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IMPACTS OF FUELS ON Ag/Al_2O_3 SCR CATALYST IN DIESEL ENGINES

by

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ABSTRACT

The combustion of propane and NH_3 in diesel engines on low load operation, produces high level of unburnt THC and NH_3 emissions. Taking advantage of the increased THC and NH_3 levels in the exhaust, the NOx reduction activities of a Ag/Al_2O_3 SCR catalyst was investigated.

Impacts of diesel fuel injection timing on the combustion, performance and emissions of a diesel engine running on diesel-propane dual fuelling system were studied. Advanced injection timing was found to improve the combustion performance at low engine load operation. The higher in-cylinder pressure and temperature due to advanced injection timing improved the combustion of the in-cylinder fuel-air mixture.

The effects of NH_3 with additionally added H_2 (mimicking engine operation with NH_3 addition) on the NOx reduction activity over Ag/Al_2O_3 catalyst were investigated in a diesel engine in the presence of low concentrations of HC reductant using a DOC+SCR aftertreatment configuration. It was found that although, part of the exhaust HC was involved in HC-SCR of NOx, the introduction of H_2 and NH_3 mixture provided the catalyst with additional reductant that supported the removal of NOx at the exhaust.

Subsequently, under diesel-propane fuelling system, where 25% of diesel fuel was replaced with low carbon fuel (i.e., propane), higher concentration of HC reductant and NO_2 were made available for the SCR Ag/Al_2O_3 catalyst in the presence and absence of H_2 and NH_3 mixture. Although, significant amount of CO and THC escaped the catalyst unconverted, NOx conversion efficiency was enhanced. This study shows that the high level of NH_3 and THC emissions in the exhaust can be beneficial to the SCR aftertreatment system.

DEDICATION

This work is specially dedicated to God almighty; my mother, Madam Evelyn Enenemiepre Amieghaye; Bro. Morris Kofi Odubo (late) and to my dear wife and children.

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LIST OF ABBREVIATIONS

AFR	Air Fuel Ratio
Ag/Al_2O_3	Silver on Alumina
AHRR	Apparent Heat Release Rate
ATDC	After Top Dead Centre
ATR	Auto-Thermal Reforming
BDC	Bottom Dead Centre
BMEP	Brake Mean Effective Pressure
BSEC	Brake Specific Energy Consumption
BSFC	Brake Specific Fuel Consumption
BTDC	Before Top Dead Centre
BTE	Brake Thermal Efficiency
CAD	Crank Angle Degree
CDC	Conventional diesel combustion
CI	Compression Ignition
CN	Cetane Number
CNG	Compressed Natural Gas
COV	Coefficient of Variation
CRT	Continuously Regeneration Trap
DI	Direct Injection
DOC	Diesel Oxidation Catalyst
DPF	Diesel Particulate Filter
EGR	Exhaust Gas Recirculation
EOC	End of Combustion
EOI	End of Injection
FC	Fuel Cell
FTIR	Fourier Transform Infrared Radiation
GHG	Greenhouse Gas
HCCI	Homogeneous Charge Compression Ignition

HC-SCR	Hydrocarbon Selective Catalytic Reduction
HRF	High Reactivity Fuel
ICE	Internal Combustion Engine
ID	Ignition Delay
IMEP	Indicated Mean Effective Pressure
LHV	Lower Heat Value
$LHV_{C_3H_8}$	Lower Heat Value of Propane
LHV_D	Lower Heat Value of Diesel
LIVC	Late Intake Valve Closing
LPG	Liquified Petroleum Gas
LRF	Low Reactivity Fuel
MFB	Mass Fraction Burn
NG	Natural Gas
NH_3-SCR	Ammonia Selective Catalytic Reduction
PCCI	Premixed Charge Compression Ignition
PGM	Platinum Group Metal
PM	Particulate Matter
ppm	Parts Per Million
PRR	Pressure Rise Rate
RCCI	Reactivity-Control Compression Ignition
REGR	Reformed Exhaust Gas Recirculation
ROHR	Rate of Heat Release
SCR	Selective Catalytic Reduction
SI	Spark Ignition
SOC	Start of Combustion
SOI	Start of Injection
SR	Steam Reforming
TDC	Top Dead Centre
UFPs	Ultrafine Particles
ULSD	Ultra Low Sulphur Diesel

VVT	Variable Valve Timing
WGSR	Water Gas Shift Reaction

LIST OF SYMBOLS

Symbol	Units	
A	m^2	Cylinder area
L	m	Engine stroke
$\dot{m}_a$	kg/s	Air mass flow rate
$\dot{m}_f$	kg/s	Fuel mass flow
rate		
GHSV	h^{-1}	Gas hourly space velocity
N	rpm	Crankshaft rotational speed
n		Number of cylinders
ρ	kg/m^3	Density
p	bar	In-cylinder pressure
P_B	kW	Engine brake power
T	Nm	Engine torque
t	s	Time
η_{th}	%	Engine brake thermal efficiency
V	cm^3	Instantaneous volume of the engine cylinder
V_d	cm^3	Displaced volume of cylinder
γ	-	Ratio of specific heats
Ø	-	Diameter
Θ	^{o}	Crank angle degree
ϕ		Local equivalence ratio
C_p	J/kgK	Specific heat capacity at constant pressure
C_v	J/kgK	Specific heat capacity at constant volume
Z	%	Propane substitution

CHAPTER 1

INTRODUCTION

1.1 Background

Years after the discovery of Diesel and Otto cycles, the internal combustion engines (ICEs) have remained the key prime mover, providing power for essential services like the automotive, rail locomotives and ships; electricity; industrial and agricultural power plants. In the transportation sector, the spark ignition (SI) and compression ignition (CI) engines constitute the major powertrain, and they are distinguished based on the fuel types, air-fuel mixing process and the mode of combustion (Ren et al. 2018). In terms of the fuel types, whilst the CI engine uses diesel and diesel-type fuels that have high cetane numbers (CNs) and support auto-ignition, the SI engine uses gasoline and gasoline-type fuels with low CN, high octane number and are resistant to auto-ignition and therefore, they require an external source for ignition.

During combustion of fossil fuels, the chemical energy stored in the fuel is converted into mechanical energy. However, due to the presence of carbon and other properties in fossil-based fuels and assisted by the prevailing conditions in the combustion chamber, the exhaust from the ICE contains a number of undesired gaseous and solid substances which are harmful to human health and the environments. Examples of these harmful products are carbon dioxide (CO_2), carbon monoxide (CO), nitrogen oxides (NOx), total hydrocarbons (THC) and particulate matter (PM) and other gaseous substances.

Even though the CO_2 emissions from transportation could be eliminated with the advent of vehicle electrification, the limited energy density, extended charging duration of batteries and high

production costs of electrified vehicles (Borchers et al. 2021) means that with the current state of technology, the transportation sector, especially the heavy-duty sector, would continue to be dominated by internal combustion engines running on renewable liquid fuels (Yousefi et al. 2022).

Unlike the stoichiometric gasoline engines, lean burn engines such as the direct injection diesel and gasoline engines consume less amount of fuel and therefore, enjoy lower running costs and produce less CO_2 emission. However, these advantages favour the formation of NOx and PM which are particularly challenging to control. NOx emissions into the atmosphere contribute to the formation of photo-chemical smog, global warming, acidification of rain and they also have direct harmful impacts on human health by affecting the respiratory system. PMs on the other hand have been linked to several ailments, including cancer, cardiovascular diseases and premature death (Macián et al. 2021).

Having acknowledged the dangers associated with these pollutants, several countries across the World (e.g., UK, US, Japan, etc.) and intergovernmental bodies (e.g., European Union and United Nations) have been promoting and upgrading legislations to regulate and limit the emissions of these pollutants from all modes of vehicular transports (Herreros et al. 2014a). For instance, in the European Union in particular, since the environmental regulations started in 1992 as shown in Table 1.1, they have evolved progressively over the years to become very stringent with the proposed EURO 7 that is scheduled to enter into force in 2025. In the same manner, the BRIC (Brazil, Russia, India and China) countries (Honardar et al. 2011), Nigeria, etc. also have their own emission standards as shown in Figure 1.1.

Table 1. 1. Past, current and future European Union emissions standards for gasoline and diesel engines.

Gasoline Engine									Diesel Engine						
Emissions	Units	Euro 1	Euro 2	Euro 3	Euro 4	Euro 5	Euro 6	Euro 7	Euro 1	Euro 2	Euro 3	Euro 4	Euro 5	Euro 6	Euro 7
		July 1992	Jan. 1996	Jan. 2000	Jan. 2005	Sept. 2009	Sept. 2014	2025	July 1992	Jan. 1996	Jan. 2000	Jan. 2005	Sept. 2009	Sept. 2014	2025
THC	g/km			0.2	0.1	0.1	0.1	0.1	-	-	-	-	-	-	0.1
CO		2.72	2.2	2.3	1.0	1.0	1.0	0.5	2.72	1.0	0.66	0.5	0.5	0.5	0.5
NOx		-	-	0.15	0.08	0.06	0.06	0.06	-	-	0.50	0.25	0.18	0.08	0.06
HC+NOx		0.97	0.5	-	-	-	-	-	0.97	0.70	0.56	0.30	0.23	0.17	-
PM		-	-	-	-	0.0045 (GDI)	0.0045 (GDI)	0.0045	0.14	0.08	0.05	0.025	0.0045	0.0045	0.0045
PN #	#/km	-	-	-	-	-	6×10^{11}	6×10^{11}	-	-	-	-	6×10^{11}	6×10^{11}	6×10^{11}

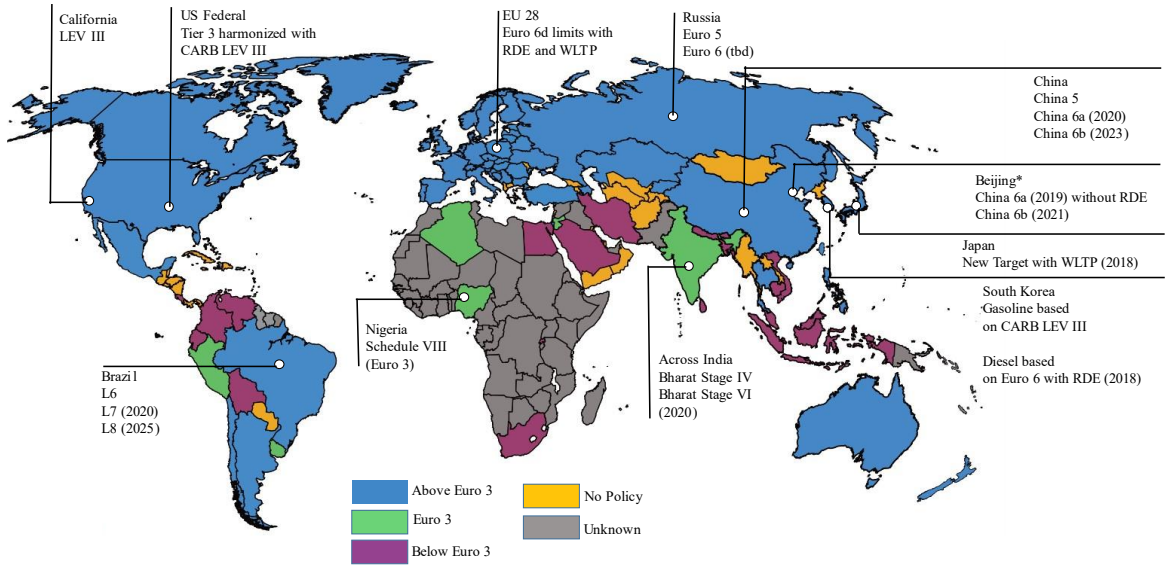


Figure 1. 1. Emission Standards of Different Countries Across the Globe. Adapted from (UNEP 2017).

The high fuel economy of modern lean burn engines; various technological innovations including exhaust gas recirculation (EGR), turbocharging and variable valve timing (VVT); advanced combustion strategies and post-combustion control techniques have contributed significantly to moderating the quantity of CO_2 and other pollutants emitted into the environment. However, as environmental legislations are becoming more and more stringent, especially with

respect to NOx and PM emissions, applications of liquefied petroleum gas (LPG) and ammonia (NH_3) as engine fuels are also possible options to achieve low pollution in transportation.

Liquefied petroleum gas and ammonia can be produced from renewables and other sources (i.e., natural gas) which are widely available in Nigeria and more economical than the conventional fuels. In addition, because both LPG and NH_3 can be stored as liquids under similar and moderate pressure, the same storage and transportation facilities for the former could also be used for the latter if all components with brass, copper and rubbers are replaced with mild steel and Teflon materials (Reiter and Kong 2011). Therefore, besides the environmental benefits of LPG and NH_3 in transportation vehicles, the application of cleaner, low to carbon-free fuels will also enhance the performance of the vehicles' aftertreatment devices to meet the tightening emission standards. In addition, as the current environmental catalysts for emission control are expensive, where alternative catalysts that could provide similar function as the PGM loaded catalysts are fitted in the engine exhaust system, the exhaust emission control techniques could be supported with less expensive but efficient emission reduction catalyst.

1.2 Research Motivation

Due to the well-known environmental and health hazards of the pollutants from the IC engines, several attempts have been made successfully in reducing the amount that is released into the environment. However, as the environmental regulations continue to evolve and become more and more stringent, it is necessary to improve upon the existing control strategies that would be able to achieve the present and future emission limits. Moreover, the trends in emissions control in recent times are being shifted to low load and cold start operations, which are typical of urban driving conditions (Bogarra et al. 2016). This is because, studies have shown that human exposure

to exhaust pollutants is higher in urban environments (Lefort, Herreros, and Tsolakis 2014), and at these low exhaust temperatures, the engine emits the bulk of the pollutants (Shen, Shamim, and Sengupta 1999; Suarez-bertoa and Astorga 2018; Tsinoglou and Koltsakis 2003).

High engine out emissions at low load and cold start operations could be the result of fuel metering deviations that is more intense at cold start (Tsinoglou and Koltsakis 2003). As the fuel is transferred into the engine cylinder in liquid phase with certain velocity, the injected fuel in the manifold or port consists of fuel droplets of which part of it evaporates and the rest falls on the intake port surface and creates a film. This becomes more intense at low engine temperature and pressure, as the liquid fuel spray will have to penetrate faster and further into the combustion chamber before vaporising (Musculus, Miles, and Pickett 2013). Furthermore, low engine temperature during idle, stop/start and low load operations of vehicles in typically congested urban environments could also lead to reduction in fuel evaporation and therefore, increasing the amount of unburnt HC (Lefort 2015). Thirdly, during cold start, a large amount of fuel is injected into the cylinder, resulting to increase in larger particles (Bogarra et al. 2017; Gaddam and Wal 2013).

1.3 Aim and Objectives of the Research

The main aim of this research is to study the impact of low carbon and carbon-free alternative fuels on Ag/Al_2O_3 catalyst in reducing NOx emissions at low exhaust gas temperature and under excess oxygen condition. To achieve the aim, this research intends to:

1. Investigate the effects of injection timings of a high reactivity diesel fuel on the combustion, performance and emissions characteristics of diesel and propane dual fuel engine at low engine load.

2 Study the effects of different concentrations of H_2 and NH_3 mixture on the activity of hydrocarbon selective catalytic reduction (HC-SCR) of NOx over silver supported alumina catalyst (Ag/Al_2O_3), where the unburnt HC contained in the exhaust gas from a diesel engine at low load was reduced with a diesel oxidation catalyst, whilst different H_2 and NH_3 concentrations considered as products of ammonia decompositions were added to the exhaust gas stream.

3 Study the NOx reduction activities over a Ag/Al_2O_3 catalyst by employing the unburnt HC from the diesel-propane dual fuel combustion at low engine load as the reducing agent and investigate the benefits of H_2 and NH_3 mixture application on the catalyst performance.

1.4 Research Outline

This thesis is divided into eight chapters. Chapter 1 presents an introduction to the challenges with the internal combustion engines, the current technological limitations with electric vehicles. Past, present and future emissions limits for different countries and regions were highlighted. Possible approaches to achieve these limits through low-carbon and carbon-free fuels as well as alternative environmental catalyst were briefly discussed. These were done to set the stage for subsequent chapters. The other chapters of the thesis are organised as follows.

Chapter 2: Literature Review

This chapter presents a general but very concise overview of diesel engine combustion, emissions formation, dual fuel, low temperature combustion and engine emission control strategies. Alternative fuels like natural gas, propane, hydrogen and NH_3 applications in compression ignition engines were discussed. Lastly, the different exhaust gas aftertreatment strategies were reviewed and their merits and demerits were discussed.

