Measurement and Characterization of In-use Emissions from Dual-Fuel Diesel Engines Operating on Alternative Fuels

by

Mang Guan

B.Eng., Beijing Jiaotong University, 2011 M.Sc., Beijing Institute of Technology, 2014

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The following individuals certify that they have read, and recommend to the Faculty of Graduate and Postdoctoral Studies for acceptance, the thesis entitled:

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submitted by **Mang Guan** in partial fulfillment of the requirements for the degree of **Master of Applied Science** in **Mechanical Engineering**.

Examining Committee:

Steven Rogak, Mechanical Engineering, UBC
Co-supervisor
Patrick Kirchen, Mechanical Engineering, UBC
Co-supervisor
Naomi Zimmerman, Mechanical Engineering, UBC
Supervisory Committee Member
Patrick Steiche, Hydra Energy Corp.
Additional Examiner

Abstract

Alternative fuels such as hydrogen (H_2) , natural gas (NG), and biodiesel can be substitutes for diesel fuel in compression ignition engines. Dual-fuel combustion technology is an effective way to utilize gaseous fuels ignited by pilot liquid fuels in existing diesel engines with minor modifications. The effects of different fuels on engine emission especially under real-world operating conditions are important information for engine manufacturers as well as vehicle operators. For this reason, this study aims to evaluate the in-use emissions for CI engines operating on the alternative fuels.

The first study focused on the unburned H_2 emission from a heavy-duty truck equipped with a 15 L diesel engine retrofitted to run in dual-fuel mode with port-injected H_2 . A Portable Emission Measurement System (PEMS) was developed integrating a semi-conductor H_2 sensor, which gives the H_2 concentration in the exhaust stream. On-road emission tests were implemented on the truck with the PEMS to measure the in-use H_2 emission under real-world operating conditions. H_2 slip maps were generated using the concentration data. The work presented the methodology to use a lowcost sensor for in-use vehicle's exhaust H_2 measurement.

In the second study, in-use emission measurements were taken for a diesel/NG dual-fuel marine vessel. The emissions under diesel mode and dual-fuel (NG + pilot fuel) mode were considered with diesel (baseline), Soybean Methyl Ester (SME), and Canola Methyl Ester (CME). It was found that under diesel mode steady states, NOx emissions were increased by $21 \pm 6\%$ on average by both biodiesels. Particle number (PN), particularly in the submicron range, were substantially increased by the biodiesels, likely an artefact of nucleation mode or volatile compounds. Under load increase conditions, transient CO and PM concentrations were substantially higher than the steady state results. Both biodiesels resulted in reduced PM emissions compared to diesel. Under dual-fuel mode, when used as the pilot fuel, SME and CME reduced NOx emissions by $14 \pm 7\%$ and $19 \pm 7\%$, respectively. The results proved that biodiesels are a potential alternative fuel for heavy-duty marine engines, though some questions remain to be answered.

Lay Summary

Heavy-duty diesel vehicles are a major source of GHG emission. Alternative fuels such as biodiesel, natural gas (NG), and hydrogen (H₂) are an attractive pathway to reduce diesel engine emissions. Dual-fuel engines can utilize gaseous fuels in diesel engines with liquid pilot fuel for ignition. This study focuses on the in-use emissions of diesel engines operating on different alternative fuels: First, a measurement system was developed to measure the unburned H₂ from a H₂/diesel dual-fuel truck. It presented a lowcost method to measure the exhaust H₂ for in-use vehicles; Second, in-use emissions from a NG/diesel dual-fuel marine vessel operating on diesel and biodiesels were characterized. It was shown that NOx emissions increased when using biodiesels under steady-state diesel operating mode. Transient PM emissions were reduced during load increases when using biodiesels as compared to diesel. In addition, when used as pilot fuels in dual-fuel mode, the biodiesels reduced NOx emissions in steady state.

Preface

This thesis includes two individual projects. I outlined the general objectives of this thesis and researched the related literature. Dr. Steven Rogak and Dr. Patrick Kirchen provided guidance and advice over the course of the two projects.

Chapter 3 was based on a collaborative project between UBC and a industrial partner. The test truck was provided by the industrial partner, who also installed and calibrated the H_2 injection system on the truck. The H_2 sensor used in this study was purchased from a commercial supplier. I did the verification test and the calibration for the H_2 sensor. The PEMS was originally designed by a previous UBC student Jeffrey Meiklejohn. I did the work to integrate the H₂ sensor and auxiliary parts into this PEMS. On-road tests were conducted while the truck was operated by a commercial fleet driver, during which I participated as a data collector and monitor in the truck cabin. I wrote the Matlab code for processing the test data with the following exception: the initial code for plotting the H_2 emissions maps were written by Pooyan Kheirkhah, a UBC PhD student at the time, and I modified it for my use. Patrick Steiche, Tyson Whyte, and Calvin Lefebre, engineers from the industrial partner also provided help on acquiring CAN-BUS data and torque data of the truck. The results from this project was published as a conference paper and presented at The Internal Combustion Engine Fall Conference (Virtual) of the ASME on Oct 13, 2021.

Chapter 4 was a collaborative project with another industrial partner. The measured marine vessel was provided by the industrial partner. The measurements were done during their regular and scheduled sailings while the vessel was operated by the Captain. I designed and installed the measurement system on the vessel with the exception: the FTIR measurements, calibration, and post-processing were carried out by another MASc student, Troy Hurren. I participated in the whole campaign activity during which I did the calibrations and regular maintenance for the equipment (except FTIR) and data recording. I wrote the Matlab codes for processing the test data. A potential journal paper from this work is in preparation at the time of writing this thesis.

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List of Abbreviations

BSFC	Brake Specific Fuel Consumption
CAN	Controller Area Network
CI	Compression Ignition
CME	Canola Methyl Ester
DAQ	Data Acquisition
ECU	Engine Control Unit
EGR	Exhaust Gas Recirculation
EGT	Exhaust Gas Temperature
ELPI	Electrical Low-Pressure Impactor
FAME	Fatty Acid Methyl Esters
FID	Flame Ionization Detector
FTIR	Fourier-transform Infrared
FTP	Federal Test Procedures
GHG	Green House Gas
GR	Gear Ratio
GVWR	Gross Vehicle Weight Rating
GWP	Global Warming Potential
HDRD	Hydrogenation Derived Renewable Diesel
HEPA	High Efficiency Particulate Air (filter)
IMO	International Marine Organization
LCA	Life Cycle Assessment
LNG	Liquefied Natural Gas
MFC	Mass Flow Controller
NDIR	Non-dispersive Infrared
NG	Natural Gas
NOx	Oxides of Nitrogen (including NO and NO_2)
OC	Organic Compound
OPC	Optical Particle Counter
PAH	Polycyclic Aromatic Hydrocarbon
PEMS	Portable Emission Measurement System
\mathbf{PM}	Particulate Matter
DN	Dantiala Numahan

PNParticle Number

RH	Relative Humidity
\mathbf{SI}	Spark Ignition
SME	Soybean Methyl Ester
TDC	Top Dead Center
UEGO	Universal Exhaust Gas Oxygen sensor
WMS	Wavelength Modulation Spectroscopy

List of Symbols

- c_p Pitot tube constant
- C_i Volumetric concentration
- D Exhaust pipe diameter
- DR Dilution ratio
- f Friction factor
- *GR* Gear ratio
- \dot{m} Mass flow rate
- m_a Mass of air
- m_f Mass of fuel
- M Molar mass
- *n* Sample size
- Δ_P Pressure difference
- P_b Brake power
- P_{gen} Generator power
- P_{max} Maximum engine power
- Q Volumetric flow rate
- R_0 Resistance of the H_2 sensor in clean air
- R_L Resistance of the load resistor
- R_s Resistance of the H_2 sensor in sample gas
- *Re* Reynolds number
- SE Standard error
- t Time
- T Torque
- v_c Centerline flow velocity
- v_m Mean flow velocity
- V_c Total voltage on the test circuit
- V_{RL} Voltage on the load resistor
- WF Weighting factor
- WSE_i Weighted specific emission of species i
- x Mass concentration
- \bar{x} Mean value

η_{gen} Generator efficiency

- λ Excess air ratio
- μ Viscosity
- ρ Density
- σ Standard deviation
- au System latency

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Chapter 1

Introduction

Compression ignition (CI) engines are widely used in various applications in industry. Due to their higher compression ratios and lean burn feature, they are the more efficient type of internal combustion engine compared to spark ignition (SI) engines [1] and are especially favored for heavy-duty applications, such as fleet trucks, construction equipment, and marine vessels. However, CI engines running on petroleum diesel fuel have a bad reputation of producing large amounts of engine-out emissions of nitrogen oxide (NOx) and particulate matter (PM), which lead to air pollution and risk human health [2]. Public attention and stringent emission regulations [3, 4, 5] have been put on diesel engine's emissions. Meanwhile, Greenhouse gases (GHG) such as carbon dioxide (CO₂) produced from burning fossil fuels are gaining more and more concern since the global climate crisis has become an urgent issue to deal with. In addition, the dependence on petroleum fuel leads to geopolitical tensions.

To address these challenges, different pathways have been put forward, aiming at improving diesel engine's fuel efficiencies as well as reducing its emission of various pollutants. The methods include technologies focused on improving in-cylinder combustion processes and after-treatment systems which purify engine-out exhausts. Apart from these, substituting diesel with alternative fuels is considered to be a potential solution, which provides diversity in fuel options and can potentially reduce emissions of GHG, PM, and NOx. Different types of alternative fuels have been considered for CI engines.

Biodiesel, as a most common liquid substitute for diesel, can be directly used (or in blends with diesel) in CI engines. Biodiesel can be produced from a wide variety of feedstocks such as vegetable oils, animal fats,or waste cooking oils through a process called transesterification [6]. Two of the common feedstocks especially in North America are soybean oil and canola oil [7]. The biodiesels produced from them are called Soybean Methyl Ester (SME) and Canola Methyl Ester (CME), respectively. Biodiesel made from plants are considered to be carbon-neutral as the plants absorb CO_2 as they grow [8], although their life-cycle carbon intensities depend on a variety of factors including feedstock options and land use [9]. Meanwhile, the risk of diverting farmland or crops for biofuel production is still in debate as it may be a detriment to the food supply [10]. Despite the controversies, numerous studies have been conducted on various diesel engines operating on different types of biodiesels [11]. However, a vast majority of the literature were based on laboratory tests in which the engines were coupled to a dynamometer and operated following a standard test cycle. As a lesson we had learned from the infamous "dieselgate" scandal [12], the emission results from laboratory tests can be significantly different from the actual tailpipe emissions in realworld conditions, which bring the most direct effects to our environment. It is thus necessary to evaluate the effects of biodiesels on engine emission under real-world operating conditions for industrially relevant engines.

Natural gas (NG), as a widely available fossil fuel in the world, is one of the most commonly used gaseous alternative fuels for CI engines. Mainly consisting of methane (CH_4) , NG is considered to produce much less CO_2 compared to diesel due to its lower carbon-to-hydrogen ratio [13]. NG has a major benefit of reducing PM emissions as its gaseous state leading to better mixing with air and the general non-existence of polycyclic aromatic hydrocarbons (PAH) in its composition [14]. As NG has high octane number and low cetane number, they are difficult to be burned alone in conventional CI engines. To solve this issue, dual-fuel combustion strategy is used. In dual-fuel combustion engines, the gaseous fuel, such as NG, is injected into the intake port or directly into cylinder and ignited by directly injected liquid fuel, such as diesel, near the end of compression stroke [15]. The performances of dual-fuel gas engines have been studied extensively both in laboratory tests or under real-world conditions in the literature [16]. In addition to the criteria pollutants, a new problem associated with dual-fuel gas engine is the methane emissions, since methane has a significant global warming potential (GWP) [17]. In a previous study [18], high CH_4 emissions were observed at low-load conditions on a dual-fuel gas engine under realworld working conditions and vessel operation strategy has been improved to effectively reduce the CH₄ emissions.

Another gaseous fuel considered for CI engines is the hydrogen (H₂). Compared to NG, H₂ is a less common fuel for CI engines especially in passenger vehicles mainly due to its limitations in storage and distribution [19]. But in heavy machinery or power generation applications where space is less of a concern, H₂ is still an attractive option. Due to its zero carbon-content nature, H₂ has the potential to reduce tail-pipe emissions, particularly CO₂ emissions. Current use of H₂ in CI engines is mainly by partial substitution for diesel. The H₂ substitution ratio in diesel/H₂ dual-fuel engines is limited by engine knocking and pre-ignition [20]. The ratio is normally controlled by the injection system according to engine loads. A previous study [21] investigated the in-use emissions of CO_2 , NOx, and PM of a diesel/H₂ truck and found reductions in CO_2 and increases in NOx. Meanwhile, there were suggestions that unburned H₂ (H₂ slip) was emitted in potentially significant amounts in some cases, though precise measurement results of H₂ emission was not possible. Although not a pollutant, H₂ slip indicates incomplete combustion of the fuel and thus reduced fuel economy and deteriorated fuel efficiency. In addition, the presence of H₂ in the exhaust can also affect the performances of the after-treatment system. Due to these reasons, quantifying the amounts of H₂ slip under various engine operating conditions is important for the engine calibrators to optimize their H₂ injection strategies.

Based on the these backgrounds, this thesis aims to answer the following questions related to heavy-duty dual-fuel engines operating on different alternative fuels:

1. How to measure the H_2 slip for an in-use vehicle in road tests? Is there an effective and low-budget method which is suitable for measuring the H_2 slip on a vehicle under real-world operating conditions?

2. How do the biodiesels (SME and CME) affect the in-use emissions of a heavy-duty marine engine under real-world conditions as compared to diesel?

To answer these questions, the in-use emissions of two types of vehicles using various alternative fuels and fueling strategies have been studied experimentally. Firstly, relevant backgrounds including the dual-fuel technology, fuel properties, and emission measurement instruments have been introduced in Chapter 2 together with a literature review. Chapter 3 describes the development and implementation of an exhaust H_2 measurement system for a diesel/H₂ dual-fuel truck. The in-use emission characteristics of a diesel/NG dual-fuel marine vessel operating on diesel and biodiesels are discussed in Chapter 4. Finally, major findings from these two studies are summarized in Chapter 5 together with recommendations for future research.

Chapter 2

Background and Literature Review

This work will consider two types of heavy-duty vehicles powered by CI engines fueled with different fuels in both diesel mode and dual-fuel mode. This section will introduce the background information regarding dual-fuel engines, alternative fuels, and emission measurement methods. The literature review will focus on two fields: the effects of different alternative fuels on engine emission; and the emission measurement methods for in-use vehicles.

2.1 Dual-fuel engines

The term "dual-fuel engines" refers to compression ignition engines that burn simultaneously two different fuels in various proportions [15]. Typically, these two fuels include a gaseous fuel, which is the primary energy source for combustion, and a liquid fuel, which provides the energy for ignition. The latter one is also called the pilot fuel.

With an independent gas injection system, dual-fuel engines can operate in two modes: (1) With only directly injected liquid fuel (such as diesel), operate as a conventional diesel engine, which is called the "diesel mode" operation; (2) With gaseous fuel as the primary energy source, and liquid fuel as the pilot fuel for ignition, which is called the "gas mode" operations. These two terms will be used in this thesis to represent the two different fueling modes of dual-fuel engines.

Based on how the gaseous fuel is introduced into the cylinder, there are two types of dual-fuel strategies: (1) The gaseous fuel is injected upstream of intake port and premixed there with the intake air, inducted into the cylinder, compressed, and then the mixture is ignited by the pilot fuel which is injected directly into the cylinder near TDC (Figure 2.1). This type of engine is called premixed dual-fuel engine; (2) The gaseous fuel is injected at a very high pressure directly into the engine cylinder after the injection and ignition of the liquid fuel. Among the two approaches, the premixed dualfuel engine is more commonly used due to its lower fuel pressure, simplicity, and lower cost.



Figure 2.1: The conceptual schematic of a premixed dual-fuel engine

In premixed dual-fuel engines, the energy content is typically dominated by the gaseous fuel, since only a small portion of liquid fuel is injected to ignite the premixed mixture. The ratio of the amount of gaseous fuel to that of the liquid fuel is an significant factor influencing engine combustion and emissions. There are different strategies to control this ratio. The easiest strategy is to inject the pilot fuel at a fixed rate regardless of variations in engine load and engine speed. A more advanced strategy is to control the amount of pilot fuel injection based on engine speed/torque map to achieve optimum performance of the engine. The development of this map needs the understanding of engine combustion and emission characteristics. For example, for a H_2 /diesel dual-fuel engine, the H_2 /diesel ratio is limited by efficiency, PM, NOx emissions as well as knock and pre-ignition behaviours [20], while in a gas engine it is also limited by CH₄ emissions.

Due to the low C/H ratio and low PAH content of gaseous fuels and the lean burn combustion feature, dual-fuel engines are considered to have the benefits of high power density, high efficiency, and reduced CO_2 , PM and NOx emissions especially at high load conditions [22]. In addition, dualfuel engines can usually also be used as a conventional diesel engine since the gas fuel injection is independent of the existing diesel system. These advantages make dual-fuel engine a feasible solution to improve existing diesel engines and a promising technology to meet the challenges of reducing GHG emission and air pollution if the fuel used can be sustainably produced and combusted in a manner to exploit its combustion, emission, and engine performance advantages.

2.2 Alternative fuels and their effects on engine emission

A variety of fuels have been considered as the substitutes for diesel. In this section, three types of alternative fuels including biodiesel, natural gas and hydrogen will be briefly introduced on their properties and applications in diesel engines. Some typical properties of these three fuels are summarized in Table 2.2.

2.2.1 Biodiesel

As a liquid fuel, biodiesel or its blends can be used as the only fuel in diesel engines or as the pilot fuel in dual-fuel engines. Biodiesel is derived from renewable sources such as vegetable oils, animal fats, or waste cooking oils. To make the biodiesel, raw feedstocks need to go through a transesterification process with an alcohol and a catalyst [23]. The product of this reaction consists of fatty acid methyl esters (FAME), namely biodiesel. Due to its high viscosity and corrosive nature which may cause problems in fuel injection system and in cold start conditions, biodiesel is usually blended with petroleum-based diesel in practical use. As an example, the label B10 indicates that the blend is made up of 10% biodiesel and 90% diesel on a volume basis. With the advancement in technology of modern diesel engine, some engine manufacturers offer warranty for up to B20 in their engines [24]. Authorities are also promoting the use of biodiesel in their policies. For instance, the Government of Canada has created the National Renewable Diesel Demonstration Initiative aiming to achieve an average 2% renewable content in the Canadian distillate pool [25].

The source of biodiesel covers a variety of feedstock. Among them, vegetable oil is the most common category. According to the Canada Biofuel Annual Report 2019 [7], canola oil and soybean oil made up 70% of all biodiesel feedstocks in Canada. The biodiesels derived from these two feedstocks are called soybean methyl easter (SME) and canola methyl easter (CME), respectively. Compared to conventional diesel, biodiesels generally have the advantageous properties of high oxygen contents and higher cetane numbers [11]. Typically, biodiesels will result in lower PM and CO emissions and higher NOx emission than diesel [26]. These effects had been reported in many studies with biodiesels made from various feedstocks and in various blend ratios [27, 28, 29, 30, 31, 32, 33, 34, 35]. For instance, Ozsezen et al [27] measured the emissions from a 6L-displacement 81kW diesel engine fueled with CME and found that CO and soot opacity were reduced by 73%and 48% respectively at full load. Except for the higher oxygen content, they believed that higher cetane number and associated shorter ignition delay of CME also played an important role in the reduction effect of CO and soot. Similar trend had been observed with SME blends on a 4-cylinder 40 kW diesel engine by Gokalp et al [30]. They found 52% reduction in CO and 74% reduction in smoke opacity when running on SME and its blends. Increases in NOx emissions had been reported in a majority of these studies. Most researchers believed that the oxygen presence in the biodiesel causes high local temperature zone in the combustion chamber, which boosted the formation of NOx [29, 36, 30, 37].

