impact throughout a product's life (i.e. cradle-to-grave) from*

raw material acquisition through production, use and disposal. The general categories of environmental impacts needing consideration include resource use, human health, and ecological consequences."

Based on this definition, a "*cradle-to-grave*" analysis is an approach used to quantify the environmental footprint of a process or product system over its entire life cycle. An LCA of a product or process is conducted to quantify the environmental burdens associated with the different stages involved throughout its lifespan, from raw material extraction, production, distribution (transportation), to the disposal or recycling, as shown in Figure 3.1. To weigh the environmental loads of a product, LCA should include the inventory data such as inputs and outputs relevant to the production process, as well as their potential environmental impacts. Moreover, the LCA should consist of the interpretation of results of the impact assessment and the inventory analysis, as highlighted by the ISO 14040 guideline. To contribute to the development of sustainable societies and effective protection of the environment and human health in the short and long term, a holistically approached based on LCA is necessary (Curran, Introduction to Life Cycle Assessment, 2015). Hence, this applies to the Maritime transport sector, especially when the environmental impacts of the fuel used are to be assessed.

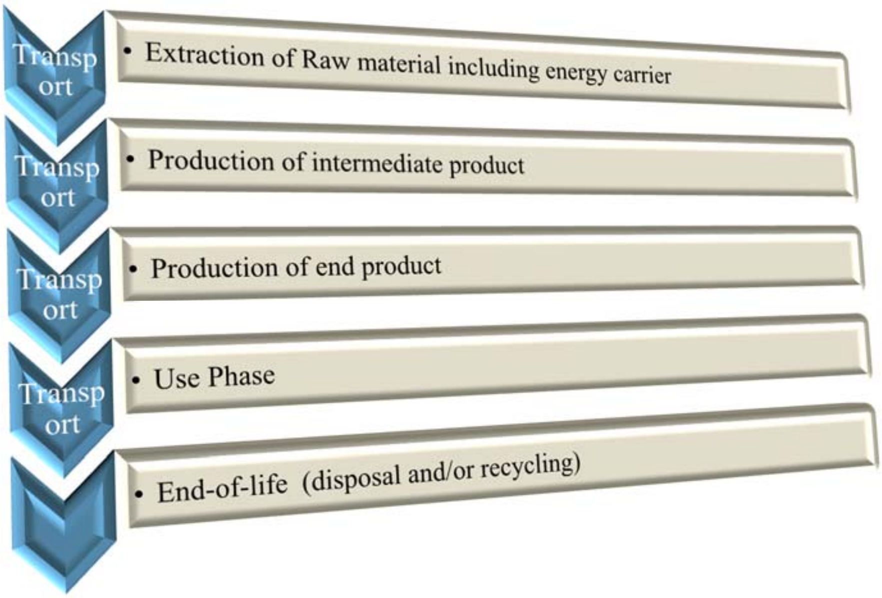

Figure 2. 9 Simplified life cycle of a selected product. Source: (Klöpffer & Grahl, 2014).

2.3.1 Previous LCA of alternative fuels and maritime transport

Different researchers have conducted LCA studies on some alternative fuels in maritime transport. This is mostly due to the level of awareness of the society about the impact of the increased anthropogenic activities on the environment. Jivén, et al., (2004) conducted a study on *LCA-ship design tool for energy efficient ships, A life Cycle analysis program for ships*, where they developed a software which will analyse the Life cycle of the ship from the construction stage to the scrapping stage. Moreover, another study conducted by Nicole, Popa & Beizadea, (2014), used the same LCA approach from ship manufacturing to scraping. They also used the life cycle cost analysisand highlighted the air acidification due to the pollutants (NO_x, So_x…) resulting from the combution process and their effect in terms of toxicity of the water and soil, but also the air. They found that the wastewater contained nitrogen that caused algal bloom and degraded the marine life by depleting the oxygen in the water.

Bicer et al. (Bicer, Dincer, Zamfirescu, Vezina, & Razo, 2016) conducted a comparative LCA for four different methods of NH_3 production from “craddle-to-grave”, using renewable energy resources. On separate occasions, they used the energy generated from nuclear, hydropower, biomass and municipal waste to produce hydrogen (through an electrolyzer) and ammonia (via a Haber-bosch synthesis), whereas nitrogen was produced using a cryogenic air separator. For one kilogram of NH_3 produced, the results indicated the lowest GHG emissions (Global warming potential) for municipal waste based NH_3 power plant (0.34 kg CO_2e), followed by hydropower (0.38 kg CO_2e), nuclear power (0.84 kg CO_2e), and biomass (0.85 kg CO_2e). Energy efficiency (and “exergency efficienecy”) for hydropower was highest (42.7%,’46.4%’), followed by nuclear (23.8%,’20.4%’), biomass (15.4%,‘15.5%’) and municipal waste (11.7%, ’10.3%’). In terms of human health, nuclear based NH_3 power plants recorded the highest (0.95 kg eq/NH_3) for human toxicity, where as municipal waste based NH_3 power plant was recorded as the lowest. Finally, in terms of recource depletion, the nuclear power plant was found to be highest due to the use of uranium as a primary energy resource, followed by the hydropower plant.

Moreover, Bengtsson, Andersson, & Fridell, (2011) presented the results of a comparative LCA of four marine fuels, namely liquefied natural gas (LNG), heavy fuel oil (HFO), gas-to-liquid (GTL) fuel, and MGO from “well-to-propeller”. Compared to HFO, LNG reported a slight decrease in Global warming potentials (GWP) due to methane slip. A significant decrease in acidification and eutrophication potentials for LNG and other alternatives due to the reduced SO_x and NO_x emissions was observed. With the coupling of scrubbers and selective catalytic reduction (SCR) with MGO and GTL, a slight increase in acididification and eutrophication potentials was recorded, whereas none of the fossil fuels were able to reduce GHG over its entire life cycle. Also, HFO was reported to be the highest in terms of energy efficiency, while GTL reported the lowest.

Bicer and Diner (2018) examined the environmental impacts of switching completely from HFO to two alternative fuels, namely NH_3 and H_2 produced from both traditional hydrocarbon and renewable energy sources. Using a "craddle-to-grave" approach, they conducted a comparative LCA of these alternative fuels per tonne-kilometr for two merchant ships including during their operation and maintenance stages. They used SimaPro and GREET sofwares to asses various impact categories and inventory data including GWP, marine eco-toxicology and ozone layer depletion to quantify the environmental burdens associated with a complete switch. Findings from this study revealed that 73 percent of marine eco-toxicology was attributed to HFO based NH_3 cargo ships, but a 47 percent reduction was recorded for a dual fuel tanker with HFO and NH_3 (generated from wind), while hydropower based H_2 fuel had the lowest in terms of marine eco-toxicology.

In terms of GWP for both cargo and tanker ships, hydropower based H_2 fuel was found to be the environmental friendiest (with 0.00198 kg CO_2 and 0.001 kg CO_2e), followed by NH_3 synthesized from wind only or combined with hydrocarbon fuels (0.0079 kg CO_2 and 0.0036 kg CO_2e), whereas a 34.5 percent reduction in GHG was attributed to NH_3 fuel in the dual mode and a 0.0018 kg CO_2e for the NH_3 fuel only, while NH_3 produced from HFO was recorded the highest GHG emissions (between 49.3 to 64 percent). In terms of abiotic resource depletion, HFO based NH_3 fuel recorded the highest, followed by wind based NH_3 fuel, due to the utiliztion of non renewable resources such as coal and fossil fuel. In terms of acidification, HFO based NH_3 fuel was found to be the highest due to the emissions of air pollutants such as SO_x and NO_x during the operation phase.

To verify compliance with stringent IMO regulations, Gilbert, et al. (2018) assessed various marine fuels that include both fossil fuels and alternatives. They presented the findings of the full LCA evaluated on the basis of suitability to readily comply with existing regulations and, at the same time, deliver environmental loads over their entire life cycles. The results indicated that there is not a single alternative fuel that is optimally suited to comply with existing IMO regulations and concomitantly offset emissions across its whole life cycle. Despite alternative fuels proving to deliver a significant reduction in local pollutant emissions, a clear reduction in GHG emissions over their life cycles remains a challenge. For H_2 produced from LNG it was subjected to steam reforming process, which is promising in terms of reducing local pollutants, but faces infrastructure challenges due to its limited supply in the electricity mix and its inability to significantly reduce GHG emissions, giving its high carbon footprint. For biofuels, they can readily deliver local pollutants, but not sustainable, due to a number of factors such as land use or the adabatic depletion of resources.

In another study, Corbett & Winebrake (2012) conducted a comparactive LCA (from "well-to-tank") of RFO, MDO and MGO for container ships. The results revealed that MDO and MGO can readily deliver a significant reduction in local pollutants, yet cannot reduce the GHG emissions across their life cycle due to the additional energy utilized for the refining or blending process. Compared to RFO, the LSF (MDO and MGO) proved to deliver significant reduction in SO_x by 70-85 percent, with 1 percent increase in CO_2 due to the additional energy utilized by the blending or refining processes.

2.3.2 Approaches and methodologies used

Most of the researchers used the life cycle inventory analysis with a "cradle-to-grave" approach in their studies. A particular assessment was made on the execution of any process or product system, from the raw material, distribution, use, to the disposal or recycling. Each step is analyzed in order to weigh the associated environmental loads and explore means to minimize its impacts on the environment in a sustainable way. Significantly, transportation is one of the most important parts of the life product, where a significant amount of energy is used.

2.4 Previous studies on the fuel performance aspect of the marine diesel engine

The diesel engine is widely used in maritime transport, due to its high efficiency, robustness and simplicity in construction, using mainly steel as its building material. This internal combustion engine, fueled by fuel oil, uses compression ignition to burn the fuel, then transforms the heat released to mechanical work. Diesel fuel is injected to the combustion chamber at a very precise moment, a few crank angles before the top dead center (TDC) (Heywood, Internal combustion engine fundamentals, 1988; 2008), when the compressed air reaches a high temperature as shown in Figure 2.2. The combustion reactions result from the interaction of the fuel with the oxygen in the air due to the high temperatures produced by the compression of the gases. The higher pressures resulting during the expansion process of the piston-cylinder arrangement produce useful mechanical energy. The diesel engine is designed with a high compression ratio that leads to a high thermal efficiency, which means that typically a better energy efficiency can be achieved than for instance for Otto-cycle engines or gas turbines. For an ideal combustion, the oxygen should mix with the fuel in sufficient quantity to allow the full oxidation of the fuel (Jääskeläinen & Khair, 2017).

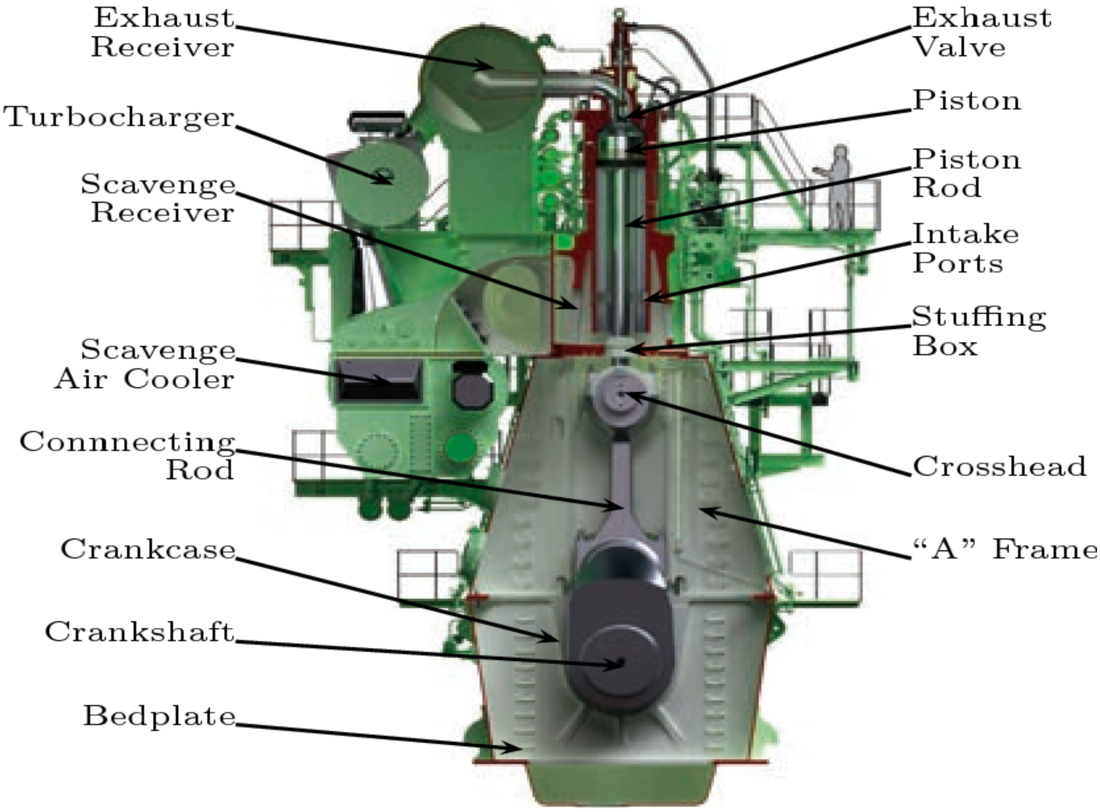

Figure 2. 10 Cross section of a two stoke marine diesel engine, MAN Diesel & Turbo G95ME-C, with description of the main components and an estimation of the engine size by comparison to the included drawing human.

Source: Llamas, 2018. (The original picture belongs to MAN Diesel & Turbo)

2.3.3 Homogeneous charge compression ignition engines (HCCI)

HCCI engines are a concept of highly efficient engines, which simultaneously have low emissions of NOx and particulate matter. In these engines the fuel is ignited by the compression ignition, but the fuel and air are premixed to a lean mixture early during the compression stroke. This largely avoids the formation of particulate matter in the fuel spray, and reduces the amount of NO_x formed by lowering the combustion temperatures.

2.4 Some previous experimental studies on the tested combustion of ammonia

The molecular geometry of ammonia offers a high flexibility that makes it an ideal vector for the easy storage and transport of hydrogen and renewable energy such as wind and solar energy. Ammonia has a low heating value and low boiling temperature. Despite its hydrogen-rich compound with high volumetric density it is characterized by poor thermal and combustion performances due to its high auto ignition temperature and low flame propagation (Kobayashi, Hayakawa, A.Somarathne, & C.Okafor, 2019 : J.Reiter & Song-CharngKong, 2011).

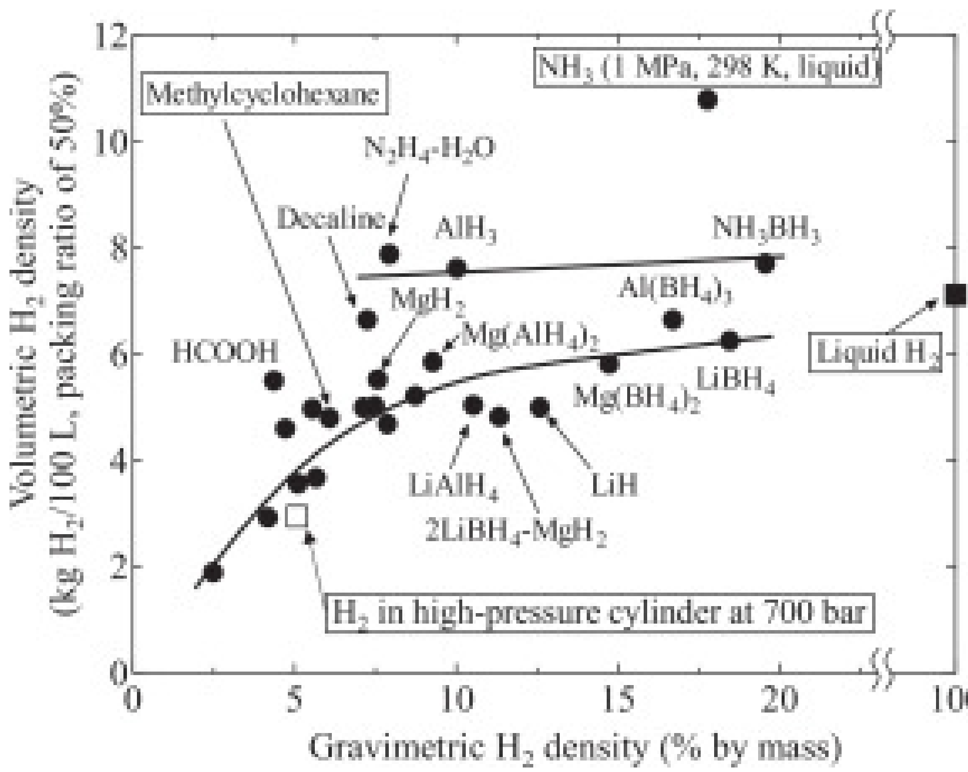

Figure 2. 11 Volumetric hydrogen density of ammonia. Adapted from (Kobayashi, Hayakawa, A.Somarathne, & C.Okafor, 2019).

As of date, no published work has been done with respect to aqueous ammonia combustion and emission characteristics in internal combustion engines. However, fewer recent publications covering ammonia combustion and emissions characteristics are available in the open literature. Different researchers have developed interest in ammonia combustion and have conducted studies on the feasibility and potential barriers for the deployment of ammonia as transport fuel.

Kobayashi, et al. (Kobayashi, Hayakawa, A.Somarathne, & C.Okafor, 2019) studied the possibility of applying ammonia as a carbon neutral fuel and outlined the progress made in the combustion of ammonia in both internal and external combustion engines. They found that hydrogen is 17.8 percent m/m of ammonia. Also, they observed that ammonia and propane are thermodynamically alike and share some chemical features. Therefore, they concluded that propane could be substituted by ammonia for propane powered ships. Compared to hydrogen, ammonia can be easily liquefied due to its low boiling temperature (-33.4 °C) , and low condensation pressure (9.9 bar), but with a high auto ignition temperature (650 °C), lower heating value (18.6 MJ/kg) and limited flame propagation (0.07 m/s). The high autoignition temperature means it is difficult to auto ignite. Moreover, they found that the combustion of ammonia in air contributes significantly to the NO_x formation. Despite some failed attempts to burn ammonia in both internal and external combustion engines due to its poor thermal characteristics, different projects to develop ammonia as a fuel for combustion have been carried out in different parts of the world. For instance, the first use of ammonia as transportation fuel is dated back to the 1940's. Yet, the technologies are still developing to overcome barriers and improve combustion chemistry for ammonia to be used as a stand-alone fuel.

J.Reiter & Song-CharngKong (2011) condcuted an experiment to investigate whether it is feasible to power inetrnal combustion engines with ammonia. To allow the ammonia to intake and adapt the engine to a dual fuel mode, they adjusted the engine manifold and modified the fueling systems. To assess the combustion and emission characteristics of the fuels, on the one hand, they used a turbocharged four-cylinder CI test engine in dual fuel mode with ammonia and diesel. On the other hand, they deployed ammonia as the main fuel while injecting diesel as a pilot fuel. To obtain an optimal fuel efficiency, they adjusted the energy to set a desired range. To attain a constant engine power, they varied the fuel energy output by increasing diesel (40-60%), while reducing ammonia (60-40%). Second, they varied the composition of the vaporized ammonia, while injecting a small amount of diesel as pilot fuel to obtain variable engine power. Using the dual fuel mode, they observed an increased CO and hydrocarbon levels, NOx emissions increased with ammonia in higer proportion, the peak cylinder pressure decreased due to lower combustion ranking of ammonia, and soot emissions were reduced due to the ammonia. However, a lowerered fuel efficiency and increased ammonia emission were observed due to the variable fuel operation since there was no ignition promoter to ignite ammonia.

3 Methodology

3.1 Overview of methodology

This chapter is divided into three sections: section 3.2 presents a brief summary of the LCA framework for life cycle assessment. Section 3.3 gives an overview of the engine simulation process, including basic equations and systematic approaches adapted. Section 3.4 gives an overview of the engine simulation and experimental tests conducted at the University College London (UCL) Engine Laboratory. This section is divided into two subsections. Subsection 3.4.1 presents the UCL engine simulation and experimental test procedure, while subsection 3.4.2 presents the UCL engine experimental methods.