Chapter 3: Experimental Equipment

This chapter describes some of the facilities that were used in running the experiments and arriving at the results. These include the engine test rigs and instrumentations, furnace, mini reactor, catalysts, engine exhaust gas emissions analysers and some selected properties of the diesel, propane and gasoline fuels and formulae.

Chapter 4: Investigating the Combustion, Performance and Emission Characteristics of Propane-Diesel Dual Fuel Engine

In this chapter, experiments were run on a diesel engine running on a diesel-propane dual fuelling system. This was done by using propane to displace 15 and 25 per cent of the diesel fuel, whilst the diesel fuel injection timing was advanced to create a better premixed in-cylinder air-fuel mixture. The study was carried out to investigate the effects of injection timings of a high reactivity fuel on the combustion, performance and emissions characteristics of a diesel engine running on diesel-propane dual fuelling system under low load engine operation.

Chapter 5: The Effects of H_2 and NH_3 Mixture on NOx Reduction Over Ag/Al_2O_3 Catalyst

Onboard applications of H_2 and NH_3 mixture in diesel vehicles for NH_3-SCR of NOx over Ag/Al_2O_3 catalyst in the presence of low amount of HC reductant was investigated in this chapter. Experiments were performed using a DOC to reduce or eliminate the exhaust HC in a DOC+SCR aftertreatment configuration. The NOx reduction activity over Ag/Al_2O_3 catalyst was investigated by injecting different concentrations of H_2 and NH_3 mixture upstream the DOC. Subsequently, the injection point for H_2 and NH_3 mixture was moved downstream the DOC.

Chapter 6: Enhancing the NOx Reduction Activities of Ag/Al_2O_3 Catalyst with Propane and H_2 and NH_3 Mixture

In this chapter, the HC-SCR activity of NOx over Ag/Al_2O_3 catalyst was investigated in the presence of H_2 and NH_3 mixture using the exhaust HC. The experiments were carried out using the exhaust from a diesel-propane dual fuel engine containing significant amount of unburnt THC and other low carbon exhaust species. Hydrogen injection cycles were carried out by injecting two different concentrations of H_2 and NH_3 mixtures upstream the SCR catalyst. The effects of the catalyst over the exhaust THC and other exhaust gas species in the presence and absence of the H_2 and NH_3 mixture were also analysed.

Chapter 7: Conclusions and Future Work

This chapter presents the summary and the important findings from this research work and the motive for each chapter is also presented. Also presented in this chapter are recommendations for future works arising from this research.

CHAPTER 2

LITERATURE REVIEW

2.1 Compression Ignition Engines

With high thermal efficiency exceeding 50% (Kim et al. 2013) and reliability, the modern direct injection (DI) diesel engines have remained not only dominant in the medium to heavy-duty transportation sector but have also gained quite a significant application in light-duty markets. The high thermal efficiency is attributed to several factors, such as the high compression ratio, lean air-fuel mixture (Lee, Song, and Chun 2010), and greater amount of work that is extracted at the expansion stroke.

Nonetheless, the trend in diesel car registration has declined significantly in the last 4 years in favour of gasoline, alternative fuel (e.g., natural gas) vehicles and hybrid and electric vehicles (Carlucci et al. 2020; Conway et al. 2021). This is due to the high NOx and PM emissions from diesel engine, resulting from localized fuel rich mixture zones and overall lean combustion (Kim, Kim and Lee 2008). Furthermore, because of the known trade-off between NOx and PM, it becomes difficult to simultaneously control these emissions as reducing one causes the other to increase.

2.1.1 Combustion Process in CI Engine

The combustion process in the diesel engine can be well explained with the heat-release history of a typical direct injection diesel engine, which is represented on the rate of heat release (ROHR) diagram as shown Figure 2.1. The ROHR which profiles the rate at which the chemical

energy stored in the fuel is converted into heat, is a function of the physicochemical properties of the fuel, instantaneous in-cylinder pressure and cylinder volume travelled by the piston (Yusri et al. 2019).

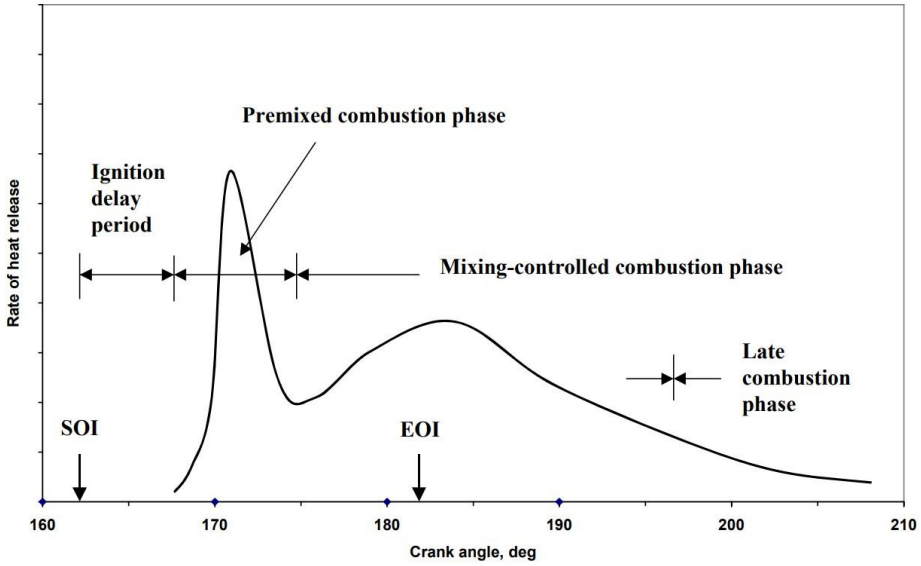


Figure 2. 1. Rate of heat release of a direct injection diesel engine (Martini and Larsen 2013).

The ROHR diagram typically consists of four phases, namely: the ignition delay (ID), premixed combustion, mixing (diffusion) control combustion and late combustion phases. Each of these phases is in principle controlled by the fuel-air-mixing process. The thermodynamic cycle begins when air is inducted into the cylinder and compressed by the upward movement of the piston. As the hot compressed air gets close to TDC, liquid fuel is injected into the cylinder. However, because the combustion of fuel only occurs in the gas phase, the injected liquid fuel has to be heated, disintegrates into submicron size droplets (atomization), evaporates and mix with the hot compressed air to form a combustible fuel-air mixture (Kavtaradze, Zeilinger, and Zitzler 2005). This means for ignition to take place, the fuel must be heated to a temperature sufficient for some of the weaker bonds to break down and form enough radicals to support auto-ignition (Murphy, Taylor, and Mccormick 2004).

The ignition delay (ID) period is the time interval between the start of fuel injection (SOI) to the start of combustion (SOC). The SOC has been determined using different metrics. The most common is the method which is based on the measured in-cylinder pressure data. With this method, the SOC has been defined by the departure from the straight line of the compression stroke just before TDC on a log (pressure) versus log (volume) indicator diagram plot (Stone 1999); point where 10% of the net accumulated heat release occurs (Hosseini and Checkel 2006); the CAD at which the ROHR curve passes the zero level from a negative value to a positive value after the start of fuel injection (Zeraati-Rezaei et al. 2020); the minimum point in the cumulative heat release curve (Stone 1999). Also, by differentiating the cylinder pressure with respect to the crank angle, the SOC can be defined as the minimum that occurs in the first derivative curve after the start of injection or at the point where the second and third derivative curves become zero and positive, respectively (Stone 1999).

The ignition delay is caused by a combination of physical and chemical processes occurring simultaneously under complex in-cylinder temperature and pressure conditions (Pham et al. 2021). The physical delay is the time interval from the instant of the liquid fuel injection, atomization, heating to when it is transformed into vapor phase. Whereas the chemical delay is the time it takes for the fuel to undergo thermal decomposition and form combustible radicals. As illustrated in Figure 2.2, the physical and chemical delays are strongly influenced by the fuel properties such as cetane number (CN), volatility, viscosity, surface tension. For instance, the higher the CN, the shorter the ignition delay and less fuel is injected into the combustion chamber. Higher volatility allows for faster evaporation and earlier formation of combustible mixture.

In the premixed combustion phase, the amount of combustible charge formed from the fuel-air mixture reaches a flammable limit and undergo a rapid combustion. Hence, the heat

released during the premixed combustion stage is strongly dependent on the amount of fuel-air mixture prepared during the ID period. The remaining fuel and gas mixtures after the premixed combustion stage burn in the diffusion-controlled phase of the combustion and the extent of this phase is a function of the available fuel-air mixture. The late combustion phase extends to the expansion stroke, and this completes the combustion cycle. At this stage, the combustion is an indication of heat released by small portion of fuel that was left unburned or from products that are still undergoing further oxidation.

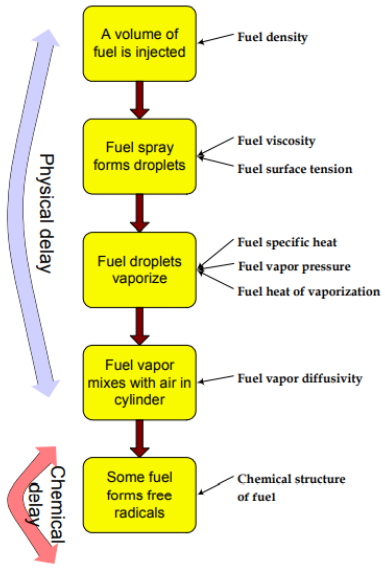


Figure 2. 2. Complete compression ignition process (Murphy, Taylor, and Mccormick 2004).

2.2 Dual Fuel Engines

Diesel engines provide highly efficient energy conversion not only with the conventional diesel fuel but also with a wide range of alternative liquid and gaseous fuels (Lapuerta et al. 2012). However, due to the high resistance of most gaseous and liquid fuels to auto-ignition by reason of their low CNs and high auto-ignition temperatures, their applications in compression ignition engines are predominantly carried out in dual fuel modes. The high compression ratio of diesel

engines makes them adaptable to alternative fuels with low CN and energy content fuels when used in co-combustion with diesel and diesel-like fuels (Mustafi, Raine, and James 2010).

Dual fuel engines are run with two fuels with different reactivity. This type of engine combines the combustion characteristics of SI and CI engines. They can operate in two ways depending on the amount of gaseous fuel relative to the liquid fuel. The first is the introduction of homogenously premixed high-octane fuel (e.g., natural gas, gasoline, hydrogen, and carbon monoxide) and air into the combustion chamber early in the intake stroke, which is then ignited by the direct injection of a small quantity of high CN liquid (i.e., pilot) fuel (Stewart, Clarke, and Chen 2007) close to TDC. In this category, the combustion of the pilot fuel generates high temperature that initiates the ignition of the surrounding premixed gaseous fuel-air mixture in the rest of the cylinder. The second category is the addition of small amount of gaseous fuel to air of a fully operational diesel engine (Karim 2003).

Bilcan et al. (2001) and Karim (2003) explained the combustion of dual fuel engines and categorized it into three phases. These are: (I) ignition of the high CN pilot fuel, (II) combustion of the remaining pilot and gaseous fuels in the immediate surrounding of the pilot fuel spray, and (III) flame propagation through the remainder of the gaseous fuel-air mixture. In a typical dual fuel engine, the bulk of the energy released comes from the combustion of the gaseous fuel with only a small fraction of the power output contributed by the pilot fuel. This is because the pilot fuel only serves as the ignition source and therefore, the amount injected is only equivalent to 5-10% of the total full load (Mustafi, Raine and James 2010; Szwaja and Grab-Rogalinski 2009).

The main objectives of the dual fuel engines are to maximize the gradual replacement of the liquid fuel with gaseous fuel (Stewart, Clarke and Chen 2007; Wagemakers and Leermakers

2012) and to reduce the emissions of NOx and PM. The ignition mode of dual fuel engines provides several ignition sources which help to optimize the gaseous fuel combustion and improve engine out emissions (Xu et al. 2016). As a common knowledge, dual fuel engines exhibit higher engine power output and efficiencies as well as lower PM and NOx emissions than the corresponding straight diesel. However, there are still some shortcomings with the application of the dual fuel engines. Under high engine load operations, the challenges are usually combustion knock and higher NOx emissions. Combustion knock is an abnormal combustion that occurs due to spontaneous ignition of a portion of the end gas mixture in the combustion chamber ahead of the propagating flame (Szwaja and Grab-Rogalinski 2009; Lounici et al. 2017). During part load operations, the lean mixture formed becomes difficult to ignite and burn completely. As the quantity of pilot fuel available is small, the flame propagation does not get to the parts of the charge located far from the ignition nuclei and therefore, slows down the burning rate (Ouchikh et al. 2022). This leads to low performance and significant amount of CO, THC emissions at part load operations (Selim 2003). However, the dual fuel engines have the advantages of utilizing a wide range of gaseous fuels and they can switch over to pure diesel fuel even under load without interruption to the engine operation.

2.3 Engine Emissions and Formation

Ideally, the combustion of hydrocarbon fuels in IC engines produces only H_2O and CO_2 as presented in the stoichiometric equation 2.1. However, due to the heterogeneity of the in-cylinder mixture and high temperature prevailing inside the combustion chamber, other gaseous and solid substances such as CO, THCs, NOx and soot are also formed as part of the combustion products. Generally, these emissions are formed inside the combustion chamber mainly due to insufficient

time needed for the oxidation of the HC fuels (Egúsquiza, Braga, and Braga 2009), non-homogeneous temperature distribution and combustion process (Tsolakis et al. 2005) and, high flame temperatures in the presence of abundant oxygen and nitrogen in the combustion chamber (Agarwal, Sinha, and Agarwal 2006).

$$C_xH_y + \left(x + \frac{y}{4}\right)[O_2 + 3.76\,N_2] \rightarrow xCO_2 + \frac{y}{2}H_2O + 3.76\left(x + \frac{y}{4}\right)N_2 \qquad 2.1$$

2.3.1 Nitrogen Oxides (NOx)

Nitrogen oxide is a common terminology for nitrogen monoxide (NO) and nitrogen dioxide (NO_2). NOx is predominantly formed as NO in the combustion chamber and is principally a product of oxidation of atmospheric nitrogen. Also, some amount of NO could be formed due to oxidation of fuel bound nitrogen (Sun et al. 2016) or prompt NO. The latter is formed due to nitrogen reacting with intermediate radicals such as C, CH, CH_2 to produce nitrogen containing species like NH, HCN, H_2CN and CN, which are subsequently oxidized to form NO (Pan et al. 2014). However, the total NOx formed through these two routes is considered less significant, as the bulk of NOx is formed as thermal NO through the Zeldovich mechanism at temperature exceeding 1800 ^oC (Leermakers, Somers, and Johansson 2012). The thermal route considered as the primary source of NO is strongly dependent on the flame temperature and residence time. The mechanism of NO formation from molecular nitrogen is governed by the equations 2.2–2.4. NO_2 on the other hand can be formed in or outside the combustion chamber by reacting with excess oxygen over an oxidation catalyst. Also, at low temperature, peroxyl radicals (RO_2) formed as intermediates of low temperature combustion of hydrocarbon fuels react with NO to form NO_2 as shown in the equation 2.5.

$$O + N_2 \rightarrow NO + N \quad (2.2)$$

$$N + O_2 \rightarrow NO + O \quad (2.3)$$

$$N + OH \rightarrow NO + H \quad (2.4)$$

$$NO + RO_2 \rightarrow NO_2 + RO \quad (2.5)$$

2.3.2 Carbon Monoxide (CO)

This is a highly toxic, colourless, tasteless, and odourless gas that is formed from incomplete combustion of hydrocarbon fuels. The formation of this gas is determined by the prevailing air-fuel (A/F) ratio during the combustion process (Heywood 1988). It could be formed at both fuel-rich and -lean regions of the cylinder. At fuel-rich regions, CO is formed when there is no sufficient oxygen to completely burn all the carbon in the fuel to CO_2. In lean mixture regions, the low temperatures could cause partial oxidation of the fuel to generate CO (Abdullah 2011). Also, decrease in burnt gas temperature during expansion process reduces the oxidation of CO and therefore, leads to the increase in the emissions of CO.