However, the studies mentioned above were mostly conducted on dynamometers and were focused on on-road diesel engines, which typically operate at higher engine speeds compared to heavy-duty applications such as marine engines. There are very limited studies conducted on heavy-duty marine engines under real-world operating conditions. One such work was done by Khan et al [38]. They investigated the in-use emissions from a marine vessel running on a 50:50 blend of diesel and algae biofuel. The vessel was powered by 4 Caterpillar D398 diesel engines (12 cylinder, 48.3 L displacement and 600 kW maximum power rating at 1200 rpm) connected with two 1600 kW propulsion motors. Their study reported overall reductions on all of the pollutants (5%, 18%, 10% and 25% reductions on CO₂, CO, NOx and PM respectively), though the reduction in PM was not statistically significant. Another similar study was done by the U.S. Army on 4 floating plant vessels fueled with B100 biodiesel (feedstock unknown) [39]. These vessels were powered by diesel engines with different power ratings ranging from 78-597kW. Reductions of CO_2 , CO and PM were found in most cases in their study, while slight increases in CO and PM was observed at 25%load on one of the measured vessels. The changes in NOx emission were found to be varying between different vessels and different load conditions.

It can be seen from the literature that, under real-world settings, there isn't a consistent trend on the effects of using biodiesels, especially on NOx and PM emissions. Meanwhile, the dataset for in-use emissions of heavyduty marine engines fueled by SME and CME has not been found. In addition, these studies were only conducted at steady states. Real-world transient emission data have not been found in literature.

2.2.2 Natural gas

Natural gas (NG) is a type of fossil fuel found in the deposits of crude oil or deep underground rock formations [40]. The NG extracted from rock formations is also called tight gas, which is accessed by drilling wells through the rocks. NG is becoming a prime energy source for major energy consumers around the world including the US, Canada and China [41]. Compared to conventional diesel fuels, natural gases have the advantages including wide availability, cleaner emissions and lower cost.

Natural gas typically consists of about 90% methane and varying amounts of other alkanes such as ethane, propane and butane as well as small amounts of carbon dioxide, nitrogen and hydrogen sulfide, as is listed in Table 2.1 [42]. The processing of raw natural gases will remove the hydrogen sulfide content and reduce water content. The major component, methane, is an odorless and nontoxic gas with a simple chemical structure. Its higher octane number relative to diesel means that it is a more knock-resistant fuel and thus can run in engines with higher compression ratios, indicating higher efficiencies [43].

Composition	Formula	Concentration(vol)					
Methane	CH_4	70-90%					
Ethane	C_2H_6	0-20%					
Propane	C_3H_8	0-20%					
Butane	C_4H_{10}	0-20%					
Carbon Dioxide	CO_2	0-8%					
Oxygen	O_2	0-0.2%					
Nitrogen	N_2	0-5%					
Hydrogen sulphide	H_2S	0-5%					
Rare gases	Ar, H_2 , Ne, Xe	Trace					

Table 2.1: Typical compositions of natural gas [42]

Natural gas is often liquefied to be transported or stored over long distances such as in marine transportation. The liquefied natural gas (LNG) is stored in specialized tanks at slightly higher-than-atmospheric pressures and very low temperatures (111 K at atmospheric pressure). To be used as a gaseous fuel in dual-fuel engines, LNG is vaporized through heat transfer from engine coolant before introduced into intake port.

The NOx and PM emissions are expected to be lower for NG/diesel dual-fuel engines due to the premixed combustion mode, while HC and CO emissions resulted from incomplete combustion can typically increase [44]. Besides the regular pollutants, unburned methane is a new concern for NG engines because of its significant global warming potential, 84 compared to CO_2 (potential of 1) over a 20-year period or 28 over 100-year period [17]. Moreover, the fact that methane is hard to oxidize with common catalysts makes it a challenge for aftertreatment systems [45]. Two previous studies had been conducted on a dual-fuel marine vessel focusing on its methane emissions [18, 46]. Sommer et al [18] measured the in-use CH₄ emissions of the vessel at steady states. They found that specific CH_4 emissions were high at low engine loads. By applying cylinder deactivation technology and optimizing vessel operation strategy, the total CH_4 emission were reduced by up to 33%. Sacal et al [46] measured the CH_4 emission under transient operations. They found that exhaust CH₄ concentration during load increases was 1.9 times relative to steady states, and total methane emissions were up to 43% higher under transient operations.

2.2.3 Hydrogen

Hydrogen (H_2) is a renewable fuel that can be produced from fossil gases, biomasses, or pure water [47]. It is normally considered as an energy carrier rather than an energy source as it must be produced from a primary source through processes which consume considerable energy and produce GHG emission. The application of hydrogen as a fuel heavily depends on its manufacture and the associated economy. Recovered hydrogen from industrial by-products can provide a viable source for hydrogen.

 H_2 has several properties which make it an attractive fuel for engines: (1) In its pure form, H_2 , when reacted with oxygen, produces no CO₂, making it a clean fuel; (2) Its high heating value on mass basis contributes to a high flame temperature and low ignition energy, though the volumetric heating value is low; (3) Its high flame speed also contributes to low ignition delay.

By principle, these mean that hydrogen works well in lean combustion and can substantially reduce CO_2 and soot emissions. However, on the other hand, as fuel/air ratio approaching stoichiometric conditions, i.e., at higher engine loads, hydrogen engines are prone to pre-ignition and high NOx emissions [51]. In addition, although hydrogen has high specific energy on mass basis (MJ/kg), the energy per volume is low. This will restrict the engine intake volumetric flows as hydrogen will replace some amount of the intake air, potentially resulting in the penalty of loss of power and higher

Property	Diesel (I)	Biodiesel (I)	Natural gas(g)	Hydrogen (g)
Formula	$C_n H_{1.8n}$	RCO_2CH_3	CH_4	H_2
Lower heating value	42.6	37.5	47.1	120.0
(MJ/kg)				
Stoichiometric A/F	14.5	12.5	17.2	34.3
ratio				
Autoignition Tem-	315	149	540	565-582
perature (°C)				
Cetane Number	40-55	48-65	N/A	N/A
Density at STP	846	888	0.777	0.090
(kg/m^3)				
Energy Density at	38.6	33	0.03	0.01
STP (MJ/L)				

Table 2.2: Typical values of selected properties of diesel, biodiesel, natural gas and hydrogen [48, 49, 50]

soot emissions.

A previous study [21] measured the real-world emissions of CO₂, NOx and PM from a H₂/diesel dual-fuel truck. It was found that, compared to pure diesel, the H₂ addition reduced CO₂ emissions by approximately 25% but increased NOx by about 10%, and the PM emission remained similar. While the effect of hydrogen addition on the emissions of criteria pollutants have been studied in literature [52], the emission of unburned H₂ (or H₂ slip) gained few attention. Although H₂ is harmless to the environment, incomplete combustion of H₂ fuel indicates poor fuel economy as well as reduced efficiency. In a study by Gatts et al [53], they measured the H₂ emission from a 10.8L heavy-duty diesel engine supplemented with H₂. They found that H₂ emission increased as decreasing load, and it changed with H₂ substitution ratios. The maximum exhaust H₂ concentration of 14,000 ppm was observed at 10% load with 4.5% H₂ substitution ratio by volume. However, this study was based on dynamometer tests. Real-world on-road test of H₂ emission is lacking in literature to the best of the author's knowledge.

2.3 Engine emission test cycle and measurement methods

The formations of pollutants in diesel engines are affected by a variety of factors. It is rather difficult to accurately estimate the exhaust composition by means of theoretical models or numerical calculation. In this background, direct measurements of engine emission are necessary for understanding the actual emission level of each pollutant. On the other hand, emission regulations have always been a driving force for emission reduction. More and more stringent emission limits are implemented in different regions and fields. These emission regulations not only are based on emission reduction technologies, but also rely on representative test cycles and accurate measurements of the pollutants. To reasonably assess the emission level of an engine, emission measurements need to conducted following a representative test cycle. This section will introduce the standard test cycles for engine emission tests.

2.3.1 Engine emission standards and test cycles

Different emissions standards are implemented in different regions and countries of the world. For instance, in Canada, the emission regulations are enforced under the Canadian Environmental Protection Act 1999 (CEPA 1999) [4]. The regulations generally align with U.S. EPA federal standards [54]. Specified regulations apply to different categories of engines and vehicles. In general, they are divided as on-road vehicles and off-road vehicles.

For on-road vehicles, the regulation defines them further by their weight classes. For instance, trucks with Gross Vehicle Weight Rating (GVWR) > 3856 kg are classified as heavy-duty vehicle [54]. Emission testing for heavy-duty vehicles is performed according to the Federal Test Procedure (FTP) heavy-duty transient cycle. This cycle considers a variety of typical driving patterns encountered in real-world conditions for heavy-duty trucks [55]. The final output from this test are brake-specific FTP emissions which are weighted emissions in grams divided by weighted brake power (bhp-hr or kWh).

For marine engines with power outputs larger than 130 kW, emission standards are authorized by the International Marine Organization (IMO) under the International Convention for the Prevention of Pollution from Ships (MARPOL) [56]. The MARPOL Annex 6 [5] set limits for major pollutants in marine engine exhaust including NOx and SOx. The test cycle for marine diesel engines is described in the ISO 8178-4 standard [57]. Particularly, for heavy-duty constant-speed propulsion engines, the cycle (E2) is made up of 4 modes with different loads. The load requirements and weighting factors for each mode in the E2 test cycle are listed in Table 2.3. Noted that all the test modes refer to steady state tests when engine is operated on a dynamometer under well controlled conditions, and transient operations are not considered in this test cycle.

Test mode	Engine load (% of maximum power)	Weighting factor
1	100	0.2
2	75	0.5
3	50	0.15
4	25	0.15

Table 2.3: Specification of engine loads and weighting factors for different test modes described in ISO 8178-4 E2 test cycle [57]

In this thesis, two different types of vehicles are considered, namely a fleet truck and a marine vessel. Based on their typical operating conditions, different test plans and test cycles are designed for each vehicle separately. A summary of the test information is listed in Table 2.4.

Table 2.4: A summary of the test modes and conditions for the two vehicles involved in this study

Chapter	Vehicle type	Engine type	Fueling mode	Test condition
Chapter 3	Fleet truck	${\sf H}_2/{\sf diesel}$ engine	Gas	Real-world (On-road)
Chapter 4	Marine vessel	NG/diesel engine	Diesel	Steady state Transient
			Gas	Steady state

2.3.2 Engine emission gas analyzers

A summary of common instruments used for gaseous pollutant measurement is shown in table 2.5. Based on their measuring principles, they can be divided into 3 major categories, namely spectroscopy, ionization, and electrochemical. The absorption spectroscopy technique measures the amount of light absorbed by the sample gas which the light passes through. The absorption (light intensity) is proportional to the concentration of the target gas. Traditional spectroscopy devices measure with an infrared at a non-dispersive wavelength range which corresponds to a certain gas species, thus it is called "non-dispersive infrared gas analyzer" (NDIR). This technique has the limitation of single gas detection capability and also suffers from crosssensitivities to the other species with overlapping spectra. An advanced version of NDIR is the Fourier-transform infrared spectroscopy (FTIR). FTIR shines multiple light beams covering the whole spectrum through the sample gas, and then uses Fourier transform to process the raw signals to obtain a wide range of spectrum at one time. To achieve fast measurements, cooled photoelectric detectors can be used. They can shorten the response time of FTIR to as fast as 10ms [58].

Ionization detectors are normally used for HC measurement. The principle of FID is based on the ionization of hydrocarbon molecules in a hydrogen flame. The number of ions generated in the flame corresponds to the number of carbon atoms in the sample gas molecules. Hence the measuring results from FID are total HC content, or commonly indicated as an equivalent HC concentration (e.g., C_3H_8).

Electrochemical sensors are also widely used for detecting pollutant gases (such as CO_2 , CO, NOx, or O_2) especially for their generally lower costs, simpler control, and mass production applications. They work by the principle of oxidization or reduction reactions in which the oxidizing or reducing sample gas reacts with the electrode and creates an electrical current. The generated current is linear to the concentration of the gas to be measured. Cross-sensitivity is a common issue for electrochemical sensors, which can be improved by applying chemical filters that can remove the interference species.

This study focuses on the in-use emission from engines, i.e. on-road or on-board testing under real-world operating conditions. The requirements of the instruments for this purpose differ from the ones used for laboratory tests, which are typically steady-state tests. Except for the variations in environment conditions such as temperature, humidity, or altitude, one additional consideration is the response time of the instruments. Faster response is desired for accurately and timely capturing of the transient changes in engine exhaust. The response times for different instruments may vary as a variety of factors including their principles, target gas, measuring environment as well as the sampling design. Even for the same type of gas analyzers, reported response times from different manufactures differ in a

Principle	Technique	Measured gas species	Typical response time (s)
Spectroscopy	NDIR	CO, CO ₂ , CH ₄	< 50
	NDUV	NO, NO $_2$	< 50
	FTIR	CO ₂ , CO, HC, NOx	< 1
Ionization	FID	HC	< 10
Electrochemical	Electrochemical sensors	Oxidizing or reducing gases	Varies

Table 2.5: Common gas analyzers/sensors for engine emission measurement and their typical response times [59, 60, 61]

wide range. Special care should be taken of response time when choosing instruments for real-world tests.

2.3.3 H_2 measurement methods

Conventional H₂ measurement methods typically include gas chromatography and mass spectrometer. For instance, in the dynamometer test by Gatts et al [53], H₂ emission was measured using an Electron Pulse Ionization Mass Spectrometer. However, these instruments are usually large, expensive, and slow in terms of their sampling and reaction times [61]. Hence, they are difficult to be implemented in on-road tests. Chemical or electronic sensors, on the other hand, are relatively compact in size, simple in structure, and low in cost. Though the application of H₂ sensor in vehicle emission test was rarely found in literature, they were very common in other fields such as fuel cell or hydrogen industries [62, 63]. Table 2.6 lists some typical available hydrogen sensors with their important parameters according to literature review. It can be seen from it that, unfortunately, cross-sensitivity to CO seems to be a common problem for H_2 sensors. The only exception, thermoconductivity sensor, has the disadvantage of detection limit. Meanwhile, some of these sensors such as semi-conductive sensors or electrochemical sensors have strong dependence on environmental parameters such as ambient oxygen content [64]. Based on these facts, a simple and effective method for in-use H₂ measurement on vehicles is not readily available. A more careful selection of H₂ sensor should be done based on the knowledge of test environment and specific requirements.

Principle	Range	Response time	Cross sensitivity	References
	(vol%)	$T_{90}(s)$	-	
Catalytic	< 4	< 10	HC,CO	[65]
Thermo-conductivity	> 1	< 5	He	[61, 66]
Electrochemical	> 0.001	2-100	CO, HC, CO ₂ ,NOx	[67]
Semi-conductive MOSFET	> 0.001 < 5	< 15 < 5	CO, CH ₄ CO	[68] [69]

Table 2.6: Typical H_2 sensors and their technical parameters

2.3.4 PM measurement methods

Particulate emission is a major concern for diesel engines and also a challenging matter to measure as the composition of diesel PM varies in chemical structures, sizes, and morphology.

Smoke opacity measurement is a widely used PM measurement method. It uses smoke opacity meters which measure the optical properties of engine exhaust, i.e. the extinction of light beam resulting from scattering and absorption by particles. This method is usually less costly and simpler compared with the other instruments, while it has limitations such as low resolution, cross sensitivity to NOx, and lack of sensitivity to nanoparticles.

A method based on light scattering principle is the optical particle counter (OPC). This is a more direct approach to measure the particles compared with the smoke opacity measurement. It measures the light scattered by the particles crossing a laser beam. The intensity of the light pulse detected by a photo detector is used to count and size the particles. The photo detector can also be calibrated against aerosol mass concentrations (mg/m³), in which case the OPC gives PM mass concentration results. An example of this device is the TSI Dusttrak aerosol monitor. This type of instruments can report real-time data on PM concentration which makes them suitable for in-use measurements. However, they are sensitive to particle size and composition [70]. This brings uncertainties to the measurement results of particles spanning a wide range of diameters such as the diesel particulates. To verify the results of light scattering methods, gravimetric samples can be collected and used as backup.

Besides the total number or mass concentration, size distribution is also an important information about the PM. An established method to measure particle size distribution is by using cascade impactors. It can divide and collect the particles at different size ranges based on their momentums, or aerodynamic diameters. The collected particles at each stage can then be used for mass or composition analysis. An advanced technique using impaction mechanism is called "Electrical Low-Pressure Impactor (ELPI)". In this device, electrometers are connected to each of the impactor stages to measure real-time particle number concentrations and size distributions. This is particularly suitable for in-use emission measurements. However, limitations also exist in this method mainly due to its algorithm for converting raw current signals to particle number or mass concentrations. For example, in Dekati ELPI+, the default algorithm assumes constant density of particle, which is not the case for engine particulate emissions. To tackle this issue, mathematical methods such as inversion and iteration are needed. Detail information on this topic can be found in literature [71].

Another important aspect of diesel PM measurement is the sampling system. Condensation and adsorption of organic compounds can happen during this process [72], which can significantly change the compositions of raw PM generated in the combustion process, and lead to inaccuracies in measurement results. Devices such as catalyst strippers can be used to remove these organic compounds. In addition, particle losses during the sampling process can also cause significant changes to the results. The loss may happen in sample extraction as well as sample transportation. Several different effects such as gravitational settling, diffusion, inertial deposition, and electrostatic deposition all contribute to the losses [73]. Measures can be taken to mitigate some of these losses such as using a conductive tube to eliminate electrostatic losses. In addition, flow modelling or calculation methods can be used to estimate these losses.

2.4 Motivation and objectives

Alternative fuels including biodiesel, NG, and H_2 are a potential solution to reduce GHG emission and the emissions of other pollutants (mainly NOx and PM) from CI engines. The premixed dual-fuel combustion strategy provides an effective pathway to burn gaseous fuels with pilot liquid fuels in conventional diesel engines. Due to the different properties of different alternative fuels, they can result in different effects on engine emissions. To evaluate the emission of dual-fuel vehicles under real-world operating conditions, in-use emission measurements need to be conducted. This thesis include two works described in Chapter 3 and Chapter 4, respectively, which aim to address different objectives on two different dual-fuel vehicles.

2.4.1 Objectives for Chapter 3

The emissions from $H_2/diesel$ dual-fuel engines have been studied mostly in the laboratory. Limited studies have focused on its real-world emissions of regular pollutants but not on the in-use H_2 emissions. This is, in part, due to the lack of a suitable exhaust stream H_2 measurement technology. Several types of H_2 sensors have been used in industry for safety monitoring but rarely for vehicle emissions tests. These sensors have certain detection limits as well as requirements for testing environment.