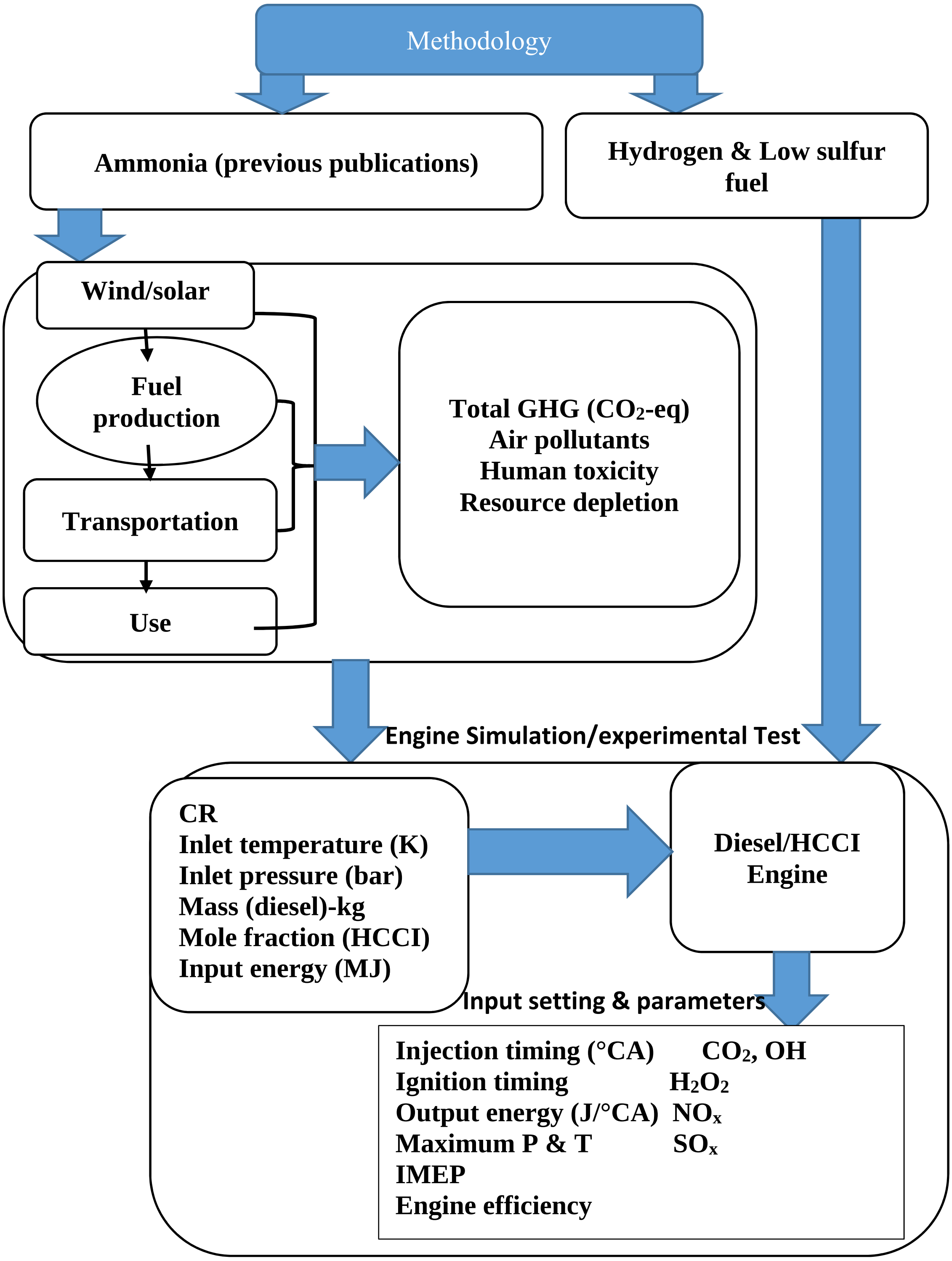

Figure 3. 1 Flow diagram of research methodology

3.2 Life cycle assessment methodology

3.2.1 Basic principles and LCA framework

Life Cycle Assessment (LCA) is a standard tool used to quantify and evaluate the environmental aspects of a certain processes or products throughout their lifespan, - from extraction of resources to disposal. An LCA is a systematic approach to analyze the environmental loads of a certain process or product or the transfer of environmental impacts from one stage to another, throughout the product's whole life cycle. Hence, a properly conducted LCA is an iterative process encompassing all stages and resources used throughout the process, thereby identifying any potential improvement or possible "trade-off" outside the scope of the process (Kun-Mo Lee; Atsushi Inaba, 2004 : Klöpffer & Grahl, 2014 : Curran, 2015).

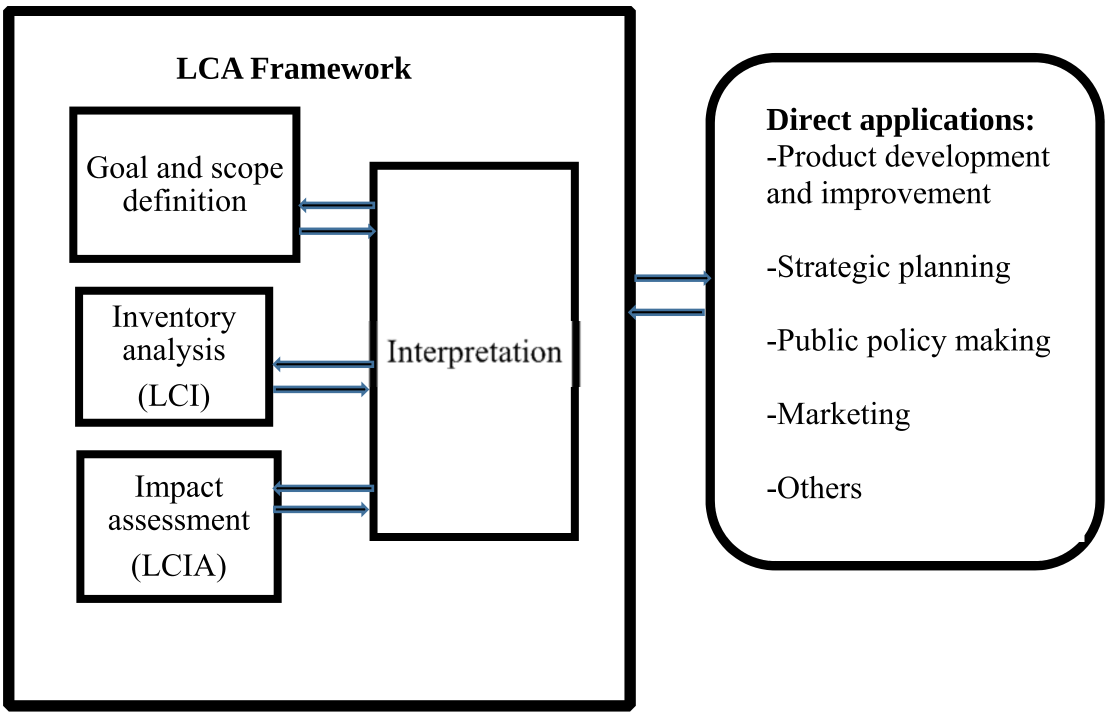

Figure 3. 2 ISO LCA Framework and its applications (Adapted from ISO 14040:2006)

LCA was purposely developed as a potential tool to minimize industrial wastes and energy consumption, and to compare different technologies having the same function with one another. The LCA framework has evolved over the years, from one form to another. An extension of its Environmental Management Standards (ISO 14000), the LCA framework was established by the ISO to evaluate environmental loads throughout the lifespan of a product system. This LCA framework (ISO 14040: 2006) is a widely accepted iterative approach that is organized into four main phases (as outlined in figure1) with three supplementary standards, including ISO 14041, 14042 and ISO 14042 (Kun-Mo Lee; Atsushi Inaba, 2004 : Curran, 2015: Klöpffer & Grahl, 2014). The structure of this LCA follows the Life Cycle Assessment Student Handbook (Curran, 2015).

Every ISO (Figure 3.2) model of LCA framework (ISO 14041) begins with the goal and scope definition phase, in which the purpose of the LCA being studied is established. The LCA framework consists of the guidelines for the collection of the inventory data. Though in the goal definition, the objective of the assessment is explicitly stated, whereas in the scope definition, the essential characteristics of a process or product system being assessed are specified, thereby providing details and identifying possible constraints. The LCA framework of the ISO standard is an iterative process, such that during the conduct of the LCA, any changes in the goal and scope can be noted and modified. Moreover, when defining the scope of the study, the following elements are to be considered: the functions of the system, the functional unit, the system boundaries must be clearly defined, the data quality requirements, impact indicators, approach and methodology for impact assessment and impact categories, and cut-off criteria must be clearly specified, and allocation procedures, inventory data needs, as well as characterization factors must be carefully selected (Curran, 2015 : Kun-Mo Lee; Atsushi Inaba, 2004 : Klöpffer & Grahl, 2014).

3.3 Engine simulation

The engine simulations conducted as part of this study were used to assess the technical viability of successfully igniting ammonia, aqueous ammonia solution, and hydrogen in a compression ignition engine, and to compare these results with the ignition of marine diesel fuel, represented by n-dodecane.

The engine simulations use a simplified thermodynamic and chemical kinetic model of a diesel engine. They use a single-zone temperature and reaction model which assumes a homogeneous composition of the engine cylinder. The single-zone model is limited in its accuracy in that it is unable to simulate differences in fuel-air stoichiometry or differences in temperature or chemical species concentrations. As a result, it overpredicts heat release rates and underpredicts the combustion's duration (Bissoli et al., 2016).

The simulations estimate pressure and temperature in a cylinder according to the compression in a piston-cylinder arrangement, and heat released from chemical reactions. They were implemented using the Cantera software package in the Python programming language. These software packages are open source software and free access to any researcher. The choice of using single-zone chemical kinetic simulations was motivated by the fact that they are simple to implement, available, and allow making an initial judgement about the ignition requirements for an engine. The source code of the simulator is based on an adaptation of the code provided by Schönborn, (2018). The engines simulated with Python were programmed based on two engines, marine diesel engine and a homogeneous charge compression ignition (HCCI) engine. Different fuels, such as Ammonia, Hydrogen and a representative of fossil fuel marine gas oil (MGO) precisely dodecane, are used for the tests.

In a diesel engine fuel is injected during the last phase of the compression stroke. The mixture starts burning at the boundary of the fuel spray where it mixes with air, creating a high efficiency, where a high percentage of fuel burned at very high temperature and with high NOx emissions. Particulates are formed in the fuel-rich center of the spray where too little oxygen is present for the full oxidation of the fuel. Given that a single-zone model is unable to accurately represent differences in stoichiometry and temperature, diesel engine simulations using a single-zone model are not very accurate.

Compare to diesel engine and gas engine, the HCCI engine uses a compression ignited homogenous charge as its working principle. Fuel and air are mixed at the start of the compression stroke; the ignition happens when the lean mixture (composed by a very high proportion of air to fuel) are compressed until they reach a very high density and temperature, leading to spontaneous reaction of the mixture. Given that inhomogeneities occur even in this combustion mode single-zone models have limited accuracy in predicting absolute emissions, but ignition timing can usually be predicted with good accuracy (Z.M. Hammond, J.H. Mack, R.W. Dibble, The effect of hydrogen peroxide addition to methane fueled homogeneous charge compression ignition engines through numerical simulations, Int. J. Engine Res. (2014) 1–12.).

In practice some HCCI engines may use a spark to control the ignition timing. When the HCCI engine is too cold, it can face some ignition problem and while it is very hot, it may lead to engine knock. However, no spark is used in the HCCI engine simulations presented herein.

Table 3. 1 Engine simulation setting (input data)

	INPUT		
Crstart	15		
Crfinish	20		
stroke	2,6		
a	1,3		
l {m}	2,5		
Diameter {m}	0,5		
Abore	0,19625		
volume {m3}	0,51025		
temperature {K}	313,15	40	
pressure {k Pa}	430	4,3	absolute pressure!
Energy use { MJ}	0,5		
Nt {mol}	84,2731122		
Perfect gas {kpa}	8,314		
NH3 low heating value LHV	18,6	http://injapan.no/wp-content/uploads/2017/02/13-Prof.-Kobayashi-Ammonia-Combustion.pdf	
H2 low heating value LHV	120,4	https://www.engineeringtoolbox.com/fuels-higher-calorific-values-d_169.html	
C12H26 low heating value LHV	44,147	https://scienceache.wordpress.com/2015/02/10/heat-content/	

Source: Authors, 2019.

Table 3. 2 Masse and mole fraction of fuel used in Diesel and HCCI engine

Diesel **HCCI**

FUEL	Mass [kg]	Molecular mass [g/mole]	Amount of substance [mole]	Molefrac-tion
NH3	0,02688172	17	1,581277672	0,018763727
H2	0,004152824	2	2,07641196	0,02463908
NC12H26	0,011325798	170	0,066622341	0,000790553

Source: Authors, 2019.

The simulation is based on the same amount of input of 0.5 megajoules (MJ) energy. We assume that the energy input is the same for the different alternatives fuel used for the tests. The energy input is used to calculate for the diesel engine, the masses of ammonia, hydrogen and dodecane fuel injected. The energy input is also the basis of calculation for the HCCI engine, the mole fraction of ammonia, hydrogen or dodecane needed for the mixture (fuel, air), which are shown by Tables 3.1 &3.2.

Different mechanisms such as Song2016, AramcoMech2.0 and Polimi-tot-nox1407 are used to simulate the chemical structure of the respective fuel ammonia, hydrogen and dodecane (Song, o.a., 2016: Li, o.a., 2017).

3.3.1 Ignition ranking

A comparative analysis of the ignition was done by ranking the fuels according to their ignition quality. Ignition timing is very important for the determination of the engine efficiency. An early ignition or late ignition affects drastically the engine performance by reducing the work output released at the end of the cycle.

3.3.2 Indication of the required compression ratio

The compression ratio was obtained by dividing the total volume before compression by the total compressed volume. Then different measurements, which are needed to determine are as following:

- Cylinder bore diameter,
- Crankshaft stroke length,
- Compressed volume.

The higher the compression ratio (14:1 to 25:1), the higher efficiency and the more power you get from the engine. In addition, the combustion chamber has often a narrower aspect ratio, which is due to a higher compression ratio. Therefore, the rate of heat released tends to be reduced due to the earliest contact between the flame and the piston (Winterbone & Turan, 2015).

The engine simulations were carried out for compression ratios between 20 and 25 for all engines and fuels. Except for the dodecane, used as fuel in the HCCI engine (CR 10 to 15).

3.3.3 Indicated mean effective pressure (IMEP)

The indicated work output per swept volume of the engine is known as the Indicated Mean Effective Pressure (IMEP). IMEP is a fundamental parameter due to its independence to the number of cylinders, displacement of the engine and the speed.

The IMEP formula (1) is derived from integration of the enclosed area of the high-pressure part of the P-V diagram (Martyr & Plint, 2012)

$$IMEP = \int PdV/V_{swept} \qquad (1)$$

$$IMEP\ (N/m^2) = \overline{p_i}$$

$$= \frac{indicated\ work\ output\ (N\ m) per\ cylindre\ per\ mechanical\ cycle}{Swept\ volumle\ per\ cyclinder\ m3}$$

$$\frac{indicated\ work\ output\ (N\ m) per\ cylindre\ per\ mechanical\ cycle}{Swept\ volumle\ per\ cyclinder\ m3}$$

3.3.4 Engine efficiency

The means of examining the thermodynamic processes in an engine is to determine the indicated efficiency through the isolation of the mechanical losses, especially when it is to compare the performance of different engines. Indicated efficiency can be seen as the ratio between the effective work output and the energy released by the fuel per cycle.

The indicative efficiency or thermal efficiency can be obtained through this formula:

$$\eta_t = \frac{w_c}{m_f Q_{HV}}$$

W_c : work per cycle

m_f : mass of fuel per cycle

Q_{HV}: heating value of fuel

3.4 UCL engine simulation and experimental test

3.4.1 UCL engine simulation methods

In this section, the engine simulations carried out were modelled based on the input setting (parameters) of the UCL experimental diesel engine (See Table 3.2). For an energy input of 0.0005MJ, a mass of 1.7301E-05 kg of was injected. The fuel consisted of pre-vaporized mixture of dimethyl ether (DME) and aqueous ammonia (26% by mass of pure ammonia and dissolved in water).

UCL Engine Input setting (parameters)

No, of Cylinders	1
Cylinder Bore (mm)	86
Cylinder Stroke (mm)	86
Swept Volume (cm3)	499,56
Geometric Compression Ratio	18,3:1

3.4.2 UCL engine experimental methods

3.4.2.1 The engine experimental laboratory Set Up

The UCL engine experimental laboratory (Engine Cell 2) is used for energy related research purposes such as development and experimental testing of new fuels. The test cell comprised a Soot Particle Aerosol Mass Spectrometer for real time (see figure 3.3) particle emissions measurement and various apparatus such as graduated cylinder, stirring rod and Erlenmeyer flask. The laboratory also houses a small control unit (see figure 3.4) equipped with four surveillance cameras for remote monitoring, and two sets of work stations consisting of three computers each and various data processing devices such as an exhaust gas particle sizer or analyzer (see figure 3.5) and a digital storage oscilloscope (see figure 3.4). The UCL experimental engine used to carry out this investigation was a single-cylinder direct-injection diesel engine. (See figure 3.3)

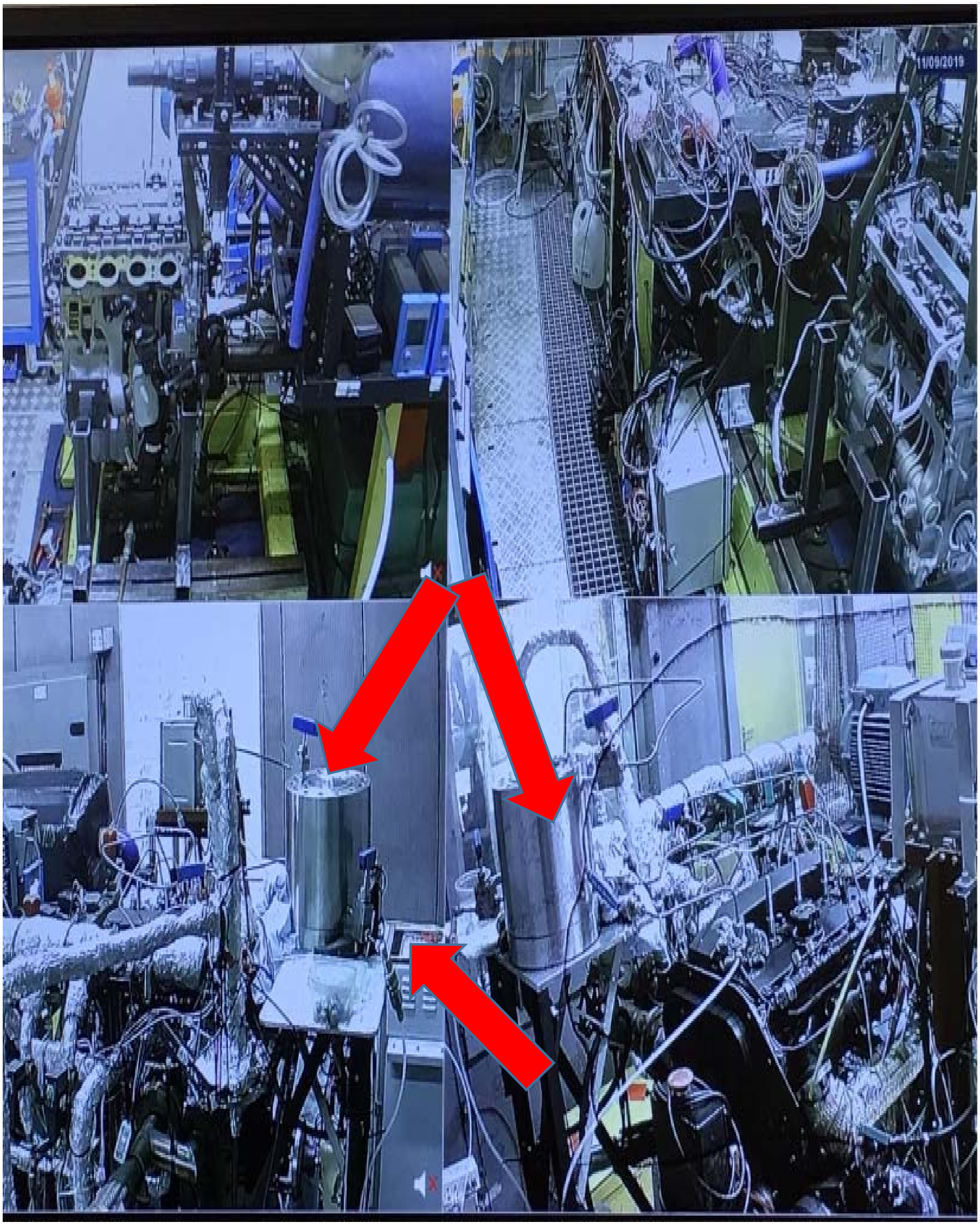

Figure 3. 3: Experimental Engine Set Up at University College London

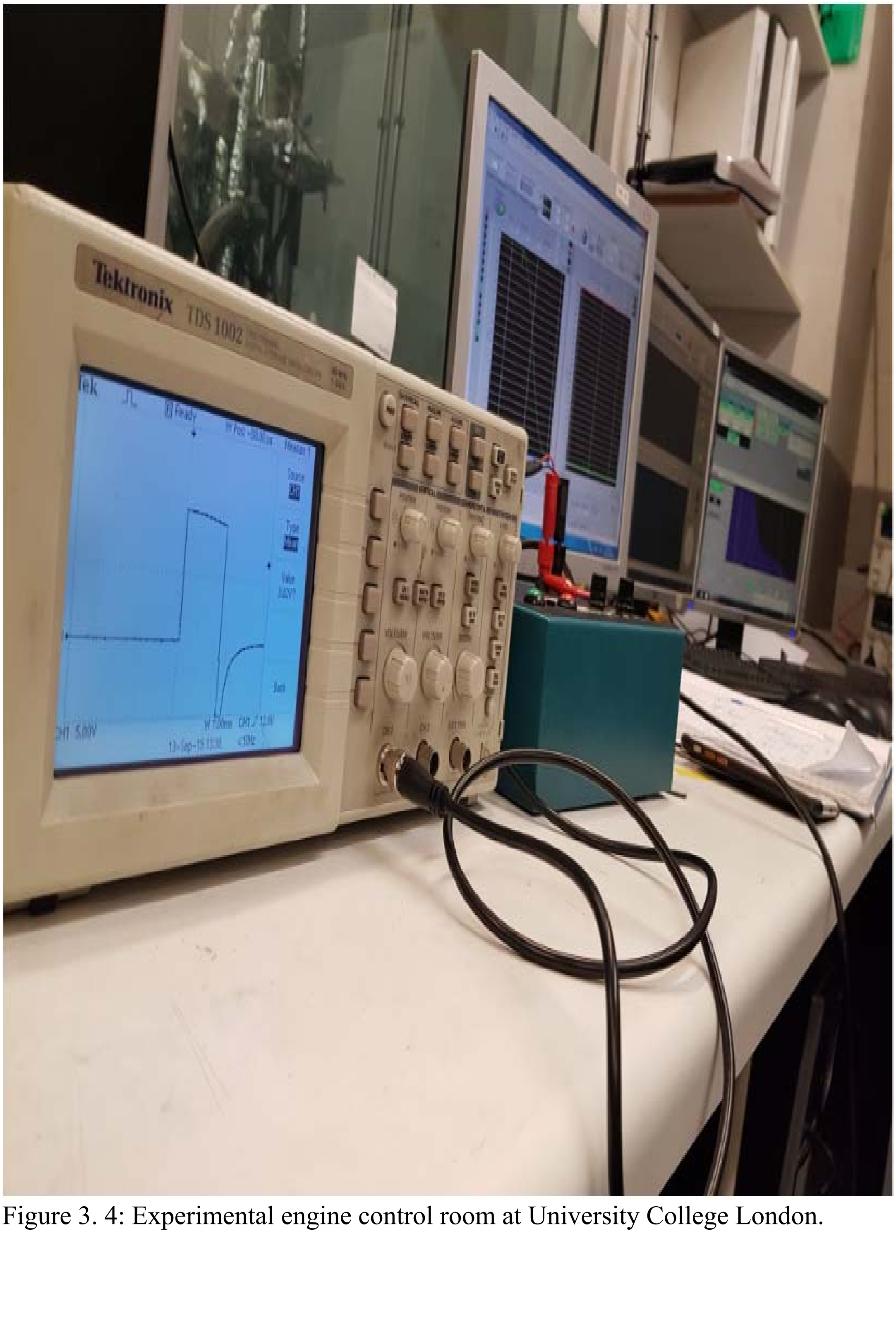

Figure 3. 4: Experimental engine control room at University College London.