2.3.3 Total Hydrocarbon Concentration (THC)

THC constitutes the total unburnt hydrocarbons or partially burnt hydrocarbons that are contained in the engine exhaust stream. The main causes of THC emission include heterogeneity of the A/F mixture resulting from the under-mixing of fuel in air and, poor fuel oxidation in the combustion chamber caused by flame quenching from cold wall (wall quenching) and low combustion temperature (bulk quenching). In additions to these, liquid fuel films formed in

combustion chamber can survive through the exhaust stroke; and when unburnt HC mixtures are forced into crevice volumes such as spaces between the piston and cylinder wall and then released during the expansion stroke as THC.

2.3.4 Particulate Matter (PM)

These are composed of solid carbonaceous materials (soot), ash, volatile organic materials (liquid phase HC), and small amount of sulphur and metallic compounds. Soots are primarily formed in the diffusion combustion phase during incomplete combustion of HC fuel at locally fuel-rich regions with elevated temperatures. At high temperature, a large portion of the unburnt HC is stripped of hydrogen (pyrolysis) to form the carbonaceous particles (Nord 2005). A tiny fraction of the fuel as well as atomized and evaporated lubrication oil, is decomposed and appears as the volatile organic fraction (VOF) or soluble organic compounds (soluble organic fraction, SOF) in the exhaust.

As shown in Figure 2.3, particles are generally classified into three modes according to their size (diameter) distribution. These are:

1. Nuclei mode particles which are the smallest and fall within the range of 5 nm < diameter < 50 nm. They are mainly the volatile organic compounds formed during exhaust gas dilution and cooling, and may contain fractions of solid carbon, sulphur and metal compounds. These classes of particles are considered the most dangerous because of their smallness in size. This makes it easier for them to penetrate deeper into the alveola region of the human lung, bloodstream and cause great damage to the body. In fact, epidemiological studies have shown a strong link between these particles and lung disease, asthma, cardiovascular ailments as well as genetic damage (Frank et al. 2007).

2. Accumulation mode particles fall within the range of 50 nm < diameter < 1000 nm and are usually the carbonaceous agglomerates with some volatile materials adsorbed on their surfaces.
3. Coarse mode, this group of particles are those with size diameter > 1000 nm. Although, they are generally not common in exhaust emissions analysis, they represent the particles from accumulation mode that have been deposited on the exhaust system surfaces and later retained.

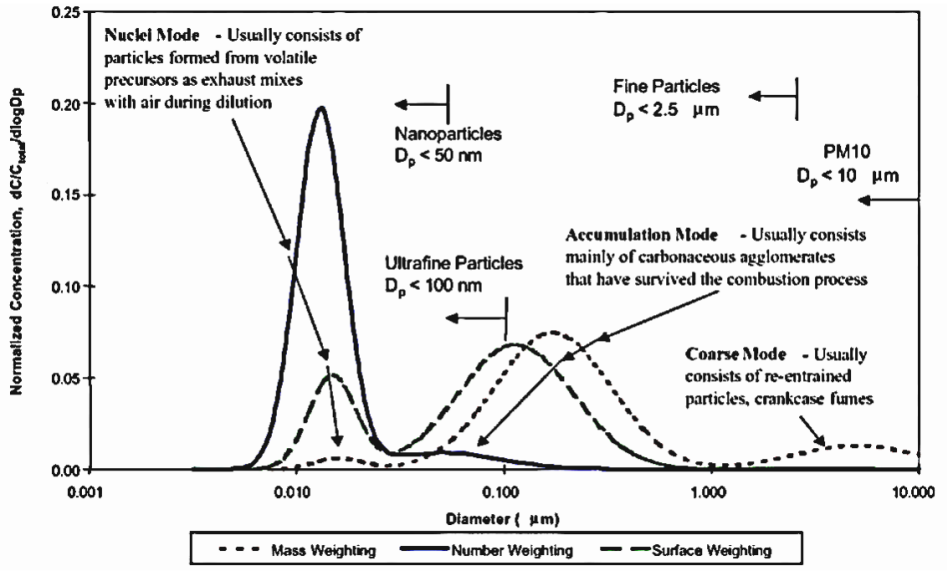


Figure 2. 3. Typical engine exhaust particle number size distributions (Kittelson et al. 2006; Bernemyr 2007).

2.4 Emissions Control Techniques

Different strategies are used to control emissions from IC engines. These could be broadly grouped into three, namely: (1) engine design modification/advanced combustion system, (2) use of cleaner alternative fuels; and (3) the application of exhaust gas after-treatment devices. This section will be concentrated in reviewing some of these techniques.

2.4.1 Engine Design Modification/Advanced Combustion Technique

Under this, exhaust gas recirculation (EGR), reformed exhaust gas recirculation (REGR), diesel fuel injection and some advanced low temperature combustion strategies are discussed.

Exhaust Gas Recirculation involves mixing part of the burnt gas with the fresh air going into the cylinder. The recircled gas could be in the form of external or internal (i.e., negative valve overlap-used in retaining part of the burnt gases by closing the exhaust valve earlier before the inlet valve opening) (Honardar et al. 2011), and the external could be in the form of cold or hot, and low or high pressure (depending on the location where the gas is extracted) (Bermúdez et al. 2011).

EGR is a very effective and widely researched in-cylinder pollution reduction technique applied in modern ICEs to reduce nitrogen oxide (NOx) emissions. The overall effect of EGR is the reduction of combustion temperature by replacing part of the cylinder inlet air with CO_2, H_2O, N_2 and other gases contained in the exhaust. This changes the combustion condition due to dilution, thermal and chemical effects. The dilution effect is caused by the displacement of part of the air with the recirculated exhaust (inert) gas which lowers the in-cylinder air-fuel ratio and increases the mixing time. The thermal effect changes the thermal properties (e.g., reduction in flame temperature) with the CO_2 and water in the exhaust gas. Replacing the cylinder oxygen content with gases with higher specific heat capacities increases the overall heat capacity of the cylinder charge and lead to reduction of flame temperature. The chemical effect is caused by the endothermic dissociation of the recirculated CO_2 and water vapor during combustion, resulting to lower flame temperature (Al-Qurashi, Zhang, and Boehman 2012).

However, as EGR leads to reduction in oxygen level and lower in-cylinder combustion temperature, the percentage of EGR supplied should be limited. This is because the application of high amount of EGR could deteriorate the combustion quality and increase the emissions of PM, HCs and CO.

Reformed Exhaust Gas Recirculation is a form of EGR but varies slightly since the recirculated exhaust gas comes in the form of synthesis gas (H_2 and CO) as well as CO_2, CH_4, H_2O and N_2. The REGR may be generated on-board as shown in Figure 2.4. This is done by incorporating a catalytic fuel reformer in the EGR loop to produce H_2-rich gas (Abu-Jrai, Tsolakis, and Megaritis 2007) which could then be fed back into the engine inlet manifold (Abu-Jrai et al. 2009) or aftertreatment system as reformed exhaust gas.

With a combined application of H_2 and EGR in the combustion process, improvements in engine performance, reduction in emissions and engine brake specific fuel consumption can be achieved (Long et al. 2021). The H_2 can extend the flammability limits of the H_2-HC mixture compared to the relatively slow reaction rates of typical HC fuels (Tsolakis, Megaritis, and Yap 2008). The CO_2 and H_2O components of the REGR reduce the combustion temperatures and assist in the reduction of NOx (Abu-Jrai et al. 2009).

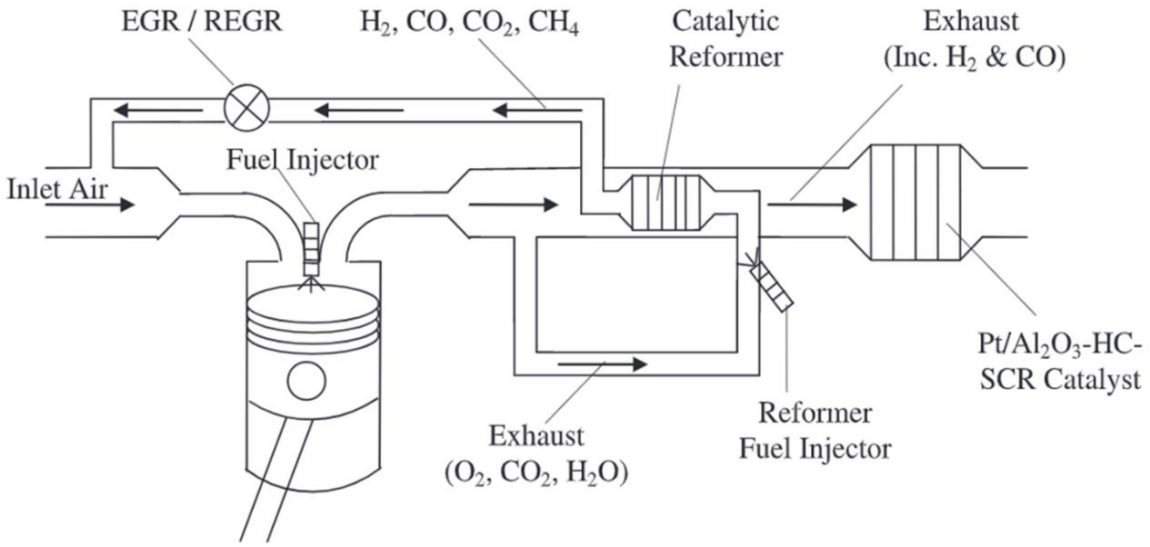


Figure 2. 4. Schematic of engine REGR and SCR aftertreatment system (Abu-Jrai, Tsolakis, and Megaritis 2007).

Diesel fuel injection pressure and timing are also very effective strategies that are used to promote the diesel engine combustion process and reduce exhaust gas emissions. For instance, increasing the injection pressure can effectively improve the fuel atomization (Ouchikh et al. 2022) and promote the quality of the fuel-air mixture (Chen et al. 2020). This provides a better and more complete combustion process, higher brake thermal efficiency and lower emissions of soot and CO into the environment (Canakci et al. 2009). Also, unlike the conventional mechanical systems of fuel injection where the fuel is injected into the cylinder once per cycle, the development of common rail electronic fuel injection systems uses split or multiple fuel injection strategies to achieve better combustion process and lower exhaust emissions. Split or multiple injection strategies allow the division of a single injection profile into pre (pilot), main and post injection pulses with a defined dwell time. For double injection systems, the fuel is split into pre- and main injections with the pre-injected fuel going in to increase the in-cylinder gas temperature and pressure before the main injection (Yousefi et al. 2022). Several studies have shown that the combustion process can be improved by splitting the fuel injection into pre- and main injections.

The reason is that the heat released from the combustion of the pre-injection (a small amount of fuel) in the compression stroke prior the main injection, increases the pressure and temperature of the in-cylinder charge and as a result, the ignition delay of the main injection is reduced (Suh 2011). The post injection on the other hand is a strategy used mainly to promote the performance of exhaust gas aftertreatment devices.

2.4.2 Low Temperature Combustion (LTC)

LTC modes are advanced combustion techniques used to achieve low combustion temperature and in-cylinder air-fuel mixture that is more homogeneous than the CDC mode inside the combustion chamber. The main benefits of LTC are the reduction in fuel consumption (i.e., low CO_2 emission) and to provide conditions that favour the simultaneous reduction of NOx and PM emissions.

Generically, LTC strategies are achieved by carefully controlling the combustion process in a way that all or most of the fuel is premixed to avoid locally rich regions in the combustion chamber (Nazemi and Shahbakhti 2016; Nieman, Dempsey and Reitz 2012). As shown in Figure 2.5, the NOx and soot formation regions and the different combustion modes are presented on the local equivalence ratio (ϕ) versus combustion temperature (T) diagram. Unlike the curve for the CDC mode, the LTC operating regimes avoided the NOx region and moved to the lower temperature side of the soot peninsula. The means, with the application of LTC strategies, both the locally fuel rich regions where soot is formed and the high temperature regions that support the formation of NOx can be simultaneously avoided (Macián et al. 2021). Another important benefit is that higher engine thermodynamic efficiency can be achieved due to reduction in heat transfer and shorter combustion duration (García et al. 2019).

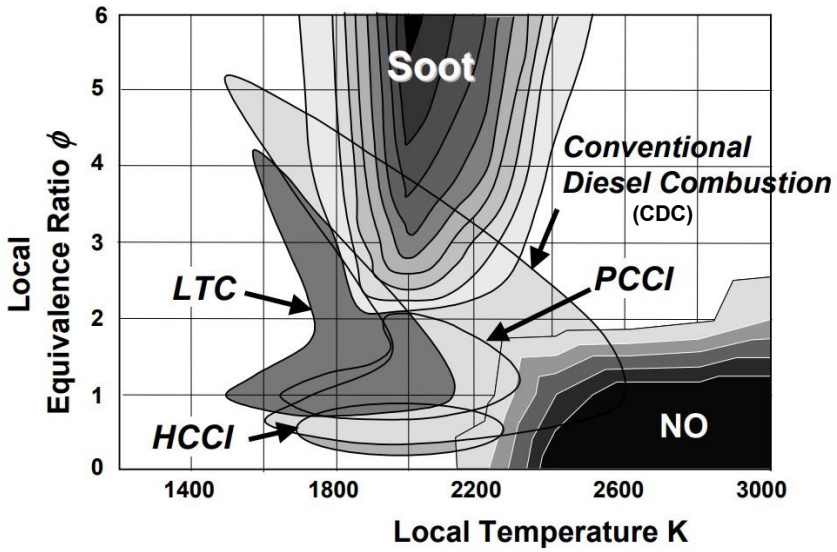


Figure 2. 5. NOx and soot formation regions with different combustion modes (Neely et al. 2005).

Although, several strategies including homogeneous charge compression ignition (HCCI), premixed charge compression ignition (PCCI) and reactivity-controlled compression ignition (RCCI) are used to achieve low temperature combustion (Figure 2.5), this section will only dwell on the RCCI strategy. RCCI is an advanced dual fuel combustion mode as it employs two fuels of different reactivity (Martin et al. 2018; Prikhodko et al. 2013) and early/and or multiple injection (Ren et al. 2018) of high reactivity fuel (HRF) to achieve an in-cylinder equivalence ratio below stoichiometric but more homogeneous than the CDC. As with the dual fuel combustion, a low reactivity fuel (LRF) like gasoline, compressed natural gas (CNG) and liquefied petroleum gas (LPG) is premixed with the fresh air inducted into the cylinder. However, the RCCI strategy differs from the dual fuelling as the HRF is injected much earlier in the compression stroke before the fuel-air charge is compressed beyond the critical compression ratio (CCR) needed to ignite the fuel (Martin et al. 2018). The early injection of the HRF increases the mixing time for the HRF and LRF fuels and creates a stratified in-cylinder mixture which is auto-ignited in an area of high

reactivity and high equivalence ratio (Martin et al. 2018) and afterward the combustion progresses sequentially from the high reactivity zone to low reactivity zone (Pedrozo et al. 2022). After the initiation of combustion, its progression thereafter will be dependent on the in-cylinder reactivity stratification that is mainly controlled by the HRF (Benajes et al. 2018).

However, where two types of fuels with different reactivity are involved, the combustion characteristics are influenced by the properties of both fuels. For example, the increase ignition delay caused by the high-octane gaseous fuel allows adequate time for the gaseous-liquid fuel to mix properly. Hence, creating a partially premixed charge that would reduce the mixture heterogeneity and thus, promotes the simultaneous reduction of NOx and soot emissions (d'Ambrosio and Ferrari 2015). NOx reduction is made possible as the diesel spray is reduced, and the gaseous fuel substitution is increased. This creates a lean mixture of the gaseous fuel with higher heat capacity, resulting to lower peak combustion temperature and oxygen content. The low soot emission is due to reduced diesel fuel utilization (Noipheng et al. 2011); improved atomization and increased diffusion combustion velocity (Tira et al. 2012) and homogeneity in fuel-air mixture (Brijesh, Chowdhury, and Sreedhara 2015). However, due to local over-mixing of fuel and air at low temperature environment, LTC combustion strategies could lead to incomplete combustion of fuel and increase in HC and CO emissions (Zeraati-Rezaei et al. 2020).

2.4.3 Alternative Fuels

To mitigate the adverse effects on health and environment from the combustion of conventional fuels, the need to explore alternative fuels in IC engines has attracted more and more interests in combustion and emission research. This recent trend in fuel research is mainly driven by the tightening environmental emission standards and to conserve the depleting energy reserves.