In the first project of this study, the objectives are to:

- Develop an economic method to measure the H₂ slip from a H₂/diesel dual-fuel truck under real-world operating conditions.
- With the developed method, try to characterize the in-use H₂ slip of the truck and to find the relation between the H₂ slip and engine operating conditions.

Chapter 3 addresses these objectives with a low-cost exhaust H_2 measurement for an in-use H_2 /diesel dual-fuel truck.

2.4.2 Objectives for Chapter 4

The effects of biodiesels on engine emissions have been studied extensively in literature but mainly on light-duty diesel engines and in steady laboratory test settings. Real-world emission data from heavy-duty marine engines is limited and transient test data is lacking. To measure the engine emissions under real-world operating conditions, mature technologies are available for criteria pollutants (e.g. CO₂, NO_x, CO, and PM), and the instruments using these technologies can be integrated into a PEMS to conduct measurements on the in-use vessel.

The objectives of the second project in this thesis include:

- Evaluate the effects of two biodiesels, namely SME and CME, on the steady-state emissions (including CO₂, CO, NOx, PM, and PN) of the marine engine in diesel operation mode, as compared to diesel.
- Characterize the emissions (including CO₂, CO, NOx and PM) of the marine engine during transient operations (i.e. load increases) in diesel operation mode. Compare the effects of diesel, SME, and CME on the transient emissions.
- Evaluate the effects of the two biodiesels on the steady-state emissions (including CO₂, CO, NOx, CH₄, and PM) of the engine when used as the pilot fuel in gas mode, as compared to diesel.

These objectives are addressed in Chapter 4, where the in-use emissions from a dual-fuel marine vessel operating under both diesel mode and gas mode with diesel, SME, and CME are characterized and compared.
Chapter 3

Measurement of the In-use H_2 Emission of a $H_2/Diesel$ Dual-Fuel Truck

In this chapter, a low-cost method is developed to measure the H_2 slip in the exhaust of a heavy-duty truck (Figure 3.1) under real-world operating conditions. The truck is equipped with a 2016 15 L Detroit diesel engine retrofitted to run in dual-fuel mode with port-injected H_2 ignited by directly injected diesel. The unburned H_2 fuel will result in H_2 slip in the engine exhaust, which indicates poor fuel economy and deteriorates engine efficiency. The H_2 /diesel injection ratio was calibrated according to engine speed and torque. With the developed method, H_2 slip can be characterized for different engine operating conditions. A relation between the H_2 slip and engine operating condition can be established with the measurement results. Section 3.1 describes the setup of the measurement system. Section 3.2 introduces the data processing methods. Road test results are discussed in Section 3.3. Conclusions are summarized in Section 3.4.



Figure 3.1: A picture of the used hydrogen dual-fuel truck

3.1 Measurement system setup

In order to measure the in-use H_2 emission of the truck in real-world on-road tests. A measurement system has been set up utilizing a low-cost H_2 sensor and a self-developed PEMS. This section describes the development of this measurement system.

3.1.1 H_2 sensor selection

 H_2 sensors are transducer devices that detect H_2 molecules and produce an electrical signal with a magnitude proportional to the H_2 gas concentration [74]. Compared with the conventional H_2 detection methods such as chromatography, H_2 sensors have several advantages including their low cost, faster response, and smaller size. These advantages make them suitable for on-road tests.

Sensor selection depends on the particular requirements of in-use vehicle measurements. In our measurements, the sample gas is sampled from the exhaust pipe of the truck and can be diluted by dried compressed air to lower the H_2 concentration as well as to prevent condensation in the sampling line. Four critical parameters must be considered when selecting the H_2 sensor:

(1) Measurement range: A previous study on a similar truck equipped with the same H_2 injection system used gas chromatography method to measure the H_2 concentration in the exhaust. The H_2 concentration in the raw exhaust was found to vary between 0-20,000 ppm. To prevent condensation in the sampling line, the dilution ratio needs to be set above 15:1. In practice, the dilution ratio was set to approximately 20:1. Thus, the estimated H_2 concentration range is 0-1,000 ppm for diluted samples.

(2) Response time: In order to resolve the transient emission data, a short response time is desired. A typical response time for a PEMS system is expected to be within 1s. Although some literature has reported a response time within this range, none of the commercially available H_2 sensors identified in this work can meet this requirement. The shortest response time reported by the sensor supplier is less than 4s. It should be noted that the actual response time of a sensor may also be influenced by test conditions and thus were determined experimentally in the road tests.

(3) Cross-sensitivity: The presence of CO, NO and HC in the exhaust gas must be considered as many of the H_2 sensors are susceptible to reducing gases. The cross-sensitivity to CO is a general issue for almost all the available H_2 sensors. However, the concentration of CO in the diesel exhaust is expected to be low because of the global lean combustion. With a dilution ratio of 20:1, the concentration of CO in the sample gas is estimated to be within 100 ppm. This value is low enough for some of the H_2 sensors to neglect its cross-sensitivity.

(4) Gas environment: The raw exhaust from a diesel engine varies in terms of temperature, relative humidity, and oxygen concentration. However, the high dilution air ratio (20:1) will constrain these variations within a small range, especially will result in an oxygen concentration close to the air. This will exclude some sensors which require lower O_2 concentrations. Meanwhile, it also makes the dependence on O_2 concentration negligible for some sensors, such as the semiconducting metal-oxide sensor.

To summarize, the H_2 sensor for this study should fulfill these requirements: 1) can detect H_2 in a concentration range of 1-1,000 ppm; 2) have a response time within or close to 1 second; 3) present no cross-sensitivity to NO and HC, and minor sensitivity to CO in less than 100 ppm; 4) can operate in gases with an O₂ concentration similar to the air.

Considering these criteria, only resistance-based sensors and work functionbased sensors are the viable options. Taking the cost into account, we chose the MQ-8 semi-conductor sensor which can meet most of the requirements at a very low cost [75]. A picture of this sensor is shown in Figure 3.2.

The sensor's resistance (R_s) changes with varying H₂ concentrations and the dependence can be approximated by the formula

$$R_s/R_0 = aC_{H_2}^b \tag{3.1}$$

where R_0 is the sensor's resistance in clean air, a and b are sensor-specific



Figure 3.2: A picture of the MQ-8 H_2 sensor (sensor housing was removed to show its circuit structure)

constants, and C_{H_2} is the H₂ concentration in the sample gas.

In order to record the changes in R_s , a test circuit (Figure 3.3) is used to convert the change in R_s into the change of the voltage on the load resistor (R_L) . A 5 V heater is used to heat up the sensor to a certain temperature to ensure the activation of the semi-conduction material. In the next step, the sensor's characteristics, such as the sensitivity to temperature, humidity, and other potential influencing factors, will be verified in a benchtop test.

3.1.2 H₂ sensor verification test setup

To quantitatively understand the critical characteristics of the H_2 sensor, verification tests were done on the bench. These benchtop tests serve for two purposes: (1) control independently each of the potential influencing factors including preheating time, flow rate, temperature and RH to investigate their influences; (2) use standard H_2/N_2 mixture gas with known H_2 concentration to calibrate the sensor, namely to find out the constants in equation 3.1.

Figure 3.4 shows the apparatus of the benchtop test for the H_2 sensor: Compressed air is used as the zero standard. An inline desiccant dryer is used to remove the water content from the compressed air. The dried air then passes through a heated tube. A heater connected with a PID controller can maintain the gas at desired temperatures. The flow rate of the heated gas is



Figure 3.3: Test circuit of the MQ-8 H₂ sensor (V_H : Heater voltage, V_c : Circuit voltage, R_L : Load resistor, V_{RL} : Load resistor voltage, 1/3/4/6: sensor pin, 2/5: heater pin)

controlled by a rotameter set after the heated tube. Finally, the flow passes through a cross fitting where a MQ-8 H_2 sensor and a temperature/RH transducer are installed. A surface-mounted thermocouple is attached to the housing of the H_2 sensor to monitor the sensor's surface temperature. The tubing starting from the entrance of the heated tube to the exhaust is thermal insulated to ensure constant gas temperature.



Figure 3.4: H₂ sensor verification test apparatus diagram

3.1.3 Verification of the influencing factors of the H_2 sensor

Using the test setup described above, we were able to control each of the potential influencing factors independently to investigate the significance of their influences. Four of the critical factors are verified here:

(1) Preheating time. The sensor is heated by an internal heater to maintain its temperature in order to produce a stable output. To find the required preheating time for the H₂ sensor, we continually monitored the R_0 , which is an indicator of the sensor element's temperature, for 2 hours after turning on the heater. During this process, gas flow rate, temperature and RH were held constant. It was found that R_0 dropped when the heater was powered on and R_0 stabilized after approximately 20 minutes, as shown in Figure 3.5 (1). To account for different starting temperatures, a preheating time of 30 minutes is suggested to ensure the stability.

(2) Flow rate. As heat can be transferred by both conduction and convection between the gas and the sensor, the velocity of the flow can affect the temperature of the sensor. Moreover, mass transfer between the sensor and the gas is also dependent on flow velocity. In the benchtop test, flow rate was changed by adjusting the rotameter. R_0 values are compared under different flow rates ranging from 0-5 lpm in Figure 3.5 (2) R_0 dropped significantly as flow was increased from 0 to 2 lpm. However, further increasing the flow rate, the change in R_0 was within 3%. This implies that R_0 should be measured with a stable flow rate higher than 2 lpm. The flow rate was maintained at 4.5 lpm in the other tests.

(3) Temperature. The temperature of the semiconductor material can influence the R_0 . However, this temperature cannot be measured directly. Instead, two temperatures were monitored during the test: flow temperature, which was measured by a Dwyer 657 RH/temperature transducer at the cross fitting, and sensor surface temperature, which was measured by a thermocouple mounted on the surface of the sensor's housing. It was found that the differences between these two temperatures were nearly constant during the test. Thus, only flow temperature was used as an indicator of the sensor temperature. Figure 3.5 (3) shows the changes in R_0 under varying flow temperatures. As the temperature increased from 10 to 50 °C, the change in R_0 was within 2%. During regular weather conditions, the temperature of the diluted exhaust sample in an on-road test is between 30-40 °C. Variation of R_0 in this temperature range is thus negligible.

(4) Relative humidity. As water is a product of the oxidation reaction of H_2 , the water content in the exhaust sample can affect the sensor's response to H_2 gas. Here we wanted to find out if RH also affects the R_0 . The

humidity of the air was changed by replacing the dryer with a sealed box containing a wet sponge. The sensor was tested in a RH range between 15% - 35%. Figure 3.5 (4) shows that R_0 dropped significantly as RH increased. In order to ensure a stable R_0 , the water content of the exhaust sample should be controlled or compensated. Because the correlation between R_0 and RH is unclear, we chose to dry the sample air completely to exclude this influencing factor.



Figure 3.5: H₂ sensor verification test results: (1) R_0 variation during the first 30 minutes of preheating; (2) R_0 under different air flow rates; (3) R_0 under different air temperatures; (4) R_0 under different air humidities

3.1.4 H₂ sensor calibration

After verifying the factors influencing R_0 , a bottle of H_2/N_2 mixture with a standard H_2 concentration of 1% was used to assess the sensor performance with H_2 . The H_2/N_2 mixture was mixed with compressed air to obtain a range of H_2 concentrations. The flow rates of the H_2 mixture and the

compressed air were controlled by two Alicat mass flow controllers with an accuracy of $\pm 0.2\%$.

As the first step, one sensor was tested under seven different H₂ concentrations spanning from 100 to 1,500 ppm to verify the linearity between $log(R_s/R_0)$ and $log(C_{H_2})$. The results are shown in Figure 3.6. Then, other sensors were calibrated using only two points to find out the constants *a* and *b* in Equation 3.1 for each individual sensor.



Figure 3.6: The linear relation between $log(R_s/R_0)$ and $log(C_{H_2})$ verified in the calibration test

Figure 3.7 (1) shows the calibration curve for the sensor used in the final road test. With the linear correlation found in this figure, we can determine the two constants in Equation 3.1: a=54.95, b=-1.24. Figure 3.7 (2) compares the measuring results of this sensor with the standard H₂ concentrations. At low concentration (480 ppm), the measured value has a difference of -7% compared with standard concentration. At high concentration (1440 ppm), the difference is -14%. For both concentrations, the standard errors of the mean value are within 0.5%.



Figure 3.7: Calibration results for the chosen H₂ sensor: (1) the correlation between $log(R_s/R_0)$ and $log(C_{H_2})$ determined with two data points; (2) the measured H₂ concentration from the sensor compared with the standard H₂ concentration

3.1.5 Portable emission measurement system

From the benchtop test, we had understood the characteristics of the H_2 sensor in clean air as well as the sensor's responses to different H_2 concentrations. In order to implement measurements on the truck with this sensor, a portable emission measurement system (PEMS) was developed to: (1) dilute the raw exhaust gas with a required dilution ratio and transfer the diluted sample to the H_2 sensor at a constant flow rate; (2) prevent condensation in the sampling line and remove the water content from the sample gas; (3) log the measurement data in a Data Acquisition (DAQ) system.

As shown in Figure 3.8, the diluted exhaust is filtered by a HEPA filter and then dried by an in-line desiccant drier before arriving at the H₂ sensor. This direr ensures the RH of the sample to be 0%. A temperature/RH transducer is installed before the H₂ sensor to monitor the temperature and RH of the diluted sample. The flow rates of MFC 1, 2 and 3 are set as 19 slpm, 4.5 slpm and 15.5 slpm respectively, such that the dilution ratio is 20:1. The system can be purged with dilution air by setting the flow rate of MFC 1 higher than 20 slpm.



Figure 3.8: Schematic diagram of the PEMS : MFC 1, 2 and 3 control the flow rates of compressed air, H_2 sensor and bypass respectively



Figure 3.9: A picture of the self-developed PEMS

3.2 Data acquisition and processing method

The resistance of the H₂ sensor (R_s) changes with H₂ concentration in the sample stream as described in equation 3.1. The change of R_s is reflected by the change in V_{RL} , which is logged with a Raspberry Pi HAT MCC118 [76] at a frequency of 4 Hz. Rs can be calculated from V_{RL} by:

$$R_s = (V_c/V_{RL} - 1)R_L (3.2)$$

where V_c , R_L are constant values measured on the test circuit.

Combining Equation (2) with Equation (1), the H₂ concentration C_{H_2} [ppm] in the sample gas is:

$$C_{H_2} = \left(\frac{R_s}{aR_0}\right)^{1/b} \tag{3.3}$$

 R_0 is a constant value decided by measuring sensor resistance in the clean air. The R_0 needs to be checked before every test by purging the PEMS with clean compressed air.

 H_2 slip rate $\dot{m}_{H_2,slip}$ [kg/hr] can be calculated with:

$$\dot{m}_{H_2,slip} = C_{H_2} \frac{M_{H_2}}{M_{exh}} \dot{m}_{exh}$$
(3.4)

where M_{H_2} and M_{exh} are the molar weights of H_2 and the exhaust, respectively. M_{exh} is approximated with a constant value of 29 g/mol, same as the air.

The mass flow rate of exhaust, \dot{m}_{exh} , and the hydrogen injection rate, $\dot{m}_{H_2,inj}$, are read from the truck's CAN messages. This H₂ injection rate is provided by the control unit of the hydrogen injection system.

The ratio of H_2 slip rate and the H_2 injection rate is calculated to obtain the percentage slippage of H_2 :

$$slippage(\%) = \frac{\dot{m}_{H_2,slip}}{\dot{m}_{H_2,inj}} \times 100 \tag{3.5}$$

Engine brake torque, T, can be calculated by dividing the drive shaft torque, T_{shaft} , which was measured by a torque transducer mounted on the drive line, by the gear ratio GR:

$$T_{brake} = \frac{T_{shaft}}{GR} \tag{3.6}$$

Data including engine speed, gear ratio, drive line engagement and transmission shift status are all available from the truck's CAN messages. These data are used to filter out the conditions when torque calculations are invalid. These conditions include: drive line unengaged, transmission in process, and negative gear ratios. Data under these conditions are excluded in the processing procedures to generate the H_2 slip map. As a necessary assumption for simplicity, gearbox efficiency is considered as 100%.

3.3 On-road test results and discussion

The developed measurement was used to measure the in-use H_2 emission from the test truck. This section will describe and analyze the test data from the on-road tests.

3.3.1 Exhaust H₂ concentration of the in-use truck

Figure 3.10 shows the variation of exhaust H_2 concentrations measured by the H_2 sensor in an H_2 /diesel dual-fuel mode on-road test. These concentrations are corrected by the dilution ratio. In a general sense, we can see that the system is capable of capturing the variation of H_2 concentrations in the truck's exhaust. The consistency between the H_2 emission and the H_2 injection rate can be observed. However, in order to use this data for further analysis, the latency of the sensor's response should be determined first.



Figure 3.10: Time series plot of the dilution ratio-corrected exhaust H_2 concentration (black curve) and the H_2 injection rate (blue curve) during an on-road test of a heavy-duty truck running in a H_2 /diesel dual-fuel mode

The sensor's latency is the time lag between the time H_2 leaves the exhaust port of the engine (t_{ex}) and the time H_2 is detected by the sensor (t_{dt}) . As the combustion time interval in the cylinder is comparably short, we can assume t_{ex} is the injection time of H_2 . Hence, the latency is:

$$\tau = t_{dt} - t_{ex} \tag{3.7}$$



Figure 3.11: Examples of detected H_2 concentrations in response to: (a) increasing H_2 concentration; (b) decreasing H_2 concentration

The total latency τ can be found by comparing the rising or falling edge of the H₂ injection rate and the exhaust H₂ concentration in time series plots. As can be seen from Figure 3.11a and 3.11b, the sensor responded very differently to rising and falling H₂ injection rates. Noted that these figures are only presented as an example of determining the latency. In fact, the latency is not a constant value through the test, as it can be affected by many factors such as flow rate, temperature, or gas compositions. The adopted sensor latency is determined by averaging the time lags in many different scenarios. For responses to increasing H₂ injection rates, a latency of 4.5 s is used. For decreasing H₂ injection rates, the latency is too long to account. Due to this reason, the periods including falling H₂ injection edges will be excluded for generating H₂ slip maps.

3.3.2 H_2 slip maps

Figure 3.12 shows the H_2 slip maps generated from the data collected on the truck running in dual-fuel mode for 1 hour under typical on-road conditions. The gray scale of each bin indicates the dwell time the engine operates at each speed and torque region. The color of the red lines indicates the H_2 concentration [ppm] and slippage [%] at this region. The dashed black line on the top is the maximum brake torque curve of the engine.

From Figure 3.12 (1), we can find that the highest H_2 concentration (14,000 ppm) occurred at speed regions over 1500 rpm for medium-to-high engine torque. This aligns with the high H_2 slippage rate (54%) in that region in Figure 3.12 (2). However, the dwell time of the engine in this region is nearly zero, which means the data for this operation region is very limited. This is because that a big proportion of the data in this region was removed due to the long response time. It implies that a reduction in H_2 injection rate is decided by the engine's operating condition and has been quantified during the H_2 injection system calibration. However, the injection map of the H_2 system is inaccessible to us for confidential reasons. This unfortunately limits the further explanation and verification of these findings.