Figure 3. 5: HORIBA Motor Exhaust Gas Analyzer at University College London.

4 Results and Discussions

4.1 Introduction

This chapter gives an overview of the engine simulation and experimental test results obtained. It comprises of four main sections, divided into subsections. Section 4.2 presents the ignition simulation of ammonia in both diesel and HCCI engines. Section 4.3 presents the ignition simulation of hydrogen in both diesel and HCCI engines. The engine parameters and the energy input remain the same for HCCI and the diesel engine except for the HCCI fueled with dodecane, as explained in subsection 4.4.2. Section 4.4 presents the ignition simulation of dodecane (MGO representative) in both diesel and HCCI engines. Section 4.5 presents the overview of UCL experiment. It is divided into two subsections: Subsection 4.5.2 gives a brief summary of UCL engine experimental test comprising of pre-mixed air and a mixture of aqueous ammonia (NH_4OH) and diethyl ether (DEE) in HCCI engine. In test two, aqueous ammonia is ignited with pilot injection of diesel fuel in a diesel engine.

4.2.1 Diesel cycle simulation

The marine diesel engine was set as fallowing:		
	Compression ratio	20 to 25
	Inlet temperature	40°C
	Inlet pressure:	4.3 bar
	fuel injection mass	0.0269 [kg]
	Ideal compression ratio	25:1

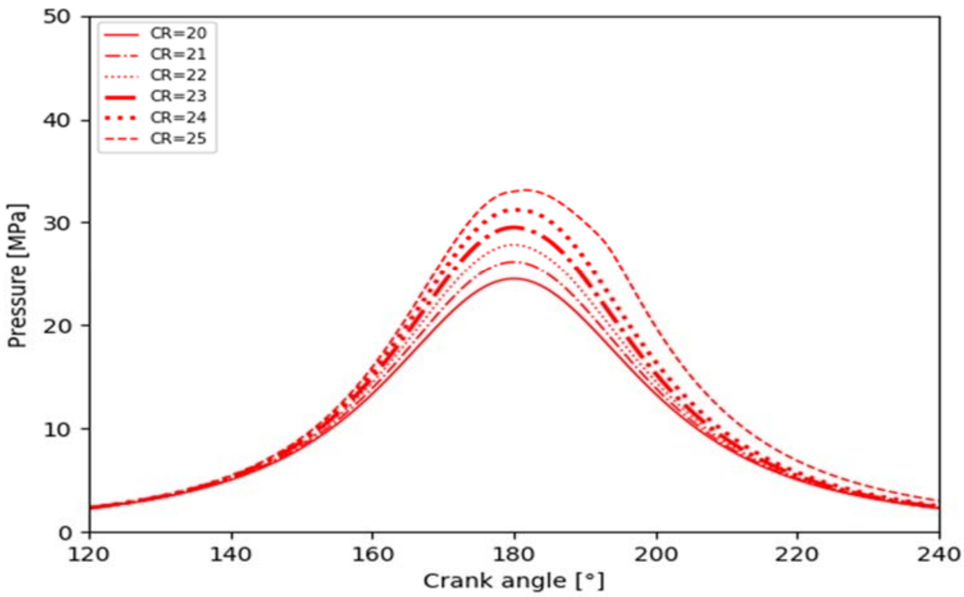

Figure 4. 1 Ignition curve of Ammonia through the diesel engine

Source: Authors, 2019

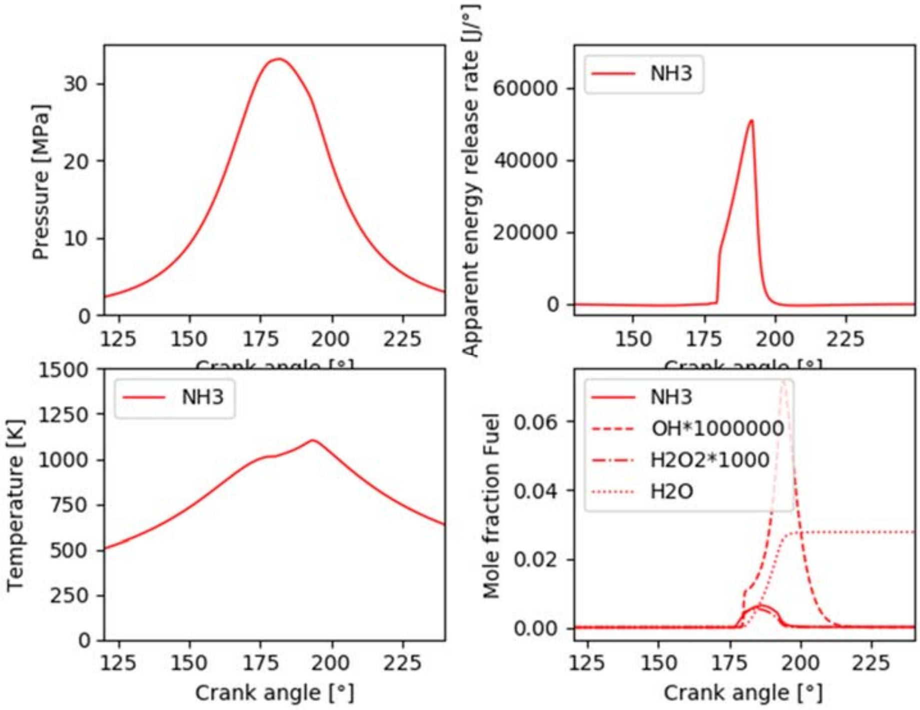

Figure 4. 2 Ammonia combustion reaction though the diesel engine at a compression ratio 25:1

Source: Authors, 2019

As shown in Figure 4.1, with 0.0269 kg of ammonia used as fuel, the fuel ignited only at a compression ratio within the range of 20 to 25. In addition, a high compression ratio involved extremely high pressures reaching the point of 35 MPa, which is likely to be a severe mechanical challenge for the engine. CR25 shows the highest pressure among other CR settings tested, because ammonia needs a high temperature for combustion. Even the highest compression ratio, 25 showed a later ignition. Combustion of ammonia at lower CRs and temperatures could be achieved with a dual fuel engine using a combustion promoter such as hydrogen and diesel to ignite the ammonia.

4.2.2 Homogeneous charge compression ignition (HCCI)

The HCCI engine was set as following:		
	Compression ratio	20 to 25
	Inlet temperature	40°C
	Inlet pressure:	4.3 bar
	Mole fraction of NH3	0.0188

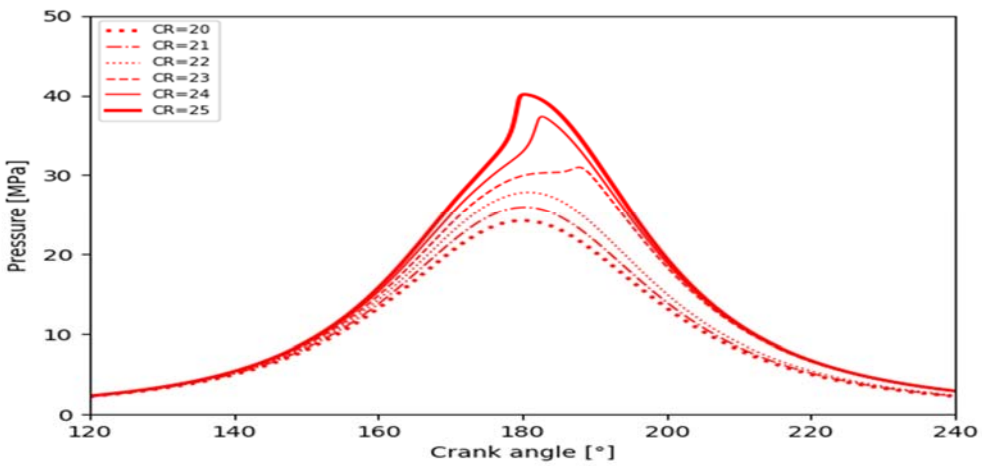

Figure 4. 3 Ignition curve of Ammonia through the HCCI engine.

Source: Authors, 2019.

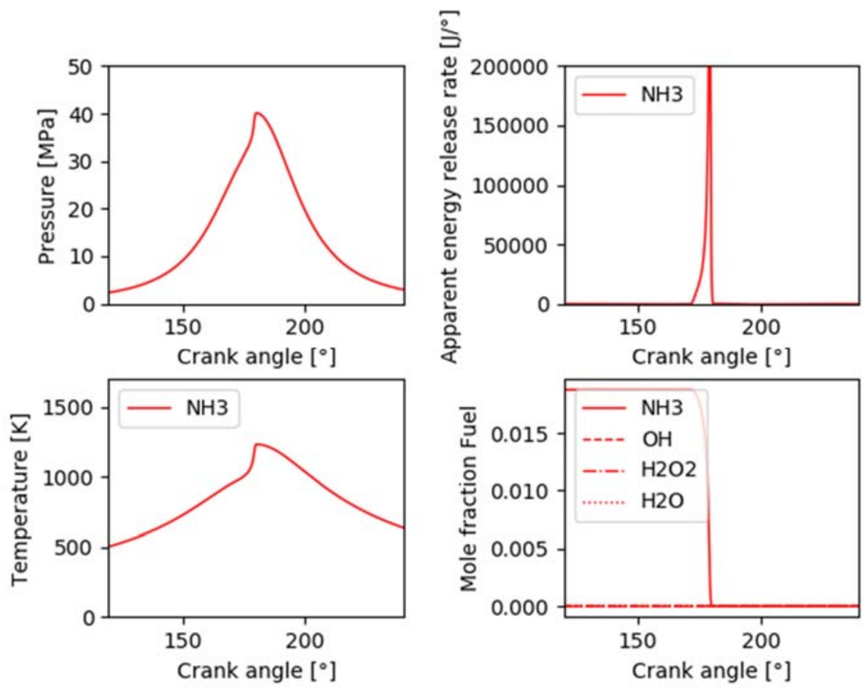

Figure 4. 4 Ammonia combustion reaction through the HCCI engine at CR 25.

Source: Authors, 2019.

Figure 4.3 shows the ignition of ammonia as fuel in different timing in relation with the different CR used for the test. The result shows that the pre-mixing of fuel and air allowed more time for ignition to take place, and full ignition was achieved both at CR 24, and CR 25 when at CR 23 late ignition was observed. Also, at the highest compression ratio, CR 25, the combustion reached the pressure of above 40MPa. Figure 4.3 shows that at the lower compression ratio 20 to 22 no ignition was simulated; this is probably due to the high-temperature needed by ammonia to ignite.

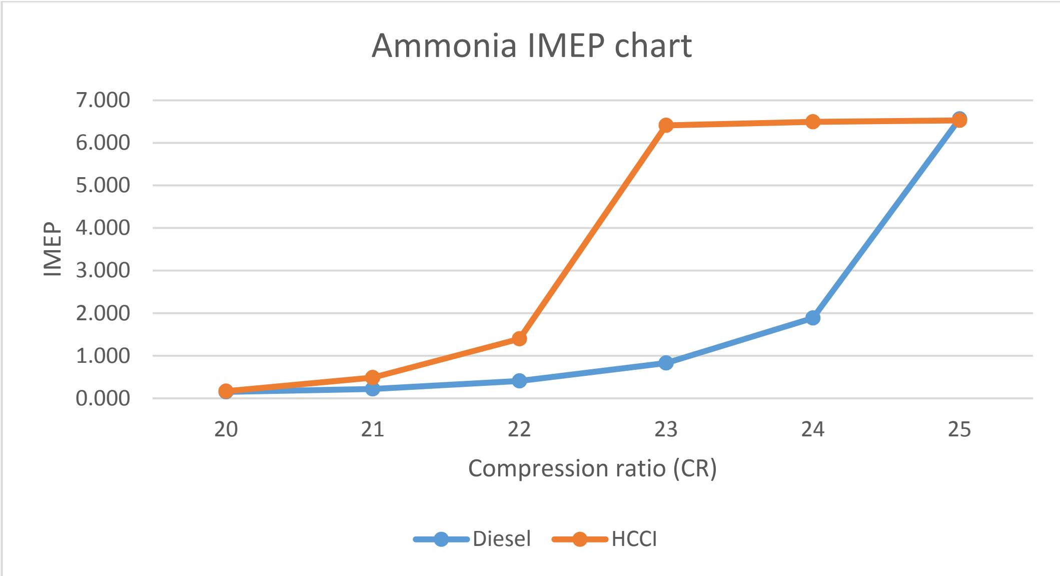

Figure 4. 5 Ammonia IMEP generate per compression ratio (20-25)

Source: Authors, 2019.

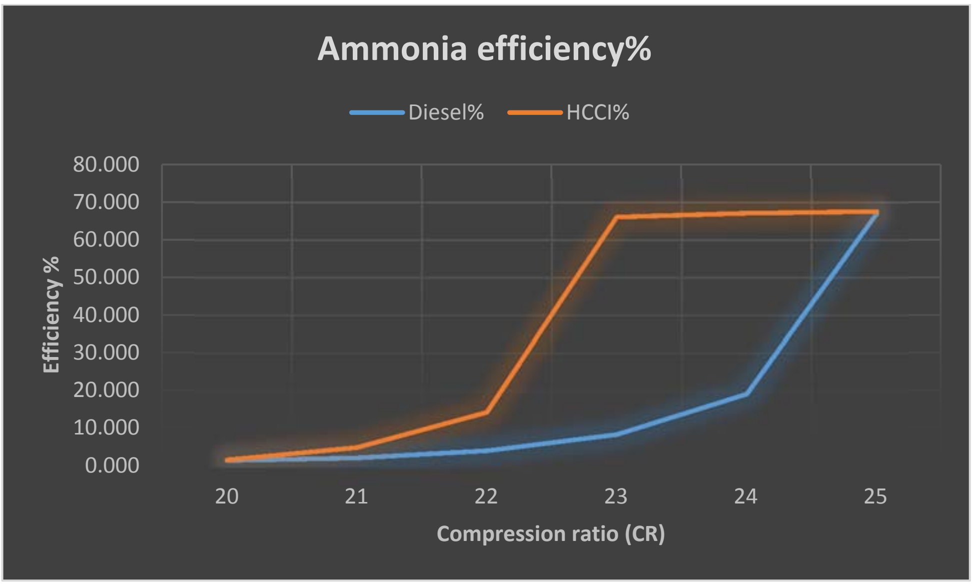

Figure 4. 6 Ammonia efficiency (%) per engines and CR

Source: Authors, 2019.

Figure 4.5 and 4.6 show that for HCCI combustion, the IMEP increases with compression ratio. At the lowest compression ratios of CR21 to CR22 there was almost no reaction. As the compression ratio was increased to CR23 the IMEP increased markedly to 6.410 bar and reached a peak of 6.526 bar at CR25. The same trend occurred for the thermal efficiency: At CR21 the efficiency was only 1.7% due to the lack of reaction. Then as ignition occurred at CR23 the thermal efficiency increased to 66.13% and reached a peak of 67.59% at CR25. The Diesel engine results showed a smooth increasing trend of IMEP and thermal efficiency between CR20 to CR23 with a respective IMEP0.151 bar ,0.828 bar and efficiency of 1.53% and 8.45%. At a compression ratio of 24 the thermal efficiency rose to 19.22%, while CR25 reached a high efficiency of 67%, which was similar to that of the HCCI engine.

The calculation of the IMEP and efficiency are shown in these two graphs highlights, the difference being between the HCCI engine and the Diesel engine in terms of performance. The HCCI trend is due to the fact that the fuel pre-mixture injects earlier have more time in the combustion chamber and therefore have a greater chance at reacting fully at lower compression ratios. Different from the HCCI engine, in the diesel engine the fuel is injected when the piston reaches top dead center. This situation gives less time to the fuel to mix well with the oxygen molecules, leading to a lower fuel burn and lower efficiency, under these conditions.

4.3 Hydrogen

4.3.1 Diesel engine

The marine diesel engine was set as fallowing:		
	Compression ratio	20 to 25
	Inlet temperature	40°C
	Inlet pressure:	4.3 bar
	fuel injection mass	0.00415 Masse [kg]
	Ideal compression ratio	23; 24; 25

The hydrogen used as fuel reacted in the diesel engine at the high compression ratios CR23 to CR25. The ideal compression ratio was around CR20-25, with the lowest peak pressure of 25MPa and the highest peak pressure was approximately 36MPa (as shown in Fig. 5.7 below).

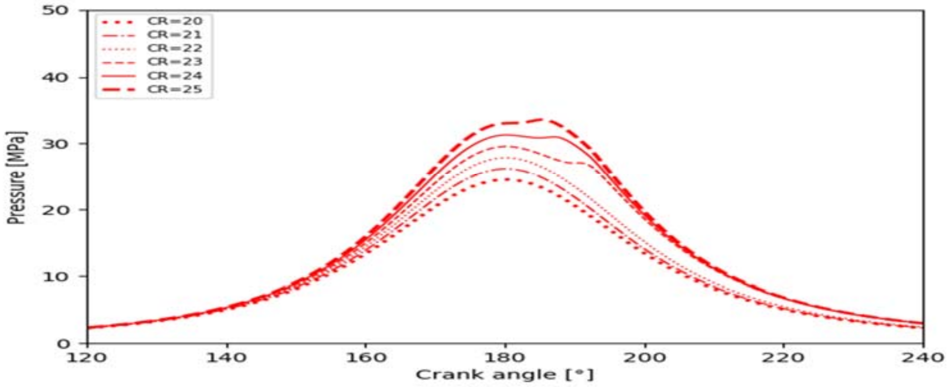

Figure 4. 7 Ignition curve of hydrogen in a marine diesel engine

Source: Authors, 2019.

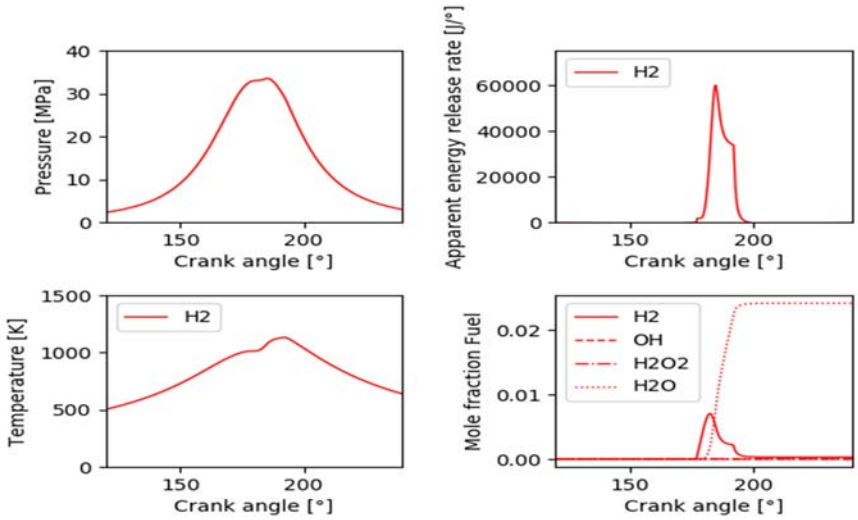

Figure 4. 8 Hydrogen combustion reaction though the diesel engine at CR 25.