Consequently, low carbon and carbon-free gaseous fuels are being actively explored as alternatives to the conventional fuels in the transportation sector. However, it is also important that these alternative fuels should have high energy density and their applications should not require major structural changes in the engines (Ekin, Ozsoysal and Arslan 2022). Some of these fuels are summarized below.

Natural Gas is a mixture of different gases with methane as the main component. Other components of natural gas are ethane, propane, butane and traces of higher hydrocarbon and inert gases (Akansu et al. 2004). Natural gas is in abundance worldwide and Nigeria in particular has an estimated reserve currently standing at 182 TCF (trillion cubic feet) with a projected growth rate of over 70% by 2025 (Odumugbo 2010). This gas normally comes in two forms, namely, as: (1) associated gas, which occurs as part of the crude oil, and (2) non-associated gas that occurs as natural gas in a reservoir with little or no crude oil content. It is a fossil-based fuel and can be used either as a compressed (CNG) or liquified natural gas (LNG). However, it is the cleanest of all fossil fuels due to its lowest carbon to hydrogen ratio (C/H) and therefore, it is capable of curbing soot and greenhouse gas emissions when used in the transportation sector as a substitute to the conventional liquid fuels. Moreover, the presence of NG in the combustion chamber increases the specific heat capacity of the air-fuel mixture and consequently, produces lower NOx emissions due to the low combustion temperature.

NG has high octane number (~120) and high auto-ignition temperature (~600 ^{o}C). These properties make it difficult for NG-air mixture to achieve auto-ignition in compression ignition engines. Also, due to the relatively slow burning rate of NG, the heat-to-work conversion efficiency and the power performance of a NG engine is limited (Shu et al. 2018). This means to achieve the high temperature required for auto-ignition and enhance the combustion of NG

engines, it must be provided with extreme levels of charge heating and/or compression (Hosseini and Chekel 2006), a high cetane number fuel or NG-hydrogenation (Shu et al. 2018). Furthermore, NG has lower volumetric energy density than the conventional fuels (Mazloomi and Gomes 2012) and therefore, more natural gas fuel would be consumed to produce equivalent energy as diesel fuel.

Numerous studies have been carried out to investigate the combustion, performance and emission characteristics of natural gas fuelled compression ignition engines. Pedrozo et al. (2022) studied the effects of NG composition on the combustion, emissions and fuel conversion efficiency of a single cylinder compression ignition engine operating on dual fuel and RCCI combustion modes. The authors combined the RCCI mode with late intake valve closing (LIVC) strategy to adjust the in-cylinder lambda and charge reactivity. The study revealed that RCCI strategy with LIVC operation could reduce NOx, CH_4, THC and CO emissions and produce higher combustion efficiency. In addition, it was shown that the presence of more reactive components like ethane and propane in NG favoured the RCCI mode. Papagiannakis and Hountalas (2004) investigated the combustion and emissions characteristics of a high-speed DI diesel engine operating in diesel-natural gas dual fuel mode under 2000 rpm engine speed at 40%, 60% and 80% of the full engine load. The authors reported lower peak cylinder pressures due to increase in NG proportion of the dual fuel mode. Also, less intense premixed combustion, lower soot and NOx emissions compared to the diesel operation were also reported. Higher BSFC, CO and HC emissions reported for dual fuel operation were attributed to poor conversion of the gaseous fuel, promoted by the lower in-cylinder temperature and slower burning rate of the air-fuel mixture in the cylinder.

Liquefied Petroleum Gas (LPG) is also referred to as ‘auto gas’ or ‘auto fuel’. It is a by-product of petroleum refineries and natural gas. The main components of LPG are propane (C_3H_8)

and butane (C_4H_{10}), with traces of other light hydrocarbons such as propylene. Also, LPG has higher volumetric energy content and density compared to NG. It is readily and widely available worldwide and is cleaner compared to conventional diesel fuel. This is due to the high hydrogen to carbon ratio, which is significant in the reduction of HC, CO and CO_2 emissions. Furthermore, LPG can be liquefied at moderate pressure of between 7-8 bar at atmospheric temperature, making storage and transportation easier compared to other gaseous fuels (Ashok, Ashok, and Kumar 2015).

While LPG enjoys a degree of popularity in spark ignition engines as transport fuel in taxis (Surawski et al. 2014), it is a low CN fuel with high auto-ignition temperature. These properties make it highly resistance to self-ignition and, therefore not suitable as a stand-alone fuel in diesel engines. In diesel engines, LPG can be fumigated into the combustion chamber along with intake air or injected directly into the combustion chamber with a cetane number enhancer to improve its auto-ignition characteristics.

Goldsworthy (2012) fumigated LPG into a heavy-duty common rail diesel engine to investigate the engine performance and emissions pattern and reported up to 4% increase in thermal efficiency. In terms of emissions, decrease in NOx but increase in HC and CO emissions were observed at all load conditions. This is a consequence of poor mixture combustion caused by reduction in diesel fuel and higher LPG auto-ignition temperature. Also, increasing the LPG fumigation depletes available oxygen which in turn leads to high consumption of pilot diesel, causing deterioration of thermal efficiency (Tira et al. 2012). However, LPG has no aromatic, and very low amount of sulphur which are beneficial for the reduction of PM and improve HC-SCR performance. In addition, LPG has higher calorific value compared to diesel fuel. This means LPG provides higher engine power with low amount of fuel consumption (Marialto et al. 2019).

Hydrogen (**H_2**) had long been considered as a promising and ideal alternative energy source in ICEs and fuel cells (FCs) (Ezzat and Dincer 2018). The fact that H_2 does not contain carbon in its molecule means that its combustion does not produce carbon-base emissions (e.g., CO, CO_2, HC, and PM) and therefore, it is an environmentally clean fuel (Castro, Toledo, and Amador 2019). In addition, H_2 can be produced from fossil fuels as well as from renewable sources such as water, biomass, and wind. Some of the technologies used in producing H_2 are water electrolysis, steam reforming and dehydrogenation of organic chemical hydrides.

Hydrogen has good combustion characteristics such as high flame speed and diffusivity. Whilst the high diffusivity allows it to easily form a homogeneous mixture with intake charge to make a better premixed and more uniform combustible mixture, the high flame speed leads to reduction in combustion duration. In addition, it has wide flammability limits, low ignition energy and high energy density on mass basis. These properties make it easier for H_2/HC mixture to ignite, reduce misfires and improve the emissions and performance of the engine and aftertreatment devices (Abu-Jrai, Tsolakis, and Megaritis 2007). However, H_2 has higher auto-ignition temperature of about 858 K (Dimitriou, Tsujimura, and Suzuki 2019) and low CN compared to conventional diesel fuel. This means it needs higher compression ratio or higher CN fuel for ignition. Other challenges with H_2 fuel include production, storage, high tendency to knock, and low volumetric energy density. Interestingly, some of these problems could be solved with the production of H_2 on-board from the endogenous fuel (e.g., hydrocarbon or ammonia).

Hydrogen can be produced onboard a vehicle using the hydrocarbon fuels or ammonia as the feed. The latter could be used to provide H_2 by employing the exhaust gas heat to thermally dissociate NH_3 into H_2 and N_2. In the case of hydrocarbon, several options are available to generate hydrogen. Amongst them include the endothermic steam reforming (SR) as illustrated in equation

2.5. In this type of reaction, high temperature steam in the exhaust stream reacts with hydrocarbon fuel in the presence of a catalyst to produce H_2-rich gas. Depending on the amount of steam available, the CO produced from the SR could react with the excess steam to produce additional H_2 gas through a secondary reaction known as the water-gas shift reaction (WGSR), shown in equation 2.6. Another option to produce H_2 onboard is the exothermic partial oxidation (Pox) of hydrocarbon fuels as shown in equation 2.7 (Tsolakis, Megaritis, and Wyszynski 2003). Auto-thermal reforming (ATR) is a combination of SR and Pox that occurs concurrently when hydrocarbon fuel reacts with both oxygen and steam in the same reactor to produce H_2-rich gas (Hjeij, Biçer, and Koç 2022). The production of H_2 onboard by combining all these techniques through a direct catalytic interaction of exhaust gas and fuel is known as exhaust gas fuel reforming (Tsolakis, Megaritis, and Wyszynski 2003).

Steam reforming reaction: $C_xH_y + xH_2O \rightarrow xCO + (x + 0.5y)H_2$ 2.5

Water-gas shift reaction: $CO + H_2O \rightarrow CO_2 + H_2$ 2.6

Partial oxidation: $C_xH_y + 0.5xO_2 \rightarrow xCO + 0.5yH_2$ 2.7

Auto-thermal reforming: $C_xH_y + 0.5(x-1)O_2 + H_2O \rightarrow xCO + 0.5(y+2)H_2$ 2.8

Ammonia (NH_3) is one of the World most synthesized chemical with around 180 M tons of annual production (Kobayashi et al. 2019) and has a well-established infrastructure for storage and handling process (Ryu, Zacharakis-Jutz, and Kong 2014). It can be synthesized from renewable (e.g., solar, wind and hydro-energy) and non-renewable (e.g., natural gas) sources using Haber-Bosch technology.

Although ammonia is traditionally used in the chemical industries to produce fertilizers, explosives, pesticides, textiles, refrigerants etc., the properties of NH_3 make it attractive as an alternative carbon free fuel. Consequently, the practical application of ammonia as a fuel in ICE has been studied some years back. In the 1940s during the World War II, due to extreme scarcity of fossil fuel, ammonia was utilized to maintain the military buses in Belgium (Zhang et al. 2021). Also, in the 1960s, the US military investigated the feasibility of ammonia as source of energy in Army vehicles (Reiter and Kong 2008).

Even though there are lots of safety concerns when handling ammonia, if the regulations and procedures are strictly adhered to, liquid ammonia can be safely transferred from the point of production, storage, transportation, filling station to the consumers. In addition, at roughly 9 bar ammonia is a liquid at environmental temperature (Li et al. 2022). This means that it can be liquefied under mild conditions. Furthermore, the properties of ammonia are similar to those of propane and therefore, it can be conveniently stored onboard in relatively small, light volume low-cost tanks (Frigo and Gentili 2013).

However, due to the high resistance of ammonia to auto-ignition and poor solubility of liquid ammonia in diesel fuel (Zhang et al. 2021), NH_3 combustion in diesel engines are mostly carried out in dual fuelling modes using a second fuel that is more reactive to serve as the combustion promoter or additive (Wang et al. 2016). Furthermore, due to the characteristic low flame speed and energy density, ammonia is suitable in high compression ratio, low speed and high load marine engines (Schramm et al. 2020).

Ammonia has high H_2 content in both volumetric and gravimetric terms. As shown in equation 2.9, 1 molecule of gaseous NH_3 can be cracked over a catalyst to generate 1.5 molecules

of H_2 which is equivalent to H_2 content of 17.8 wt.% (Comotti and Frigo 2015). As a result, it is capable of providing a cheaper solution to the H_2 storage problem, because storing NH_3 is three times cheaper than storing H_2 (Ezzat and Dincer 2018).

$$NH_3(g) \rightarrow 1.5H_2\,(g) + 0.5N_2\,(g) \qquad \Delta H = +46\ \mathrm{kJ/mol} \qquad 2.9$$

Application of different combinations of NH_3 in co-combustion with diesel fuel was investigated by Reiter and Kong (2011). The authors reported drastic reduction of CO_2, soot and NO. It was observed that although, the low temperature from NH_3 combustion suppresses NO formation, as the energy contribution from NH_3 went beyond 40 %, higher amount of NO was formed due to the fuel-bound nitrogen. On the other hand, it was also observed that higher diesel fuel displacement produced higher exhaust emissions of HC, CO and soot compared to when the engine was operated with pure diesel. This was attributed to incomplete combustion of fuel due to low flame temperature from NH_3 substitution.

Gill et al. (2012) studied NH_3 combustion in diesel engine by assessing possible options of introducing NH_3 to the engine. The options that were considered are: (1) gaseous NH_3; (2) H_2 and NH_3 mixture (i.e., assuming a product of incomplete dissociation of gaseous NH_3); and (3) pure H_2 (i.e., where NH_3 is considered to have dissociated completely). It was concluded in the study that, although the combustion of pure H_2 increases NOx due to its high flame temperature, overall, it performs better in terms of emissions and fuel consumption than pure gaseous NH_3. In terms of engine stability and thermal efficiency, at high load conditions, pure gaseous NH_3 showed better performance than H_2 and dissociated NH_3 because of lower cooling losses attributed to the larger quenching distance and smaller flame speed of NH_3. However, the advantage of using the H_2 and

NH_3 mixture is, it can be used as both reductant and promoter of NH_3-SCR. This has the advantage of simultaneously decreasing the emissions of NH_3 and NO_x.

In practical applications, ammonia would be supplied in liquid form into a storage tank from where it would be channelled to a heat exchanger that captures the hot gases from a reactor and convert the liquid NH_3 to gas. Since the ammonia decomposition is an endothermic reaction, the energy source is expected to come from the high temperature exhaust heat. The gaseous ammonia is then passed through a commercial ruthenium-based catalytic reactor that employs the hot exhaust gas heat to transform it into H_2 and NH_3 for the purpose of SCR aftertreatment system. However, temperature of about 650-700 ^oC is required to efficiently crack NH_3 over most of the catalysts employed (DOE 2006). As these temperatures are well above typical diesel exhaust temperatures, an electrical heating element would be required to provide additional heat to the catalyst.

2.4.4 Exhaust Gas After-treatment

Exhaust gas after-treatment system is the application of one or more devices in the engine exhaust system to reduce specific pollutants emanating from the engine. As the exhaust gases transit through these devices, they are involved in different chemical and physical processes in a thermally and chemically controlled environment (Rappé 2014) to reduce the most hazardous substances (García et al. 2019). For the stoichiometric gasoline engine, a Three-Way-Catalyst (TWC) is used to convert CO, HCs, and NO into harmless substances. In lean burn (e.g., diesel) engine, the presence of excess oxygen in the exhaust makes the control of NOx with the conventional TWC difficult. The reason is that the NOx + CO reaction which is the key pathway

for NOx reduction in TWC is bypassed as CO is preferentially consumed by directly reacting with O_2 (Houel et al. 2007).

In diesel engines, different after-treatment techniques are used, each of which serves to eliminate specific pollutant(s). The exhaust gases from diesel engines are control through diesel oxidation catalyst (DOC), diesel particulate filters (DPF), lean NOx trap (LNT) and selective catalytic reduction (SCR). This section is going to dwell on DOC, DPF and SCR.

Diesel Oxidation Catalyst is designed to reduce tailpipe emissions through the oxidization of gaseous HC and CO emissions from diesel engine exhaust. In addition to these, it also oxidizes the volatile components of the PM, and NO to NO_2. The main reactions that take place in a DOC are illustrated in equations 2.10 to 2.12. Increase in NO_2 is useful for downstream aftertreatment devices like SCR and DPF. State-of-the-art technologies of emission reduction from commercial automobile DOC applications have been estimated to be over 90% CO and more than 70 to 80% of THC (Wang, Baek, and Lee 2008).

DOC is a flow through device that has a honeycomb metallic or ceramic monolith substrate which is made up of thousands of small channels. Each channel is coated with a highly porous washcoat layer containing precious metal catalysts such as Platinum (Pt), Palladium (Pd) or a blend of Pt and Pd. The washcoat layer assists in increasing the exposed surface area and the number of precious metal sites available for oxidation reactions (Kurien and Srivastava 2019). As the exhaust gases transit through the channels, HCs and CO react with oxygen within the porous catalyst layer to form CO_2 and H_2O.

$$CO + \frac{1}{2}O_2 \rightarrow CO_2 \qquad 2.10$$

$$C_xH_y + (x + \frac{y}{4})O_2 \rightarrow xCO_2 + \frac{y}{2}H_2O \quad 2.11$$

$$NO + \frac{1}{2}O_2 \rightarrow NO_2 \quad 2.12$$

The activity of the DOC depends on a range of factors, including the temperature and GHSV of the exhaust gas, level and nature of PM, the different species in the exhaust and inhibitions/synergies between them (Fayad et al. 2017; Irani, Epling, and Blint 2009). As a consequence, many studies have used hydrogen to promotes the oxidation of THC, CO and NO to NO_2 over the DOC catalyst (Herreros, et al. 2014b; Salomons et al. 2006), mainly at low temperature where most of the emissions are produced. This is because H_2 supports the catalyst thermally as it increases the catalyst local temperature and reduces reaction inhibitors through chemical effects. The latter is due to the production of hydrogen-containing oxidising species (e.g., OH and HO_2) which promote the oxidation of adsorbed HC and NO to NO_2 (Herreros et al. 2014b). Due to competition of HC, CO and NO for access to the limited catalysts' active sites, the H_2 effects promote the oxidation of adsorbed hydrocarbons and as a result, increases the amount of adsorbed CO or NOx on the catalyst.