An increasing H_2 slip trend can be observed with increasing engine speed and increasing engine load. At the 1200 rpm and 1200-1600 Nm region, where the engine operated most frequently, the H_2 slip was at a relatively low level, namely 3500-7500 rpm or 9% relative to H_2 injection rate. This indicates that the engine operated efficiently at its frequently encountered conditions. However, it should be noted that these H_2 slip maps are not complete since some important operating conditions, including idling and gear transition, were not included. Furthermore, some of the operating conditions (e.g. low load and high speed) shown in these maps might be rarely encountered in typical operations. These shortcomings presented the limitations of the method for evaluating H_2 slip for in-use vehicles.



Figure 3.12: In-use H_2 slip maps of the measured truck: (1) H_2 slip in concentration [ppm]; (2) percentage H_2 slippage [%]

3.4 Summary and conclusions

In this chapter, a method was developed aiming to measure the H_2 slips from a H_2 /diesel dual-fuel truck under real-world operating conditions. This method utilized a low-cost semi-conductor sensor, which could give the H_2 concentration in a range of 1-1000 ppm. A PEMS was designed to control the flow rate, dilution ratio, and the RH of the sample gas to ensure stable output of the sensor. With the developed method, 1 hour of on-road test data was collected for the truck during road tests in real-world city traffic conditions. System latency was determined by comparing the time series plots of the exhaust H_2 concentration and the H_2 injection rate. It was found that the system responded to an increasing H_2 concentration in approximately 5s; However, its response time for a decreasing H_2 concentration was longer than 100s. Data processing was implemented to synchronize the exhaust H_2 concentration and the H_2 injection rate and to remove the proportions with long latency. Finally, H_2 slip maps were generated which provided preliminary insights into the in-use H_2 slip characteristics of the truck.

Following conclusions can be drawn from this work:

- With a low-cost semi-conductor H_2 sensor, the developed PEMS was able to capture the variations of H_2 concentration in the engine exhaust. The results generally showed consistency with the injected H_2 flow rates.
- During highly transient conditions, particularly when the injected H_2 flow rate abruptly decreased, this system responded to the decreasing H_2 concentration slowly (>100s). This resulted in inaccuracy of the measurement system. Though data processing could be done to remove these conditions, the processing would remove some important operating conditions of the engine and result in an incomplete H_2 map.
- Overall, the developed method was able to provide rudimentary results of the in-use H₂ slip for the vehicle in a low cost. To achieve higher accuracy, a more advanced measurement system with faster response time and more precise calibration is desired. In addition, to obtain a more representative H₂ slip map, more road test data needs to be collected, system latency can be more accurately determined, and data exclusion criteria can be improved.

Chapter 4

Characterization of the In-use Emission from a Dual-Fuel Marine Vessel Fueled with Biodiesels

Biodiesels are a common substitute for diesel in CI engines. As the feedstocks of biodiesels vary, the properties of the biodiesels are different, which results in changes in engine performances and emission characteristics. To evaluate the effects of two common types of biodiesels, namely SME and CME, on engine emission, this chapter describes the implementation and the results of an emission measurement campaign conducted on a marine vessel, which was powered by a dual-fuel engine fueled by diesel and biodiesels. The evaluations include: (1) The effect of using the biodiesels as the liquid fuel in diesel mode on engine emission, as compared to diesel; (2) The emission characteristics of the engine under transient operations with the different fuels; (3) The effect of using the biodiesels as the pilot fuel in gas mode on engine emission, as compared to diesel. The methodology used in this measurement is introduced in Section 4.1. Data processing methods and error analysis are described in Section 4.2 and 4.3, respectively. Section 4.4 discusses the engine parameters as well as the emission characteristics for the different fuels under diesel mode steady state, diesel mode transient operation, and gas mode steady state, respectively. Finally, conclusions are summarized in Section 4.5.

4.1 Experimental

This section describes the methodology of the measurement campaign. First, important parameters of the measured vessel and its engine will be introduced. Then, the fuels used in this campaign will be discussed. The measurement system will be described next, and the test cycles will be introduced at last.

4.1.1 Measured vessel and engine information

The measured vessel, Seaspan Reliant, is an A-class cargo ferry built in 2016. It has a carrying capacity of 4810 Gross Tonnage and a summer deadweight of 2767 t [77]. Its main propulsion system consists of two NG/diesel dual-fuel engines coupled with constant-speed generators. The combination can produce 9000 kW of power at constant speed of 750 rpm under dual-fuel mode [78]. In this campaign, the emissions from one of the two engines were measured, while the other engine provided operational stability for the vessel. In a previous unpublished work, the engines were found to have very similar emission characteristics. Hence, the tailpipe emissions from the vessel under bi-engine operations could easily be estimated if the emissions of a single engine under a certain load condition is known.

Important parameters of the engine are listed in Table 4.1. This engine was equipped with a turbo charger and without an EGR system. The exhaust gas was sampled downstream of the turbo charger. Two different fueling modes were considered: In diesel mode, the engine was fueled with directly injected diesel or biodiesel at a fixed injection timing; In gas mode, NG was the primary fuel and was injected into intake port, and later ignited by a small amount ($\sim 2\%$ of total energy content) of diesel or biodiesel. The injection timing of the pilot fuel was controlled by the stock ECU. Unfortunately, detail information of the engine mapping was inaccessible.

Parameters	Specification
	-1
Number of Cylinders	9
Stroke	4
Diesel Fueling	Direct injection
NG Fueling	Port injection
Ignition	Compression ignition
Displacement [L/cyl]	36
Mean piston speed [m/s]	10

Table 4.1: Specifications of the measured engine



Figure 4.1: A picture of the measured vessel- Seaspan Reliant [79]

4.1.2 Test fuels

As mentioned in Section 2.2.1, SME and CME are two most common biodiesels in North America. In this campaign, engine operation with SME, CME, and one reference diesel fuel was considered. Some selected properties of the three fuels are listed in Table 4.3. The labels used for the different fuels are summarized in Table 4.2. The baseline diesel originally contains approximately 5% of biodiesel content. For simplicity, it is labeled as "D100" in this thesis. SME and CME are pure biodiesels and are labeled as "SB100" and "CB100", respectively. To qualitatively evaluate the effect of blending fuels, a blend of 80% SME and 20% diesel by volume was tested and labeled as "SB80". In addition, a commercial fuel additive (Aderco 2055G) was applied to the SME100, and this combination is label as "SBAdd". As the chemical composition and the volumetric ratio of the additive in the SBAdd were unknown, this test was only to provide a qualitative evaluation of the effect of the fuel additive. The biodiesels and diesel were stored in separated day tanks on the vessel which prevented the mixing of the fuels.

Table 4.2: Labels of the test fuels

Labels	Fuel content
D100 (baseline)	100% Diesel
SB100	100% SME
SB80	80% SME + 20% Diesel
SBAdd	100% SME + Fuel additive
CB100	100% CME

Another important factor for evaluating the fuels is the GHG emissions across the entire life cycle of their production and use. Life cycle assessment (LCA) is a commonly used approach to quantify these effects. A typical LCA includes activities related to feedstock production, fuel production, transportation, distribution, and combustion of the fuel. This study didn't conduct an actual LCA for the test fuels. However, literature [80] has reported that biodiesels produced from soybean and canola generally have lower life cycle GHG emissions than petroleum diesel (Figure 4.2).

Table 4.3: Selected properties of the test fuels (data provided by the industrial partner)

Properties	Units	D100	SB100	CB100	Test method
Viscosity at 40 $^\circ C$	mm^2/s	3.6	4.3	4.7	ASTM D7042
Density at 15 $^\circ C$	${\sf kg}/{\sf m}^3$	848.86	884.01	884.39	ASTM D4052
Cetane Index	-	51.2	56.9	55.8	ASTM 6890
Sulfur Content	mg/kg	40	2.5	4	ASTM D5453
Ash Content	mass%	0	0	< 0.005	ASTM D874
Calorific Value at 25 $^\circ C$	${\sf MJ/kg}$	45.49	39.95	40	ASTM D4809



Figure 4.2: GHG emissions (g CO_2e/MJ fuel) for canola, soybean, yellow grease, and tallow neat biodiesel (B100) by life cycle stage[80]

4.1.3 Instrumentation

An on-board measurement system was implemented on the vessel to measure the engine-out exhaust. A schematic diagram of the measurement system is shown in Figure 4.3. Two streams were sampled separately from the exhaust pipe through a flange: Stream 1 was heated to prevent condensation and filtered by a particulate filter to remove the PM in the raw exhaust; Stream 2 was diluted by clean compressed air. The volumetric concentrations of gaseous species, mass or number concentrations of PM, and some engine parameters were measured and recorded by various instruments.

A portable multi-gas analyzer (ECOM J2KN Pro) was used to measure the gaseous species including CO₂, CO, NOx, CH₄, and O₂ in the filtered stream (stream 1). The ECOM integrates multiple gas sensors as listed in Table 4.4. An internal cooler condenses the water content in the heated sample gas and ensures the sample gas dry before entering the sensors. In this way, the ECOM measures the dry-basis concentrations of the pollutants. Each of the sensors in the ECOM was calibrated with standard gas bottles before the starting of a measurement to ensure accuracy. The test data of the ECOM was recorded continuously at 1Hz at its internal memory during the measurements.

An FTIR (Bruker MATRIX-MG5) was used to measure CO_2 , CO, NOx, CH_4 , and H_2O concentrations in stream 1 simultaneously with the ECOM.



Figure 4.3: Schematic diagram of the measurement system

FTIR measures by the principle of absorption spectroscopy and uses Fourier transform to obtain a wide range of spectrum at the same time. Liquid nitrogen was used to cool the photoelectric detector, which enables fast response time. A 20 s average concentration was provided by the FTIR.

Stream 2 was diluted in order to match the PM concentration to the detection range of the instrument (TSI DustTrak). The dilution ratio (DR) of stream 2 was controlled with 3 Mass Flow Controllers (MFC). The DR was then set as the ratio of the total gas flow rate versus the raw exhaust sample flow rate. This ratio was ultimately determined by the ratio of undiluted CO_2 concentration (measured by the ECOM) and the diluted CO_2 concentration (measured by an infrared analyzer, LICOR). DR typically ranged between 4:1 to 9:1 depending on the actual PM mass concentration.

PM mass concentration in the diluted sample was measured by a 90° light scattering aerosol monitor (DustTrak II 8530). The DustTrak II provides the total PM mass concentration (mg/m³) for particles in the size range of approximately 0.1-10 μm . It is a simple and compact instrument with high sensitivity and time resolution. However, the correlation between scattering and particle mass density is a strong function of particle size and refractive index [81]. As particle size distributions and particle compositions in diesel exhaust may vary as engine operating conditions change, the calibration of DustTrak II may vary as well. To validate the PM concentration



Figure 4.4: A real picture of the measurement system for the vessel emission campaign

results, gravimetric samples were collected in parallel using $2\mu m$ PTFE filters. These filter samples were weighed before and after the measurements in a temperature/humidity-controlled microbalance room to obtain the mass of the PM collected. The comparison between DustTrak PM concentrations and gravimetric sample results are given in Appendix A.

Particle number (PN) concentrations as well as particle size distributions were measured by an Electrical Low Pressure Impactor (Dekati ELPI+). In the ELPI+, the particles were first charged into a known charge level in a corona charger, and then size classified in a low-pressure cascade impactor according to their aerodynamic particle size. Real-time particle size distributions in 14 size fractions ranging from 6 nm to 10 μ m were provided by the ELPI+. The raw data from ELPI+ were currents from each stage. The raw currents were recorded at 1 Hz in its memory and later used to calculate number or mass concentrations through processing.

Some engine performance parameters were measured and monitored in

Emission Parameter	Instruments	Model
CO ₂ (raw) [%]	IR sensor	ECOM J2KN
CO_2 (diluted) [%]	NDIR	LICOR 820
NOx (raw,dry) [ppm]	Electrochemical sensor	ECOM J2KN
NOx (raw,wet) [ppm]	FTIR	Bruker MATRIX-MG5
CO (raw,dry) [ppm]	Electrochemical sensor	ECOM J2KN
CO (raw,wet) [ppm]	FTIR	Bruker MATRIX-MG5
CH_4 (raw,dry) [ppm]	IR sensor	ECOM J2KN
CH_4 (raw,wet) [ppm]	FTIR	Bruker MATRIX-MG5
H_2O (raw) [%]	FTIR	Bruker MATRIX-MG5
PM concentration (diluted) $[mg/m^3]$	Light scattering	Dusttrak II 8530
PM weight (diluted) $[\mu g]$)	Gravimetric sample	MTL PT47DMCAN
PN concentration (diluted) $[\#/cm^3]$	ELPI	Dekati ELPI+
Engine operating parameter	Instruments	Model
Engine load [kW]	Vessel	-
Exhaust temperature [°C]	Thermocouple	-
Exhaust flow pressure [Pa]	Pitot tube + Manometer	Fluke 922
Equivelence ratio	UEGO	Bosch LSU 4.9

Table 4.4: Measured parameters and their measuring instruments

the system. Engine load was recorded by the vessel system from the generator output. A pitot tube connected with a Manometer (Fluke 922) measured the differential pressures in the exhaust stream, which was used to calculate the exhaust volumetric flow rate. Exhaust temperature was monitored by a thermocouple during the measurements. The exhaust temperatures were used to calculate the density of the exhaust stream based on ideal gas law. For steady-state measurements, the variation in exhaust temperature was required to be within 3°C. Excess air ratio was recorded by means of a universal exhaust gas oxygen sensor (UEGO, Bosch LSU 4.9). A summary of all measured parameters and their measuring instruments are listed in Table 4.4. All the signals except FTIR results were logged using an NI data acquisition system at a frequency of 1 Hz.

4.1.4 Test cycles

In-use emission tests were carried out on the vessel during regular operational sailings and sea trials in coastal waters. Measurements were done under steady states or transient operations. The steady-state measurements were taken at loads of 10%, 25%, 50%, 75% and 90% of maximum power, each for a duration of 5-10 min. Before recording the steady state data, the variation in engine load was checked to be within 1 Nm, and that in engine exhaust temperature was required to be within 3° C.

The transient test consisted of 3 consecutive load increase scenarios: 10-90%, 10-50%, and 50-90% in a time duration of approximately 100 s, 50 s, and 50 s, respectively. The duration of each transient test represents the shortest duration permitted by the power management system. It should be noted that these transients were significantly more aggressive than those encountered during typical vessel operation. The test sequence was repeated three times for each fuel. The load was controlled by the vessel operator during the transient tests. In addition, to exclude the potential influences from the battery banks used for load balancing, the power management system of the vessel was shut down during the transient tests.

To prevent the influence of cold start, all measurements were taken at least 1 hour after engine started. In addition, because increased emissions had been observed upon fuel switching during the sailing, the measurements were required to be taken at least 2 hours (~ 4 hours in most cases) after fuel switching. For each fuel type and fueling mode, a dedicated sea trial was carried out to ensure no fuel switching happened during the measurements. The fuel types and testing conditions considered for each mode are summarized in Table 4.5.

Fueling mode	Test condition	Load mode	Fuel type
Diesel mode	Steady state	10%, 25%, 50%, 75%, 90%	D100, SB100, SB80
			SBAdd, CB100
	Transient	10-90%, 10-50%, 50-90%	D100, SB100, CB100
Gas mode	Steady state	10%, 25%, 50%, 75%, 90%	D100, SB100, CB100

Table 4.5: Summary of test conditions considered in this campaign

4.2 Data processing

In order to compare the emissions under various engine loads between different fuels, brake specific emission factors (g/kWh) were required. The raw data from the exhaust analyzers include volumetric concentrations of the gaseous pollutants and mass/number concentrations of the PM. To convert the raw concentrations to specific emissions, exhaust flow rate is needed, which can be calculated from the pitot tube data. This section describes the calculations involved in these conversion processes.

4.2.1 Engine load

Generator powers (P_{gen}) were recorded from the vessel system. In order to compute the engine brake power (P_b) , generator efficiencies (η_{gen}) were applied according to a pre-stored table. P_b were calculated by Equation 4.1.

$$P_b = \frac{P_{gen}}{\eta_{gen}} \tag{4.1}$$

Engine load in percentage was then calculated with Equation 4.2.

$$Load = \frac{P_b}{P_{max}} \times 100 \tag{4.2}$$

where P_{max} is the maximum output power of the engine (4320 kW).

4.2.2 Excess air ratio (λ)

Excess air ratio λ is an important parameter which describes the richness of the fuel/air mixture and affects engine combustion and emissions. It is calculated by:

$$\lambda = \frac{(m_a/m_f)_{actual}}{(m_a/m_f)_{stoich}} \tag{4.3}$$

where m_a and m_f are the inducted air and fuel masses, respectively, and "stoich" refers to the stoichiometric condition.

The univeral oxygen sensor used in this campaign was pre-calibrated based on the fuel setting of CH₄. Thus, its outputs were considered to be accurate only for the gas mode. As an alternative way, λ can be calculated from exhaust gas compositions (CO₂, O₂, and CH₄). To do this, the C/H ratio of the fuels need to be known. While typical formulas for diesel and natural gas are available, the formula for biodiesels varies as the specific fatty acids contained in them. It was assumed as C₁₈H₃₂O₂ (linoleic acid),

Table 4.6: Chemical formulas and stoichiometric A/F ratios for the three different fuels

Fuel	Formula	Molecular weight (g/mol)	Stoichiometric A/F
Diesel	$C_{12}H_{23}$	167	14.5:1
Biodiesel	$C_{18}H_{32}O_2$	280	12.3:1
NG	CH_4	16	17.2:1

which is a typical content in oil-derived biodiesels [82]. As a simplification, SB80 and SBAdd were assumed to have the same chemical composition as SB100. The formulas and stoichiometric A/F ratios of these fuels are listed in Table 4.6. Details of the λ calculation can be found in Appendix C.

4.2.3 Exhaust gas flow rate

A pitot tube positioned at the center line of the exhaust duct was used to measure the pressure difference between the static and dynamic pressure (ΔP) at the exhaust pipe centreline. Centreline flow velocity (v_c) can be calculated by Equation 4.4.

$$v_c = c_p \sqrt{\frac{\Delta P}{\rho_{ex}}} \tag{4.4}$$

where c_p is the pitot tube coefficient based on calibration, and ρ_{ex} is the density of exhaust gas, which can be estimated by ideal gas law. Exhaust pressure is assumed to be the same as the atmospheric pressure, and the exhaust gas molecular weight (M_{ex}) is estimated with the concentrations of CO_2 , H_2O , O_2 , and CH_4 .

Average velocity, v_m , is calculated from the velocity profile of a turbulent pipe flow as in Equation 4.5 [83, chapter 6].

$$v_m = \frac{v_c}{1 + 1.3\sqrt{f}} \tag{4.5}$$

where f is the friction factor which can be decided with exhaust gas Reynolds number, Re. Ideally, this is a iterative process since Re and v_m are dependent. However, calculations suggested that the combination $1+1.3\sqrt{f}$ varies in a very narrow range with the calculated v_m . For simplicity, a constant fvalue (0.04) was used here as an approximation.

Then, exhaust gas volumetric flow rate (Q_{ex}) can be calculated with v_m and pipe diameter (D), by:

$$Q_{ex} = v_m \pi (D/2)^2$$
 (4.6)

Exhaust gas mass flow rate can (\dot{m}_{ex}) be calculated from the volumetric flow rate (Q_{ex}) and the exhaust gas density (ρ_{ex}) .