Source: Authors, 2019.

The fist ignition occurred around 185° crank angle with a compression ratio of 23 and a pressure of 29.36Mpa. It is worth noting that the ignition occurred from the compression ratio 23 to 25. However, the inlet temperature played a very important and relevant role in the combustion process as we can see in Figure 4.8. The highest peak pressure happened at a CR of 25 with a peak of pressure of about 35.9MPa.

4.3.2 Homogeneous charge compression ignition (HCCI)

The settings used for hydrogen HCCI were as follows:

	Compression ratio	20 to 25
	Inlet temperature	40°C
	Inlet pressure:	4.3 bar
	Mole fraction	0.0246

The hydrogen used as fuel reacted very well in the engine as shown in Figure 3; the ignition was simulated to take place at 180° with an ideal compression ratio of 16 combined with a pressure around 20MPa.

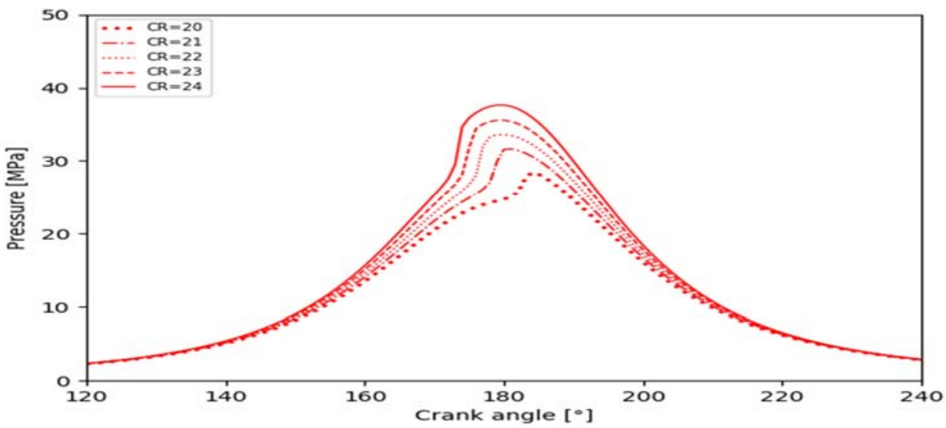

Figure 4. 9 Ignition curve of hydrogen through the HCCI engine

Source: Authors, 2019

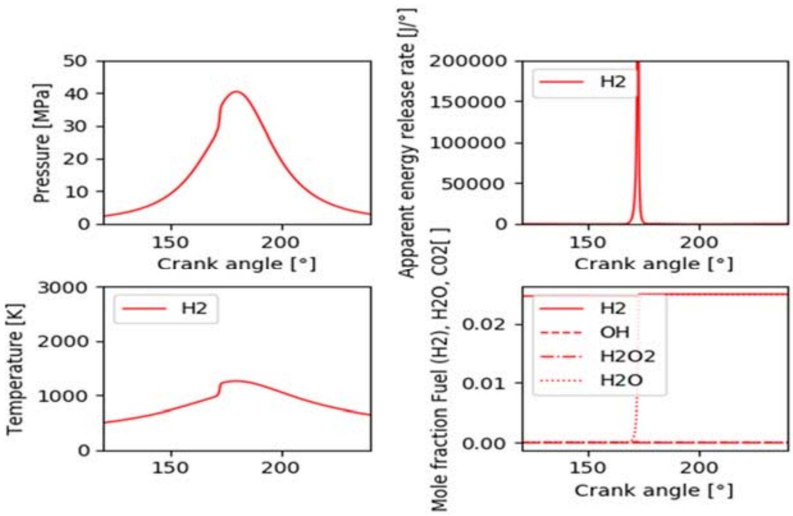

Figure 4. 10 Hydrogen combustion reaction through? the HCCI engine at CR 25.

Source; Authors, 2019.

Hydrogen was easier to ignite than ammonia. Figure 4.9, shows that the ignition time became earlier as the compression ratio was increased. CR25, being the higher compression ratio, showed an early ignition due to the fuel-air pre-mixture, a peak pressure of 40MPa and an internal temperature around 1500K as presented in figure 4.9 & 4.10.

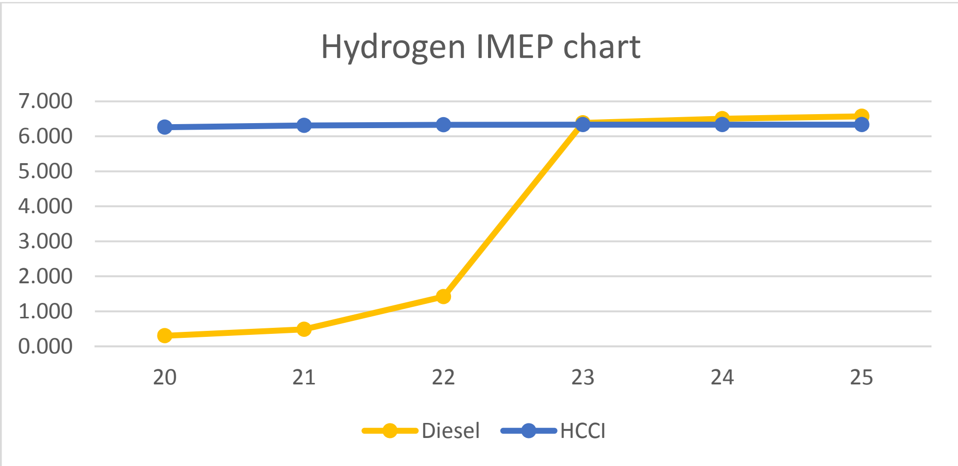

Figure 4. 11 Hydrogen IMEP generate per compression ratio (20-25)

Source: Authors, 2019.

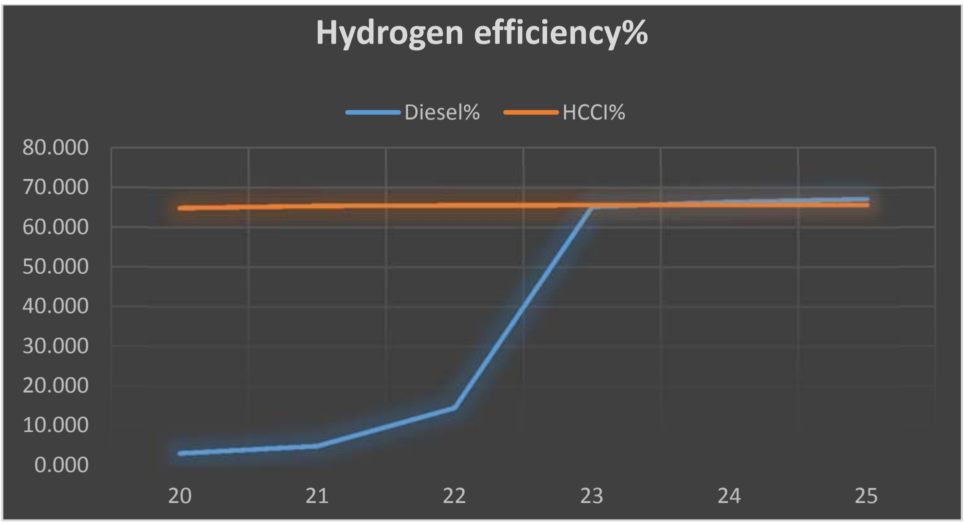

Figure 4. 12 Hydrogen Efficiency(%) per engine and CR. Source: Authors, 2019.

The diesel engine fueled with hydrogen showed a low IMEP of 0.3 bar at CR20, while at a CR20 in the HCCI engine the IMEP was around 6.262 bar present in figure 4.11. The IMEP trend reached 1 bar for the diesel engine at CR22 and kept growing up to 6.383 bar at CR23, where the same IMEP was noted for the HCCI engine. A slight difference was showing between the diesel and HCCI engine at CR25 with respectively IMEP 6.572 & 6.335 bar and efficiency 67.1% & 65.6%; see figure 4.11 and 4.12.

The difference in performance trend can be explained by the fact that with the HCCI engine, the hydrogen had more time to disperse and ignite and is already mixed with air before the injection. For the diesel engine the delay injection reduces the amount of fuel burn, because the fuel has less time to mix with the oxygen molecule. We notice also that at a higher compression ratio (25:1), the reducing volume of the combustion chamber facilitates air fuel mixing, therefore increasing the efficiency as we can see in figure 4.12.

4.4 Marine gas oil representative (Dodecane)

4.4.1 Diesel engine

The marine diesel engine was set as fallowing:		
	Compression ratio	20 to 25
	Inlet temperature	40°C
	Inlet pressure:	4.3 bar
	fuel injection mass	0.0113 [kg]
	Ideal compression ratio	21

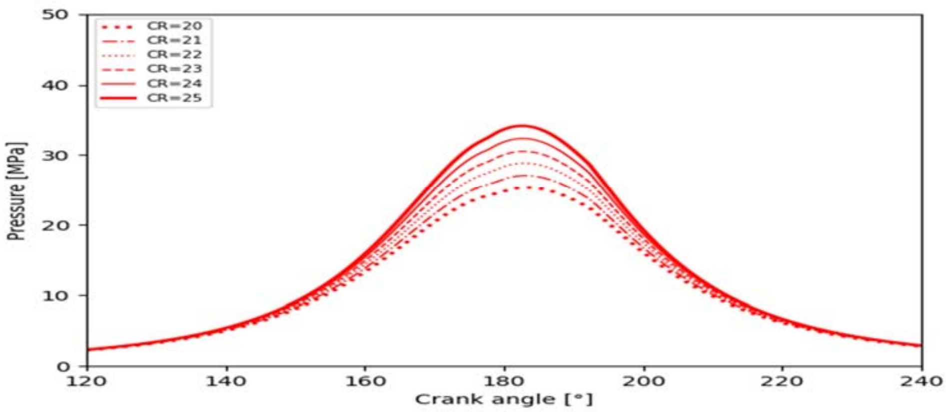

Figure 4. 13 Dodecane ignition curve through the diesel engine

Source: Authors, 2019.

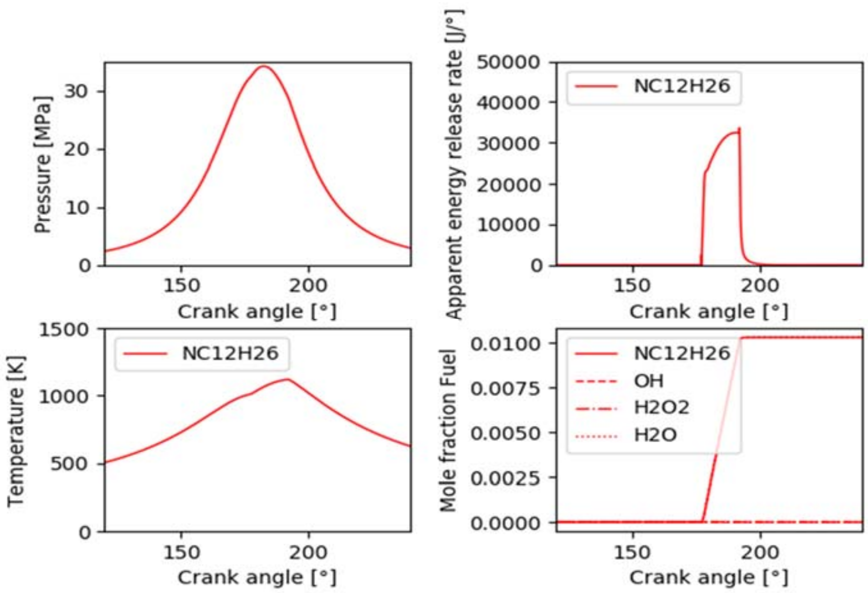

Figure 4. 14 Dodecane combustion reaction though the diesel engine at CR25.

Source: Authors, 2019.

The dodecane fuel reaction at CR 20 to 25 gave a high pressure of 33.98MPa. The lowest pressure was 25.46MPa, which is high for a diesel engine as we can see in Figure 5.8. It should be noted that the reaction of the injected fuel during compression occurred when the crank reaches the angle of 180°. Eventually, as shown in Figure 4.9, the temperature in the combustion chamber reached 1135 K.

4.4.2 Homogeneous charge compression ignition

The ideal setting of the homogeneous charge compression ignition engines is as follows:

Compression ratio	10 : 15
Inlet temperature	40°C
Inlet pressure:	4.3 bar
Mole fraction	0,000791

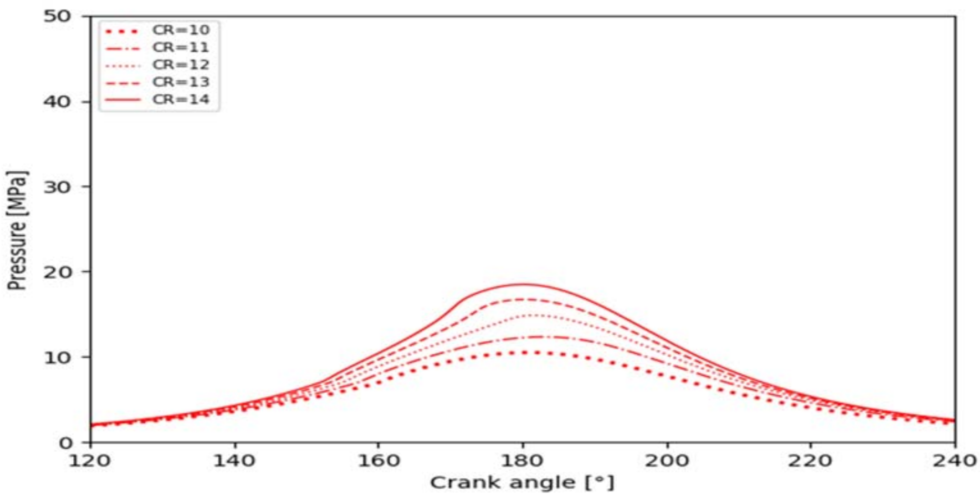

Figure 4. 15 Ignition curve of dodecane through the HCCI engine

Source: Authors, 2019.

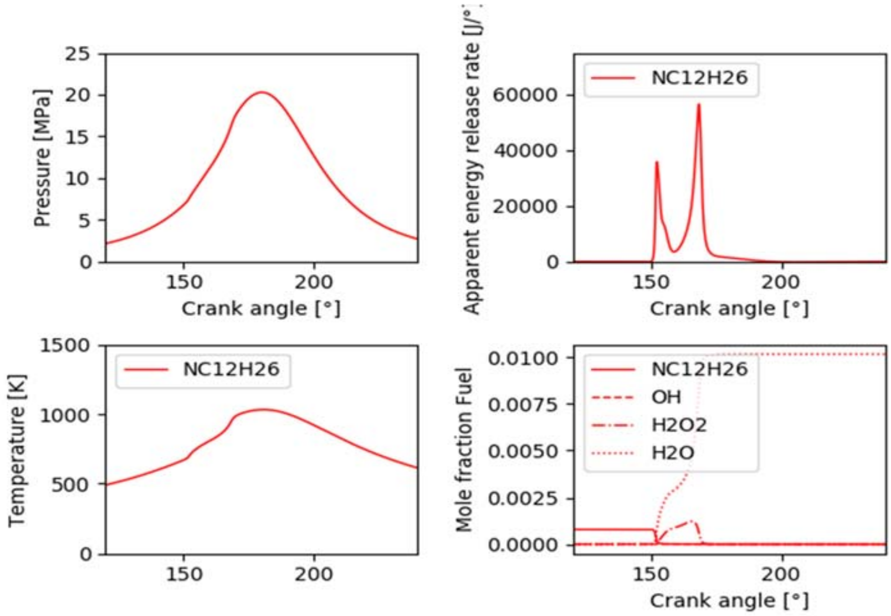

Figure 4. 16 Dodecane combustion reaction though the HCCI engine at CR 15.

Source: Authors, 2019.

Figures 4.15 & 4.16 show the highest compression ratio of the 15 used in these simulations reaching a pressure of 18.45MPa, which is lower than 20MPa at a crank angle of 180°. The compression ratio was lower in these simulations, which was more suitable for the early ignition of dodecane in the HCCI engine mode.

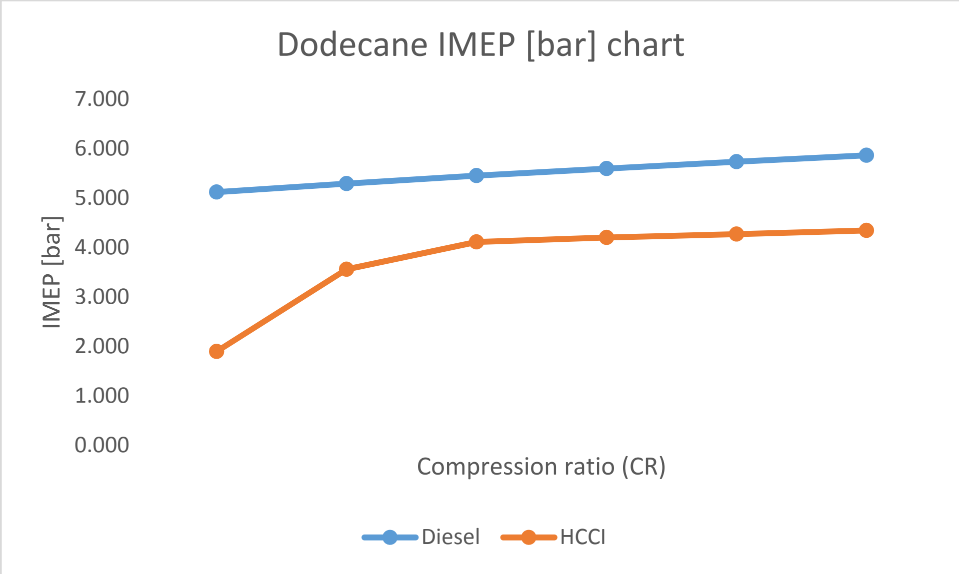

Figure 4. 17 Dodecane IMEP generate per compression ratio (HCCI 10-15; diesel 20-25)

Source: Authors, 2019.

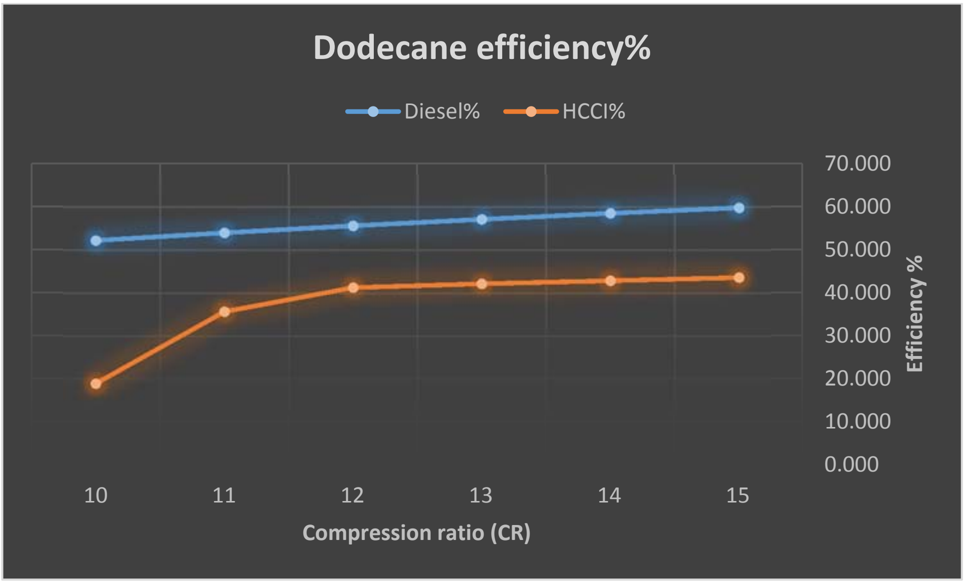

Figure 4. 18 Dodecane diesel efficiency (CR20-25) & HCCI efficiency (CR10-15)

Source: Authors, 2019.

The diesel fuel is of a very high cetane number making it easy for self-ignition. As seen in figure 4.15, an early ignition was simulated due to the high cetane number of dodecane. Since the diesel engine used a higher compression ratio efficiency of the HCCI engine, it was lower than for the diesel engine as presented in figure 4.18.

4.5 UCL engine experimental test results

4.5.1 Engine experimental test 1 (results)

The first two tests were carried out on a 100% (percent) diesel combustion. The conditions were 4 bar IMEP, injection timing 10 degrees BTDC, 1200 rpm crankshaft speed, 550 bar injection pressure and the ignition delay period was 10.4 degrees. The compression ratio was kept constant, while the volumetric flow rates of the inlet air and fuel were kept at 2.5 L/s and 1.07 L/s.