Diesel Particulate Filter is a filtration device commonly used for the removal of particles from diesel exhaust system. It is capable of filtering particles of very fine size. The basic particles removal operations of DPF include inertial impaction, interception, diffusion, sieving and the catalytic removals of semi-volatile organic HC components (ultrafine particles-UFPs), which could become new particles (Kwon, Ryu, and Carlsten 2020) or adsorbed/condensed in the already formed particles. Figure 2.6 shows the flows of exhaust gases through a typical DPF commonly used for diesel engines.

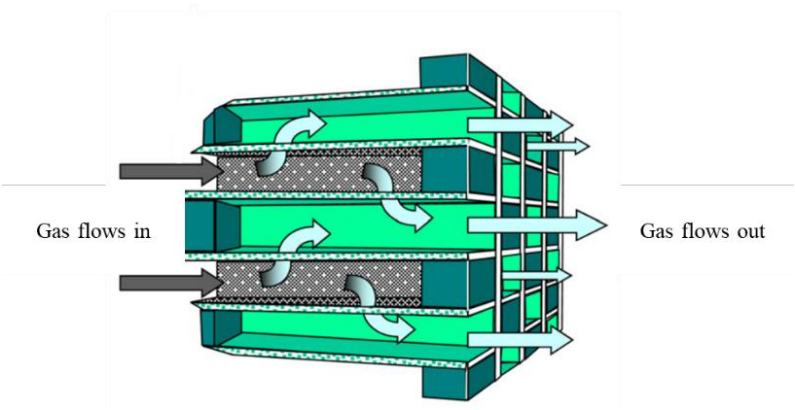


Figure 2. 6. Image of a wall flow diesel particulate filter (Tsuneyoshi and Yamamoto 2012).

DPFs are mostly made of cordierite and silicon carbide materials and are wall-flow with honeycomb monolithic structures in which the ends of alternate channels are plugged. The blocking of the alternate ends forces the exhaust gas to flow, transported and diffuse through the porous honeycomb filter or substrate wall. As the particles transit through the wall of the porous substrates resulting in physical separation of the solid particles, it also causes a gradual reduction of porosity and permeability. This is due to the deposition and accumulation of soot within the porous microstructure of the filter wall. And as the soot layers continue to build up, soot cake is formed which in turn causes reduction in permeability at the point of maximum packing density or upstream surface of the filter wall (Bensaid et al. 2009). This increases the pressure drop and consequently, leads to increase in fuel consumption, high CO_2 emission and loss of power output. These drawbacks can be avoided through periodic regeneration process of the soot.

Soot regeneration can be done passively (normal engine driving with the assistance of NO_2) or actively. Regeneration of soot requires both heat and oxidants (i.e., O_2 and NO_2) as shown in equations 2.13-2.15. However, NO_2 is known to be a better oxidant at low temperatures compared to O_2 and can oxidize soot at typical diesel engine temperature of 250 ^oC encountered during

normal driving cycle. Moreover, lower DPF regeneration temperature eliminates thermal fatigue and minimizes energy used for the regeneration (Shrivastava et al. 2010).

Passive regeneration is achieved with an oxidation catalyst placed upstream of the DPF as shown in the continuously regeneration trap (CRT) in Figure 2.6. The NO_2 formed from the oxidation of NO over the DOC promotes the continuous combustion of the soot deposited on the DPF (equations 2.13-2.14). The active regeneration is carried out in the presence of O_2 and exhaust gas temperatures higher than those of modern diesel engines. To achieve this condition, either late cycle post-injection or fuel injection upstream of the (DOC) is used to activate the active regeneration. The oxidation of the injected HC on the DOC raises the exhaust gas temperature that burns off the soot as represented in equation 2.15.

$$C + NO_2 \rightarrow CO + NO \quad 2.13$$

$$C + 2NO_2 \rightarrow CO_2 + 2NO \quad 2.14$$

$$C + O_2 \rightarrow CO_2 \quad 2.15$$

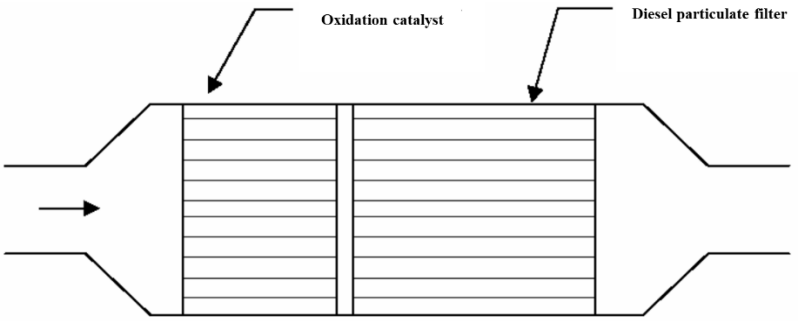


Figure 2. 7. Schematic of a continuously regenerated filter (Nord 2005).

NOx Reduction Techniques apply devices at the exhaust to reduce the NOx emitted into the environment**.** The most widely studied NOx reduction strategies for diesel engine exhaust are selective catalytic reduction (SCR) and lean NOx trap (LNT). In addition, there are also many

studies of LNT + SCR hybrid system. In this hybrid strategy, the LNT is used to remove the bulk of NOx, whilst the NH_3 generated during the rich operation phase acts as a reductant to further reduce the remaining NOx in the downstream SCR catalyst (Lee et al. 2010). This section, however, is going to review only the SCR of NOx. Selective catalytic reduction is a very effective after-treatment technique for the abatement of NOx under lean burn engine conditions. It requires the reaction of exhaust gases with reducing agents in the presence of a catalyst to convert NOx in the exhaust stream to N_2 and H_2O. There are generally two types of SCR namely: ammonia/urea-SCR and hydrocarbon-SCR.

Ammonia/Urea Selective Catalytic Reduction (NH_3-SCR) is a well-established after-treatment technique with high NOx conversion efficiency commonly applied in heavy-duty trucks and stationary machineries. Ammonia is used as a reducing agent with usually Vanadia-based catalyst like V_2O_5–WO_3/TiO_2 and V_2O_5− MoO_3/TiO_2, and zeolite-based catalysts (e.g., Fe- and Cu-zeolites). But then the corrosive and toxic nature of NH_3 as well as infrastructures make the direct application of NH_3 a challenge especially in automotive applications. As a remedy, aqueous urea solution (NH_2CONH_2) commonly known as "Adblue" is used as a source of NH_3. But then, there is the problem with high urea freezing point at -12 ^oC (Gu, Chun, and Song 2015; Schmieg, Blint, and Deng 2009).

When urea solution is injected into the exhaust gas stream, three reactions as shown below occur consecutively. Firstly, change of phase takes place where the H_2O representing about 67% of the urea solution evaporates leaving behind pure urea (Resitoglu, Altinisik, and Keskin 2015) (equation 2.16). Secondly, which is also known as pyrolysis reaction or urea thermolysis involves the thermal decomposition of the pure urea and the subsequent formation of NH_3 and isocyanic acid (HNCO) (equation 2.17). Thirdly, hydrolysis of HNCO on the catalyst surface to produce

additional NH_3 molecule (equation 2.18). The NH_3 molecule is adsorbed on the catalyst substrate, which would later be desorbed from the substrate. Therefore, the NH_3-SCR is the catalytic reaction of the desorbed NH_3 with NOx to produce N_2 and H_2O.

Urea evaporation reaction: $CO(NH_2)_2(solution) \rightarrow CO(NH_2)_2(pure\ urea)$ 2.16

Thermolysis reaction: $NH_2CONH_2\ (pure) \rightarrow NH_3 + HNCO$ 2.17

Hydrolysis reaction: $HNCO + H_2O \rightarrow NH_3 + CO_2$ 2.18

The NH_3-SCR could be a result of NH_3 reacting with pure NO in the presence of O_2 as in equation 2.19 (standard SCR), NO and NO_2 as seen in equation 2.20 (fast SCR) or NO_2 as in equation 2.21. According to studies, the speed of conversion of NOx is determined by the ratio $NO:NO_2$ as the reaction becomes faster when the ratio $NO:NO_2$ approaches 1 (Schwidder et al. 2008).

$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O$ 2.19

$2NH_3 + NO + NO_2 \rightarrow 2N_2 + 3H_2O$ 2.20

$4NH_3 + 3NO_2 \rightarrow 3.5N_2 + 6H_2O$ 2.21

Hydrocarbon Selective Catalytic Reduction (HC-SCR) is a De-NOx technique in which hydrocarbon fuels are used as the reducing agents. Although several catalysts including Cu-ZSM5 and PGM catalysts (e.g., Pt/Al_2O_3) have been investigated for HC-SCR, silver alumina catalyst (Ag/Al_2O_3) has been identified as the most effective for this De-NOx technology with a wide variety of HCs in an O_2-rich environment (Schmieg, Blint, and Deng 2009). Increase in O_2 concentration supports the activation of both HC and NO by promoting the hydrocarbon partial

oxidation to form reactive intermediate species which in turn, react with O_2-containing intermediates (e.g., NO_2 or nitrates) to form N_2 (Iliopoulou et al. 2004).

There are two types of HC-SCR, namely: passive and active HC-SCR. The passive HC-SCR uses the unburnt HCs contained in the exhaust gas as the reductant, whilst the active type is achieved by providing the exhaust with additional HC. This is usually done through late in-cylinder post fuel injection or by externally spraying fuel into the exhaust line. The HC reacts with NOx on the catalyst active sites as shown in equation 2.22 (Chong et al. 2010) to convert the NOx to N_2.

The advantage of HC-SCR over the conventional NH_3-SCR is that the on-board fuel can be utilized as the reducing agent which makes the system more simplified. In addition, Ag/Al_2O_3 catalyst is less expensive and has better sulphur durability compared to the PGM catalysts (Gu, Chun, and Song 2015). It has been shown that the NOx reduction activities of HC-SCR over Ag/Al_2O_3 is dependent on the type of HC reductant (Herreros et al. 2014a; Houel et al. 2007). Consequently, several hydrocarbons including the conventional diesel, GTL, the oxygenated hydrocarbons such as ethanol, methanol, propanol, aromatic hydrocarbons, biodiesels, and gaseous fuels (e.g., propylene, hydrogen, etc.) have been investigated as reducing agents in HC-SCR.

$$C_xH_y + \left(2x + \frac{y}{2}\right)NO \rightarrow \left(x + \frac{y}{4}\right)N_2 + xCO_2 + \frac{y}{2}H_2O \qquad 2.22$$

However, as the exhaust gas temperatures of modern diesel engines become lower due to fuel economy, the catalysts become ineffective in their activities (Herreros et al. 2014b). This is because the Ag/Al_2O_3 catalyst is sensitive to carbonaceous species and nitrates poisoning, and most of the CO and unburnt THC are produced during periods of low temperatures such as cold

start or stop and start operations. Some of the reasons for poor catalysts' performance at low temperature are: (1) formation and accumulation of stable surface nitrates (Theinnoi et al. 2008), and (2) transformation of gas-phase hydrocarbons into C-containing species (e.g., HC and/or soot) (Sitshebo, Tsolakis, and Theinnoi 2009). These nitrates and C-containing species block both the internal and external pores of the catalyst active sites and as a result, decreases the pore volume and specific surface area of the catalyst (Junhua et al. 2010; Theinnoi et al. 2008).

A number of studies have used hydrogen to promote the reduction of NO over HC-SCR at catalysts low temperatures (Breen et al. 2005). Several reasons have been advanced to explain the role of H_2 in enhancing the NOx reduction over Ag/Al_2O_3. Some of the reasons are that H_2 activates molecular oxygen to reactive species (e.g., superoxide O_2^-) (Shimizu and Satsuma 2007) at low temperature; promotes the activation of NO to NO_2 and the subsequent reaction of NO_2 with the adsorbed HC on the catalyst sites (Herreros et al. 2014a) to form N_2, CO_2 and H_2O. This provides additional benefit as it reduces the concentration of accumulated surface nitrates which block the active sites of the catalyst (Kondratenko et al. 2008). H_2 also promotes the formation of radicals that participate and enhance the NOx reduction process at lower temperature (Gu, Chun, and Song 2015).

As the activity of Ag/Al_2O_3 is strongly influenced by the nature of the reducing agent, several studies including (Tamm 2013) have shown increase in NOx conversion efficiency with NH_3 as a reducing agent over the same catalyst in the presence of H_2. Therefore, the moderately high amount of unconverted NH_3 (Reiter and Kong 2011) contained in the exhaust of ammonia-diesel co-fuelled engines or produced from onboard NH_3 cracking could be employed to reduce NOx over Ag/Al_2O_3 catalyst in the presence of low or high concentration of HC reductants.

2.5 Summary

The modern IC engines have undergone significant technological improvements with the introduction of lean burn engines which also provides environmental benefits. However, a larger proportion of the ICEs still run on fossil-based fuels. In addition, high combustion temperature and in-cylinder conditions such as lean air-fuel mixture; fuel impingement on pistons and wall wetting; incomplete fuel vaporization and heterogeneity in air-fuel mixture after fuel injection and before ignition, have made the formation of harmful emissions as part of the combustion products. With the environmental emission standards becoming more and more stringent, using the conventional diesel fuel as a source of energy in compression ignition engines will create a drawback to the current emission control strategies. Therefore, low carbon and carbon-free alternative fuels as well as advance combustion systems have to be explored to achieve the current and future emissions limits.

Although, NH_3-SCR is a well-established NOx reduction strategy with a high level of success, there are challenges with the reductants and catalyst compared to HC-SCR. In HC-SCR, the type of reducing agent affect the performance of the catalyst in achieving high emissions conversion. Therefore, different hydrocarbons have been studied as reductants over silver alumina catalyst. However, the HC-SCR requires relatively high temperature to achieve reasonable amount of NOx conversion. This is due to the formation of stable surface nitrates by silver that result in self-poisoning, and transformation of gas-phase hydrocarbons into carbonaceous species leading to the masking of catalyst active sites. As a solution, hydrogen has been used to promote the low temperature limitations of HC-SCR. In the same manner, evidence of improved NOx conversion with ammonia reductant over the same catalyst have been observed in the presence of H_2.

Therefore, there is need to investigate how to provide both NH_3 and H_2 mixture and practically implement it onboard vehicles. The NH_3 and H_2 mixture that is produced onboard can be used to eliminate NOx at the exhaust in the presence of low HC reductant and exhaust gas that is enriched with unburnt HC from diesel-propane dual fuel engine.

CHAPTER 3

EXPERIMENTAL EQUIPMENT

3.1 Test Engine and Instrumentation

This chapter introduces some of the facilities that were used to run the experiments for this research. These include the test engine, emission analysers, furnace, reactor and the catalysts. Some of the formulae used to analyse the experimental results are also presented.

3.1.1 Test Engine

The experimental engine used for this research is shown in Figure 3.1. The engine is a water-cooled research diesel engine with main specifications as shown in Table 3.1. It is equipped with a high-pressure common-rail fuel injection system that permits the control of pilot, main and post injections (i.e., pressure, injection rate and fuel quantity). The fuel injection timings in crank angle degrees (CADs) before TDC are presented in the following chapters. The fuel injector was set at an opening pressure of 550 bar.

Table 3. 1. Diesel engine parameters.

Engine type	1-cylinder
Stroke type	Four-stroke
Bore/stroke (mm)	84.0 / 90.0
Connecting rod length (mm)	160
Displacement volume (cm^3)	499
Compression ratio	16:1
Engine speed range (rpm)	900-3000
IMEP range (bar)	<7
Common rail fuel injection pressure range (bar)	500-2000
Number of injections	3 injection events



Figure 3. 1. Single cylinder experimental diesel engine.

3.1.2 Engine Instrumentation

An electric dynamometer with a motor and load cell coupled to the engine was used to control the engine load and speed. Other standard test rig instrumentations such as thermocouples and Kistler 6125B pressure transducers were positioned at relevant places to monitor the intake air, oil, exhaust temperatures and pressures. The details of the engine's instrumentations are described in the respective chapters.