4.2.4 Brake specific fuel consumption

The brake specific fuel consumption (BSFC) rates could not be measured directly. Instead, they were estimated with exhaust emission data. For an arbitrary fuel composition of $C_x H_y O_z$, the fuel consumption rate (\dot{m}_f) can be calculated from formula 4.7.

$$\dot{m}_f \frac{12x}{12x + y + 16z} = \dot{m}_{CO_2} \frac{12}{44} + \dot{m}_{CO} \frac{12}{28} + \dot{m}_{CH_4} \frac{12}{16}$$
(4.7)

where \dot{m}_{CO_2} , \dot{m}_{CO} , and \dot{m}_{CH_4} are the mass flow rates of exhaust CO_2 , CO, and CH_4 , respectively. Then, BSFC can be calculated by:

$$BSFC = \frac{\dot{m}_f}{P_b} \tag{4.8}$$

4.2.5 Specific emissions

For gaseous species, raw emission data from the instruments were volumetric concentrations (C_i) , where *i* indicates a specific species. Note that the drybasis concentrations $(C_{i,d})$ from the ECOM need to be converted to wet-basis concentrations $(C_{i,w})$ by:

$$C_{i,w} = C_{i,d}(1 - C_{H_2O}) \tag{4.9}$$

The wet-basis concentrations were converted to brake specific emission (BSE_i) using Equation 4.10.

$$BSE_{i,g} = \frac{\dot{m}_{ex}C_{i,w}M_i}{P_b M_{ex}} \tag{4.10}$$

where M_i is the molecular weight of the species.

For PM emission, the Dusttrak provided the mass concentration $x [mg/m^3]$, and the specific emission can be calculated by:

$$BSE_{pm} = \frac{xDRQ_{ex}}{P_b} \tag{4.11}$$

where DR is the dilution ratio obtained from the diluted and undiluted CO_2 concentration.

To provide an emission performance indicator for each fuel type, the weighted specific emission factor (WSE_i) was calculated with the weighting

factors (WF_k) established in ISO 8178-4 E2 test cycle [57] as listed in Table 2.3. Note that the 100% load condition was replaced by 90% as 100% load operation was not possible for the measured vessel.

$$WSE_i = \frac{\Sigma(\dot{m}_{i,k}WF_k)}{\Sigma(P_{b,k}WF_k)}$$
(4.12)

where $\dot{m}_{i,k}$ refers to the mass flow rate of species *i* at load point *k*.

It should be noted that while the ISO 8178-4 E2 weighting factors were used, the emission measurement methods implemented here and the experimental procedure are not identical to those in the standard. The WSE were intended to provide a convenient metric for comparison between the emissions for the operations with different fuels.

4.3 Error analysis

This section describes the errors associated with the measurement results. The errors involve two categories: 1) systematic errors, or instrument errors, which originated from the instruments; and 2) statistical errors, which were related to the random variations within a measurement.

4.3.1 Systematic errors

The systematic errors come from the instruments when their results deviate from the actual values. For the ECOM, FTIR, and LICOR, these errors were characterized by measuring standard gas mixtures. Additionally, ECOM and FTIR can be mutual references during the measurements. The results from these two instruments have been compared for all the tests, and they showed good consistencies on CO_2 , CO, and NOx, while big discrepancies existed in CH_4 results (details of the comparison are included in Appendix B). By comparing to other reference instruments (Wavelength Modulation Spectroscopy and Flame Ionization Detector) in a laboratory test, it was found that the CH_4 results from FTIR were accurate while the ECOM results were untrustable. Hence the CH_4 results from the ECOM were not used.

For PM measurements, the accuracy of the Dusttrak is difficult to determine explicitly. Although gravimetric samples were collected and can be compared with Dusttrak results, the sensitivity of light scattering method to particle size and properties affected the agreement between these two methods. According to a previous study [21], the accuracy of DustTrak was estimated as approximately 10% for measuring diesel exhaust PM. The accuracy of PN concentrations from the ELPI varies with a variety of factors such as particle diameters, temperature and gas composition. According to manufacturer data, the sensitivity of ELPI+ number concentration varies in a wide range of 0.1-100 $\#/\text{cm}^3$ [84].

Torque data was provided by the vessel's system and the error was unknown. The accuracy of the thermocouple, manometer, and λ sensor are acquired from the manufacturer specifications. [85, 86, 87].

Propagated errors of the calculated parameters are summarize in Table 4.7.

Parameter	Error sources	Propagated error
Q_{ex}	$\Delta P:\pm 1.0\%$	$\pm 0.5\%$
DR	$\begin{array}{c} {\sf CO}_2 \ ({\sf raw}): \ 0 \\ {\sf CO}_2 \ ({\sf diluted}){:}{\pm}2.0\% \\ {\sf H}_2{\rm O}{:}{\pm}5.0\% \end{array}$	$\pm 5.4\%$
T_{ex}	T_{ex} : 0.75%	-
λ (sensor) λ (calculated)	$\lambda \text{ sensor: } \pm 3\% \ { m CO}_2 \ ({ m raw}): \ 0 \ { m CH}_4{:}{\pm}5\% \ { m H}_2{ m O}{:}{\pm}5\% \ { m O}_2{:}0$	±7.0%
BSCO ₂	$\begin{array}{c} {\rm CO_2} \ ({\rm raw}): \ 0 \\ Q_{ex}: \pm 0.5\% \\ {\rm H_2O}{:} \pm 5\% \end{array}$	$\pm 5.0\%$
BSCO	CO: $\pm 4.3\%$ Q_{ex} : $\pm 0.5\%$ H_2 O: $\pm 5\%$	$\pm 6.6\%$
BSNOx	NOx: $\pm 2.0\%$ Q_{ex} : $\pm 0.5\%$ H ₂ O: $\pm 5\%$	±5.4%
BSPM	PM: $\sim 10\%$ $Q_{ex} : \pm 0.5\%$ DR: $\pm 5.4\%$	> 10%

Table 4.7: Instrument errors and propagated errors

4.3.2 Statistical errors

Compared with systematic errors, statistical errors are more important in this study as the primary purpose is to comparatively assess the emissions of different fuels. Under steady state engine operation, the measurements were taken in a duration of 5-10 min. During this period, data was logged at a frequency of 1 Hz. Therefore, 300-600 continuous data were recorded for each load point. However, these data points cannot be considered as independent samples as the measurement was taken continuously. The sample size (n) was instead determined by the number of repetitions of a load point in the whole campaign, ranging between 1 to 3 in this study. Standard error (% SE) for the mean value (\bar{x}) can be calculated by

$$\% SE = \frac{\sigma}{\sqrt{n}\bar{x}} \tag{4.13}$$

Standard errors of the calculated parameters are computed with the SE of each measured parameter based on error propagation rules. They are presented as the error bars in the figures in the following sections.

4.4 Results and discussion

This section describes the results from the vessel emission campaign. It includes three parts: First, engine performance parameters (exhaust gas temperature, λ , BSFC) of all the fuels under both fueling modes will be compared together; Secondly, steady state and transient emissions for diesel mode will be discussed; Finally, steady state emissions for gas mode will be presented.

4.4.1 Engine performance parameters

Engine exhaust gas temperature

Exhaust gas temperature (EGT) is representative of the time-averaged exhaust temperature [88, chapter 6] and is also an reflection of the combustion process– late combustion results in high EGT. The variations of exhaust temperature versus engine load are shown in Figure 4.5. As a general trend, the exhaust temperature peaked at 50% load for all fuels measured except diesel in dual-fuel mode. Overall, higher exhaust temperatures were observed in gas mode as compared to diesel mode. This was mainly due to the richer F/A ratio of gas mode.

In diesel mode, the biodiesel fuels resulted in slightly lower exhaust temperatures at 25% and 90% loads compared to diesel. At other loads, the differences were minor (< 10%). In gas mode, the variations in exhaust temperature were generally small. Exhaust temperature is a resulting product of many factors. Besides the λ , the lower heating value of the biodiesels may also reduce the EGT [89]. In addition, the higher cetane rating of biodiesel may result in modified combustion phasing and affect the EGT [30].



Figure 4.5: Exhaust temperature at various engine loads (d: diesel mode; g: gas mode)

Excess air ratio

The excess air ratio (λ) is a critical parameter which directly affects engine combustion behavior and the resulting emissions. In this study, λ was controlled according to the mapping in the ECU. The λ values obtained by two methods (electrochemical sensor and based on exhaust composition) are presented together in Figure 4.6a and 4.6b. It can be observed that the general trends of λ for the different fuels agreed well with the two methods, although some minor discrepancies existed at some conditions such as the 10% load. Overall, diesel mode λ were higher than gas modes particularly at low loads. λ of diesel mode dropped rapidly as increasing load until 50% load and then kept stable. In diesel mode, the λ for diesel and biodiesels were typically very similar, except a 10% difference were found at 10% load between SB80 and diesel as measured by the sensor. In gas mode, the differences between fuels were also minor. Due to the higher oxygen contents of the biodiesels, λ with using biodiesels were expected to be higher given the air mass was constant. However, this was not observed here in this study. The reason may be that the baseline λ was sufficiently lean that the use of an oxygenated fuel did not significantly affect it.



Figure 4.6: Excess ratios (λ) at various engine loads: (a) measured by λ sensor; (b) calculated based on exhaust composition. (d: diesel mode; g: gas mode)

Brake Specific Fuel Consumption

Brake specific fuel consumption (BSFC) is a measure of fuel efficiency. The BSFC shown in Figure 4.7 were estimated based on mass balance of carbon. As a general trend, BSFC decreased with increasing load and stabilized after 75% load, indicating that the engine approached its maximum fuel efficiency when reaching maximum load. In diesel mode, biodiesels resulted in 17-20% higher BSFC at 25% and 90% loads compared to diesel, while the differences at other loads were small. The BSFC for different pilot fuels in gas mode were similar except at 10% load, where high fluctuations in the exhaust flow rates resulted in high statistical errors. The slight increase in BSFC with biodiesel is typical and generally attributed to the lower heating value and the higher density of biodiesel compared to diesel [11].


Figure 4.7: Calculated BSFC at various engine loads (d: diesel mode; g: gas mode)

4.4.2 Diesel mode steady-state emissions

Carbon dioxide emissions

CO₂ is a major GHG and is originated from the complete combustion of the fuel. The variations of exhaust CO₂ concentration and BSCO₂ for different fuels are shown in Figure 4.8a and 4.8b, respectively. As can be seen from Figure 4.8a, the trends of CO₂ concentrations for different fuels were similar and were roughly the reverse of the trends of λ . BSCO₂ is directly determined by the λ . As a result, the differences in BSCO₂ between diesel, SB100, and CB100 were overall small (<5%), except the high statistical errors at 10% load condition. In general, SB80 had similar BSCO₂ as SB100. The additive slightly reduced BSCO₂ compared to SB100 at most load conditions. Slight reductions on BSCO₂ with biodiesel (when λ is constant) are typically reported by other researchers and are related to their higher oxygen contents [89, 38, 28, 90].



Figure 4.8: Variations of (a) CO_2 concentration, (b) $BSCO_2$ at various engine loads in diesel mode

Carbon monoxide emissions

CO was mainly resulted from incomplete combustion of the fuel. As is shown in Figure 4.9a, exhaust CO concentrations decreased as increasing engine load with all the fuels. The high CO emission at low loads were probably due to very lean mixtures which resulted in low combustion temperature. Compared to diesel, biodiesels produced lower CO emissions over the whole load range. Highest reductions were observed at 10% load, where 28.2% and 40.6% reductions were reported for SB100 and CB100, respectively. As load increased, BSCO dropped rapidly and the differences became smaller. Again, SB80 had similar performance as SB100 in BSCO. The additive slightly reduced BSCO at low loads. The reduction of CO emission with biodiesel can be explained by the extra oxygen content in the biodiesel which enhances the oxidization of the fuel [27, 28].



Figure 4.9: Variations of (a) CO concentration, (b) BSCO at various engine loads in diesel mode

Nitrogen oxides emissions

The formation of NOx in diesel engines is mainly influenced by local combustion temperature as well as the oxygen content in the mixture. As can be seen from Figure 4.10a, the trends of exhaust NOx concentrations were consistent with the tends of EGT in Figure 4.5 and both reached a maximum at 50% load. Compared to diesel, SB100 and CB100 resulted in similar increases in BSNOx over the whole load range. Despite the higher uncertainty at 10% load, 20-30% increases were observed at 25-90% loads with SB100 and CB100 compared to diesel. SB80 produced similar NOx emissions as SB100 at 25-75% loads and slightly lower BSNOx at 90% load. The additive reduced NOx emissions for SB100 at most loads. A potential cause of the increased NOx emission when using biodiesels is related to the oxygen content in the biodiesel, which enhanced the oxidization of the nitrogen in the air and also may result in an increase in the flame temperature, as indicated by some researchers [29, 36, 30, 37].



Figure 4.10: Variations of (a) NOx concentration, (b) BSNOx at various engine loads in diesel mode

PM mass concentration

PM in diesel exhaust is primarily formed by soot agglomerates which are composed of primary particles and absorbed organic compounds (OC). Figure 4.11a and 4.11b show the variations of PM mass concentration and BSPM for the different fuels in diesel mode. As a general trend, PM mass concentration decreased with increasing engine load. This was opposite to a common PM trend which increases when the mixture becomes richer at higher load. The reason was possibly related to the OC, which are unburned HC in the fuel and could be high due to very lean mixtures. A noticeably high BSPM of 2.44 g/kWh was observed at 10% load with CB100, which was 36.8% higher than the baseline diesel. As the load passed 25%, BSPM dropped substantially to a very low level (< 0.1 g/kWh) for all the fuels. The differences between SB100 and diesel were insignificant at all loads considering the statistical errors. BSPM of SB80 were similar to SB100. SBAdd produced lower PM emissions than SB100 at low loads.

By principle, the oxygen content in biodiesel should reduce incomplete combustion of the fuel and help reduce the PM emission [27]. On the other hand, as a secondary effect, pyrolysis of heavy HC in the fuel at high temperature could contribute to the soot formation, although the oxygen content in biodiesels again inhibits this formation. The actual reason for the particularly high BSPM with CB100 at 10% load is unclear. A possible reason can be related to the uncertainty of the light scattering method as it was found to be sensitive to particle sizes and compositions, which are affected



Figure 4.11: Variations of (a) PM mass concentration, (b) BSPM at various engine loads in diesel mode

by engine operating conditions and the implemented fuel.

Particle number concentration and size distribution

Particle number (PN) concentration and their size distribution are important parameters which have significant effects on health implications. Total PN and size distribution not only are decided by the particles' origin which is the combustion process, they are also highly sensitive to sampling system and processes [72]. The variations of total PN concentration versus engine load in diesel mode are shown in Figure 4.12. It can be seen from the figure that, generally, biodiesels produced higher total PN compared to diesel over the whole load range. In particular, at 50% load, SB100 and CB100 resulted in increases of 121% and 158%, respectively. It is worth noting that the addition of the additive (SBAdd) had greatly reduced total PN for SB100 particularly at 50-90% loads.

PN were dominated by the particles in the diameter range of $0.04 - 0.2\mu m$, where SB100 and CB100 both produced significantly higher PN than diesel at 50% and 75% loads. The increases in this range correlated well with the increases in total PN for the biodiesels. However, it should be noted that the increase of PN in the submicron range doesn't necessarily lead to higher total mass concentration. Unlike the total PN, total PM mass concentrations are dominated by larger particles at micron range. Unfortunately, this couldn't be verified by the ELPI+ data due to the limitation of its algorithm. Since the ELPI+ assumed constant particle density, the

ELPI+ data could not be used to accurately estimate particle mass concentrations. Nonetheless, the increases in PN of submicron particles when using biodiesels should be of more concern since they may have health effect implications.



Figure 4.12: Variations of total PN at various engine loads in diesel mode



Figure 4.13: PN size distributions for different fuels under (a)10% (b)25% (c)50% (d)75% (e)90% engine loads in diesel mode (D_a : aerodynamic diameter)

Summary of diesel mode steady-state emissions

To simplify comparison of operation with the different fuels, the weighted specific emissions were calculated based on Equation 4.12. It should be noted that emissions at 10% load are not included in this weighted value. The results for different fuels are summarized in Table 4.8. In addition, change rates of the specific emissions for the biodiesels relative to baseline diesel are shown in Figure 4.14.

Compared to diesel, SME and CME resulted in similar changes in the emissions of CO_2 , CO, and NOx. The increase in PM emission when using CME may be an artificial effect resulting from the measurement method and needs to be reexamined. The changes in CO_2 , CO, and NOx emissions were overall consistent with the majority of the literature [27, 28, 29, 30, 31, 32, 33, 34, 35]. In particular, the increase in NOx emission was a common issue associated with biodiesels due to their high oxygen content. This may bring extra challenges to the engine operator if stringent NOx limits are enforced. The increase in PN of submicron particles when using both biodiesels might be an artefact related to particle nucleation or OC in the PM.

Fuel	\mathbf{CO}_2	CO	NOx	РМ
D100	706 ± 13	0.82 ± 0.02	12.0 ± 0.24	0.077 ± 0.005
SB100	700 ± 21	0.60 ± 0.02	14.53 ± 0.48	0.082 ± 0.011
SB80	725 ± 23	0.63 ± 0.02	13.56 ± 0.41	0.094 ± 0.015
SBAdd	677 ± 15	0.58 ± 0.01	13.64 ± 0.29	0.069 ± 0.008
CB100	687 ± 21	0.54 ± 0.01	14.54 ± 0.43	0.108 ± 0.012

Table 4.8: Weighted brake specific emissions $(\pm 1\sigma) [g/kWh]$ for different fuels in diesel mode



Figure 4.14: Biodiesel's percentage change rate of weighted specific emissions relative to D100 in diesel mode

4.4.3 Diesel mode transient emissions

The real-world working conditions of diesel engines involve transient operations. Compared with steady state operation, transient operation can result in changes in fuel/air ratio which will affect the resulting emissions. In particular, for turbo charged diesel engines, the fundamental discrepancies between steady state conditions and transient ones mainly originate from the characteristics of the turbo charger [91]. Namely, the delay in changes in the air path (air pressure, air flow rate) relative to the changes in the injected fuel quantity can result in short-term deviations from the ideal air-fuel ratio.

This section aims to characterize the differences between the emissions under transient operations and "estimated" steady-state emissions for 3 types of fuels: D100, SB100, and CB100. As described in Section 4.1.4, the transient test cycle includes 3 load increase scenarios: 10-90%, 10-50%, and 50-90%. This sequence was repeated 3 times for each fuel type. The steady-state emissions were estimated based on 4-th order polynomial fitting of engine loads and pollutant concentrations. As an example, Figure 4.15 shows the fitting between engine load and CO_2 concentration for diesel under steady state. The polynomial function found by this method was then used to predict the steady-state concentrations of a pollutant at a given load during transient conditions. This prediction assumes that the engine performance and emissions are only a function of engine load for a certain fuel type. This assumption neglected the influences from other parameters such as temperature and fuel efficiency. In the next step, the actual transient concentration of the pollutant was compared with the steady-state prediction to obtain the change of transient concentrations relative to steady-state concentrations. The results will be presented in 2 forms: First, as in Figure 4.16, the absolute transient concentrations of a pollutant will be compared with the steady state estimations; Second, as in Figure 4.17, the emission changes of transient operation relative to steady-state ones will be compared for the 3 fuels. And all 3 repetitions will be presented in both 2 figures.