In HCCI conditions, the above process was repeated for tests 3 onwards, using a 28% m/m ammonia in water blended with 10% m/m diethyl ether (DEE).
During the tests, diesel fuel was first injected directly into the combustion chamber at 10 degrees before TDC as a pilot fuel. The amount of ammonia and DEE mixture was increased incrementally into the engine manifold, creating a homogeneous fuel and air mixture. The amount of ammonia and DEE mixture was increased until the diesel was completely replaced in terms of energy amount, but when the pilot injection was removed, the ammonia and DEE mixture did not ignite on its own. When running on 100% ammonia and DEE mixture with the pilot injection still on, it was observed that the inlet air temperature and the cylinder pressure dropped rapidly due to the cooling of the engine. This rapid cooling effect of the engine was attributed to the ammonia hydroxide solution. Then, a heater was used to increase the inlet air temperature to 90 ^{0}C. Yet, still no ignition was observed.

The composition of the % m/m DEE in the mixture was then varied from 2-12 %. From 2-9% m/m DEE, no combustion occurred, whereas at 12% m/m DEE, a delay but very high combustion was suddenly observed. It was later understood that this mixture was not properly mixed and that the ignition was just DEE igniting. The process was repeated for tests 7-9 and the same result was observed. This experiment was not a successful implementation of HCCI combustion, because the aqueous ammonia and DEE blends were not soluble within one another and kept separating out. This resulted in almost pure DEE being injected and igniting on its own. In these tests, it was observed that aqueous ammonia could not be ignited under these engine conditions.

A Motor Exhaust Gas Analyzer and Fast Particles Spectroscope were used to measure the exhaust emission species. The engine exhaust gas was passed through a heater to further increase its temperature. This prevented the exhaust gas from condensing. Then, it was sent to the Motor Exhaust Gas Analyzer, where its concentration was measured based on a calibrated value.

The recordings were made during steady states. Some results from this experiment have been excluded due to some errors in the readings of the exhaust gas pressure and temperature, this as a result of the equipment breakdown. However, only results from tests 7-9 were considered since they provided the most valid data.

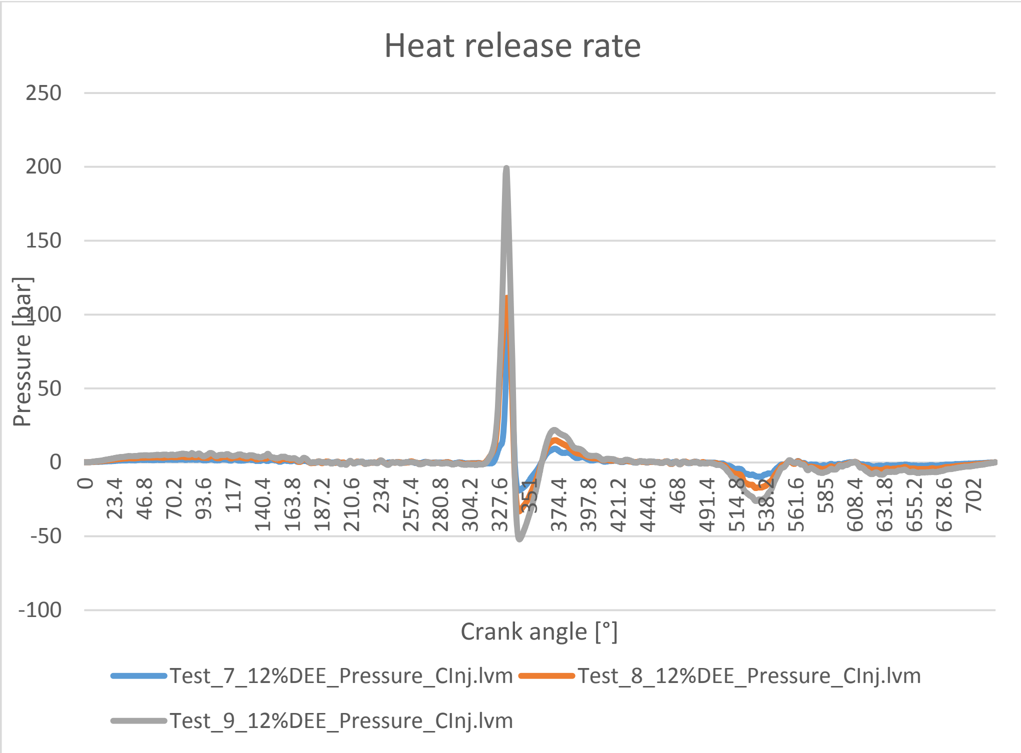

Figure 4. 19 Heat release rate of combustion during test 7, 8 and 9.

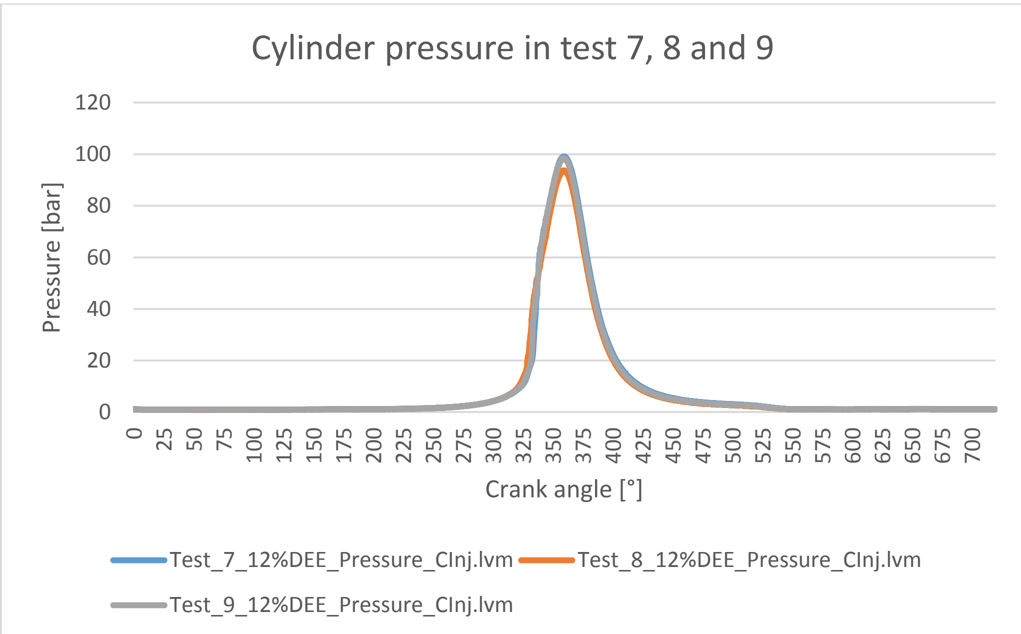

Figure 4. 20: Cylinder pressure in tests 7,8 and 9

As shown in figure 4.19, a high pressure reaching 200 bar was observed during the combustion, releasing a lot of energy. By the same time the cylinder pressure reached a peak of 100 bar as presented in figure 4.20. These two graphs present an early and high ignition during tests 7, 8 and 9 where no diesel was used and only the mixture (DEE/aqueous ammonia) was burning as fuel. The peak combustion is due to the DEE igniting after the aqueous ammonia. Because it was later noticed that there was not a perfect mixture in the fuel tank, and two layers were formed, these results probably represent only the DEE combustion, without ammonium hydroxide. It is known that DEE is very flammable and has a high cetane number.

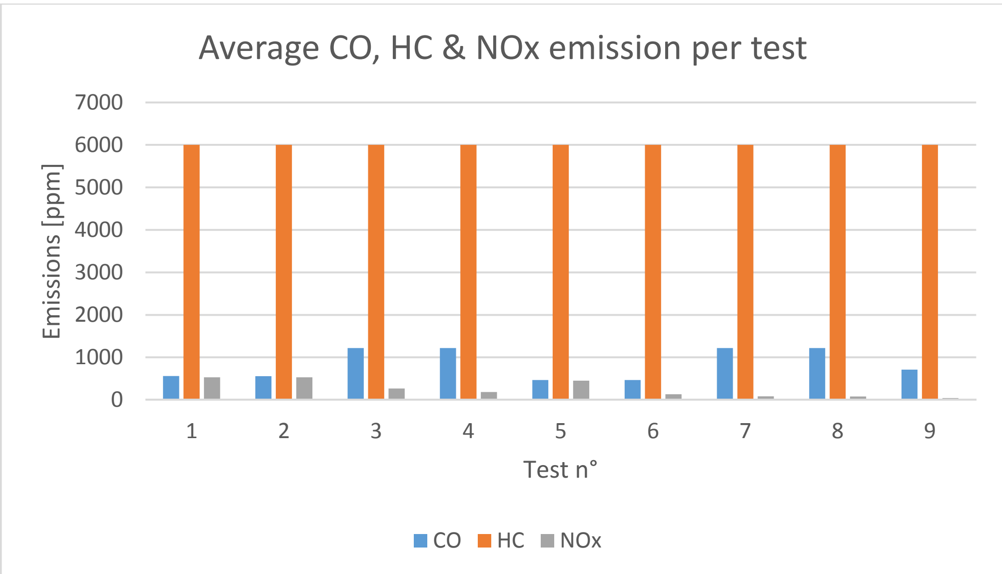

Figure 4. 21: Average CO, HC & NOx per test in ppm

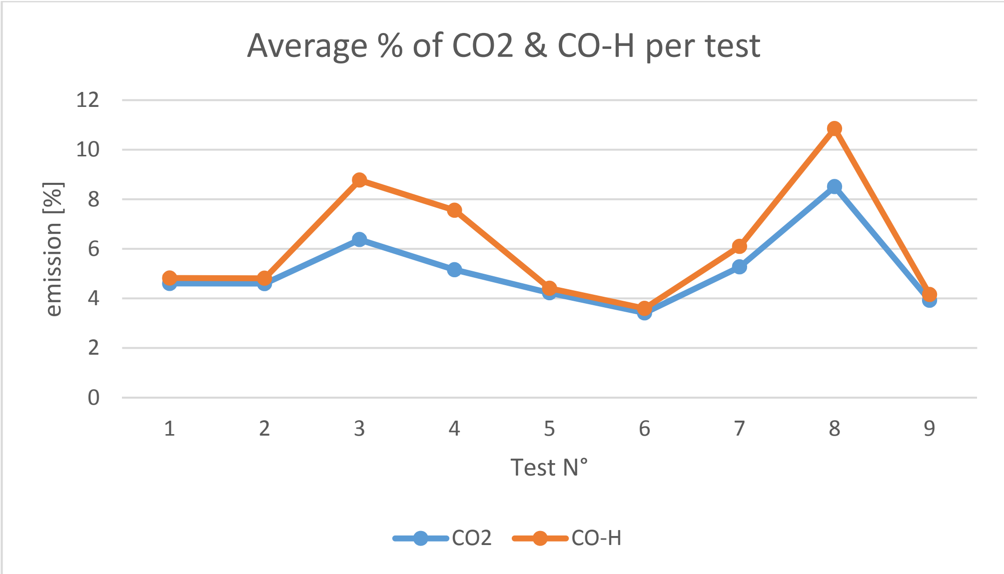

Figure 4. 22: Average % of CO2 & CO-H per test

However, the test allowed us to get some information about the exhaust composition and an average emission of CO_2, CO-H, CO, HC and NO_X as we can see in figures 4.21 & 4.22. The Hydrocarbon (HC) has an average of 6000 ppm during all 9 tests performed, while the Carbon monoxide (CO) reached the peak during test 7 with 1220.6ppm. On the other hand, the highest NO_x emissions are noticed in tests 1 and 2 with an average of 532ppm. Additionally, the highest concentrations in CO_2 and CO-H are noticed in test 8 with respectively 8.5% and 2.34%..

4.5.2 Engine experimental test 2 (results)

In this test, an ignition of aqueous ammonia mixture with diesel pilot injection was investigated. The same conditions in the Engine experimental test 1 were repeated. While the timing of the diesel injection was kept constant, the ammonia hydroxide injection timing and the IMEP varied. (see Table 3.3).

Table 3. 3: Table of parameters

Test Number	IMEP bar	Diesel Injection Duration ms/s	SOC	Ammonia Injection
1	4	648	360,6	0
2	4	648	360,6	0
3	4,5	648	361	1,07
4	4,5	648	361	1,07
5	5	648	362,2	2,6
6	5	648	362,8	2,1
7	5	648	363	2,1
8	5,2	648	363	3,19
9	5,2	648	363	3,19
10	5	640	362,8	3,2
11	5	640	363	3,2
12	4	589	362,2	2,6
13	4	587	362,4	2,6
14	4	596	362,2	2,6
15	5	646	362,2	3
16	5	726	361,6	0
17	5	646	361,8	2
18	5	634		2,2
19	5	629		2,4
20	5	620	362,2	2,6
21	5	616	362,4	2,8
22	5	614	362,6	3

Figure 4.23, 4.24 and 4.25 represent the cylinder pressure and temperature per test. The most focused points are tests 8,9,10,22 where the aqueous ammonia was injected at 3bar. Additional heat and pressure can be noticed in these chosen tests. However, the peak pressure was achieved in test 16, where no aqueous ammonia was injected. Also, for test 16, it was observed that, the more aqueous ammonia injection was increased, the more the ignition delay increased. With respect to exhaust emissions,

whereas the more the average CO_2 emissions were reduced

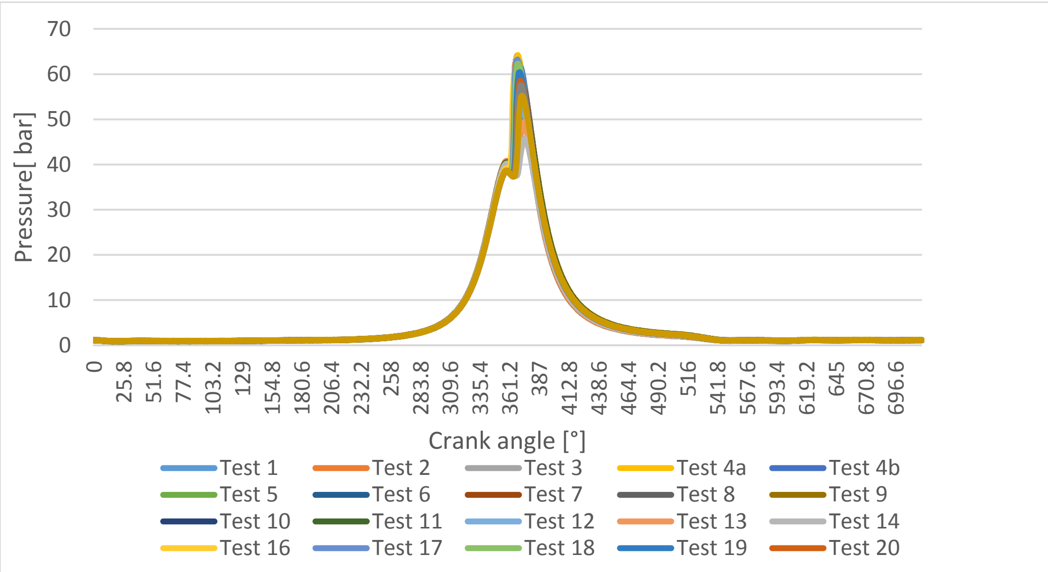

Figure 4. 23: Cylinder pressure [bar] per crank angle per test

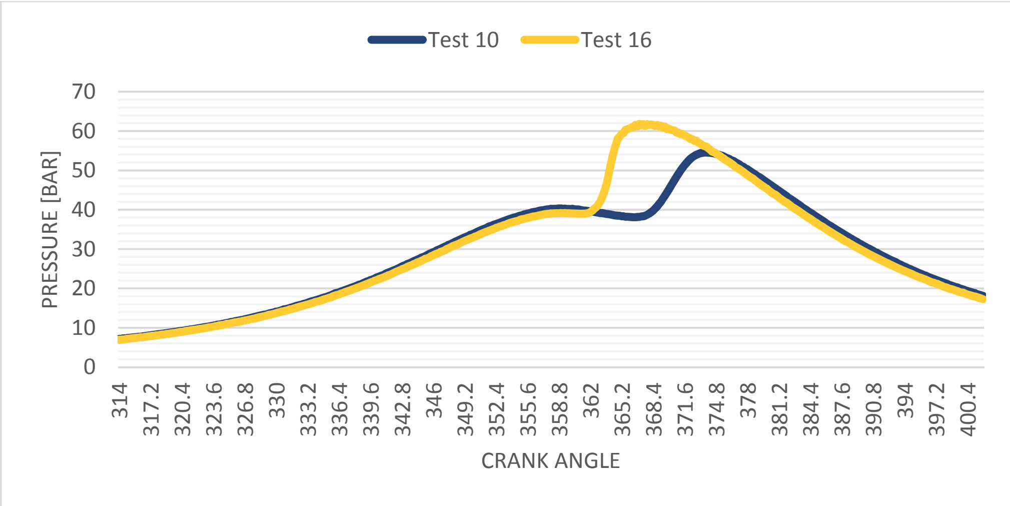

Figure 4. 24: Cylinder pressure [bar] per crank angle (test 10 &16)

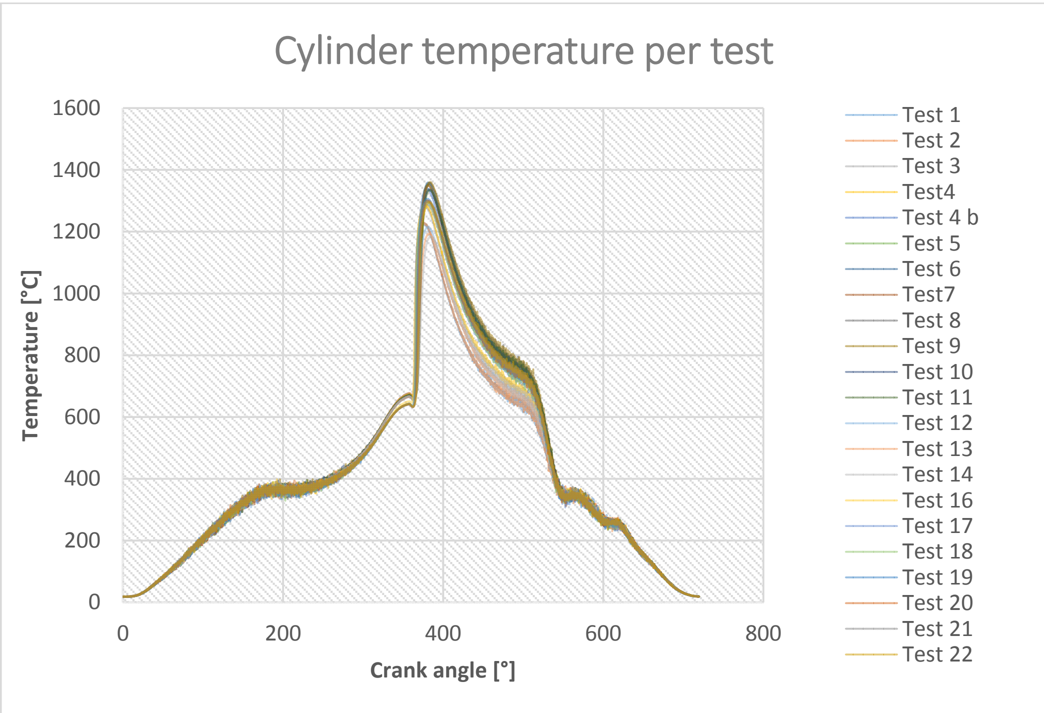

Figure 4. 25: cylinder temperature [°C] per test

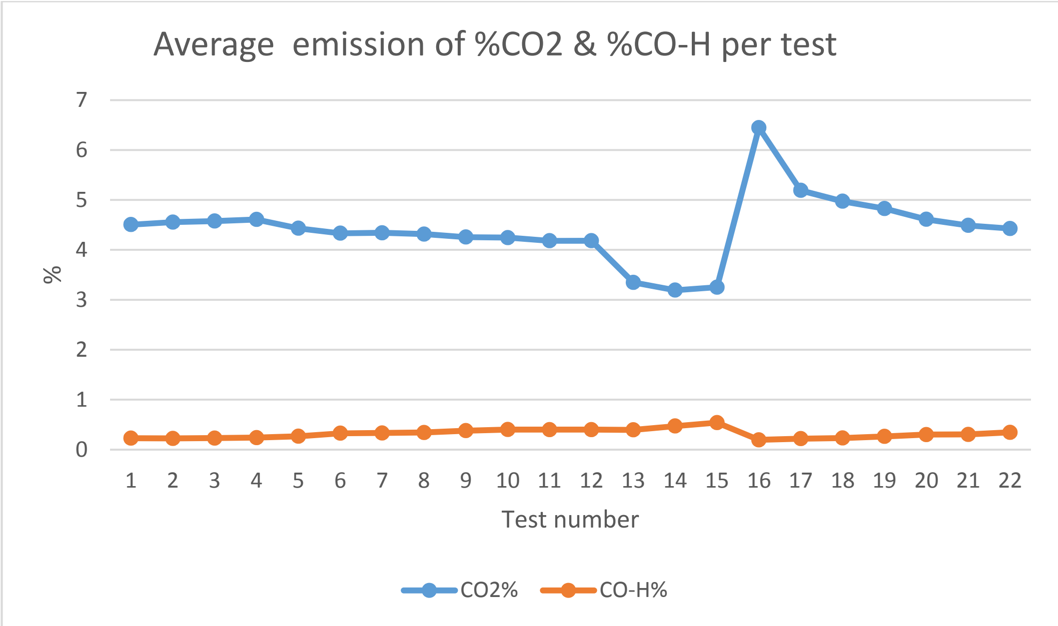

Figure 4.26: Average emission in percentage of CO_2 & CO-H per test

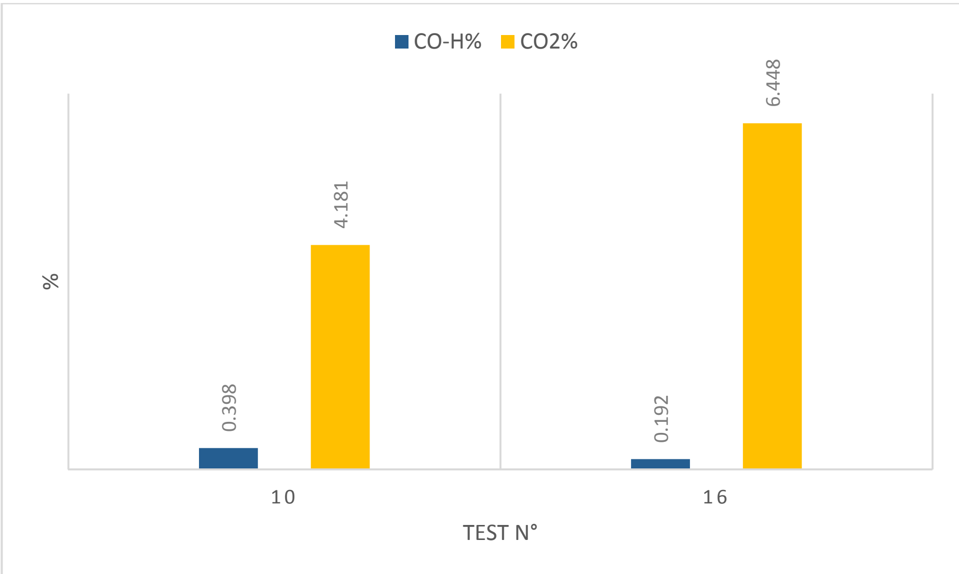

Figure 4.27: Average emission in percentage of CO_2 & CO-H for the most representative tests (test10 & 16).