3.2 Fuels

The fuels used to run the engine for this thesis are ultra-low sulphur diesel (ULSD) and propane gas. Whilst the ULSD fuel was provided by Shell Global Solutions, UK, the propane gas supplied from a gas bottle was purchased from BOC. The diesel fuel flow rate was measured in volumetric basis. This was done using a volumetric pipette and a stopwatch to monitor the time taken for the engine to consume 44 ml of the diesel fuel. Table 3.2 shows the physical and chemical

properties of the fuels adopted from (Serhan, Tsolakis, and Martos 2018; Surawski et al. 2014). The propane supply system consists of a high-pressure propane cylinder, regulator that brings down the cylinder pressure, a digital flow meter that allows a precise control of the propane flow rates, a check valve and a shut off valve to control the flow of propane.

Table 3. 2. Properties of ultra low sulphur diesel and propane fuels.

Property	ULSD	Propane
Chemical formula	$C_{14}H_{26.1}$	C_3H_8
Cetane number	43.4	5
Density @ 15^{o}C (kg/m^3)	826.9	1.861
Lower heating value (MJ/kg)	43.11	46.3
Sulphur (mg/kg)	6.1	<1
Specific heat capacity (kJ/kgK)	1.87	2.07
Stoichiometric air-fuel ratio	14.6	15.6
Aromatics (wt.%)	24.4	0
Auto-ignition Temperature (^{o}C)	180-220	472

3.3 Exhaust Emission Analysis

Engine exhaust emissions such as regulated and unregulated gases like CO, NOx (NO NO_2), NO, NO_2, THC, NH_3, propylene, ethane, methane, N_2O were measured with a Fourier Transform Infrared Radiation (FTIR) gas spectrometric analyser. Although, propane was not part of the emissions that were analysed with the FTIR, it is believed that the higher THC emission from diesel-propane dual fuel combustion compared to single diesel was contributed largely by the presence of unburnt propane in the exhaust. The FTIR consists of a light source, interferometer, detector, and a computer. The light source emits infrared radiation which is then converted into interference ray by the interferometer. The interference ray passes through the exhaust samples, and in the process, the interference pattern containing the sample information is obtained. Thereafter, the interference pattern is obtained with a computer and then subjected to a fast Fourier transform to get the infrared spectrum. For different gaseous pollutants in exhaust gas, there are

molecular structures with different vibration modes corresponding to specific infrared absorption spectrum.

Nitrogen gas contained in a cylinder was introduced into the FTIR equipment before and after using it. This is to prevent contamination and condensation of exhaust gas species and water on the equipment channels and mirror. Prior to the gas sampling, the FTIR was warmed up to 191 ^{o}C and the interferometer and optic detector purge were set to 0.2 l/m, whilst liquid nitrogen is constantly introduced to cool the system. Exhaust samples were directly drawn at the relevant sampling points along the exhaust system of the engine using a heated polytetrafluoroethylene tube. The heated tube was maintained at 191 ^{o}C to prevent the condensation of water and HCs that would affect the readings.

3.4 Hydrogen Measurement

Hydrogen measurements were carried out by sampling part of the exhaust gas through an H-sense H_2 mass spectrometry operated, based on the Electron Impact Ionization Mass Spec (EIMS) analyser. Because the H-Sense is temperature sensitive, it was thoroughly purged with nitrogen gas and calibrated with a gas mixture containing 5% H_2 in N_2 from a gas cylinder before it was used to take measurements of the hydrogen concentration over a range of 0 – 50,000 ppm H_2.

3.5 Catalysts

The catalysts used for this research were provided by Johnson Matthey Plc. The flow of gases passing through the catalysts were controlled by a parameter known as the gas hourly space velocity (GHSV). The GHSV with the unit h^{-1} is defined as the volumetric flow rate of the reactant

feed (i.e., exhaust gas) divided by the external volume of the monolith catalyst and is presented in equation 3.1. The volumetric flow rate was controlled and kept constant using a suction pump and a calibrated glass tube flow meters located downstream of the furnace.

$$\text{GHSV } (\text{h}^{-1}) = \frac{\text{Flow rate of exhaust gas over catalyst } \left(\frac{\text{m}^3}{\text{h}}\right)}{\text{Catalyst Volume } (\text{m}^3)} \qquad 3.1$$

3.5.1 Diesel Oxidation Catalyst

A diesel oxidation catalyst (DOC) (ø = 56 mm, L = 102 mm) coated onto a ceramic cordierite honeycomb monolith substrate with cell density (surface area) and wall thickness of 600 cpsi and 3 mm, respectively, was supplied by Johnson Matthey PLC. The DOC was coated with platinum group metal (PGM) catalyst loading of 100 g/ft^3 with platinum, palladium and rhodium (Pt/Pd) formulation of 3:1. The DOC was wrapped with an interam matting material to prevent gases from slipping between the monolith and reactor wall before inserting into the exhaust system.

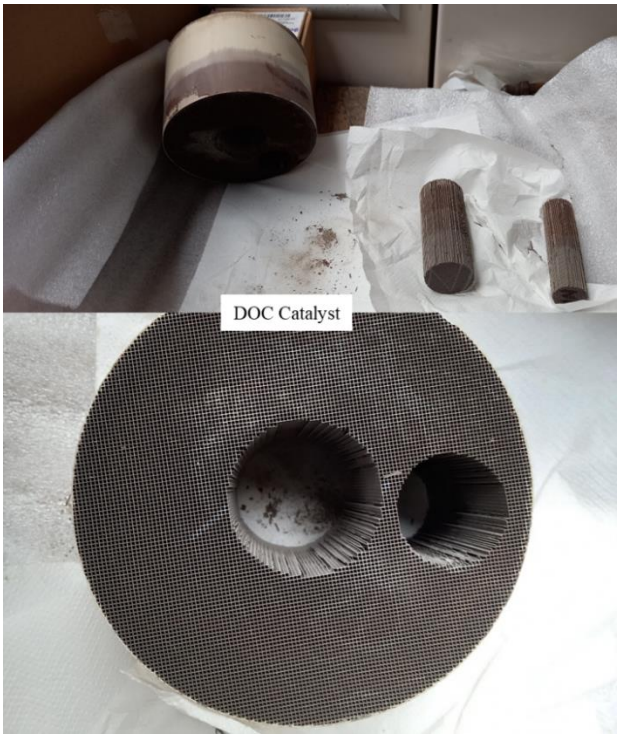


Figure 3. 2. Diesel oxidation catalyst.

3.5.2 HC-SCR Catalyst

The HC-SCR catalyst used is a 2 mass % Ag/Al_2O_3 coated monolith catalyst (Ø = 40 mm, L = 120 mm) supplied by Johnson Matthey Plc with a high cell density of 600 cpsi. Similar to DOC, the HC-SCR catalyst monolith was wrapped with a matt before inserting it into a reactor. The reactor is then placed inside a tubular furnace with a K-type thermocouple positioned upstream of the catalyst and a temperature controller was used to control the inlet reaction temperatures of the furnace.

Before inserting the DOC and SCR catalysts into the exhaust system and the reactor, they were thermally conditioned in an oven at 500 ^{o}C for 5 hours. This was done to limit any possible physisorption or chemisorption effects on the catalysts.

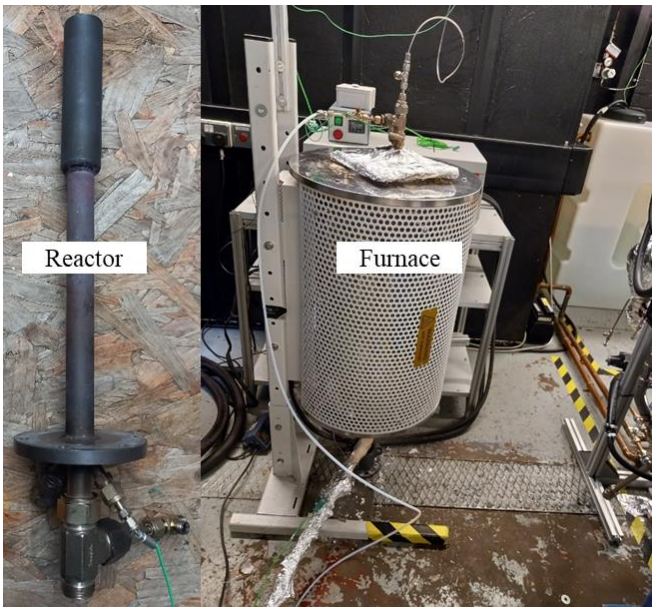


Figure 3. 3. Reactor and tubular furnace.

3.6 Combustion Data Processing

The in-cylinder pressures data for combustion analysis were acquired using an AVL GH13P pressure transducer mounted on the cylinder head and signals were amplified by an AVL FlexiFEM 2P2 Amplifier. A digital shaft encoder (producing 360 pulses per revolution) fitted to the engine was used to record the instantaneous crankshaft positions. A bespoke lab-View software was used to acquire the in-cylinder pressures. Pressure variations corresponding to 200 consecutive engine cycles at intervals of 1^{o} CAD were acquired. The outputs from the analysis of the engine cycles includes the in-cylinder pressure, indicated mean effective pressure (IMEP), apparent net heat release rate (AHRR), cumulative heat released and percentage coefficient of variation (COV) of IMEP values.

- Apparent net heat release rate (AHRR) as shown in equation 3.2 was used to calculate the heat released in the combustion chamber. Therefore, the heat transfer with the cylinder wall was not considered in the calculation.

$$\mathrm{AHRR} = \frac{\gamma}{\gamma-1}\mathrm{p}\frac{\mathrm{dV}}{\mathrm{d\theta}} + \frac{1}{\gamma-1}\mathrm{V}\frac{\mathrm{dp}}{\mathrm{d\theta}} \qquad 3.2$$

Where, θ is the engine instantaneous crank angle, γ is the ratio of specific heats (C_p/C_v) obtained by plotting the log (pressure) versus log (volume) curves using the pressure data generated from the experiment and the calculated volume. The γ value used was the average of the slope of the compression and expansion lines. Also, p (Pa) and V (m^3) are the respective instantaneous cylinder pressure and volume which are dependent on the position of the piston inside the cylinder. While the change in instantaneous volume and pressure with respect to the piston position ($\frac{dV}{d\theta}$ and $\frac{dp}{d\theta}$), were respectively calculated from the parameters acquired from the LabView software.

- The IMEP represents the ideal average output pressure over a cycle of the engine and is calculated from the cylinder pressure using the equation below:

$$\mathrm{IMEP} = \frac{\text{Indicated Work per Cycle}}{\text{Displaced Volume}} = \frac{\oint \mathrm{pdV}}{\mathrm{V_d}} \qquad 3.3$$

Where, p and V are the in-cylinder pressure and the corresponding cylinder volume.

- In this work, due to the differences in the lower heating values of propane and diesel, brake specific energy consumption (BSEC) was used to analyse the fuel energy consumption using the following equation:

$$\mathrm{BSEC} = \frac{\dot{\mathrm{m}}_\mathrm{D} \times \mathrm{LHV_D} + \dot{\mathrm{m}}_{\mathrm{C_3H_8}} \times \mathrm{LHV_{C_3H_8}}}{\mathrm{P_B}} \qquad 3.4$$

Where, P_B is the engine brake power output (kW), $\dot{m_D}$ and $\dot{m_{C_3H_8}}$ (kg/s) are the mass flow rates of diesel and propane, and LHV_D and $LHV_{C_3H_8}$ (MJ/kg) are the respective lower heating values.

- Brake thermal efficiency (η_{th}), which is an indication of how much heat energy from the fuel is converted into mechanical work is calculated from:

$$\eta_{th} = \frac{P_B}{\dot{m}_{fuel} \times LHV_{fuel}} \quad 3.5$$

Where, $\dot{m}_{fuel}$ is the fuel mass flow rate and LHV_{fuel} is the lower heating value of the fuel.

- Coefficient of variation of IMEP (COV_{IMEP}) was used to evaluate the combustion stability and it is defined as:

$$COV_{IMEP} = \frac{\sigma_{IMEP}}{\overline{IMEP}} \quad 3.6$$

Where, σ_{IMEP} is the standard deviation of IMEP and $\overline{IMEP}$ is the mean of IMEPs.

- Brake Power (P_B) is expressed as:

$$P_B(kW) = 2\pi TN \quad 3.7$$

Where, T is the engine torque (Nm).

- Displaced Volume (V_d): this is a measure of the volume swept by the pistons inside the cylinders and is calculated with the following equation.

$$V_d = A \times L \times n \quad 3.8$$

Where, A is the cylinder area (m^2), L is the stroke (m) and n is the number of cylinders.

3.7 Experimental Errors and Repeatability

In this thesis, the experiments were carefully carried out to minimize uncertainties and test-to-test variability resulting from equipment and random errors. To ensure repeatability and accuracy of the experimental procedures, each measurement was taken at least three times, and therefore, the results presented in this thesis are the average values from three different measurements. At the beginning and end of every test, the exhaust gas sampling tubes were purged

with compressed air. This is done to reduce the impacts of residual HC, CO_2, H_2O from previous tests on subsequent measurements. The gas analysers were calibrated using specific gases before measurements were taken. The error bars for emissions and other combustion performance results represent the standard deviations of the analysed results.

CHAPTER 4

INVESTIGATING THE COMBUSTION, PERFORMANCE AND EMISSION CHARACTERISTICS OF PROPANE-DIESEL DUAL FUEL ENGINE.

4.1 Introduction

This chapter presents the combustion, performance and emission results of a compression ignition engine running on a diesel-propane dual fuel system at low engine load. It is well known that at low load engine operation, the dual fuel engines suffer from low performance and higher engine out THC and CO emissions compared to the conventional diesel fuel engines. The reason is that the homogeneous in-cylinder air-fuel mixture formed due to the presence of gaseous fuel (including propane) becomes difficult to ignite and burn completely under low load condition (Selim 2003). As the mixture is lean, it takes a longer time to burn in the expansion stroke where the pressure and temperature are lower (Abu-Jrai, Al-Muhtaseb, and Hasan 2017). However, the performance and emission characteristics of the diesel engine are normally influenced by the start of injection timing (Teoh et al. 2018). Advancing the injection timing of the diesel fuel would allow more fuel energy to be released in the combustion chamber and increases the in-cylinder pressure and temperature. Therefore, application of this strategy to a diesel-propane dual fuel engine can promote the combustion of the propane-air mixture and consequently, provides additional benefits to the environment. The aim of this chapter is to investigate the effects of early injection timings of the diesel fuel on the combustion, performance and emissions characteristics of a compression ignition engine running on a diesel-propane dual fuelling system at low load

engine condition. This will help to offer further information on the advantages of advancing the pre- and main injection timings of the diesel fuel on dual fuel engines. In this study, propane is used as the LRF and the diesel as the HRF.

The schematic of the experimental set-up, showing the engine with the emissions and pressure analysers as well as propane supply system is presented in Figure 4.1. The experimental condition and procedure are described in Section 4.2. Sections 4.3 discusses the details of the effects of propane substitutions and diesel fuel injection timings on the engine combustion, performance and emissions characteristics. The overall results are summarised in Section 4.4.