Figure 4.15: The 4-th order polynomial fitting of engine load and exhaust CO_2 concentrations for D100 fuel under diesel mode steady states

Transient carbon dioxide emissions

As can be seen from Figure 4.16, transient CO_2 emissions were overall higher than the steady states for all the fuels. From Figure 4.17: During 10-50% load increase, high CO_2 increases (30-40%) were observed with diesel and SB100, whereas the increase with CB100 was relatively lower (~ 10%). However, CB100 tended to result in a more substantial CO_2 increases for loads > 60% compared to the other two fuels during 10-90% load increase. Due to the fact that the steady-state CO_2 emissions of the three fuels were similar, the actual CO_2 concentration for CB100 during load increases was lower than the others at 10-50% load, but were increased at higher loads. The trends of CO_2 concentrations might be related to the changes in fuel/air ratio. The higher CO_2 concentrations relative to steady states imply that the mixture became richer under transient operations, which would be expected due to the turbo charger lag.



Figure 4.16: Transient CO_2 concentrations during load increases for D100, SB100, and CB100 in diesel mode (the three repetitions of each load increase operation were indicated in the legend)



Figure 4.17: Percentage change of the transient CO_2 concentration relative to steady state during: A: 10-90% load increase; B: 10-50% load increase; C: 50-90% load increase (lines of the same color represent 3 repetitions)

Transient carbon monoxide emissions

The transient CO emissions during load increases exhibited greater differences relative to steady states than CO_2 as shown in Fig 4.18 and 4.19. In particular, during the first 10-90% load increase, a nearly 300% increase was found in CO concentration in the 60-70% load region, for operation with diesel. The increased CO emissions during transient operations could be related to the richer mixture. Meanwhile, variations in the CO emissions between repetitions were high for diesel and CME as can be seen in the Scenario A in Figure 4.19. Higher CO emissions were measured during the first repetition of 10-90% load increase as compared to the subsequent two. A possible reason for this is the low temperature of the first repetition. As is shown in Figure 4.20, the exhaust temperatures of the first repetitions were lower than the other ones. Operation with SME and CME resulted in lower CO increases during transient operation, relative to diesel. This reduction is more significant than the variations between the repetitions.



Figure 4.18: Transient CO concentrations during load increases for D100, SB100, and CB100 in diesel mode

Transient NOx emissions

The transient NOx emissions were generally close to steady states for all 3 fuels, as can be seen from Figure 4.21 and 4.22. All the differences were within 10% at 30-90% load range, and slight reductions were observed at the start of the load increase, which could be explained by the decease of oxygen content in the mixture. Compared to diesel and CB100, SB100 tended to result in a slightly more significant NOx reduction, particularly around 20% load. However, since the steady-state NOx emissions for SB100 and CB100 were both higher than the D100, the biodiesels still produced higher NOx emissions than diesel during transient operations.



Figure 4.19: Percentage change of the transient CO concentration relative to steady state during: A: 10-90% load increase; B: 10-50% load increase; C: 50-90% load increase (lines of the same color represent 3 repetitions)



Figure 4.20: Transient engine exhaust temperatures during load increases for D100, SB100, and CB100 in diesel mode



Figure 4.21: Transient NOx concentrations during load increases for D100, SB100, and CB100 in diesel mode



Figure 4.22: Percentage change of the transient NOx concentration relative to steady state during: A: 10-90% load increase; B: 10-50% load increase; C: 50-90% load increase (lines of the same color represent 3 repetitions)

Transient PM emissions

As can be seen from Figure 4.23 and 4.24, PM mass concentrations were significantly affected by transient operations for all the fuels. Over 300% increases were observed at 20-50% load with D100 and CB100, possibly due to the rich mixture at the beginning of load increase. The first repetition of 10-90% load increase, which also caused the high CO emissions, appears to be an outlier especially for CB100. The PM emission for SB100 and CB100 were less sensitive to transient operation than diesel fuel, particularly during 50-90% load increases. Both biodiesels produced lower PM emissions at most load conditions.



Figure 4.23: Transient PM mass concentrations during load increases for D100, SB100, and CB100 in diesel mode



Figure 4.24: Percentage change of the transient PM mass concentration relative to steady state during: A: 10-90% load increase; B: 10-50% load increase; C: 50-90% load increase (lines of the same color represent 3 repetitions)

Summary of diesel mode transient emissions

Compared to steady state operation, all the pollutants were affected by transient operation for all 3 fuels. In Particular, the increases in CO and PM emissions were substantial. These could both be related to the fuelrich conditions due to the turbo charger lag effect. However, more detailed explanation of these effects is hindered as several key operating parameters were not available from the engine control and data acquisition system (e.g., intake pressure). Further investigation of the turbo charger behaviors as well as fuel injection rates would be helpful to reveal more facts underlying.

Comparing between the different fuels, it could be found that both biodiesels resulted in slightly improved emission increases under transient operations relative to steady-state emissions. For instance, the CO_2 and CO emissions with SB100 and CB100 during 10-50 % load increases were less sensitive to transient operations compared to that with diesel. Particularly, SB100 and CB100 both resulted in much less PM increases compared to diesel, resulting in lower PM emissions. The extra oxygen content in the biodiesels could be a possible reason resulting in these PM reductions. However, due to the uncertainties brought by the cycle-to-cycle variations as well as the measurement method itself, these findings may need further verification.

4.4.4 Gas mode steady-state emissions

In gas mode, the primary energy source was NG, which was injected into the upstream of the intake port and premixed with air. A small amount of diesel (~ 2% of total energy content) was injected into the cylinder near TDC to promote ignition of the premixed mixture. The present study will investigate the effects of biodiesel as a pilot fuel on emissions of CO₂, CO, CH₄, NOx, and PM under gas mode.

Carbon dioxide emissions

CO₂ emissions were mainly influenced by λ . As a general trend seen in Figure 4.25a and 4.25b, CO₂ concentrations increased, while BSCO₂ decreased with increasing load. The differences between CO₂ concentrations for diesel and biodiesel were minor over the load range. However, differences on BSCO₂ could be observed between the fuels. In particular, at 50% load, SB100 and CB100 increased BSCO₂ by 26.3% and 10.9%, respectively, as compared to diesel. These increases could be related to two factors: (1) Variations of the exhaust mass flow rate (Figure 4.26), which contributed the most significant differences at 50% load (22.1% and 12.7% increases for operations with SB100 and CB100 relative to D100, respectively). The reason for the substantial variations in exhaust mass flow rate is unclear, which could possibly be due to the operations of the vessel; (2) The λ (Figure 4.6a) for operations with SB100 and CB100 were 9.8% and 2% lower than diesel operation at 50% load. It should also be noted that the wide error bars at 10% load were caused by highly fluctuating exhaust flow rates.



Figure 4.25: Variations of (a) CO_2 concentration, (b) $BSCO_2$ at various engine loads in gas mode



Figure 4.26: Variations of exhaust mass flow rate under various engine loads in gas mode

Carbon monoxide emissions

CO was mainly a product of incomplete combustion of NG in gas mode. The variations of CO concentrations and BSCO against engine load are shown in Figure 4.27a and 4.27b. Compared to diesel mode, generally, gas mode exhaust CO concentrations were almost an order of magnitude higher. This was mainly due to the lower λ of gas mode. As a general trend, a high CO emission was observed at 10% load for all the fuels, and CO emissions decreased rapidly with increasing engine load. The differences in both CO concentration and BSCO between the pilot fuels were typically small.



Figure 4.27: Variations of (a) CO concentration, (b) BSCO at various engine loads in gas mode

Methane emissions

Unburned CH₄ in gas mode is a significant concern for dual-fuel engines. It could be observed from Figure 4.28a and 4.28b that high CH₄ emissions happened particularly at low loads. This finding is consistent with a previous work on the same vessel [18] and the findings by other researchers [92, 93]. The reason was mainly due to the high λ at low loads which resulted in lower flame speeds. The general trends of CH₄ emissions for the different fuels were similar based on the measurements. However, the variations in engine load will affect the weighted emission factors, which was actually not an effect from using the different fuels.



Figure 4.28: Variations of (a) CH_4 concentration, (b) $BSCH_4$ at various engine loads in gas mode

Nitrogen oxides emissions

The NOx emissions in gas mode were substantially lower than those in diesel mode, as is shown in Figure 4.29a and 4.29b. This could be due to the premixed flame in the gas mode which resulted in a lower peak combustion temperature. The trend of NOx concentrations fluctuated as increasing engine load, while BSNOx kept decreasing. At all loads except 50%, both SB100 and CB100 resulted in lower NOx emissions as compared to diesel. The biggest reductions on BSNOx were observed at 10% load, though high fluctuations caused uncertainties here. The reason for these NOx reductions are unclear yet. Two potential factors could be: (1) higher cetane number of the biodiesels advanced ignition timing and changed the progress of heat release rate; (2) higher viscosities of biodiesels affected the injection and the distribution of the fuel spray, and further changed the combustion temperature.



Figure 4.29: Variations of (a) NOx concentration, (b) BSNOx at various engine loads in gas mode

PM emissions

As can be seen in Figure 4.30a and 4.30b, PM emissions under gas mode were significantly lower than those under diesel mode, which is a well expected effect of using the NG fuel. Particularly at loads over 10%, BSPM became less than 0.01 g/kWh regardless of the pilot fuel. At 10% load, statistical errors in PM results were high, meaning that the differences between pilot fuels becoming insignificant. The differences at higher loads were also indistinguishable due to the very low PM emission levels. In addition, at this very low level of PM concentrations, the confidence in results from the DustTrak became lower. Hence, overall, the effect of using biodiesels on PM emissions under gas mode was insignificant.



Figure 4.30: Variations of (a) PM mass concentration, (b) BSPM at various engine loads in gas mode

Summary of gas mode steady-state emissions

To evaluate the overall emission levels for the different pilot fuels, the weighted specific emission factors are summarized in Table 4.9 for gas mode. The change in emission for operation with the biodiesels relative to diesel are shown in Figure 4.31.

The effects of using biodiesels as the pilot fuel in gas mode on emissions were generally insignificant except for the NOx emissions, where SB100 and CB100 resulted in reductions on NOx emissions by $14 \pm 7\%$ and $19 \pm 7\%$ than diesel, respectively. The exact reason for these reductions is unclear. Possible causes could be related to the fuel properties such as cetane number and viscosity. To better explain this phenomenon, further research on the fuel injection and combustion processes are suggested. On the other hand, by comparison to diesel mode, gas mode produced significantly less NOx and PM emissions. These proved the benefits of dual-fuel mode operation.

Table 4.9: Weighted brake specific emissions $(\pm 1\sigma) [g/kWh]$ for different pilot fuels in gas mode

Fuel	\mathbf{CO}_2	CO	NOx	РМ	CH_4
D100	521 ± 14	4.50 ± 0.13	1.41 ± 0.04	0.0021 ± 0.0002	15.66 ± 0.53
SB100	516 ± 19	4.76 ± 0.30	1.21 ± 0.06	0.0025 ± 0.0003	17.96 ± 0.59
CB100	510 ± 23	4.54 ± 0.15	1.14 ± 0.06	0.0023 ± 0.0004	18.85 ± 0.73



Figure 4.31: Biodiesel's percentage change rate of weighted specific emissions relative to D100 in gas mode

4.5 Summary and conclusions

In-use emission measurements were conducted for a marine vessel operating on diesel, SME, and CME under diesel mode and gas mode. Steady-state tests were taken for both fueling modes. Weighted specific emission factors were calculated for each fuel type. The weighted specific emission of operations with SME and CME were compared to that with diesel. Transient emission was characterized for diesel mode. The differences between transient emissions and estimated steady-state emissions were calculated and compared between diesel, SME, and CME. Following conclusions can be drawn from these results:

Under diesel mode steady-state operations:

- NOx emissions were increased by $21\pm6\%$ when using SME or CME as compared to diesel.
- CO emissions were reduced by $26\pm5\%$ and $33\pm4\%$ by using SME and

CME, respectively, as compared to diesel.

- CO₂ emissions were similar with operations on diesel, SME, and CME. However, considering the life cycle assessment, SME and CME can result in reductions on net life-cycle GHG emissions compared to diesel, according to the literature [80].
- The PM emission resulting from using CME was higher than from using diesel. However, these changes are based on light-scattering measurements which might reflect changes in particle size distribution and particle composition as much as changes in mass.
- Total PN were substantially increased particularly in the submicron particle size range when using SME and CME as compared to diesel. These increases could be an artefact of nucleation mode or be related to OC in the PM.

Under diesel mode transient operations:

- PM emissions were significantly affected by transient operations for all the three fuels. The increases in PM emission ranged between 100-200% with diesel, while the increases with SME and CME were within 50% for most conditions. This indicates that the biodiesels can result in improvements on PM emissions during transient operations.
- CO were increased by 40-100% compared to the steady-state emissions. SME and CME were both less sensitive to transient operations as compared to diesel.
- CO₂ were increased by 20-40% compared to the steady-state emissions. CME resulted in less CO₂ increases as compared to diesel and SME during 10-50% load increase.
- NOx were reduced by 10-20% during 10-30% load increases. The reduction with SME was slightly more obvious than those with diesel and CME.
- Since variations existed between the repetitions of tests, particularly in CO and PM emissions, verification tests were needed to confirm these results.

Under gas mode steady state operations (when used as the pilot fuel):

- NOx emissions were reduced by $14 \pm 7\%$ and $19 \pm 7\%$ when using SME and CME, respectively, as compared to diesel.
- CO₂, CO, CH₄, and PM emissions were not significantly changed by using different pilot fuels.

In summary, when operating on diesel mode, SME and CME resulted in slight changes in engine-out emissions as compared to diesel, and they have the potential benefits of reducing the life-cycle GHG emissions according to literature [80]. In gas mode, the biodiesels resulted in slight reductions on engine-out NOx emission as compared to diesel.

Chapter 5

Conclusions and Recommendations

Alternative fuels are an attractive solution to reduce the emissions of GHG and other pollutants of diesel engines; however, the emission and engine performance impacts of these alternative fuels need to be evaluated especially under real-world working conditions. Based on their states at normal conditions, they can be categorized into gaseous fuels and liquid fuels. Dualfuel engines, especially the premixed mode, can utilize clean gaseous fuels in conventional diesel engines with liquid fuels for ignition. Gaseous fuels, such as H_2 and NG, have the potential benefits of reducing the emissions of HC and PM, but meanwhile bring new challenges since the unburned gaseous fuels indicate poor fuel economy and may also be a significant GHG as in the case of NG. Liquid fuels, such as biodiesel, are similar in properties as diesel and can be directly used in conventional CI engines.

In this study, two issues associated with two types of dual-fuel engines operated on different alternative fuels are investigated and addressed:

(1) The measurement of the in-use H_2 slip from a H_2 /diesel dual-fuel truck under real-world operating conditions;

(2) The effects of using biodiesels, namely SME and CME, on a dual-fuel marine engine under real-world operating conditions, including steady-state operations and transient operations, under diesel mode and gas mode.

5.1 Conclusions

On the $H_2/dissel$ dual-fuel truck, H_2 slip was measured using a low-cost semi-conductor sensor. The feasibility of this sensor for on-vehicle, exhaust stream H_2 measurement was evaluated. Influencing factors of flow rate, temperature, RH, and preheating time have been identified. The error of this sensor was found to be 7-14% when compared to H_2 calibration standards. Approximately one hour of exhaust H_2 concentration data had been collected. System latency was found to be long when an decreasing H_2 injection rate happened. H_2 slip maps generated from raw data revealed some preliminary relations between H_2 slip and engine operating parameters under real-world working conditions: H₂ slip increased with increasing engine speed and increasing torque, and the highest H_2 slip, which was around 14,000 ppm and 54% (of injection amount), happened at 1500-1700 rpm and 1400-1800 Nm region. However, further explanation of these results was limited by the knowledge of H_2 injection map which remained confidential. This work presented a low-cost method to measure the H_2 slip on in-use vehicles. Compared to commercial instruments, the semi-conductor sensor and the self-developed PEMS used in the study are cheaper in cost and are simpler to be implemented. However, the developed method still has limitations. For instance, the system latency was too long for transient H_2 concentrations, and the data processing excluded a lot of important operating conditions such as idling and gear transitions. Due to these limitations, the current system was not fully capable of accurate measurement of vehicle H_2 slips. To obtain results with higher accuracy particularly for transient operations, a H₂ sensor with shorter response time is desired.

In the second project, in-use emissions were measured and characterized for a NG/diesel marine vessel when operating on biodiesels relative to operating on diesel. The results showed that in diesel mode, the two biodiesels (SME and CME) in general had similar emission characteristics as conventional diesel under steady states, though they both increased NOx emissions (by $21 \pm 6\%$) and tended to increase total PN in the exhaust. The increases in NOx emissions when using biodiesels were a common finding in literature. and it could be related to the higher oxygen contents of the biodiesels. The increase of PN, particularly in the size range of 0.04-0.2 μm , require further analysis to reveal the real cause as they might be an artefact of nucleation mode or OC in the PM. PM mass concentrations were measured with lightscattering method which was sensitive to particle sizes and compositions. The 20-60% increase in PM mass concentration when using CME as compared to diesel was possibly related to OC in the PM. To further validate the results regarding PM and PN, some improvements need to be done to the measurement method including: (1) Separating OC and elementary carbon in the PM (e.g., by using a catalytic stripper); (2) Chemical analysis of the particulate composition, which could be done with the filter sample.

During load increases, emissions were significantly affected by the transient operations especially for CO and PM, which were both significantly increased. These could be related to the fuel-rich conditions resulting from the turbo charger lag. Compared to diesel, SME and CME both resulted in lower PM increases during load increases relative to steady states. The reason could be related to the extra oxygen contents in the biodiesels.

In gas mode, only a small amount (~ 2% of total energy content) of liquid fuel (diesel or biodiesel) was injected as the pilot fuel, emissions were less affected by using biodiesels. However, reductions by $14\pm7\%$ and $19\pm7\%$ in NOx emissions were observed when using SME and CME, respectively, as compared to diesel. This could be related to the higher cetane numbers, or higher viscosities of the biodiesels, which may have changed the combustion processes, while an exact reason is to be revealed by further studies.

Overall, SME and CME have proved to be potential substitutes for diesel in marine engines to reduce GHG emissions while meeting the emission regulations. Comparing between SME and CME, they in general had similar effects on emissions, despite the uncertainties in PM concentrations. Due to these facts, a choice between these two biodiesels may need to be made by considering other factors such as the life-cycle carbon intensities and the economics.

In summary of the two works, which both focused on the in-use emissions from dual-fuel vehicles, it can be found that the in-use engine-out emissions from the vehicles heavily depend on operating conditions, which vary significantly in real-world uses. It is therefore important to implement in-use emissions measurements to evaluate the vehicle's emission under real-world operating conditions.