During the tests, it was observed that the CO_2 emission dropped at an average of 4,5%, when the aqueous ammonia was injected, as compared to test16 which reached 6.44%. (see figure 4.26). This observation is more visible in Figure 4.27, where the comparison between ammonia mixture combustion (test10) and diesel combustion was great (test 16). In addition to CO_2 and CO, some other emission species, such as HC, measured at 6000ppm for all tests, and CO-H, which varied depending on the amount of aqueous ammonia injected. In the dual fuel mode, the emissions of CO and HC were very high, as compared to using diesel only as fuel. Hence, this sudden rise in CO and HC emissions was attributed to the increased ammonia injection.

In Figure 4.28, it can be seen that the average CO emissions increased with an increased aqueous ammonia injection. The increase in CO was mostly due to the water content in the aqueous ammonia, which was cooling down the combustion process, thus leading to an incomplete combustion. As the aqueous ammonia injection was varied, so the change in the average value of CO was emitted. As illustrated below, this change is more visible between tests 2 and 7, and tests 15 to 22. In addition, it was observed that CO emissions were lowered during test 16, upon switching to diesel as the only fuel.

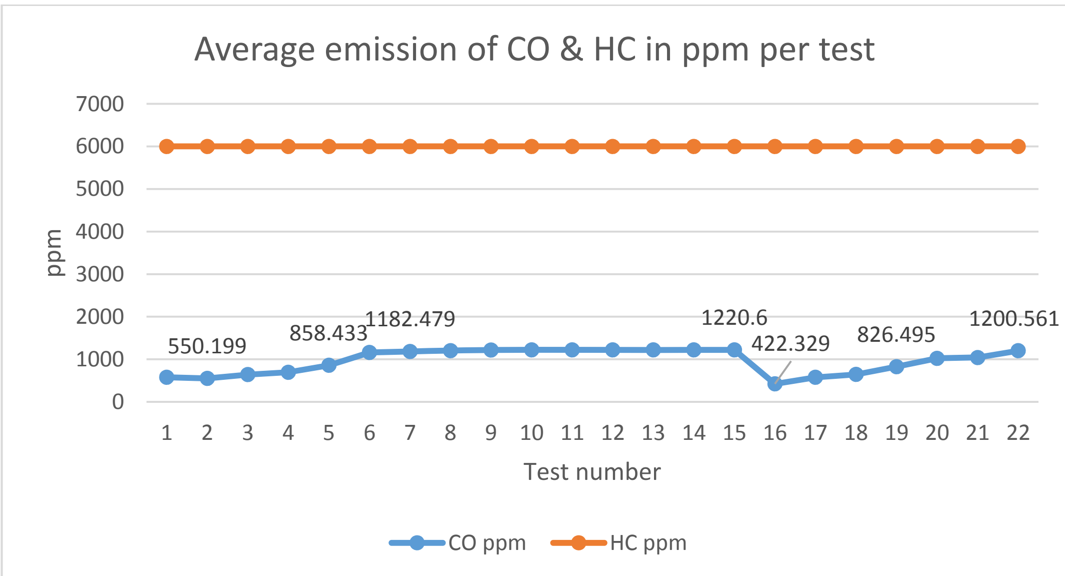

Figure 4. 28: Average emission of CO & HC in ppm per test

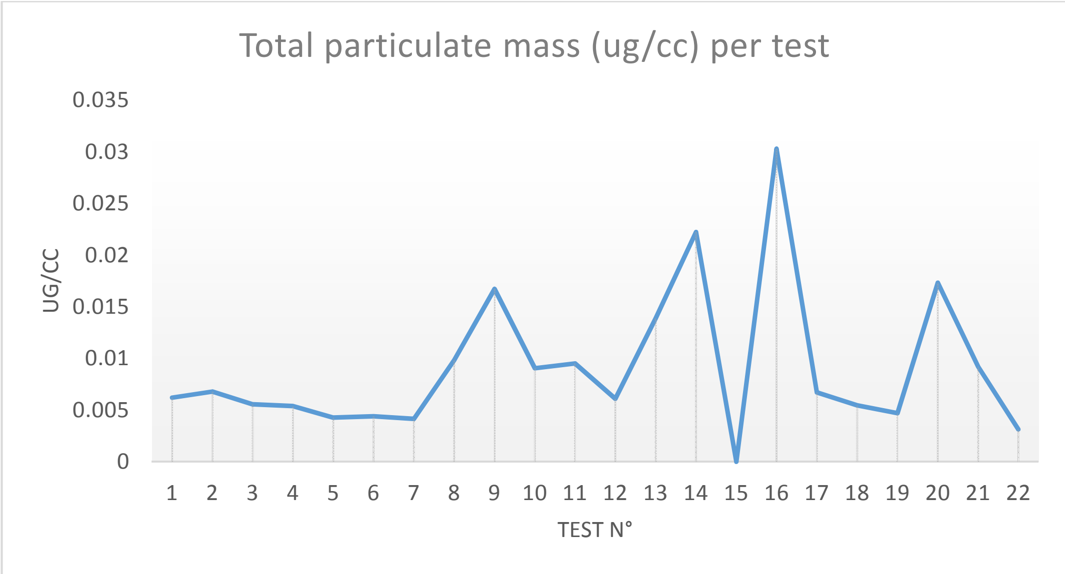

Figure 4.29Figure 4.27: Total particulate mass (µg/cc) per test

Furthermore, the Particulate Matters recorded during the tests followed an evolution based on the types of fuel injected, but also the IMEP and the ammonia pressure. Figure 4.29 shows the highest PM produced which is around 0.03µg/cc in test 16. Similarly, the tests 7, 9 and 20 gave a high PM emission.

In summary, the aqueous ammonia was combusting, but it was delaying ignition and decreasing combustion efficiency, as could be seen by the increase in carbon monoxide (CO) emissions. The water contained in the solution, cooled down the combustion and reduced the efficiency.

5 Conclusion and Recommendations

5.1 Conclusion

Today, the world is becoming more globalized and industrialized through shipping. However, for the past decades, the overdependence of the shipping industry on fossil fuel has caused the environment to suffer and threaten the health and existence of humans especially those living close to the coast. Even so, if shipping is to thrive amidst unstable energy resources and regulatory constraints it has to become sustainable in the future. In addition to energy efficiency measures, reducing the carbon footprint of fossil fuel and employing current best low or carbon neutral fuels such as alternative fuels, greenhouse emissions and air pollutants from shipping could be offset incrementally. Hence, ammonia has been proposed as a carbon neutral fuel and potential energy carrier for renewable energy.

The aim of this study was to establish whether it is feasible to use ammonia in marine diesel engines to reduce air pollutants and decarbonize shipping. Findings from previous publications indicate that some ammonia production methods are already matured, though some of the novel technologies are still developing. Ammonia is highly flexible with high volumetric density. It is relatively cheap and safe to transport. It is easy to be liquefied and has a widely available production and distribution network. Results from a number of publications indicate that ammonia can be produced from both hydrocarbon based fuels and renewable energy resources using conventional and novel technologies. The Haber Bosch process remains the most dominant pathway for ammonia synthesis, albeit it is energy intensive with the highest carbon footprint, when the energy required for the process is utilized from conventional fuels. Other studies have revealed that the energy utilized by the process can be sourced from renewable energy resources. Hence, wind, solar and hydropower based ammonia productions were found to have the lowest carbon footprint, thus making them the most environmentally friendly.

Ammonia is a nexus of food production and energy generation because it is currently used as fertilizers and, concomitantly used on land transport, either as direct fuel or precursor for hydrogen fuel that could be used in fuel cells. Even though ammonia is widely used in agriculture, and the land transport sector, there are very few publications available in the literature about its use as fuel. Still and all, a number of studies have reported that ammonia is a promising fuel with respect to reducing GHG emissions and air pollutants. Ammonia has been analysed using various routes to assess its performance indicators such as efficiency, exergy, global warming potentials, human toxicity, adiabatic depletion, among others. Yet, there is not a single well-researched assessment covering the full life cycle of ammonia, especially as a marine fuel available in the open literatures. Despite this, it has a growing interest from the shipping community to assess ammonia, albeit findings from said projects will be available in the coming years.

Furthermore, findings from the study reveals the inclusive results of the simulation of ammonia, hydrogen, and marine diesel fuel in a model diesel engine, based on the working principles of two-stroke compression ignition and homogeneous charge compression ignition engines. Results from the simulations indicate that when using ammonia as a direct fuel in diesel engine, a late ignition is observed at high temperatures and the highest compression ratio of 25 was necessary to ignite ammonia in a diesel engine. This means that ammonia has a high ignition temperature, and a low ignition quality. This could potentially be overcome by using an ignition promoter such as hydrogen, which simulations show to ignite at lower compression ratios in the range of 20-23. In homogenous mode, a premixed ammonia-air mixture was simulated to be ignited at the highest compression ratios of 24 and 25. Compared to the diesel mode, the output energy was high, indicating a higher indicative mean pressure. In both cases, there was zero CO_2 or air pollutants emitted. Hence, this proves ammonia produced from renewable sources could be a potential marine fuel for the future.

5.2 Recommendations

This research examines the possibility to employ ammonia as marine fuel to decarbonize shipping and reduce local pollutants. Having reviewed a number of publications on the life cycle assessment of ammonia, the following recommendations for the use of ammonia as marine fuel are given:

i. There is a need to conduct extensive research on the life cycle assessment of ammonia as shipping fuel. This will help establish reliable values for different performance indicators including efficiency, global warming potential, among others. Moreover, enhancing the ignition rating of ammonia should be one of the key focuses especially for institutions involved in energy research and engine designs.
ii. The IMO should encourage member states to embark on research that assesses the feasibility of using ammonia as marine fuel. Such research should cut across various dimensions including the ammonia generation on board, or using renewable energy resources such as wind and solar, and tidal power. Moreover, this research should include space availability in the case of solar and wind power, whereas safety of the vessel and crew occupational health and safety should be well established.
iii. The Maritime Safety Committee (MSC) of the IMO should closely assess the negative effects of handling, storage and use of ammonia fuel on board the ship as a fuel. This should include its impacts on equipment and the ecosystem health. Based on the findings, it would be prudent to establish guidelines with respect to its employment as marine fuel.
iv. The Marine Environment Protection Committee (MEPC) of the IMO should also assess benefits and the environmental benignity of ammonia, weighing it against fossil alternatives to make it more viable in the shipping context.
v. There is a need to develop more data for software packages used in the life cycle assessment of ammonia, especially in the maritime industry. Such

software should cover the entire life cycle of ammonia, from feedstock, production, transportation, use on board, and disposal. In addition, the software should include the crews' occupational health and safety.

vi. To ensure the availability of ammonia fuel supply in port for safe bunkering purposes, it would be prudent to do extensive research in that respect.

List of References

ABS. (2019, 05 17). *Air Pollution and Energy Efficiency: Draft Ammendment to MARPOL Annex VI*. Retrieved from ABS: https://ww2.eagle.org/content/dam/eagle/regulatory-news/2019/MEPC-74-Brief-r4.pdf

AirClim. (2011). *Air pollution from ships.* Laho: Miljöinformation Åström & Nilsson AB. Retrieved from https://www.cleanshipping.org/download/111128_Air%20pollution%20from%20ships_New_Nov-11(3).pdf

Alyson Azzara; Dan Rutherford; Haifeng Wang. (2014). *Feasibility of IMO Annex VI Tier III Implementation using Selective Catalytic Reduction.* Washington, DC: ICCT.

Atkinson, G., Nguyen, H., & Binns, J. (2018). Considerations regarding the use of rigid sails. *MECHANICAL ENGINEERING | REVIEW ARTICLE, 5*(1543564), 1543564. doi:https://doi.org/10.1080/23311916.2018.1543564

AValera-Medina, Xiao, H., Owen-Jones, M., W.I.F.David, & P.J.Bowen. (2018). Ammonia for power. *Progress in Energy and Combustion Science, 69*, 63-102. doi:https://doi.org/10.1016/j.pecs.2018.07.001

Bengtsson, S., Andersson, K., & Fridell, E. (2011). A comparative life cycle assessment of marine fuels: liquefied natural gas and three other fossil fuels. *Engineering for the Maritime Environment, 225*(2). doi:https://doi.org/10.1177/1475090211402136

Bicer, Y. (2017, 04). *Investigation of novel ammonia production options using photoelectrochemical hydrogen production.* doi:http//:www.doi. 10.13140/RG.2.2.12618.26569

Bicer, Y., & Dincer, I. (2018, 01 11). Clean fuel options with hydrogen for sea transportation: A life cycle approach. *International Journal of Hydrogen Energy, 43*(2), 1179-1193. doi:https://doi.org/10.1016/j.ijhydene.2017.10.157

Bicer, Y., Dincer, I., Zamfirescu, C., Vezina, G., & Razo, F. (2016). Comparative life cycle assessment of various ammonia production methods. *Journal of Cleaner Production*, 1379-1395.

Bodansky, D. (2018). Regulating greenhouse gas emissions from ships: The role of the International Maritime Organization. In Ocean Law Debates (pp. 478-501). In D. Bodansky, *Ocean Law Debates* (pp. 478-501). Brill Nijhoff. doi:https://doi.org/10.1163/9789004343146_019

Bouman, E. A., Lindstad, E., Rialland, A. I., & H.Strømman, A. (2017, 05). State-of-the-art technologies, measures, and potential for reducing GHG emissions from shipping – A review. *Transportation Research Part D: Transport and Environment, 52*(Part A), 408-421. Retrieved 04 04, 2017, from https://doi.org/10.1016/j.trd.2017.03.022

Brain, M. (2000, April 1). *How diesel engines work*. Retrieved August 8, 2019, from Howstuffwork: https://auto.howstuffworks.com/diesel.htm

Brown, T. (2015, 06 29). *Ammonia is a genuine contender, perhaps the contender, for carbon-free energy*. Retrieved from NH3 Fuel Association: https://nh3fuelassociation.org/2015/06/29/ammonia-is-a-genuine-contender-perhaps-the-contender-for-carbon-free-energy/

Brynolf, S., Taljegard, M., Grahn, M., & Hansson, J. (2018). Electrofuels for the transport sector: A review of production costs. *Renewable and Sustainable Energy Reviews, 81*(2), 1887-1905. doi:https://doi.org/10.1016/j.rser.2017.05.288

Burnett, R., Chen, H., Szyszkowicz, M., Fann, N., Hubbell, B., III, C. A., . . . Katherine. (2018, 09 18). *Global estimates of mortality associated with long-term exposure to outdoor fine particulate matter*. Retrieved from Proceedings of the National Academy of Sciences of the United States of America: https://doi.org/10.1073/pnas.1803222115

Caron, D. D. (2013). Climate Change and the Oceans. In D. D. Caron, *Regions, Institutions, and the Law of the Sea* (pp. 516-). Brill ; Nijhoff. doi:https://doi.org/10.1163/9789004220218_029

CE Delft. (2017). *Update of maritime greenhouse gas emissions projections.* London: IMO.

CE Delft. (2019, 08 23). *Third IMO GHG Study 2014: Final Report*. Retrieved from CE Delft: https://www.cedelft.eu/publicatie/third_imo_ghg_study_2014/1525

Chatzinikolaou, S. D., & Ventikos, N. P. (2015). Holistic framework for studying ship air emissions in a life cycle perspective. *Ocean Engineering, 110*(Part B), 113-122. doi:https://doi.org/10.1016/j.oceaneng.2015.05.042

Chena, H.-I., Cheng-YuHsiao, Wei-Cheng, Chang, C. C.-H., Chou, T.-C., Liu, I.-P., . . . Liu, W.-C. (2018). Characteristics of a Pt/NiO thin film-based ammonia gas sensor. *Sensors and Actuators B: Chemical, 256*, 962-967. doi:https://doi.org/10.1016/j.snb.2017.10.032

Cheng, C. K., Vo, D. V., & Ideris, A. (2018). Preface to the special issue 4th ICCEIB 2018. *Special Issue on Toward a Sustainable Hydrogen Production and Utilization* (p. 20633). Kuala Lumpur: International Journal of Hydrogen Energy. doi:https://doi.org/10.1016/j.ijhydene.2019.06.110

Christopher, K., & Dimitrios, R. (2012). A review on exergy comparison of hydrogen production methods from renewable energy sources. *Energy & Environmental Science*(5), 6640-6651. doi:https://doi.org/10.1039/C2EE01098D

Clean Shipping Coalition. (2015, 09 30). *The global environmental coalition exclusively dedicated to shippin.* Retrieved from Clean Shipping Coalition: http://www.cleanshipping.org/tag/imo/

Conor Walsh, N.-J. L. (2019). Trade and trade-offs: Shipping in changing climates. *Marine Policy*, 103537.

Corbett, J. J., & Winebrake, J. J. (2012). Emissions Tradeoffs among Alternative Marine Fuels: Total Fuel Cycle Analysis of Residual Oil,and Marine Diesel

Oil. *Journal of the Air & Waste Management Association, 58*(4), 538-542. doi: https://doi.org/10.3155/1047-3289.58.4.538

Curran, M. A. (2015). *Life Cycle Assessment Dtudent Handbook.* Salem, Massachusetts, USA: John Wiley & Sons, Inc. Hoboken and Scrivener Publishing LLC.

Curran, M. A. (2015). *Life Cycle Assessment Student Handbook.* Massachusetts: Scrivener Publishing.

Enerdata. (2019). *GLOBAL ENERGY SCENARIOS THROUGH 2040.* Grenoble: Enerdata. Retrieved from https://eneroutlook.enerdata.net/highlights-energy-forecasting-2040-enerfuture.pdf

EU. (2019). *Directive (EU) 2016/802 of the European Parliament and of the Council of 11 May 2016 relating to a reduction in the sulphur content of certain liquid fuels*. Retrieved from EUR-Lex: http://data.europa.eu/eli/dir/2016/802/oj

EUR-Lex. (2002). *Strategy to reduce atmospheric emissions from seagoing ships.* EUR-Lex. Retrieved from https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=LEGISSUM:l28131

European Environment Agency. (2018, 09 05). *Greenhouse gas emissions from transport*. Retrieved from European Environment Agency: https://www.eea.europa.eu/data-and-maps/indicators/transport-emissions-of-greenhouse-gases/transport-emissions-of-greenhouse-gases-11

Eyring, V., Ko¨hler, H. W., Lauer, A., & Lemper, B. (2005). Emissions from international shipping: Impact of future technologies on scenarios until 2050. *JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 110*. doi:http//www.doi:10.1029/2004JD005620

Eyring, Veronika; Corbett, James J.; Lee, David S. ; Winebrake, James J. (2007). *Brief Summary of the imppact of ship emissions on atmospheric composition, climate and human health.* London: International Maritime Organization.