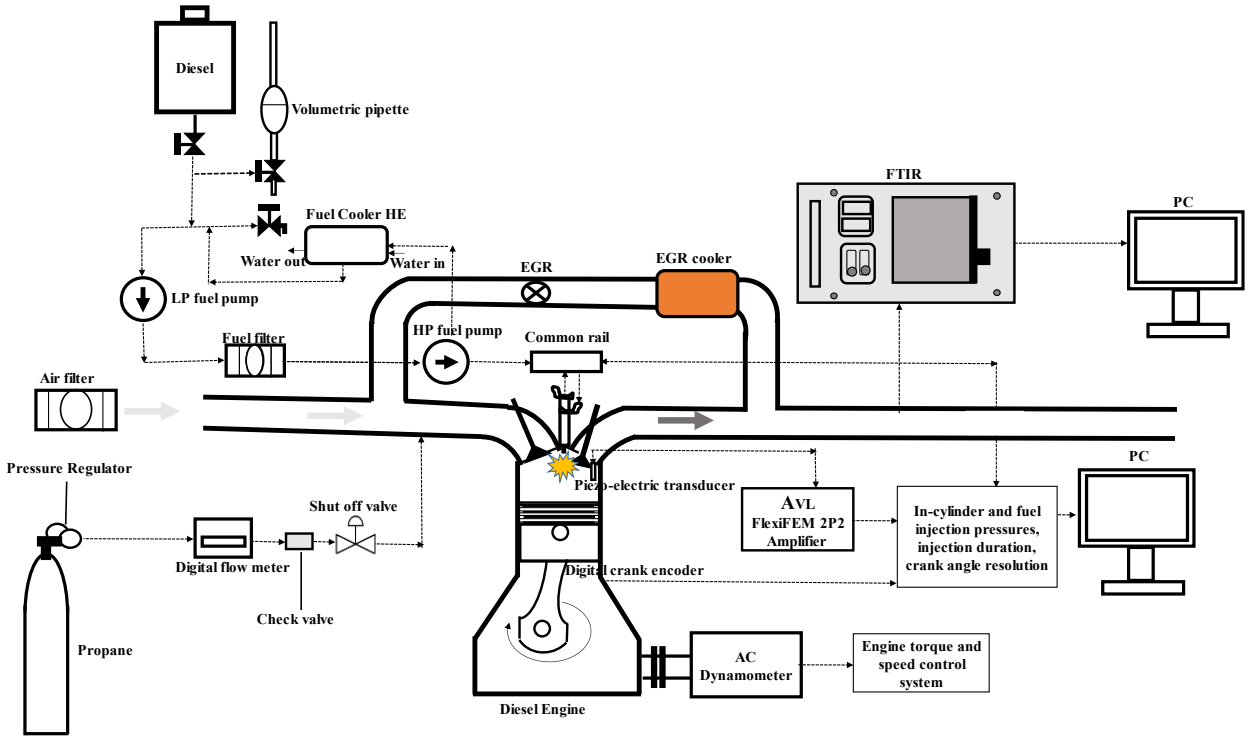


Figure 4. 1. Schematic of experimental set-up.

4.2 Experimental Condition and Procedure

Prior to the commencement of the test, the engine was warmed up until lubricating oil and coolant temperatures reached 61 ^{o}C and 33 ^{o}C, respectively. This was done to minimize emissions

fluctuations due to cold starts operation and ensure uniformity of the results (Serhan et al. 2019). The experiments were carried out based on the matrix presented in Table 4.1. All experiments were carried out under steady-state engine condition corresponding to 1500 rpm engine speed and 2 bar IMEP load, whilst the common rail fuel injection pressure was maintained constant at 550 bar.

Although, different injection timings were tried, in all cases, the dwell angle (i.e., the interval between the end of pre-injection and the start of main injection) as shown in Figure 4.2 were maintained constant. Due to excessive in-cylinder pressure rise and engine knock observed with different injection timings considered during preliminary tests, D18-8 (pre-18^{o} crank angle degree before top dead centre (bTDC), and main 8^{o}bTDC); and D21-11 (pre- 21^{o}bTDC and main, 11^{o}bTDC) were chosen for this study as the engine only became stable at these conditions. Therefore, only these two injection timings were investigated in this research.

To run on dual fuel operations, propane from a high-pressure cylinder was decompressed as it flows through a pressure regulator and then supplied to the engine intake manifold to displace 15% and 25% of the liquid diesel fuel on energy basis. The propane flow rates into the engine, calculated from equation 4.1 was controlled by a digital flow meter. Premixing of the gaseous propane and the inlet air was achieved as the propane was injected through a port located at the intake manifold. Thus, allowing the propane to diffuse and mix homogeneously with the air going into the combustion chamber. During the compression stroke and before the TDC, diesel fuel was injected directly into the combustion chamber. However, to investigate the effects of injection timing, the diesel fuel injection timing was set at D18-8 and D21-11 earlier than the original engine timing of D15-5 bTDC with injection pressure of 550 bar. This is to ensure that more time is

provided for the fuel and air to mix properly and consequently, allows more fuel energy to be released at the start of auto-ignition.

$$\text{Propane flow rate } (^{L}/_{min}) = \frac{\dot{m}_D \times LHV_D \times Z\%}{\rho_{C_3H_8} \times LHV_{C_3H_8}} \times 1000 \quad 4.1$$

Where, Z% is the propane energy fraction, $\dot{m}_D$ (kg/min) is the diesel fuel mass flow rates, $\rho_{C_3H_8}$(kg/L) is the propane density, LHV_D and $LHV_{C_3H_8}$ (MJ/kg) are the respective lower heating values of diesel and propane.

Table 4. 1. Experimental test matrix.

Engine conditions			Propane substitution Z (%)	Propane flow rates (l/min)	Diesel injection timing (CAD bTDC)	
Load (IMEP)	Speed (rpm)	Diesel injection pressure (bar)			Pre-injection	Main injection
2	1500	550	15	0.58	18	8
			25	0.96	18	8
			15	0.56	21	11
			25	0.94	21	11

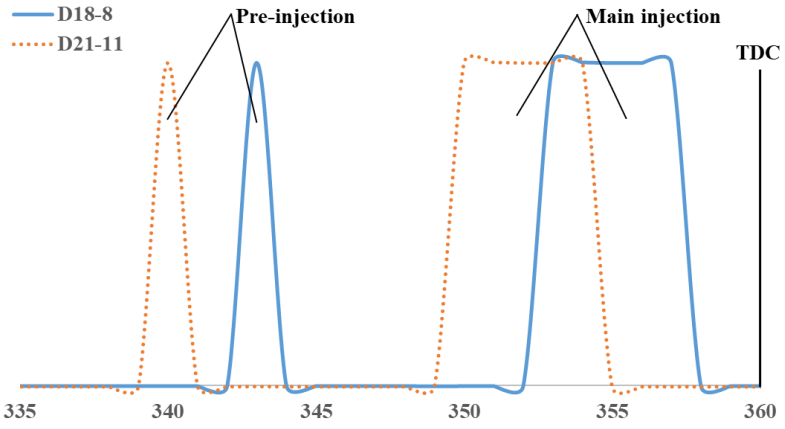


Figure 4. 2. The split injection timing scheme adopted for the experiment.

4.3 Results and Discussions

In this section, the results of diesel fuel injection timings on combustion, performance and emission characteristics of a compression ignition engine running on diesel and diesel-propane fuels are presented and discussed. The combustion analyses were carried out using the in-cylinder pressure data as they vary with the crank angle degrees at a uniform interval. From the %MFB (percent mass fraction burnt), which is the cumulative heat released (d'Ambrosio and Ferrari 2015), the combustion phasing and end of combustion are respectively defined as the positions of the CAD corresponding to 50% and 90% of the cumulative heat released.

4.3.1 Engine Combustion Characteristics

Figures 4.3 (a) and (b) show the characteristics of the in-cylinder combustion pressures and AHRR profiles for the diesel fuel injection timings of D18-8 and D21-11 for the single diesel fuel and with all two fractions of propane.

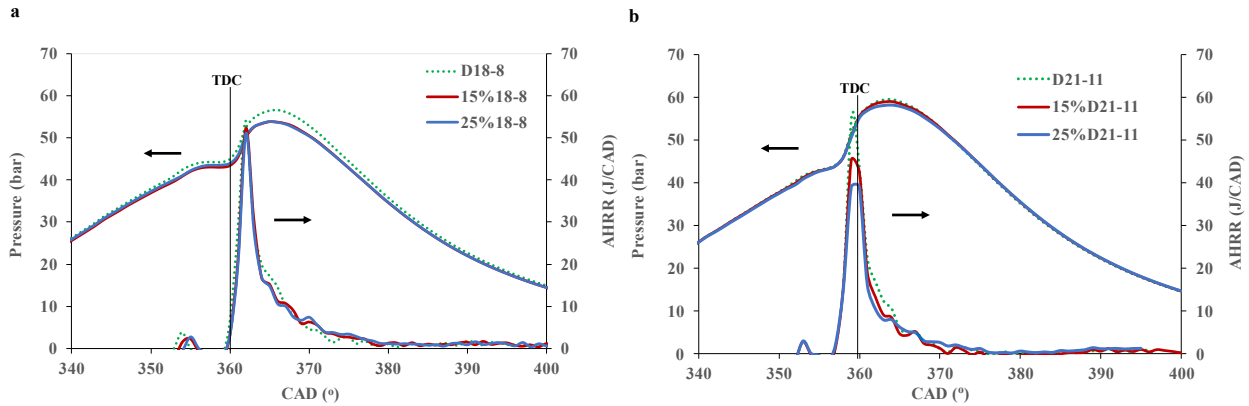


Figure 4. 3. Apparent heat release rate and in-cylinder pressure diagrams for: (a) diesel injection timing of pre-18, main 8 and (b) diesel injection timing of pre-21, main 11 with propane substitution ratios of 15% and 25%.

As can be observed in both Figures 4.3 (a and b), the peak of the in-cylinder pressures and premixed combustion phase are higher for the single diesel compared to the dual fuel conditions.

In addition, except in the case of where propane constituted 25% of the engine fuel, as the diesel fuel injection timing was advanced, the ignition delay becomes shorter as evidenced in Figure 4.4. With the split diesel injection system used for this research engine as shown in Figure 4.2, the ignition delay here was calculated as the CAD interval between the commencement of diesel main injection into the cylinder and the point at which the AHRR curve passes the zero level from a negative value to a positive value. Xu et al. (2016) and Cameretti et al. (2016) in their respective studies, reported that early direct diesel fuel injection timing led to an increase in the in-cylinder pressure and AHRR. The early injection timing allows more fuel energy to be released during the compression stroke (Shu et al. 2018). This increases the in-cylinder air temperature and enhances the fuel evaporation rate (Mathivanan, Mallikarjuna, and Ramesh 2016). Consequently, both the physical preparation time and the chemical reaction time (Wei et al. 2017) of the air-fuel mixture is reduced before the SOC. It is believed that these reasons may have led to the shorter ignition delay, higher peak premixed combustion phase and in-cylinder pressure as the injection was advanced to D21-11.

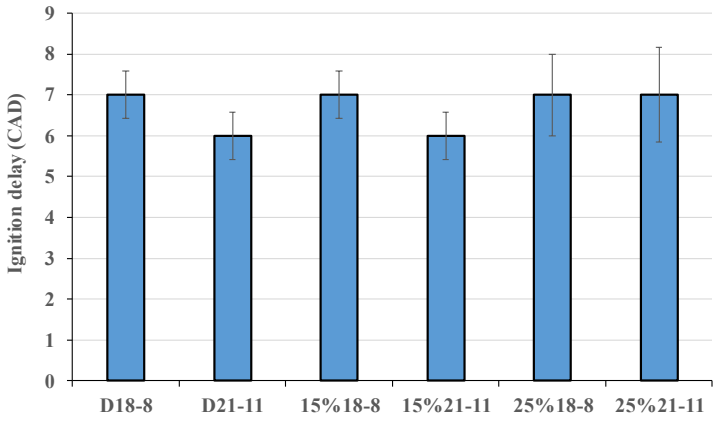


Figure 4. 4. Ignition delays for different injection timings and propane fractions.

However, the addition of propane reduces the peak cylinder pressures and the premixed combustion phase of the AHRR for the two injection timings. In addition, it is observed that with

D21-11 diesel injection timing, increasing the propane fraction to 25% prolongs the ignition delay. The ignition delay for diesel engine is influenced by the changes in the physical and chemical properties of the cylinder charge. In dual fuel engines, due to the differences in the physicochemical properties of the two fuels involved as well as the injection of gaseous fuel through inlet manifold, the specific heat capacity of the cylinder charge, oxygen concentration, pre-ignition reaction and the formation of active species during combustion are affected (Lata and Misra 2011).

With the addition of propane being the fuel with the lower CN and higher specific heat capacity with respect to diesel, it is believed that while the low CN slowed down the chemical reaction rate (Brijesh, Chowdhury, and Sreedhara 2015) of the in-cylinder mixture, the high specific heat capacity and reduction in partial pressure of oxygen due to increase in propane substitution contributed to the reduction of the adiabatic flame temperature (Molina et al. 2021). The effects of these are the longer ignition delay and decrease in the peak pressure and premixed combustion phase which become more pronounced as the concentration of the gaseous fuel was increased to 25%. Furthermore, the lower cylinder pressures observed under dual fuel operation duration the compression stroke is due to the higher specific heat capacity of the gaseous fuel-air mixture (Papagiannakis and Hountalas 2004). The difference becomes less obvious in Figure 4.3 (b) as a result of the higher temperature of the in-cylinder mixture which also positively enhanced the combustion of the gaseous fuel.

Moreover, when Figures 4.3 (a) and (b) are compared, the former is observed to exhibit slightly lower peak in-cylinder pressure and the AHRR moved into the expansion stroke. This could be attributed to the injection timing of D18-8 being closer to TDC than D21-11. Therefore, since more fuel was injected into the cylinder during the main injection than during pre-injection,

as can be seen in Figure 4.2, it is likely that a larger proportion of the fuel was combusted in the expansion stroke where the temperature and pressure are lower. When this kind of low temperature and pressure prevail inside the combustion chamber, it could lead to shorter combustion reaction time of the injected fuel before the opening of the exhaust valve (Serhan et al. 2019). This means that when compared to D21-11, less fuel energy was converted to useful work when the injection timing was set at D18-8.

4.3.2 Engine Performance Characteristics

Combustion duration for all the studied cases as presented in Figure 4.5 were calculated as the difference in CAD corresponding to 90% and 10% of the cumulative heat release. For diesel fuel injection timing of D18-8, the combustion duration for the single diesel fuel is similar to that of 15% C_3H_8, but then it becomes shorter when the energy contribution from propane is increased to 25%. This could be attributed to increase in the specific heat capacity of the in-cylinder fuel-air mixture and consequently, flame extinction (quenching) in the expansion stroke reduces the overall rate of flame propagation. As for the effect of injection timing, Xu et al. (2016) carried out a study on a diesel-gas dual fuel engine and obtained similar result. The explanation was that the advance injection timing produces a leaner fuel-air mixture and consequently, retards the burning rate of the in-cylinder mixture and increase the combustion duration. As it can be seen in Figure 4.5, as the diesel fuel injection timing was advanced to D21-11, the combustion duration increases.

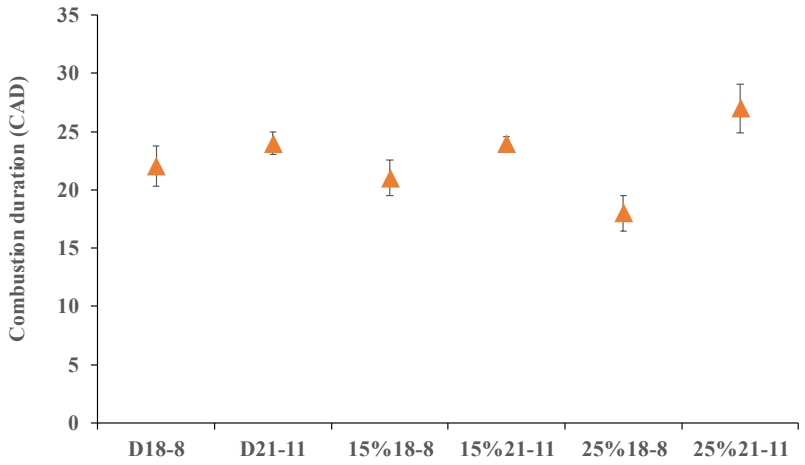


Figure 4. 5. Combustion duration for different injection timings and propane fractions.

Again, it can be observed that as the diesel injection timing was advanced to D21-11, increasing the amount of propane energy contribution of the engine fuel to 25% results to longer combustion duration. This means that even though the combustion is known to be affected by the physico-chemical properties of the fuel, under this condition, the increase in the combustion duration was mainly due to the advance injection timing. The advance fuel injection timing provided favourable in-cylinder conditions which allowed more fuel to be burnt over a longer time and therefore, could be a strategy to promote the combustion of diesel-propane dual fuel engine at low load.

Moreover, the conversion of energy from the start of combustion to the end of combustion can be explained by the cumulative heat release (or MFB) analysis (Yusri et al. 2019). As it can be seen in Figure 4.6, the effect of gaseous fuel in the cylinder becomes obvious with 25% propane energy fraction as the 50% cumulative heat release point is moved away from TDC. This can be explained by the high specific heat capacity and low CN of propane which combined to prolong the ignition delay. For D18-8, whilst the 50% cumulative heat release with 15% propane remains at the same CAD with single diesel combustion, it changes when the propane fraction was

increased to 25%. Similar results are also produced with D21-11 injection timing. However, in this case, the 50% cumulative heat release seems to be closer to the TDC than with D18-8. This shows that the injection timing is very important as it can be used to fix the combustion phasing (Zeraati-Rezaei et al. 2020) even in the presence of low reactivity fuel.