5.2 Recommendations for future work

While the main objectives of this work have been achieved, some additional questions remain to be addressed in future work:

- In order to better understand the behavior of the H₂ sensor, more benchtop tests need to be done about the response time and the cross sensitivities. In addition, more careful data processing methods should be applied to the raw H₂ concentration data in order to acquire more comprehensive and representative H₂ slip maps.
- Further analysis of the NOx emission changes brought by using biodiesels on the marine engine is needed. For instance, more fuel property data can be obtained by chemical analysis, and the combustion process can be studied on a research engine to reveal the heat release rate and the fuel distribution.
- The results under transient operations showed significant differences between diesel and biodiesels. These findings look promising but lack of further analysis and verification. To verify these results, transient tests can be done under better controlled conditions, e.g. on a research engine. Improvements also need to be done especially for the PM measurement method (details described below).
- Light-scattering PM measurement methods are sensitive to particle sizes and properties. Measures can be taken to separate the soot and organic compounds in the PM (e.g. using a catalytic stripper). Chemical analysis could be done with the collected PM samples. In addition, more precise particle size distribution can be obtained with more advanced instruments such as the SMPS.
- The particle number or mass concentrations from the ELPI are calculated based on the assumption of constant particle density, while actual particle densities vary significantly over the size range. This could result in a wrong particle size distribution. Due to this reason, the ELPI data for the biodiesel campaign should be used with special care. For better interpretation of ELPI data, mathematical methods such as data inversion need to be performed.
- Particle losses in sampling tubes can affect the measured PM or PN concentrations. Although this may not change the results on a relative basis, estimation of particle losses can be done to improve the result's accuracy.

Bibliography

- EPA. About diesels. https://www.fueleconomy.gov/feg/di_ diesels.shtml. Online; accessed 18 October 2021.
- [2] A. C. Lloyd and T. A. Cackette. "Diesel Engines: Environmental Impact and Control". In: Journal of the Air & Waste Management Association 51.6 (2001), pp. 809–847. DOI: 10.1080/10473289.2001. 10464315.
- [3] U. S. EPA. Heavy-Duty Highway Engine: Clean Fuel Fleet Exhaust Emission Standards. Standard EPA-420-B-16-017. EPA, 2016.
- [4] Canadian Environmental Protection Act, 1999. https://laws-lois. justice.gc.ca/eng/acts/c-15.31/. Online; accessed 29 September 2021.
- I. M. Organization. Revised MARPOL annex VI : regulations for the prevention of air pollution from ships and NOx technical code 2008. English. 2nd ed. International Maritime Organization London, 2009, vi, 212 p. : ISBN: 9789280142433.
- [6] D.-S. Kim, M. Hanifzadeh, and A. Kumar. "Trend of biodiesel feedstock and its impact on biodiesel emission characteristics". In: *Environmental Progress & Sustainable Energy* 37.1 (), pp. 7–19. DOI: https://doi.org/10.1002/ep.12800.
- [7] B. Harvey. Canada Biofuels Annual 2019. Report CA19017. USDA, 2019.
- [8] F. S. Zeman and D. W. Keith. "Carbon neutral hydrocarbons". In: Philosophical Transactions of the Royal Society A: Mathematical, Phys- ical and Engineering Sciences 366.1882 (2008), pp. 3901–3918. DOI: 10.1098/rsta.2008.0143. URL: https://royalsocietypublishing. org/doi/abs/10.1098/rsta.2008.0143.

- T. E. McKone et al. "Grand Challenges for Life-Cycle Assessment of Biofuels". In: *Environmental Science & Technology* 45.5 (2011). PMID: 21265567, pp. 1751–1756. DOI: 10.1021/es103579c. eprint: https://doi.org/10.1021/es103579c. URL: https://doi.org/10. 1021/es103579c.
- [10] HLPE. Biofuels and food security. A report by the High Level Panel of Experts on Food Security and Nutrition of the Committee on World Food Security. Report. Rome: HLPE, 2013.
- [11] C. Mohd Noor, M. Noor, and R. Mamat. "Biodiesel as alternative fuel for marine diesel engine applications: A review". In: *Renewable and Sustainable Energy Reviews* 94 (2018), pp. 127-142. ISSN: 1364-0321. DOI: https://doi.org/10.1016/j.rser.2018.05.031. URL: https://www.sciencedirect.com/science/article/pii/S1364032118303770.
- [12] BBC news. Volkswagen: The scandal explained. https://www.bbc. com/news/business-34324772. Online; accessed 18 October 2021.
- T. Korakianitis, A. Namasivayam, and R. Crookes. "Natural-gas fueled spark-ignition (SI) and compression-ignition (CI) engine performance and emissions". In: *Progress in Energy and Combustion Science* 37.1 (2011), pp. 89–112. ISSN: 0360-1285. DOI: https://doi.org/10.1016/j.pecs.2010.04.002. URL: https://www.sciencedirect.com/science/article/pii/S0360128510000377.
- [14] A. Boretti. "Advantages and Disadvantages of Diesel Single and Dual-Fuel Engines". In: Frontiers in Mechanical Engineering 5 (2019), p. 64.
 ISSN: 2297-3079. DOI: 10.3389/fmech.2019.00064. URL: https: //www.frontiersin.org/article/10.3389/fmech.2019.00064.
- [15] G. Karim. "Introduction". In: Dual-fuel Diesel Engines. Taylor & Francis Group, 2015. Chap. 1, pp. 1–9.
- [16] L. Wei and P. Geng. "A review on natural gas/diesel dual fuel combustion, emissions and performance". In: *Fuel Processing Technology* 142 (2016), pp. 264-278. ISSN: 0378-3820. DOI: https://doi.org/10.1016/j.fuproc.2015.09.018. URL: https://www.sciencedirect.com/science/article/pii/S0378382015301715.
- [17] G. Myhre and D. Shindell. IPCC WGI Fifth Assessment Report: Chapter 8: Anthropogenic and Natural Radiative Forcing. Report. IPCC, 2013.

- [18] D. E. Sommer et al. "Characterization and Reduction of In-Use CH4 Emissions from a Dual Fuel Marine Engine Using Wavelength Modulation Spectroscopy". In: *Environmental Science & Technology* 53.5 (2019). PMID: 30712340, pp. 2892-2899. DOI: 10.1021/acs.est.
 8b04244. eprint: https://doi.org/10.1021/acs.est.8b04244. URL: https://doi.org/10.1021/acs.est.8b04244.
- H. T. Hwang and A. Varma. "Hydrogen storage for fuel cell vehicles". In: Current Opinion in Chemical Engineering 5 (2014). Energy and environmental engineering / Reaction engineering, pp. 42-48. ISSN: 2211-3398. DOI: https://doi.org/10.1016/j.coche.2014.04.004. URL: https://www.sciencedirect.com/science/article/pii/ S2211339814000446.
- [20] T. Tsujimura and Y. Suzuki. "The utilization of hydrogen in hydrogen/diesel dual fuel engine". In: International Journal of Hydrogen Energy 42.19 (2017). Special Issue on The 21st World Hydrogen Energy Conference (WHEC 2016), 13-16 June 2016, Zaragoza, Spain, pp. 14019-14029. ISSN: 0360-3199. DOI: https://doi.org/10.1016/ j.ijhydene.2017.01.152. URL: https://www.sciencedirect.com/ science/article/pii/S036031991730318X.
- J. D. Meiklejohn. "The effect of hydrogen substitution on the real-world CO2, NOx, and PM emissions of a heavy-duty diesel truck". PhD thesis. University of British Columbia, 2019. DOI: http://dx. doi.org/10.14288/1.0380509. URL: https://open.library.ubc.ca/collections/ubctheses/24/items/1.0380509.
- [22] C. S. Weaver and S. H. Turner. "Dual Fuel Natural Gas/Diesel Engines: Technology, Performance, and Emissions". In: International Congress & Exposition. SAE International, 1994. DOI: https://doi.org/10.4271/940548. URL: https://doi.org/10.4271/940548.
- [23] C. K. Westbrook. "Chemistry of Biodiesel Fuels based on Soybean Oil". In: Biodiesel Fuels Based on Edible and Nonedible Feedstocks, Wastes, and Algae. CRC Press, 2021. Chap. 22, pp. 459–475.
- [24] Fleetowner.com. Biodiesel and warranties. https://www.fleetowner. com/emissions-efficiency/article/21668230/biodiesel-andwarranties. Online; accessed 24 September 2021. 2008.
- [25] The Government of Canada. Report on the Technical Feasibility of Integrating an Annual Average 2% Renewable Diesel in the Canadian Distillate Pool by 2011. https://www.nrcan.gc.ca/energyefficiency/transportation-alternative-fuels/national-renewable-

diesel-demonstration-initiative/nrddi-final-report/nrddifr-introduction/3669. Online; accessed 24 September 2021.

- [26] D. Korotney. EPA Analysis of the Exhaust Emission Impacts of Biodiesel. Report. US EPA, 2002.
- [27] A. N. Ozsezen et al. "Performance and combustion characteristics of a DI diesel engine fueled with waste palm oil and canola oil methyl esters". In: Fuel 88.4 (2009), pp. 629-636. ISSN: 0016-2361. DOI: https: //doi.org/10.1016/j.fuel.2008.09.023. URL: https://www. sciencedirect.com/science/article/pii/S0016236108003694.
- [28] O. Ogunkunle and N. A. Ahmed. "Exhaust emissions and engine performance analysis of a marine diesel engine fuelled with Parinari polyandra biodiesel-diesel blends". In: *Energy Reports* 6 (2020), pp. 2999-3007. ISSN: 2352-4847. DOI: https://doi.org/10.1016/j.egyr. 2020.10.070. URL: https://www.sciencedirect.com/science/article/pii/S2352484720314232.
- [29] S. Simsek. "Effects of biodiesel obtained from Canola, safflower oils and waste oils on the engine performance and exhaust emissions". In: *Fuel* 265 (2020), p. 117026. ISSN: 0016-2361. DOI: https://doi.org/ 10.1016/j.fuel.2020.117026. URL: https://www.sciencedirect. com/science/article/pii/S0016236120300211.
- [30] B. Gokalp, E. Buyukkaya, and H. Soyhan. "Performance and emissions of a diesel tractor engine fueled with marine diesel and soybean methyl ester". In: *Biomass and Bioenergy* 35.8 (2011), pp. 3575-3583. ISSN: 0961-9534. DOI: https://doi.org/10.1016/j.biombioe.2011.05.
 015. URL: https://www.sciencedirect.com/science/article/pii/S0961953411002881.
- [31] S. Manigandan et al. "Performance, noise and emission characteristics of DI engine using canola and Moringa oleifera biodiesel blends using soluble multiwalled carbon nanotubes". In: *Fuel* 289 (2021), p. 119829. ISSN: 0016-2361. DOI: https://doi.org/10.1016/j.fuel.2020. 119829. URL: https://www.sciencedirect.com/science/article/pii/S0016236120328258.
- [32] M. R. Seraç et al. "Evaluation of comparative combustion, performance, and emission of soybean-based alternative biodiesel fuel blends in a CI engine". In: *Renewable Energy* 148 (2020), pp. 1065–1073.

- [33] S. Orjuela-Abril, J. Rojas-Suárez, and J. Forero. "Study of performance and emissions in diesel engines operating with biodiesel from soybean oil and water emulsions". In: Aibi revista de investigación, administración e ingeniería (Jan. 2021), pp. 19–29. DOI: 10.15649/ 2346030X.935.
- [34] R. S. Gavhane et al. "Effect of Soybean biodiesel and Copper coated Zinc oxide Nanoparticles on Enhancement of Diesel Engine Characteristics". In: Energy Sources, Part A: Recovery, Utilization, and Environmental Effects 0.0 (2020), pp. 1–19. DOI: 10.1080/15567036.
 2020.1856237. URL: https://doi.org/10.1080/15567036.2020. 1856237.
- [35] U. J.C. "Impact Of Used Soya Oil Biodiesel On The Performance And Emission Of Diesel Engine". In: Journal of Multidisciplinary Engineering Science and Technology 7 (2020), pp. 12704–12716. ISSN: 2458-9403.
- [36] M. Veinblat et al. "Impact of various blends of linseed oil-derived biodiesel on combustion and particle emissions of a compression ignition engine A comparison with diesel and soybean fuels". In: Energy Conversion and Management 178 (2018), pp. 178-189. ISSN: 0196-8904. DOI: https://doi.org/10.1016/j.enconman.2018.10.028. URL: https://www.sciencedirect.com/science/article/pii/S0196890418311294.
- [37] W. J. Pitz and C. J. Mueller. "Recent progress in the development of diesel surrogate fuels". In: *Progress in Energy and Combustion Science* 37.3 (2011), pp. 330-350. ISSN: 0360-1285. DOI: https://doi.org/10.1016/j.pecs.2010.06.004. URL: https://www.sciencedirect.com/science/article/pii/S0360128510000535.
- [38] M. Y. Khan et al. "Impact of Algae Biofuel on In-Use Gaseous and Particulate Emissions from a Marine Vessel". In: *Energy & Fuels* 26.10 (2012), pp. 6137–6143. DOI: 10.1021/ef300935z. URL: https://doi. org/10.1021/ef300935z.
- [39] M. W. Tubman et al. Evaluation of biodiesel fuels to reduce fossil fuel use in Corps of Engineers floating plant operations. Tech. rep. U.S. Army Engineer Research, Development Center, Coastal, and Hydraulics Laboratory, 2016.
- [40] U.S. Energy Information Administration. Natural gas explained. https: //www.eia.gov/energyexplained/natural-gas/. Online; accessed 24 September 2021.

- [41] I. E. Agency. Database documentation:NATURAL GAS INFORMA-TION 2021 edition. Report. International Energy Agency, 2021.
- [42] Natualgas.org. Overview of Natural Gas:background. http://naturalgas. org/overview/background/. Online; accessed 24 September 2021.
- [43] J. Zhao et al. "Effects of compression ratio on the combustion and emission of a hydrogen enriched natural gas engine under different excess air ratio". In: *Energy* 59 (2013), pp. 658–665. ISSN: 0360-5442. DOI: https://doi.org/10.1016/j.energy.2013.07.033. URL: https:// www.sciencedirect.com/science/article/pii/S0360544213006385.
- [44] H. Chen, J. He, and X. Zhong. "Engine combustion and emission fuelled with natural gas: A review". In: *Journal of the Energy Institute* 92.4 (2019), pp. 1123-1136. ISSN: 1743-9671. DOI: https://doi.org/10.1016/j.joei.2018.06.005. URL: https://www.sciencedirect.com/science/article/pii/S1743967118304446.
- [45] G. Karim. "Methane and Natural Gas as Engine Fuels". In: Dual-fuel Diesel Engines. Taylor & Francis Group, 2015. Chap. 6, pp. 55–58.
- [46] D. C. Sacal et al. "Characterization of Methane Emissions from a Natural Gas-Fuelled Marine Vessel under Transient Operation". In: SAE Technical Paper 01.0631 (2021). ISSN: 0148-7191. DOI: https: //doi.org/10.4271/2021-01-0631. URL: https://www.sae.org/ publications/technical-papers/content/2021-01-0631/.
- [47] C. Song. "Introduction to Hydrogen and Syngas Production and Purification Technologies". In: Hydrogen and Syngas Production and Purification Technologies. John Wiley & Sons, Ltd, 2009. Chap. 1, pp. 1–13. ISBN: 9780470561256. DOI: https://doi.org/10.1002/9780470561256.chl. eprint: https://onlinelibrary.wiley.com/doi/pdf/10.1002/9780470561256.chl. URL: https://onlinelibrary.wiley.com/doi/pdf/10.com/doi/abs/10.1002/9780470561256.chl.
- [48] T. L. Alleman et al. "Biodiesel Handling and Use Guide (Fifth Edition)". In: (Nov. 2016). URL: https://www.osti.gov/biblio/ 1347103.
- [49] *Physical Properties*. https://methanolfuels.org/about-methanol/ physical-properties/. Online; accessed 24 September 2021.
- [50] Fuel Properties Comparison. https://afdc.energy.gov/fuels/ properties. Online; accessed 24 September 2021.
- [51] N. Saravanan and G. Nagarajan. "Performance and emission studies on port injection of hydrogen with varied flow rates with Diesel as an ignition source". In: *Applied Energy* 87.7 (2010), pp. 2218-2229. ISSN: 0306-2619. DOI: https://doi.org/10.1016/j.apenergy.2010.01.
 014. URL: https://www.sciencedirect.com/science/article/ pii/S0306261910000279.
- [52] H. A. Alrazen et al. "A review of the effect of hydrogen addition on the performance and emissions of the compression Ignition engine". In: *Renewable and Sustainable Energy Reviews* 54 (2016), pp. 785–796.
 ISSN: 1364-0321. DOI: https://doi.org/10.1016/j.rser.2015.
 10.088. URL: https://www.sciencedirect.com/science/article/pii/S1364032115011673.
- [53] T. Gatts et al. "An experimental investigation of incomplete combustion of gaseous fuels of a heavy-duty diesel engine supplemented with hydrogen and natural gas". In: International Journal of Hydrogen Energy 37.9 (2012). 7th Petite Workshop on the Defect Chemical Nature of Energy Materials, 14-17 March 2011, Storaas, Kongsberg, Norway, pp. 7848-7859. ISSN: 0360-3199. DOI: https://doi.org/10.1016/j. ijhydene.2012.01.088. URL: https://www.sciencedirect.com/ science/article/pii/S036031991200184X.
- [54] Emission Standards: Canada. https://dieselnet.com/standards/ ca/. Online; accessed 29 September 2021.
- [55] Heavy-Duty FTP Transient Cycle. https://dieselnet.com/standards/ cycles/ftp_trans.php. Online; accessed 29 September 2021.
- [56] I. M. Organization. MARPOL 73/78 : articles, protocols, annexes, unified interpretations of the International Convention for the Prevention of Pollution from Ships, 1973, as modified by the protocol of 1978 relating thereto. English. Consolidated ed., 1991. IMO London, 1992, v, 485 p. : ISBN: 9280112805.
- [57] Reciprocating internal combustion engines Exhaust emission measurement — Part 4: Steady-state and transient test cycles for different engine applications. Standard. International Organization for Standardization, June 2020.
- [58] Fourier-transform infrared spectroscopy. https://en.wikipedia. org/wiki/Fourier-transform_infrared_spectroscopy. Online; accessed 29 September 2021.

- [59] Absorption and Transmission Spectroscopy (UV, Visible, NIR). https: //www.horiba.com/en_en/products/by-technique/molecularspectroscopy/absorption-and-transmission-spectroscopy-uvvisible-nir/. Online; accessed 29 September 2021.
- [60] A. Martyr and M. Plint. "Chapter 16 Engine Exhaust Emissions". In: Engine Testing (Fourth Edition). Ed. by A. Martyr and M. Plint. Fourth Edition. Oxford: Butterworth-Heinemann, 2012, pp. 407-450. ISBN: 978-0-08-096949-7. DOI: https://doi.org/10.1016/B978-0-08-096949-7.00016-9. URL: https://www.sciencedirect.com/ science/article/pii/B9780080969497000169.
- [61] T. Hübert et al. "Hydrogen sensors A review". In: Sensors and Actuators B: Chemical 157.2 (2011), pp. 329-352. ISSN: 0925-4005. DOI: https://doi.org/10.1016/j.snb.2011.04.070. URL: https://www.sciencedirect.com/science/article/pii/S0925400511003674.
- [62] S. G. Leonardi et al. "Development of a hydrogen dual sensor for fuel cell applications". In: International Journal of Hydrogen Energy 43.26 (2018). HYdrogen POwer THeoretical and Engineering Solutions -International Symposium (Hypothesis XII), pp. 11896-11902. ISSN: 0360-3199. DOI: https://doi.org/10.1016/j.ijhydene.2018.02.
 019. URL: https://www.sciencedirect.com/science/article/ pii/S0360319918303975.
- Y. S. Najjar. "Hydrogen safety: The road toward green technology". In: International Journal of Hydrogen Energy 38.25 (2013), pp. 10716–10728. ISSN: 0360-3199. DOI: https://doi.org/10.1016/j.ijhydene. 2013.05.126. URL: https://www.sciencedirect.com/science/article/pii/S036031991301358X.
- [64] L. Boon-Brett, J. Bousek, and P. Moretto. "Reliability of commercially available hydrogen sensors for detection of hydrogen at critical concentrations: Part II selected sensor test results". In: International Journal of Hydrogen Energy 34.1 (2009), pp. 562-571. ISSN: 0360-3199. DOI: https://doi.org/10.1016/j.ijhydene.2008.10.033. URL: https://www.sciencedirect.com/science/article/pii/S0360319908013128.
- [65] HYDROGEN SAFETY BARRIERS AND SAFETY MEASURES. http: //www.hysafe.org/download/1200/BRHS_Chap5_V1p2.pdf. Online; accessed 29 September 2021.