Fertilizers Europe. (2018). *FEEDING LIFE 2030 THE EUROPEAN FERTILIZER INDUSTRY AT THE CROSSROADS BETWEEN NUTRITION AND ENERGY.* Brussels: Fertilizers Europe. Retrieved from https://www.fertilizerseurope.com/fileadmin/user_upload/Staff_2018/Staff_2018_cropped/Fertilizers_Europe_Feeding_Life_2030_The_European_Fertilizer_Industry_at_the_crossroads_between_Nutrition_and_Energy.pdf

Fridell, E. (2019). Emissions and Fuel Use in the Shipping Sector. *Green Ports*, 19-33. Retrieved 09 28, 2018, from https://doi.org/10.1016/B978-0-12-814054-3.00002-5

Giddey, S., Badwal, S., & A.Kulkarni. (2013). Review of electrochemical ammonia production technologies and materials. *International Journal of Hydrogen Energy, 38*(34), 14576-14594. doi:https://doi.org/10.1016/j.ijhydene.2013.09.054

Gilbert, P., & Bows, A. (2012). Exploring the scope for complementary sub-global policy to mitigate CO2 from shipping. *Energy Policy, 50*, 613-622. doi:https://doi.org/10.1016/j.enpol.2012.08.002

Gilbert, P., Walsh, C., Traut, M., Kesieme, U., Pazouki, K., & AlanMurphy. (2018, 01 20). Assessment of full-life cycle air emissions of alternative shipping fuels. *Journal of Cleaner Production, 172*, 855-866. doi:https://doi.org/10.1016/j.jclepro.2017.10.165

Goldsworthy, L. (2010). EXHAUST EMISSIONS FROM SHIP ENGINES - SIGNIFICANCE, REGULATIONS, CONTROL TECHNOLOGIES. *Australian and New Zealand Maritime Law Journal, 24*(1), 21-30.

Goldsworthy, L. (2010). Exhaust emissions from ship engines-significance, regulations, control technologies. *Law Journal* , Mar. LJ, 24, 21.

Gong, W., & Will, M. L. (2010). *USA Patent No. US 2010/0019506 A1.*

Guo, C., Ran, J., Vasileffa, A., & Qiao, S.-Z. (2018). Rational design of electrocatalysts and photo(electro)catalysts for nitrogen reduction to ammonia (NH3) under ambient conditions. *Energy and Environmental Science*, 45-56.

Guo, M., Fu, Z., Ma, D., Ji, N., Song, C., & Liua, Q. B. (2015). Ashort review of treatment methods of marine diesel engine exhaust gases. In M. Guo, Z. Fu, D. Ma, N. Ji, C. Song, & Q. B. Liua, *Procedia engineering* (pp. 938-943). Weijin: Elsevier.

Hanssona, J., Månsson, S., Brynolf, S., & Grahn, M. (2019). Alternative marine fuels: Prospects based on multi-criteria decision analysis. *Biomass and Bioenergy*, 159-173.

Harz, D. C. (2014). Green Ammonia to Fuel International Security. *11th Annual NH3 Fuel Conference.* Florida: NH3 Fuel Association. Retrieved from https://nh3fuelassociation.org/2014/09/07/green-ammonia-to-fuel-international-security/

Herdzik, J. (2011). EMISSIONS FROM MARINE ENGINES VERSUS IMO CERTIFICATION. *Journal of KONES Powertrain and Transport, 18*(2), 162-167. Retrieved from http//:www_bg_utp_edu_plartjok22011jok22011161.pdf

Heywood, B. J. (1988; 2008). *Internal combustion engine fundamentals.* New York: Mc Graw-hill, Inc.

Heywood, B. J. (1988; 2008). *Internal combustion engine fundamentals.* New York: Mc Graw-hill, Inc.

Hofstrand, D. (2009, May). *Ammonia as a Transportation Fuel*. Retrieved from Agricultural Marketing Resource Center: https://www.agmrc.org/renewable-energy/renewable-energy/ammonia-as-a-transportation-fuel

Holladay, J., Hu, J., King, D., & Wang, Y. (2009). An overview of hydrogen production technologies. *Catalysis Today*, 244-260.

ICCT. (2015). *Black carbon emissions and the fuel use in global shipping.* Washington DC: International Council on Clean Transportation.

Icct. (2017). *Greenhouse Gas Emissions from International Shipping, 2013-2015.* Washington: Icct.
ICCT. (2019). *A global snapshot of the air pollution-related health impacts of transportation sector emissions in 2010 and 2015.* Washington, San Francisco, Berlin, Beijing: Susan Anenberg; Joshua Miller, Daven Henze, Ray Minjares.
ICS. (2019, 07 09). *International Chamber of Shipping*. Retrieved from Shipping and World Trade: http://www.ics-shipping.org/shipping-facts/shipping-and-world-trade
IEA . (2013). *Alternative Fuels for Marine Applications.* Paris: International Energy Agency.
IEA. (2018). *CO2 EMissions from Fuel Combustion 2018: Overview.* Paris: International Energy Agency.
IEA. (2019). *Inernational Shipping: Tracking Clean Energy Progress*. Retrieved from International Energy Agency: https://www.iea.org/tcep/transport/shipping/
IEA. (2019). *The Future of Hydrogen.* Paris: International Energy Agency. Retrieved from https://webstore.iea.org/download/summary/2803?fileName=English-Future-Hydrogen-ES.pdf
IMO . (2014). *Third IMO GHG Study-Final Report.* International Maritime Organization , Marine Environment Protection Committee. London: International Maritime Organization.
IMO. (2011). *REDUCTION OF GHG EMISSIONS FROM SHIPS* . MEPC 62/INF.7. London: International maritime Organization.
IMO. (2015, 11 25). *Resolution A.1097(29): STRATEGIC PLAN FOR THE ORGANIZATION.* London: IMO. Retrieved from International Maritime Organization (For the Next Six-Year Perior 2016-2021): https://docs.imo.org/Search.aspx?mode=advanced&datetype=last&documentlang=en&cid=1&keywords=globalization
IMO. (2015). *Third IMO GHG Study* . London: International Maritime Organization.
IMO. (2016). *MEPC 70.* London: International Maritime Organization.
IMO. (2018). *MEPC 72.* London: International Maritime Organization.
IMO. (2018). *MEPC 73.* London: International Maritime Organization .
IMO. (2019). *Nitrogen Oxides (NOx) – Regulation 13*. Retrieved from IMO: http://www.imo.org/en/OurWork/Environment/PollutionPrevention/AirPollution/Pages/Nitrogen-oxides-(NOx)-%E2%80%93-Regulation-13.aspx
IMO. (2019, 08 25). *Prevention of Air Pollution from Ships*. Retrieved from International Maritime Organization: http://www.imo.org/en/OurWork/Environment/PollutionPrevention/AirPollution/Pages/Air-Pollution.aspx
IMO. (2019, 08 25). *Sulphur oxides (SOx) and Particulate Matter (PM) – Regulation 14*. Retrieved from IMO:

http://www.imo.org/en/OurWork/Environment/PollutionPrevention/AirPollution/Pages/Sulphur-oxides-(SOx)-%E2%80%93-Regulation-14.aspx
International organization for Standardization. (1997). *Environmental management-Life cycle assessment - Principles and framework.* Genève: ISO.
IPCC. (2014). *Mitigation of Climate Change.* New York: Intergovernmental Panel on Climate Change.
ISPT. (2018). *Power to Ammonia.* Delft: Institute for Sustainable Process Technology. Retrieved from https://www.ispt.eu/media/Final-report-P2A-def.pdf
J.Reiter, A., & Song-CharngKong. (2011). Combustion and emissions characteristics of compression-ignition engine using dual ammonia-diesel fuel. *Fuel*, 87-97.
JerzyKowalski. (2014). An experimental study of emission and combustion characteristics of marine diesel engine with fuel pump malfunctions. *Applied Thermal Engineering*, 469-476.
Jivén, K., Sjöbris, A., Nilsson, M., Ellis, J., Trägardh, P., & Nordström, M. (2004). *LCA SHIP -Design tool for energy efficient ships - A Life Cycle Analysis program for ship.* Lunds Universitet. Gothenburg: Vinnova and Energimyndigheten.
Jääskeläinen, H., & Khair, M. K. (2017, 08). *Combustion in diesel engines.* Retrieved from DieselNet: https://www.dieselnet.com/tech/diesel_combustion.php
Kalgora, B., & Christian, M. (2016). The Financial and Economic Crisis, Its Impacts on the Shipping Industry, Lessons to Learn: The Container-Ships Market Analysis. *Open Journal of Social Sciences, 4*(1), 38-44. doi:http//:www.10.4236/jss.2016.41005.
KlÖpffer, W., & Grahl, B. (2014). *Life Cycle Assessment (LCA).* Frankfurt: WILEY-VCH.
Klöpffer, W., & Grahl, B. (2014). *Life Cycle Assessment (LCA) : AGuide to Best Practice.* Weinheim, Germany: Wiley-VCH Verlzg GmbH & Co. KGaA.
Kobayashi, H., Hayakawa, A., A.Somarathne, K. K., & C.Okafor, E. (2019). Science and technology of ammonia combustion. *Proceedings of the Combustion Institute*, 109-133. doi:https://doi.org/10.1016/j.proci.2018.09.029
Kopela, S. (2017, November 28). Making ships cleaner: Reducing air pollution from international. *Review of European, Comparative & International Environmental Law, 26*(3), pp. 231-242. doi:https://doi.org/10.1111/reel.12220
Kun-Mo Lee; Atsushi Inaba. (2004). *Life Cycle Assessment: Best Practices of ISO 14040 Series.* Seoul : Asia-Pacific Economic Cooperation .
Lehigh University. (2018, 07 09). *Electrochemically-produced ammonia could revolutionize food production.* Retrieved from Phys.org: https://phys.org/news/2018-05-green-approach-ammonia-world.html

Lindgren, F. J., Andersson, Karin, Brynolf, Selma, Wilewska-Bien, & Magda. (2016). *Shipping and environment: improving environmental performance in maritime transportation.* Berlin Heidelberg: Springer.

Löö, J. M., Alfold, B., Gas, L. F., Hjort, J., Lagle, F., Mellqvist, J., . . . Borowiak, A. (2014). Field test of available methods to measure remotely SOx and NOx emissions from ships. *Atmospheric Measurement Techniques*, 2597-2613. doi:http//:www.doi:10.5194/amt-7-2597-2014

Makhlouf, A., Serradj, T., & Cheniti, H. (2015). Life cycle impact assessment of ammonia production in Algeria: A comparison with previous studies. *Environmental Impact Assessment Review*, 35-41. doi:https://doi.org/10.1016/j.eiar.2014.08.003

Martyr, A. J., & Plint, M. A. (2012). The Combustion process and combustion analysis. In A. J. Martyr, & M. A. Plint, *Engine Testing* (pp. 375-406). Elsevier LTd.

Nazemi, M., Panikkanvalappila, S. R., & A.El-Sayed, M. (2018). Enhancing the rate of electrochemical nitrogen reduction reaction for ammonia synthesis under ambient conditions using hollow gold nanocages. *Nano Energy*, 316-323. doi:https://doi.org/10.1016/j.nanoen.2018.04.039

Nicolae, F., Popa, C., & Beizadea, H. (2014, June). Application of life cycle assessment (LCA) in shipping industry. *Air polllution and climate change*, pp. 5-6.

Ölcer, A., & Ballini, F. (2015, June). The development of a decision making framework for evaluating the trade-off solutions of cleaner seaborne transportation. *Transportation Research Part D: Transport and Environment, 37*, 150-170. doi:https://doi.org/10.1016/j.trd.2015.04.023

Olmer, N., Comer, B., Roy, B., Mao, X., & Rutherford, D. (2017). *Greenhouse gas emissions from global shipping, 2013-2015.* Washington, DC: The International Council on Clean Transportation. Retrieved from https://safety4sea.com/wp-content/uploads/2017/10/ICCT-Greenouse-gas-emissions-from-global-shipping-2013-2

Pattabathula, V., & Richardson, J. (2016, 09). *Introduction to Ammonia Production*. Retrieved from AIChE Global Home of Chemical Engineers: https://www.aiche.org/resources/publications/cep/2016/september/introduction-ammonia-production

Ramberg, D., & Vactor, S. V. (2014). Implication of Residual Fuel Oil Phase Out. *In Energy & the Economy.* New York: International Association for Energy Economics.

Rehmatulla, N., Parker, S., Smith, T., & VictoriaStulgis. (2017). Wind technologies: Opportunities and barriers to a low carbon shipping industry. *Marine Policy, 57*, 217-226. doi:https://doi.org/10.1016/j.marpol.2015.12.021

Reiter, A. J., & Kong, S.-C. (2008). Demonstration of Compression-Ignition Engine Combustion Using Ammonia in Reducing Greenhouse Gas Emissions.

American Chemical Society Publications, 22(5), 2963-2971. doi:https://pubs.acs.org/doi/pdf/10.1021/ef800140f?rand=po8383yo

S.Seddiek, I., & M.Elgohary, M. (2014). Eco-friendly selection of ship emissions reduction strategies with emphasis on SOx and NOx emissions. *International Journal of Naval Architecture and Ocean Engineering, 6*(3), 737-748. doi:https://doi.org/10.2478/IJNAOE-2013-0209

Saiyasitpanich, P., Lu, M., Keener, T. C., & Khang, F. L.-J. (2005). The Effect of Diesel Fuel Sulfur Content on Particulate Matter Emissions for a Non road Diesel Generator. *Journal of the Air & Waste Management Association, 55*(7), 993-998. doi:https://doi.org/10.1080/10473289.2005.10464685

Shipman, M. A., & D.Symes, M. (2017). Recent progress towards the electrosynthesis of ammonia from sustainable resources. *Catalysis Today, 286*, 57-68. doi:https://doi.org/10.1016/j.cattod.2016.05.008

Stone, R. (1999). Thermodynamic principles. In R. Stone, *Introduction to internal combustion engines* (Third edition ed., pp. 32-35). New York: Palgrave.

THE DANISH ECOLOGICAL COUNCIL. (2018). *Cleaner shipping.* Copenhagen: DANISH ECOLOGICAL COUNCIL.

Tzannatos, E. (2010). Ship emissions and their externalities for the port of Piraeus – Greece. *Atmospheric Environment, 44*(3), 400-407. doi:https://doi.org/10.1016/j.atmosenv.2009.10.024

UN. (2012). *The future we want.* New York: United Nationas. Retrieved from https://undocs.org/en/%20A/RES/66/288

UNCC. (2017, 05 18). *Shipping Aviation and Paris*. Retrieved from United Nations Climate Change: https://unfccc.int/news/shipping-aviation-and-paris

UNCTAD. (2016). *Review of Maritime Transport* . New York: United Nations Conference on Trade and Development.

UNCTAD. (2016; 2018). *Review of Maritime Transport.* New York: United Nations Conference on Trade and Development.

United Nations. (1998). *Kyoto Protocol to the United Nations Framework Convention on Climate Change.* Retrieved from Kyoto Protocol-UNFCCC: https://unfccc.int/resource/docs/convkp/kpeng.pdf

University of central Florida. (2018, 05 15). *A green approach to making ammonia could help feed the world*. Retrieved from Phys.org: https://phys.org/news/2018-05-green-approach-ammonia-world.html

Walsh, C., Lazarou, N.-J., Traut, M., Price, J., Raucci, C., Sharmina, M., . . . Smith, T. (2019). Trade and trade-offs: Shipping in changing climates. *Marine Policy, 106*, 103537. doi:https://doi.org/10.1016/j.marpol.2019.103537

Van, T. C., Ramirez, J., Rainey, T., Restovski, Z., & Brown, R. J. (2019, May). Global impacts of recent IMO regulations on marine fuel oil refining processes and ship emissions. *Transportation Research Part D: Transport and Environment, 70*, 123-134. doi:https://doi.org/10.1016/j.trd.2019.04.001

Viana, M., Hammingh, P., Colette, A., Querola, X., Degraeuwe, B., Vlieger, I. d., & Aardenne, J. (2014). Impact of maritime transport emissions on coastal air quality in Europe. *Atmospheric Environment*, 96-105. doi:https://doi.org/10.1016/j.atmosenv.2014.03.046

Winebrake, J. J., Corbett, J. J., & Meyer, P. E. (2012). Energy Use and Emissions from Marine Vessels: A Total Fuel Life Cycle Approach. *Journal of the Air & Waste Management Association, 57*(1), 102-110. doi:https://doi.org/10.1080/10473289.2007.10465301

Winterbone, D. E., & Turan, A. (2015). Reciprocating internal combustion engines. In D. E. Winterbone, & A. Turan, *Advanced thermodynamics for engineers (second edition)* (2nd ed., pp. 345-379). Oxford: Butterworth-Heinemann.

WMO. (2017). *WMO Statement on the State of the Global Climate* . Geneva: World Meteorological Organization.

World Economic Forum. (2019). *The Global Risks Report 2019 14th Edition.* Cologny: World Economic Forum. Retrieved from https://www.weforum.org/reports/the-global-risks-report-2019

World Energy Council. (2018). *World Energy Trilemma Index.* London: World Energy Council. Retrieved from https://www.worldenergy.org/wp-content/uploads/2018/10/World-Energy-Trilemma-Index-2018.pdf

YARA. (2017). *Yala Fertilizer Industry Handbook.* Oslo: YARA. Retrieved from https://www.yara.com/siteassets/investors/057-reports-and-presentations/other/2017/fertilizer-industry-handbook_2017_slides_only.pdf/

Yoo, C. -y., Yoon, H. -c., Yu, J. -h., Joo, H., & Kim, J. -n. (2018). *United States of America Patent No. US 10 , 017 , 866 B2.* Retrieved from https://patentimages.storage.googleapis.com/82/06/e2/fe93b42e9615d0/US10017866.pdf

YubingShi. (2016). Are greenhouse gas emissions from international shipping a type of marine pollution? *Marine Pollution Bulletin*, 187-192. doi:https://doi.org/10.1016/j.marpolbul.2016.09.014

Ölçer, A., Kitada, M., Dalaklis, D., & Ballini, F. (2018). *Trends and Challenges in Maritime Energy Management.* Malmo: World Maritime University.

Appendices

Appendix A: Ammonia diesel engine code.

*AmmoniaMarineDiesel_V3 100%_revised IMEP &EFFI new vers 16-08 Appendix A.py - C:\User...

File Edit Format Run Options Window Help

```
# ***********************************************************************
# *** Ammonia Diesel engine simulation code adopted from Prof. Schönborn (2018)
# ***********************************************************************
def convert_composition_dict_to_string( d ):
    """
    Converts a composition dict of stype composition['CH4'] = 0.02,
    into a string like "CH4: 0.02"
    """
    X = ""
    for item in d:
        X += "%s:%.16f"%(item,d[item])
        X += ", "
    X=X[:-2]
    return X

import cmath

import os

import sys

import numpy as np

import cantera as ct

import matplotlib.pyplot as plt

CRstart=20
CRfinish=26
CRdif= CRfinish-CRstart+1
number=1
Cyclepoints=int(3600)
PComp = np.zeros((CRdif, number+1, Cyclepoints))
TIMEP = np.zeros((CRdif, number+1))
TEFFIC = np.zeros((CRdif, number+1))
CompRat = np.zeros((CRdif, number+1))
Work = np.zeros((CRdif,number+1, Cyclepoints))

for Comp in range (CRstart, CRfinish, 1):
    EnergyFactor=3.816815657*2          #*0+0.8
    Fueltot=0.01*EnergyFactor
```

Appendix B: Ammonia HCCI engine code

AmmoniaMarineHCCI_1_revised 2 (316200m) msj v2.py - C:\Users\V110\Documents\WMU 20...

File Edit Format Run Options Window Help

```
TEFFIC = np.zeros((CRdif, number+1))
CompRat = np.zeros((CRdif, number+1))
molefractionNH3 = 0.018763727
Work = np.zeros((CRdif,number+1, Cyclepoints))#moved
V1 = np.zeros((CRdif,number+1, Cyclepoints)) #moved


for Comp in range (CRstart, CRfinish, 1):
    EnergyFactor=3.816815657*2           #*0+0.8
    Fueltot=0.01*EnergyFactor
    PeroxidFractMax=1

    rpm=100

    # Define engine geometry

    CR=Comp       # Compression ratio

    stroke=2.6
    a=(stroke)/2
    l=2.50
    D=0.5
    Abore = ((D**2)/4)*cmath.pi


    # Define injector parameters:
    T_injector = 300.                                  # K
    p_injector = 1000e5                                # Pa
    injector_opening = int(177*(Cyclepoints/360))                        #
    injector_duration = int(15*(Cyclepoints/360))                         #
    injector_closing = injector_opening + injector_duration  # CA deg
    #injector_mass = 0.1*0                             # kg
    injector_t_open = (60/rpm)*(injector_closing - injector_opening) / 360 *(360

    # End of injector parameters

    # Inlet valve conditions
    # turbocharger temperature, pressure, and composition
    T_inlet = 273.15+40  # K
    p_inlet = 4.3e5  # Pa
    comp_inlet = 'O2:1, N2:3.76'
```

Ln: 77 Col: 0

Appendix C: Hydrogen diesel engine code

Hydrogen MarineDiesel_revised IMEP&EFF v2.py - C:\Users\V110\Documents\WMU 2018\Dis...

File Edit Format Run Options Window Help

```
    # outlet pressure
    T_outlet = 300.  # K
    p_outlet = 4.2e5  # Pa
    comp_outlet = 'O2:1, N2:3.76'

    # Inlet valve friction coefficient, open and close timings
    inlet_valve_coeff = 1.e-3
    inlet_opening = int(0*(Cyclepoints/360))
    inlet_closing = int(30*(Cyclepoints/360))

    # Outlet valve conditions
    p_outlet = 4.2e5  # Pa

    # Outlet valve friction coefficient, open and close timings
    outlet_valve_coeff = 1.e-3
    outlet_opening = int(330*(Cyclepoints/360))
    outlet_closing = int(360*(Cyclepoints/360))

    # End of valve parameters

    tim = []
    p1 = []
    t1 = []
    t2 = []
    v1 = []
    v2 = []
    v = []
    HRR = []
    xFuel = []
    xco = []
    xh2 = []
    xOH = []
    xPEROX = []
    deg = []
    d = []
    IMEP0 = []
    IMEP1 = []
    IMEP2 = []
    IMEP3 = []
    IMEP4 = []
    IMEP5 = []
```

Ln: 76 Col: 21

Appendix D: Hydrogen HCCI enngine code

HydrogenMarineHCCI_1 massfraction IMEP & EFF (240800) v2.py - C:\Users\V110\Document...

File Edit Format Run Options Window Help

```
    IMEP5 = []
    IMEP6 = []
    IncrWork = []
    dQdT = []


    Tim = np.zeros((number+1, Cyclepoints))
    P1 = np.zeros((number+1, Cyclepoints))


    T1 = np.zeros((number+1, Cyclepoints))
    M = np.zeros((number+1, Cyclepoints))
    MF = np.zeros((number+1, Cyclepoints))
    V1 = np.zeros((number+1, Cyclepoints))
    HRRT = np.zeros((number+1, Cyclepoints))
    XFuel = np.zeros((number+1, Cyclepoints))
    Xco = np.zeros((number+1, Cyclepoints))
    Xh2 = np.zeros((number+1, Cyclepoints))
    XOH = np.zeros((number+1, Cyclepoints))
    XPEROX = np.zeros((number+1, Cyclepoints))
    XNC3H7O = np.zeros((number+1, Cyclepoints))
    XH2O2 = np.zeros((number+1, Cyclepoints))
    XH = np.zeros((number+1, Cyclepoints))
    XHO2 = np.zeros((number+1, Cyclepoints))
    XH2O = np.zeros((number+1, Cyclepoints))
    XCH2O = np.zeros((number+1, Cyclepoints))
    XCH3O = np.zeros((number+1, Cyclepoints))
    XCH3 = np.zeros((number+1, Cyclepoints))
    XH2 = np.zeros((number+1, Cyclepoints))
    XCO2 = np.zeros((number+1, Cyclepoints))
    XCH3CHO = np.zeros((number+1, Cyclepoints))
    XCH3OO = np.zeros((number+1, Cyclepoints))
    XCH3COCH3 = np.zeros((number+1, Cyclepoints))
    XC2H4 = np.zeros((number+1, Cyclepoints))
    Deg = np.zeros((number+1, Cyclepoints))
    Injected = np.chararray(number+1)

    for m in range(number+1):

        if m == 0:
            notm = 1
```

Ln: 1 Col: 0

Appendix E: Dodecane diesel engine code

Dodecane diesel engine simulation_revised IMEP & EFF v2.py - C:\Users\V110\Documents\WMU 2018\Dissertation with Sherif...

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```
    if m == 0:
        notm = 1
    else:
        notm = 0

    print(m)
    fmt = '%10.6f  %10.1f  %10.4f  %10.4g  %10.4g  %10.4g  %10.4g  %10.4g  %10.4g'
    print('%10s  %10s  %10s  %14s  %10s  %10s  %10s %10s %10s' % ('time [s]','T1 [K]','P1 [bar]',
                                                   'V1 [m^3]', 'V2 [m^3]', 'Pist. Vel. [m/s]',
                                                   'XNC12H26','XH2O','CA deg'))

    comp_injector = {'NC12H26':1}
    injector_mass = 0.011325798      # Injected mass

    PeroxidFract=(m)*(PeroxidFractMax*Fueltot/1)
    FuelFract=Fueltot-PeroxidFract
    d = {'O2':21, 'N2':79}

    d=convert_composition_dict_to_string(d)
    print(d)
    print(notm)

    gas1 = ct.Solution('POLIMI_TOT_NOX_1407.cti')
    gas1.TPX = T_inlet, p_inlet+0.02e5, d

    gas2 = ct.Solution('gri30.xml')
    gas2.TPX = 900.0, ct.one_atm, 'N2:2, H2O:0.01, O2:5'


    # Reactors
    r1 = ct.IdealGasReactor(gas1)
    r1.volume = Abore*stroke+(1/(CR-1))*Abore*stroke   # Volume of the reactor          # 0.0065
    r2 = ct.IdealGasReactor(gas2)
    r2.volume = 10

    # Define injector state (gaseous!)
    gas1.TPX = T_injector, p_injector, comp_injector
    injector = ct.Reservoir(gas1)

    injector_mfc = ct.MassFlowController(injector, r1)
```

Ln: 1 Col:

Appendix F : Dodecane HCCI engine code

*DodecanMarineHCCI_1 massfraction IMEP & Eff v2.py - C:\Users\V110\Documents\WMU 2018\Dissertation with Sherif\a...

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```python
        # Define valves

        # define inlet state
        gas1.TPX = T_inlet, p_inlet, comp_inlet
        inlet = ct.Reservoir(gas1)

        # define outlet pressure (temperature and composition don't matter)
        gas1.TPX = T_outlet, p_outlet, comp_outlet
        outlet = ct.Reservoir(gas1)

        inlet_valve1 = ct.Valve(inlet, r1)      # allows air to flow into the cylinder
        inlet_valve2 = ct.Valve(r1, inlet)     # allows air to flow out of the cylinder

        outlet_valve1 = ct.Valve(r1, outlet)    # allows air to flow out of the cylinder
        outlet_valve2 = ct.Valve(outlet, r1)    # allows air to flow into the cylinder

        # Define piston (wall)
        w = ct.Wall(r1, r2, K=0.0, velocity=0, Q=0, A=Abore)

        net = ct.ReactorNet([r1, r2])

        step = (60/rpm)*1/360*(360/Cyclepoints)

        for n in range(Cyclepoints):

            if n == 0:
                sigma_old = a*cmath.cos(0)+cmath.sqrt(l**2-(a*(cmath.sin(0)))**2)
                PistonVel_old = 0
                V_old=r1.volume
                P_old=r1.thermo.P

    # Set injection

            if int(n) in range(injector_opening, injector_closing):

                injector_mfc.set_mass_flow_rate(injector_mass / injector_t_open)

            else:

                injector_mfc.set_mass_flow_rate(0)
```

Ln: 238 Col: 16

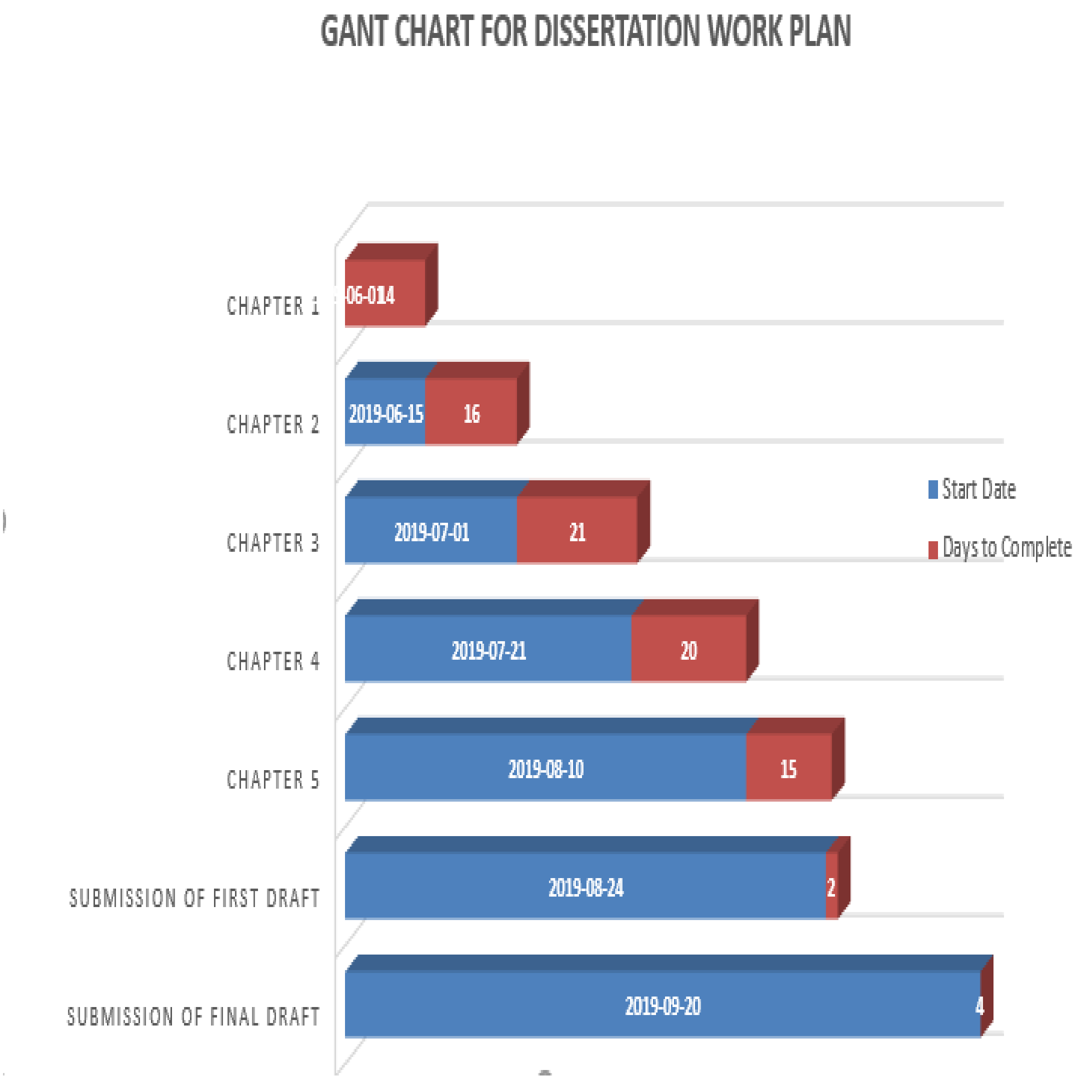
Appendix G : Engines IMEP resluts

IMEP RESULTS						
	Ammonia		Hydrogen		Dodecane	
IMEP-CR	**Diesel**	**HCCI**	**Diesel**	**HCCI**	**Diesel**	**HCCI**
10						1,8923
11						3,55541
12						4,1084
13						4,19947
14						4,26879
15						4,34149
16						
17						
18						
19						
20	0,151	0,166	0,300	6,262	5,117	
21	0,218	0,485	0,483	6,312	5,289	
22	0,407	1,396	1,421	6,327	5,452	
23	0,828	6,410	6,383	6,333	5,595	
24	1,883	6,493	6,503	6,334	5,734	
25	6,561	6,526	6,572	6,335	5,861	

Appendix H : Engines efficiencies result

Engines Efficiencies results												
	Ammonia				Hydrogen				Dodecane			
EFFI-CR	Diesel%		HCCI%		Diesel%		HCCI%		Diesel%		HCCI%	
10											0,19	19,01
11											0,36	35,73
12											0,41	41,28
13											0,42	42,20
14											0,43	42,90
15											0,44	43,63
16												
17												
18												
19												
20	0,02	1,54	0,02	1,70	0,03	3,07	0,65	64,86	0,52	52,24		
21	0,02	2,23	0,05	4,98	0,05	4,93	0,65	65,38	0,54	54,00		
22	0,04	4,16	0,14	14,37	0,15	14,50	0,66	65,53	0,56	55,66		
23	0,08	8,45	0,66	66,13	0,65	65,17	0,66	65,59	0,57	57,13		
24	0,19	19,22	0,67	67,12	0,66	66,39	0,66	65,61	0,59	58,54		
25	0,67	66,99	0,68	67,59	0,67	67,10	0,66	65,62	0,60	59,84		

Appendix I: Dissertation work plan (Gant Chart)



Appendix J: UCL results test 1

Test Numl	CO ppm	HC ppm	NOx	CO2%	E-CO2	O2	CO-H%	MFC1	MFC2	MFC3	COV CO	COV HC	COV NOx	COV CO2	COV E-CO	COV O2
1	576,452	6000	4,324	4,506	0,031	14,722	0,226	0	0	0	0,016	0	1,159	0,003	0,015	0,001
2	550,199	6000	4,221	4,555	0,031	14,66	0,222	0	0	0	0,011	0	0,944	0,004	0,016	0,002
3	639,963	6000	3,228	4,575	0,031	13,953	0,228	0	0	0	0,013	0	1,194	0,003	0,013	0,002
4	694,649	6000	4,106	4,607	0,031	13,805	0,237	0	0	0	0,012	0	0,954	0,004	0,009	0,002
5	858,433	6000	2,454	4,432	0,032	13,06	0,264	0	0	0	0,046	0	1,931	0,006	0,022	0,005
6	1159,347	6000	2,421	4,332	0,032	12,854	0,325	0	0	0	0,052	0	1,697	0,005	0,02	0,008
6	1182,479	6000	2,221	4,34	0,032	12,814	0,331	0	0	0	0,035	0	1,488	0,008	0,019	0,006
7	1202,68	6000	2,402	4,315	0,032	12,973	0,34	0	0	0	0,021	0	1,874	0,005	0,021	0,007
8	1217,415	6000	1,834	4,256	0,033	12,796	0,377	0	0	0	0,009	0	2,455	0,007	0,036	0,008
9	1220,6	6000	2,593	4,244	0,033	12,766	0,399	0	0	0	0	0	1,698	0,006	0,039	0,004
10	1220,6	6000	1,497	4,181	0,031	13,053	0,398	0	0	0	0	0	2,721	0,006	0,013	0,006
11	1220,6	6000	2,035	4,182	0,031	12,999	0,398	0	0	0	0	0	2,204	0,012	0,008	0,005
12	1220,6	6000	1,644	3,347	0,031	14,485	0,393	0	0	0	0	0	2,63	0,007	0,011	0,002
13	1220,6	6000	2,067	3,192	0,031	14,554	0,47	0	0	0	0	0	2,144	0,009	0,022	0,003
14	1220,6	6000	1,811	3,252	0,031	14,443	0,538	0	0	0	0	0	2,037	0,012	0,011	0,003
16	422,329	6000	1,312	6,448	0,03	11,988	0,192	0	0	0	0,024	0	3,139	0,005	0,038	0,004
17	577,348	6000	1,054	5,191	0,028	12,046	0,217	0	0	0	0,013	0	3,809	0,004	0,035	0,003
18	644,726	6000	1,762	4,973	0,029	12,008	0,229	0	0	0	0,015	0	2,642	0,007	0,04	0,005
19	826,495	6000	0,899	4,827	0,029	11,986	0,262	0	0	0	0,027	0	5,244	0,004	0,043	0,003
20	1021,819	6000	1,505	4,611	0,03	12,074	0,298	0	0	0	0,061	0	2,89	0,004	0,045	0,006
21	1042,094	6000	1,563	4,489	0,03	12,177	0,302	0	0	0	0,074	0	3,012	0,003	0,034	0,008
22	1200,561	6000	0,503	4,426	0,03	12,109	0,343	0	0	0	0,031	0	7,564	0,006	0,036	0,003

Test No.	NIMEP	tPP	tPHRR	Ignition timing	max In_cyl Temp	CAD at max in_cyl_T	T at SOC	pHRR	p_incyl_Pres	spark timi
1	4,011	367,2	365,4	360,6	1226,998	374,8	670,663	63,92	63,213	0
2	4,035	367,8	365,2	360,4	1230,294	374,8	673,309	63,877	63,342	0
3	4,528	368,4	365,8	360,8	1282,676	377,6	668,272	68,064	64,122	0
4	4,588	368,6	366,2	361,2	1288,668	376,8	666,144	68,567	64,226	0
4	5,053	370,6	368	362,2	1340,561	378,8	657,754	68,086	61,629	0
5	5,138	372,4	369,6	362,8	1353,71	380,8	657,554	62,643	58,177	0
6	5,186	373	370	362,8	1359,579	381,4	657,873	60,836	57,29	0
7	5,102	372,8	369,8	362,8	1350,453	381,6	658,125	61,221	57,568	0
8	5,177	374,2	370,8	363	1358,099	383,6	658,898	54,553	54,35	0
9	5,171	375	371,4	363	1360,87	384	663,053	54,017	53,582	0
10	5,007	373,8	370,8	363	1337,181	383	658,83	55,651	54,548	0
11	5,011	374,6	371,2	362,8	1335,689	383,2	660,005	52,965	53,151	0
12	4,089	372,2	369,2	362,2	1216,421	381,4	656,986	48,186	53,153	0
13	3,965	373	370,2	362,4	1194,463	382,2	657,324	41,921	49,369	0
14	3,939	374,8	371,6	362,2	1185,117	384,2	657,387	36,818	45,709	0
16	5,018	367	364	359,4	1286,371	382	648,435	57,184	61,839	0
17	5,027	368,4	365,4	360,6	1295,906	380,2	636,891	67,933	63,245	0
18	5,037	369	366,2	361	1300,239	379,8	635,706	68,056	62,312	0
19	5,071	370,4	367,4	361,8	1306,83	380,8	633,529	66,527	60,409	0
20	5,005	371	368,2	362,2	1301,24	380,4	632,308	63,033	58,525	0
21	4,997	371,4	368,4	362,2	1300,122	382	632,909	60,946	57,555	0
22	4,99	372,6	369,4	362,4	1296,234	382,6	633,275	56,832	55,216	0

Appendix K: UCL results test 2

Test Num	CO	HC	NOx	CO2	E-CO2	O2	CO-H	MFC1	MFC2	MFC3	COV CO	COV HC	COV NOx	COV CO2	COV E-CO	COV O2
1	561,882	6000	531,347	4,601	0,02	14,565	0,219	0	0	0	0,015	0	0,014	0,003	0,031	0,001
2	556,934	6000	532,076	4,592	0,02	14,566	0,218	0	0	0	0,016	0	0,011	0,003	0,013	0,001
3	1220,6	6000	268,723	6,37	0,02	0,169	2,4	0	0	0	0	0	0,33	0,112	0,019	0,542
4	1220,6	6000	184,375	5,155	0,019	0,1	2,4	0	0	0	0	0	0,101	0,014	0,036	0,031
5	465,731	6000	452,877	4,221	0,02	1,717	0,186	0	0	0	0,002	0	0,183	0,063	0,026	0,375
6	466,217	6000	132,993	3,414	0,02	0,294	0,179	0	0	0	0,002	0	0,034	0,04	0,024	0,421
7	1220,6	6000	84,139	5,268	0,02	7,954	0,824	0	0	0	0	0	0,044	0,125	0,027	0,425
8	1220,6	6000	80,042	8,505	0,02	12,323	2,342	0	0	0	0	0	0,078	0,065	0,017	0,103
9	711,294	6000	42,52	3,918	0,02	0,122	0,236	0	0	0	0,212	0	0,094	0,343	0,018	0,44

Test No.	NIMEP	tPP	tPHRR	Ignition ti	max In_cy	CAD at ma	T at SOC	pHRR	p_incyl_P	spark timi
1	4,044	367	365,2	360,4	1226,252	374,6	666,587	64,888	63,5	0
2	4,025	367,8	365,2	360,4	1223,621	374,6	666,852	64,773	63,553	0
3	5,247	359	335	318,8	1687,631	347,4	523,008	90,348	96,996	0
4	3,489	369	366,2	359	1094,233	379,6	689,865	31,107	51,971	0
5	4,28	359	335,2	320	1789,46	340,4	530,332	76,962	97,276	0
6	0,692	360,8	325,2	321	860,482	367,2	541,411	3,866	51,064	0
7	5,117	360	335,6	323	1817,3	339	530,826	91,944	99,075	0
8	3,377	359,4	331,2	314,4	1670,338	336,8	507,673	69,124	93,663	0
9	4,271	359,2	333,4	320,6	1831,242	339,6	527,705	89,439	98,573	0

Test numb	T_oil	T_coolant	T_air_inle	T_air_mar	T_fuel_PR	T_fuel_co	T_fuel_co	T_exhaust	Ts_2	T_DMS50(	T_CO2_sa	T_dil_sam	T_N2	T_samplir	T_fuel_pu
1	77,274	73,14	23,294	27,555	62,548	46,975	40,538	111,965	351,548	19,784	19,611	19,546	21,394	23,42	35,653
2	76,792	73,724	23,33	27,571	63,489	47,809	40,115	114,485	349,206	19,836	19,623	19,568	21,42	23,469	36,835
3	76,598	74,069	24,784	35,428	67,421	51,126	40,567	189,238	351,292	21,185	20,412	20,426	22,525	25,906	39,795
4	79,817	72,81	24,808	42,06	67,529	51,399	40,649	206,879	351,289	21,278	20,449	20,445	22,547	26,08	39,943
5	79,395	74,655	25,523	46,272	67,355	51,565	40,689	191,351	349,308	21,606	20,678	20,758	22,375	25,866	39,723
6	76,849	73,094	25,469	50,213	67,48	51,472	41,717	153,556	349,774	21,669	20,705	20,775	22,405	25,658	39,794
7	78,619	73,659	26,694	40,747	68,011	51,607	40,376	224,15	347,628	23,331	22,165	21,962	23,878	28,072	40,291
8	76,329	74,555	26,666	44,006	68,071	51,767	41,748	220,081	348,78	23,418	22,226	22,032	23,952	28,085	40,241
9	75,484	72,28	26,854	35,755	67,627	51,674	38,521	219,01	348,877	23,113	22,204	22,153	24,148	28,274	40,245