- [66] L. Boon-Brett et al. "A comparison of test methods for the measurement of hydrogen sensor response and recovery times". In: International Journal of Hydrogen Energy 35.14 (2010), pp. 7652-7663. ISSN: 0360-3199. DOI: https://doi.org/10.1016/j.ijhydene.2010.04.
 139. URL: https://www.sciencedirect.com/science/article/pii/S0360319910008414.
- [67] "Solid-state potentiometric gas sensors—current status and future trends". In: Journal of Solid State Electrochemistry 13.1 (2009), pp. 3–25. ISSN: 1433-0768. DOI: https://doi.org/10.1016/j.ijhydene.2010.04. 139.
- [68] Y. Luo et al. "Hydrogen sensors based on noble metal doped metaloxide semiconductor: A review". In: International Journal of Hydrogen Energy 42.31 (2017), pp. 20386-20397. ISSN: 0360-3199. DOI: https: //doi.org/10.1016/j.ijhydene.2017.06.066. URL: https://www. sciencedirect.com/science/article/pii/S0360319917323376.
- [69] G. Black et al. "Performance Testing of a MOSFET Sensor". In: (Jan. 2010).
- [70] W. C. HINDS. "Aerosol Technology: Properties, Behavior, and Measurement of Airborne Particles". In: 2nd ed. New York: John Wiley & Sons, Inc., 1998. Chap. 16.
- [71] M. Lemmetty, J. Keskinen, and M. Marjamäki. "The ELPI Response and Data Reduction II: Properties of Kernels and Data Inversion". In: Aerosol Science and Technology 39.7 (2005), pp. 583–595. DOI: 10.1080/027868291009224. URL: https://doi.org/10.1080/ 027868291009224.
- [72] J. B. Heywood. "Internal Combustion Engine Fundamentals". In: 1st ed. New York: McGraw-Hill, 1988. Chap. 11.
- [73] J. Brockmann. "Aerosol Transport in Sampling Lines and Inlets". In: July 2011, pp. 68 –105. ISBN: 9781118001684. DOI: 10.1002/ 9781118001684.ch6.
- [74] A. Hulanicki, S. Glab, and F. Ingman. "Chemical sensors: definitions and classification". In: Pure and Applied Chemistry 63.9 (1991), pp. 1247–1250. DOI: doi:10.1351/pac199163091247. URL: https://doi.org/10.1351/pac199163091247.

- [75] L. Zhengzhou Winsen Electronics Technology Co. Flammable Gas Sensor (Model: MQ-8) Manual. https://cdn.sparkfun.com/datasheets/Sensors/Biometric/MQ-8%20Ver1.3%20-%20Manual.pdf. Online; accessed 16 Dec 2021.
- [76] M. M. Cumputing. Voltage Measurement DAQ HAT for Raspberry Pi. https://www.mccdaq.com/PDFs/specs/DS-MCC-118.pdf. Online; accessed 16 Dec 2021.
- [77] Seaspan Reliant. https://www.marinetraffic.com/en/ais/details/ ships/shipid:4689965/mmsi:316033814/imo:9764233/vessel: SEASPAN_RELIANT. Online; accessed 04 Oct 2021.
- [78] K. Hocke. Seaspan takes delivery of second LNG hybrid cargo ferry. Last accessed 27 February 2017. 2017. URL: https://www.workboat. com/shipbuilding/seaspan-takes-delivery-second-ferry.
- [79] J. Taylor. Seaspan Ferries Corporation Announces Arrival of Second New Liquefied Natural Gas (LNG) Fuelled Vessel. shorturl.at/ fuzTV. Online; accessed 04 Oct 2021.
- [80] U. of Toronto. Evaluation of the Impact of Using Biodiesel and Renewable Diesel to Reduce Greenhouse Gas Emissions in City of Toronto's Fleet Vehicles. Report. University of Toronto, 2019.
- [81] H. Moosmüller et al. "Time Resolved Characterization of Diesel Particulate Emissions. 1. Instruments for Particle Mass Measurements". In: *Environmental Science & Technology* 35.4 (2001). PMID: 11349292, pp. 781–787. DOI: 10.1021/es0013935. URL: https://doi.org/10.1021/es0013935.
- [82] S. K. Hoekman et al. "Review of biodiesel composition, properties, and specifications". In: *Renewable and Sustainable Energy Reviews* 16.1 (2012), pp. 143-169. ISSN: 1364-0321. DOI: https://doi.org/ 10.1016/j.rser.2011.07.143. URL: https://www.sciencedirect. com/science/article/pii/S136403211100390X.
- [83] F. M. White. *Fluid mechanics*. 7th ed. Mcgraw-Hill, 2009.
- [84] D. Ltd. Dekati ELPI+ user manual. English. Version 1.56. Dekati Ltd. 2019.
- [85] Omega. Thermocouple types. https://www.omega.ca/en/resources/ thermocouple-types. Online; accessed 05 Oct 2021.
- [86] F. Corporation. Fluke 922 airflow meter users manual. English. Version 1. Fluke Corporation. 2006.

- [87] Lambda Sensor LSU 4.9. English. BOSCH. 2020.
- [88] J. B. Heywood. Internal Combustion Engine Fundamentals. 1st ed. New York: McGraw-Hill, 1988.
- [89] "Combustion and emissions characteristics of diesel engine fueled by biodiesel at partial load conditions". In: *Applied Energy* 99 (2012), pp. 363-371. ISSN: 0306-2619. DOI: https://doi.org/10.1016/j. apenergy.2012.05.049.
- [90] A. Petzold et al. Particle emissions from marine Diesel engines operating on biofuels. ETH - Conference on Nanoparticles 2008. 2008. URL: https://www.nanoparticles.ch/archive/2008_Petzold_PR.pdf.
- [91] C. D. Rakopoulos and E. G. Giakoumis. Diesel Engine Transient Operation. Springer, 2009.
- [92] S. Ushakov, D. Stenersen, and P. M. Einang. "Methane slip from gas fuelled ships: a comprehensive summary based on measurement data". In: Journal of Marine Science and Technology 24.4 (2019), pp. 1308–1325. ISSN: 1437-8213. DOI: 10.1007/s00773-018-00622-z. URL: https://doi.org/10.1007/s00773-018-00622-z.
- [93] J. Zheng et al. "Effect of equivalence ratio on combustion and emissions of a dual-fuel natural gas engine ignited with diesel". In: Applied Thermal Engineering 146 (2019), pp. 738-751. ISSN: 1359-4311. DOI: https://doi.org/10.1016/j.applthermaleng.2018.10.045. URL: https://www.sciencedirect.com/science/article/pii/S1359431118339875.

Appendix A PM Result Comparison

Gravimetric samples were collected at 25-90% loads for the different fuels. The PM mass obtained from the filter samples was converted to mass concentration and compared to DustTrak results in Figure A.1. The variations of the comparison under various engine loads are shown in Figure A.2.



Figure A.1: The comparison between DustTrak PM concentration and gravimetric sample results (diluted): the yellow line represents the linear fitting between the two concentrations



Figure A.2: PM concentrations (DR corrected) from the DustTrak and the gravimetric samples under various engine loads for the different fuels: black markers represent DustTrak results, red markers represent filter sample results

Appendix B

ECOM and FTIR Comparison



Figure B.1: The comparison between CO_2 concentrations from ECOM and FTIR



Figure B.2: The comparison between NOx concentrations from ECOM and FTIR



Figure B.3: The comparison between CO concentrations from ECOM and FTIR



Figure B.4: The comparison between $\rm CH_4$ concentrations from ECOM, FTIR, AVL, and WMS

Appendix C

Data Processing Script

```
%%Matlab codes for processing raw test data
%%Author: M.Guan
%%Oct, 2021
%%dry to wet conversion for ECOM using FTIR water
   concentrations
clear all
clc
load('data_summary-0830.mat'); %raw data named 's'
load('error_0830.mat'); %standard errors named 'e'
%%dry to wet basis conversion
s.cf=1-s.H20_FTIR/100; %conversion factor
e.cf=e.H20_FTIR/100;
s.CO2w=s.co2.*s.cf; %
e.CO2w=s.CO2w.*sqrt((e.co2./s.co2).^2+(e.cf./s.cf)
   .^2);
s.02w=s.o2.*s.cf; %
e.O2w=s.O2w.*sqrt((e.o2./s.o2).^2+(e.cf./s.cf).^2);
s.NOxw=s.nox.*s.cf; %ppm
e.NOxw=s.NOxw.*sqrt((e.nox./s.nox).^2+(e.cf./s.cf)
   .^2);
s.COw=s.co.*s.cf; %ppm
e.COw=s.COw.*sqrt((e.co./s.co).^2+(e.cf./s.cf).^2);
s.CH4w=s.ch4.*s.cf; %ppm
e.CH4w=s.CH4w.*sqrt((e.ch4./s.ch4).^2+(e.cf./s.cf)
   .^2);
%% lambda calculation
s.x(s.Fuel=='D')=12;
s.x(s.Fuel=='BF1' | s.Fuel=='BF2' | s.Fuel=='B80' |
   s.Fuel == 'BF1 + add ') = 18;
```

```
s.x(s.Fuel=='D/LNG' | s.Fuel=='BF1/LNG' | s.Fuel=='
   BF2/LNG') = 1;
s.z(s.Fuel=='D')=0;
s.z(s.Fuel=='BF1' | s.Fuel=='BF2' | s.Fuel=='B80' |
   s.Fuel == 'BF1 + add ') = 2;
s.z(s.Fuel=='D/LNG' | s.Fuel=='BF1/LNG' | s.Fuel=='
   BF2/LNG') = 0:
s.Mf(s.Fuel=='D')=167;
s.Mf(s.Fuel=='BF1' | s.Fuel=='BF2' | s.Fuel=='B80' |
    s.Fuel == 'BF1+add') = 280;
s.Mf(s.Fuel=='D/LNG' | s.Fuel=='BF1/LNG' | s.Fuel=='
   BF2/LNG') = 16;
s.AF(s.Fuel=='D')=14.5;
s.AF(s.Fuel=='BF1' | s.Fuel=='BF2' | s.Fuel=='B80' |
    s.Fuel == 'BF1 + add ') = 12.3;
s.AF(s.Fuel=='D/LNG' | s.Fuel=='BF1/LNG' | s.Fuel=='
   BF2/LNG') = 17.2;
s.Y=1/0.42*(s.x./((s.CO2w+s.CH4_FTIR/10000)./(2*s.
   CO2w+s.H2O_FTIR+2*s.O2w))-s.z);
e.Y=e.CH4_FTIR/10000;
s.lamc=s.Y./s.AF*28.97./s.Mf;
e.lamc=s.lamc.*e.Y./s.Y;
%% calculate exhaust gas molar weight by assuming a
   mixture of
%%CO2,O2,H2O,CH4 and N2
s.Mexh=44.01*s.CO2w/100+32*s.O2w/100+18.01*s.
   H20_FTIR/100+16.04*s.CH4_FTIR/10^6+28.01*(1-s.02w
   /100-s.CO2w/100-s.H20_FTIR/100-s.CH4_FTIR/10<sup>6</sup>);
e.Mexh=sqrt(0.4401^2*e.CO2w.^2+0.32^2*e.O2w
   .^2+0.18^2*e.H20_FTIR.^2+(16.04e-6)^2*e.CH4_FTIR
   .^2+0.28^2*(e.02w.^2+e.C02w.^2+e.H20_FTIR.^2)+(28
   e-6)^2*e.CH4_FTIR.^2);
%%
p=101325; %Pa
R=8.314; %J/mol-K
%%Calculate density of exhaust using ideal gas law
s.rho_ex=p*s.Mexh/R./(s.tex+273.15)/1000;
e.rho_ex=s.rho_ex.*sqrt((e.Mexh./s.Mexh).^2+(e.tex
   ./(s.tex+273)).^2);
```

```
%%Calculate Exhaust flow rate based pitot tube
   voltage
ratio=68.923*s.dp./s.rho_ex;
eratio=ratio.*sqrt((e.dp./s.dp).^2+(e.rho_ex./s.
   rho_ex).^2);
c_pt=sqrt(2)*1.344; %pitot tube constant
Vc=c_pt*sqrt(ratio); %center line velocity [m/s]
eVc=Vc/2.*eratio./ratio;
Vm=Vc/(1+1.33*0.2); %mean velocity [m/s]
eVm = eVc/(1+1.33*0.2);
D=0.7; %pipe diameter [m]
mu_air=3.3e-7*(s.tex+273.15).^0.7;
mu_ex=mu_air./(1+0.027*s.phi);
s.Rex=s.rho_ex.*Vm*D./mu_ex;
s.Qexh=Vm*pi*(D/2)^2; %flow rate [m3/s]
e.Qexh=eVm*pi*(D/2)^2;
%%
%%Exhaust mass flow rate
s.m_ex=s.Qexh.*s.rho_ex; %kg/s
e.m_ex=s.m_ex.*sqrt((e.Qexh./s.Qexh).^2+(e.rho_ex./s
   .rho_ex).^2);
%% emission mass flow rate
s.CO2m=s.CO2w*44./s.Mexh/100.*s.m_ex*3.6e6; %%mass
   flow rate [g/hr]
e.CO2m=s.CO2m.*sqrt((e.CO2w./s.CO2w).^2+(e.Mexh./s.
   Mexh).^2+(e.m_ex./s.m_ex).^2);
s.02m=s.02w*44./s.Mexh/100.*s.m_ex*3.6e6; %%mass
   flow rate [g/hr]
e.02m=s.02m.*sqrt((e.02w./s.02w).^2+(e.Mexh./s.Mexh)
   .^2+(e.m_ex./s.m_ex).^2);
s.NOxm=s.NOxw*44./s.Mexh/10^6.*s.m_ex*3.6e6; %%mass
   flow rate [g/hr]
e.NOxm=s.NOxm.*sqrt((e.NOxw./s.NOxw).^2+(e.Mexh./s.
   Mexh).^{2+}(e.m_ex./s.m_ex).^{2};
s.COm=s.COw*44./s.Mexh/10^6.*s.m_ex*3.6e6; %%mass
   flow rate [g/hr]
e.COm=s.COm.*sqrt((e.COw./s.COw).^2+(e.Mexh./s.Mexh)
   .^2+(e.m_ex./s.m_ex).^2);
s.CH4m=s.CH4_FTIR*44./s.Mexh/1e6.*s.m_ex*3.6e6; %%
   mass flow rate [g/hr]
```

```
e.CH4m=s.CH4m.*sqrt((e.CH4_FTIR./s.CH4_FTIR).^2+(e.
   Mexh./s.Mexh).^2+(e.m_ex./s.m_ex).^2);
%% Brake specific emissions
s.BSC02=s.C02m./(4320*s.load/100); %g/(kW-h)
e.BSC02=s.BSC02.*sqrt((e.C02m./s.C02m).^2+(e.load./s
   .load).^2);
s.BSCO=s.COm./(4320*s.load/100);
                                   %g/(kW-h)
e.BSCO=s.BSCO.*sqrt((e.COm./s.COm).^2+(e.load./s.
   load).^2);
s.BSO2=s.O2m./(4320*s.load/100);
                                   %g/(kW-h)
e.BS02=s.BS02.*sqrt((e.02m./s.02m).^2+(e.load./s.
   load).^2);
s.BSNOx=s.NOxm./(4320*s.load/100); %g/(kW-h)
e.BSNOx=s.BSNOx.*sqrt((e.NOxm./s.NOxm).^2+(e.load./s
   .load).^2);
s.BSCH4=s.CH4m./(4320*s.load/100);
                                     %g/(kW-h)
e.BSCH4=s.BSCH4.*sqrt((e.CH4m./s.CH4m).^2+(e.load./s
   .load).^2);
%% BSFC calculation
s.CW(s.Fuel=='D')=0.86;
s.CW(s.Fuel=='BF1'|s.Fuel=='BF2'|s.Fuel=='B80' | s.
   Fuel == 'BF1 + add ') = 0.77;
s.CW(s.Fuel=='D/LNG' | s.Fuel=='BF1/LNG' | s.Fuel=='
   BF2/LNG') = 12/16;
s.BSFC=(s.BSC02*12/44+s.BSC0*12/28+s.BSCH4*12/16)./s
   . CW;
e.BSFC=(e.BSC02*12/44+e.BSC0*12/28+e.BSCH4*12/16)./s
   .CW;
%% dilution ratio
s.dr=s.CO2w./s.co2_li;
e.dr=s.dr.*sqrt((e.CO2w./s.CO2w).^2+(e.co2_li./s.
   co2_li).^2);
%% PM raw
s.pmraw=s.pm.*s.dr;
e.pmraw=s.pmraw.*sqrt((e.pm./s.pm).^2+(e.dr./s.dr)
   .^2);
s.pmfilter=s.filter.*s.dr;
e.pmfilter=s.pmfilter.*sqrt((e.filter./s.filter)
   .^2+(e.dr./s.dr).^2);
s.PMm=s.pmraw.*s.Qexh*3.6; %[g/hr]
```

```
e.PMm=s.PMm.*sqrt((e.pmraw./s.pmraw).^2+(e.Qexh./s.
   Qexh).^2);
s.PMf=s.pmfilter.*s.Qexh*3.6;
e.PMf=s.PMf.*sqrt((e.pmfilter./s.pmfilter).^2+(e.
   Qexh./s.Qexh).^2);
s.BSPM=s.PMm./(4320*s.load/100);
e.BSPM=s.BSPM.*sqrt((e.PMm./s.PMm).^2+(e.load./s.
   load).^2);
s.BSPMf=s.PMf./(4320*s.load/100);
e.BSPMf=s.BSPMf.*sqrt((e.PMf./s.PMf).^2+(e.load./s.
   load).^2);
%% PN raw
s.pnraw=s.pn.*s.dr;
e.pnraw=s.pnraw.*sqrt((e.pn./s.pn).^2+(e.dr./s.dr)
   .^2);
s.PNm=s.pnraw.*s.Qexh*3.6e9; %[#/hr]
e.PNm=s.PNm.*sqrt((e.pnraw./s.pnraw).^2+(e.Qexh./s.
   Qexh).^2);
s.BSPN=s.pnraw.*s.Qexh*3600e6./(4320*s.load/100);
   %[#/kwh]
e.BSPN=s.BSPN.*sqrt((e.pnraw./s.pnraw).^2+(e.Qexh./s
```

.Qexh).²⁺(e.load./s.load).²);