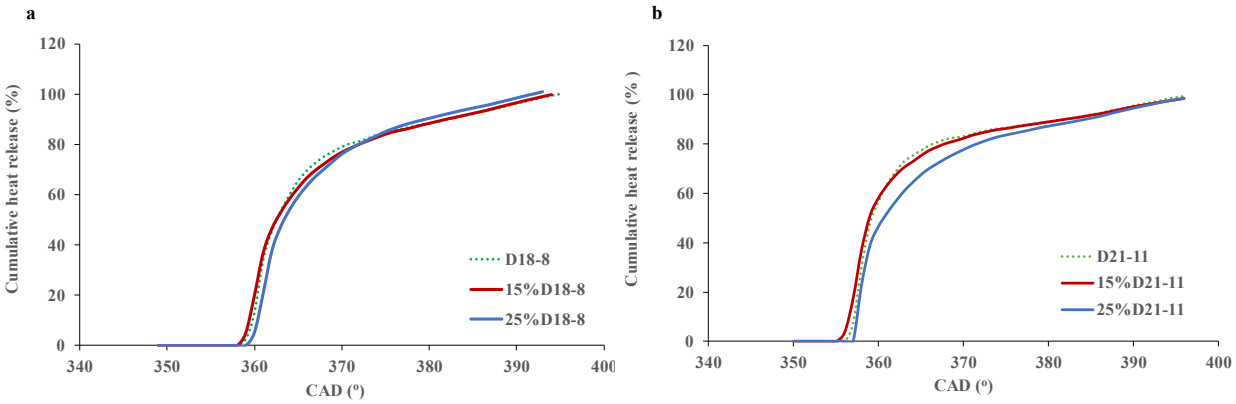


Figure 4. 6. Cumulative heat release for: (a) diesel injection timing of pre-18, main 8 and (b) diesel injection timing of pre-21, main 11 with propane substitution ratios of 15% and 25%.

Brake thermal efficiency (BTE) presented in Figure 4.7 shows how much fuel energy was converted to work for all the conditions investigated. It is observed that the brake thermal efficiency increases as the injection timing is advanced for the diesel combustion. The higher in-cylinder pressure and temperature due to the advanced diesel fuel injection timing enhanced the atomization and evaporation of the fuel. This provided a better combustible air-fuel mixture that led to more efficient conversion of the fuel energy (Ryu 2013). Also, as the injection timing was advanced, more of the diesel fuel injected was burnt to increase the peak combustion pressure and release more heat around the TDC as in Figure 4. 3 (b) and this resulted to more useful work. However, with diesel fuel injection timing of D18-8, a lower BTE was obtained.

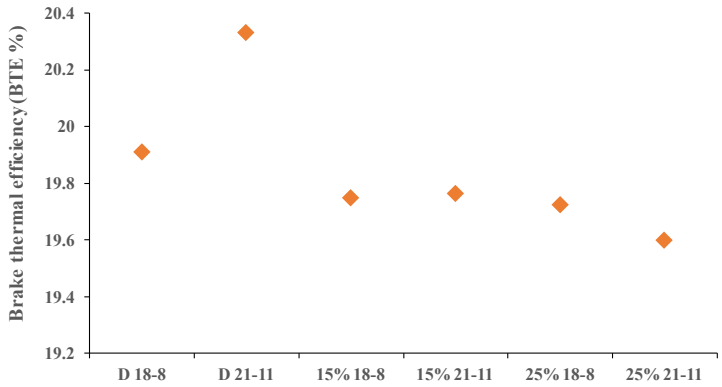


Figure 4. 7. Brake thermal efficiency under diesel and propane fuels with injection timings.

In all the two fractions of propane investigated, BTE are obviously lower compared to the straight diesel operations. This could be explained as follows: (1) as the propane is injected into the manifold, it displaces part of the intake air resulting to the reduction of volumetric efficiency of the dual fuel mode; (2) lower premixed control combustion rate associated with dual fuel operation (Papagiannakis, Hountalas, and Rakopoulos 2007). The consequences of these are that less oxygen and heat were made available for fuel combustion; therefore, more fuel was consumed in the cylinder to maintain the same engine load. Although, the advanced diesel fuel injection timing obviously improves the BTE, increasing the propane fraction from 15% to 25% results to further reduction in BTE. The higher specific heat capacity due to propane led to the reduction of the in-cylinder charge temperature and therefore, deteriorated the fuel conversion rate (Papagiannakis, Hountalas, and Rakopoulos 2007). However, the lower BTE with 25%D21-11 compared to 25%D18-8 could be an evidence of higher heat transfer in the combustion chamber or incomplete combustion of fuel, meaning that less fuel energy was converted to brake power.

Coefficient of variation of indicated mean effective pressure (COV_{IMEP}) was used as a criterion for the combustion stability. A higher value of COV_{IMEP} shows that the combustion is more unstable. Although in most conventional engines, COV_{IMEP} value exceeding 10% results to

operational problem (Heywood 1988; Ouchikh et al. 2019), for this study, the COV_{IMEP} values for all the cases were within the acceptable range of less than 2%. As it can be noticed in Figure 4.8, the COV_{IMEP} increases under diesel-propane fuel operation due to the non-uniformity of the cylinder mixture (Tira et al. 2012). However, advancing the diesel fuel injection to D21-11 leads to lower COV_{IMEP} and therefore, better combustion process for all the two fractions of propane compared to D18-8. The meaning of lower COV_{IMEP} value is that the engine operation is more stable because the uncertainties between the start of energizing and ignition of the cylinder mixture are reduced due to the multi-stage combustion (Suh 2011). This shows that with similar engine, running on diesel-propane dual fuel mode under low load operation, utilizing the D21-11 injection timing could be an effective strategy to achieve a better combustion process. This improvement in the dual fuel combustion process is attributed to better in-cylinder mixture, higher in-cylinder temperature and pressure resulting from advancing the injection timing.

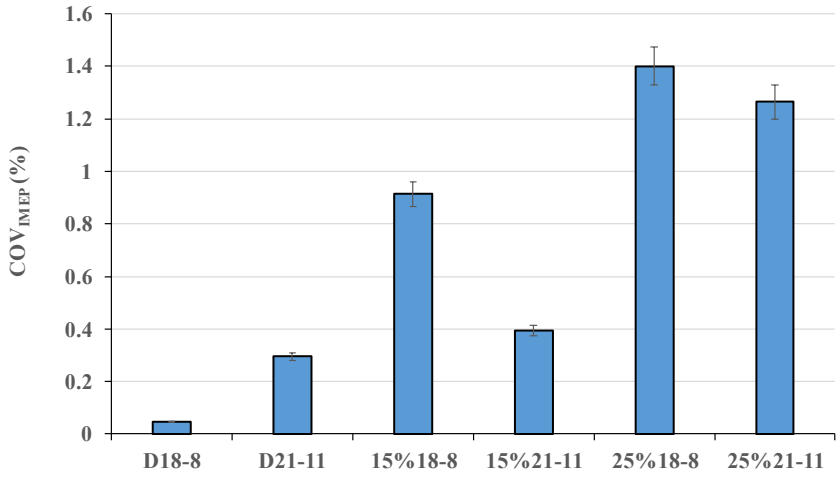


Figure 4. 8. Coefficient of variation of the indicated mean effective pressure for the different injection timings and propane fractions.

4.3.3 Emissions

Carbon monoxide and total hydrocarbon emissions for all studied injection timings and propane substitutions are presented in Figure 4.9. Typical of a low load dual fuel combustion, significantly higher level of CO and THC emissions were recorded for the dual fuel combustions when compared to the straight diesel. However, for the diesel fuel modes, when D21-11 and D18-8 are compared, slight increase in CO emissions can be observed as the injection timing was advanced to D21-11. Advancing the injection timing provides higher in-cylinder temperature to promote the oxidization of THC. However, it is thought that the temperature was not high enough to completely convert the THC to CO_2 and therefore, produced more CO emissions as product of partial THC oxidization.

Similar trend is observed where propane was burnt as part of the engine fuel for both diesel injection timings. Since both CO and THC can also be produced due to under-mixing, wall quenching and incomplete combustion (Wang et al. 2016), they are formed at regions where the diluted air and fuel mixture caused the prevailing temperature to drop and consequently, prevents the combustion process from going to completion (Suh 2011). It is believed that due to the relatively cold in-cylinder charge and low engine load, the in-cylinder conditions did not adequately support the combustion of the propane gas. Consequently, part of the THC emitted originated from the partially or unburnt propane that escaped into the crevice volumes of the combustion chamber during compression stroke and released during the expansion stroke.

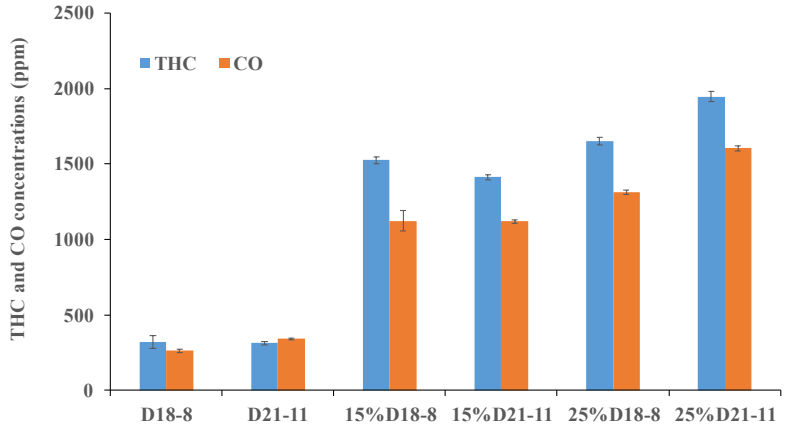


Figure 4. 9. Effects of injection timings and propane substitutions on CO and THC emissions.

In the presence of propane and D21-11 diesel injection timing, the in-cylinder charge becomes leaner and slow to vaporise, and the effect of this is that the fuel-air mixture becomes more difficult to burn completely. At the same time, the higher in-cylinder temperature provided by the more advanced injection timing compensated to somewhat, the effect of propane in the cylinder, thereby, resulting to the lower THC emissions observed with the advanced injection timing. However, as the propane fraction was increased to 25%, low combustion temperature and reduction in oxygen concentration in the cylinder caused by the addition of propane resulted to the reduction in the rate of THC and CO.

Nitrogen Oxides (NO and NO_2) emissions from the two diesel injection timings and propane fractions are shown in Figure 4.10. NO is formed in the combustion chamber due to high temperature, oxygen content and the reaction residence time. As it can be observed, NO is seen to be higher as the injection timing was advanced. The effect of advanced injection timing on NOx emissions had been previously reported by (Leermakers, Somers, and Johansson 2012). One explanation is that the earlier premixing due to advanced injection timing caused ignition and combustion to occur earlier and as a result, produced high in-cylinder peak pressure and

temperature close to TDC (Lee et al. 2015). Another reason that might probably be linked to the increase in NO is evidenced in Figure 4.6 as the BTE is higher as the injection timing was advanced to D21-11.

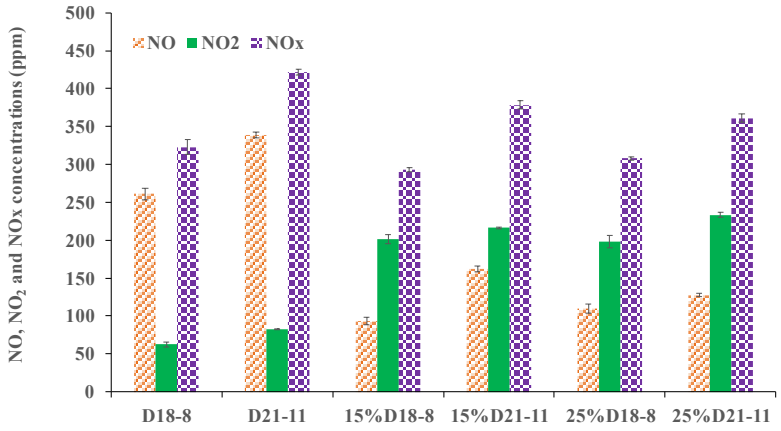


Figure 4. 10. Effects of injection timings and propane substitution on NO and NO_2 emissions.

Although, the NO emissions show significant level of reduction with the addition of propane, when D18-8 and D21-11 injection timings with the diesel-propane dual fuel systems are considered, it is clear that the latter favours the formation of NO emissions as it becomes higher compared to when D18-8 was used in the diesel-propane combustion. The reduction of NO as propane was added could be attributed to the following reasons. (1) The higher specific heat capacity of propane is believed to have assisted in suppressing the in-cylinder temperature. (2) The overall lean air-fuel mixture as propane was inducted leads to a decrease in the local high burnt gas temperature (d'Ambrosio and Ferrari 2015). Furthermore, with the delay of the combustion phasing into the expansion stroke as propane was added, the residence time for NO formation in the high temperature compression stroke is reduced (Sun et al. 2016).

On the other hand, the higher in-cylinder peak pressure and temperature from D21-11 injection timing seems to somewhat counteract the contribution from the propane addition and consequently, increased the NO level more than with D18-8. This is because the longer ignition

delay due to the presence of propane and advanced injection timing is believed to have enhanced the air-fuel mixing process and therefore, increased the amount of combustible diesel at the point of ignition.

The effect of propane gas on the engine out NO_2 emission is also presented in Figure 4.10. As it can be noticed, increasing the propane fractions also resulted to an increase in NO_2 emission. Under same injection timing, higher propane fraction seems to favour the formation of NO_2. The effect of HC on NO_2 formation under low temperature condition has been reported in previous studies by Yu, Yu, and Zheng (2019), Liu et al. (2012) and Chong et al. (2010). Also, Li et al. (2018) in reporting the influence of HC on NO_2 formation, stated that the NO_2 formation in a dual fuel engine could be due to increased HO_2 (hydroperoxyl radical) production in the relatively low temperature of unburnt-fuel-air mixture region. Therefore, it is thought that the increase in NO_2 is due to the high concentration of propane to enhance the production of more HO_2 radicals which is the main determinant for the conversion of NO to NO_2 through reaction $NO + HO_2 \leftrightarrow NO_2 + OH$ (Li et al. 2018). As the injection timing is advanced to D21-11, the increase in NO_2 is seen almost becoming a function of the amount of propane burnt. The possible speculation to this trend is that as the injection timing is advanced the residence time becomes longer, and more of the HO_2 radicals were generated to favour the formation of NO_2. Although NO_2 is a more harmful gas compared to NO, it is beneficial for downstream aftertreatment control of NOx and PM.

4.4 Summary

Dual fuel engines take advantage of the different properties of the two fuels to achieve optimum combustion and emissions benefits. However, under low temperatures and load operations, these engines suffer from relatively poor performance and produce high level of CO

and THC emissions. In this chapter, experiments were conducted to investigate the effects of advanced diesel fuel injection timing on the combustion, performance and emissions characteristics of a diesel-propane dual fuel engine. The study shows that advancing the diesel fuel injection timings favours the combustion and performance of diesel-propane fuel engine by increasing the in-cylinder pressure and temperature. It was found that the higher in-cylinder pressure and AHRR produced due to the advance injection timing to some extent, created a favourable in-cylinder environment that compensated the cooling effects from propane addition and consequently, the BTE was not significantly affected. Both THC and CO emissions under the dual fuel combustion were observed to be higher compared to the straight diesel fuel condition. These emissions are products of unburnt propane and under the two injection timings considered, the addition of propane resulted to the increase in the level of THC and CO emissions. On the other hand, while decrease in NO emissions were observed, higher amount of NO_2 emissions were recorded under diesel-propane dual fuelling condition. And as the injection timing was advanced to D21-11, longer residence time for the production of HO_2 radicals resulted to more NO_2 emissions. It was suggested that with diesel fuel injection timings of D18-8 and D21-11, 15-25% of propane could be used to displace diesel fuel and conveniently run this engine to produce a very low amount of NO emission. Furthermore, whilst DOC can be used to control CO and HC, the high level of NO_2 produced can be beneficial for the reduction of the remaining NO and PM with the appropriate exhaust gas aftertreatment devices.

CHAPTER 5

THE EFFECTS OF H_2 AND NH_3 MIXTURE ON NOx REDUCTION OVER Ag/Al_2O_3 CATALYST.

5.1 Introduction

This chapter presents the results of the effects of different concentrations of H_2 and NH_3 mixture on the NOx reduction activities over a Ag/Al_2O_3 catalyst. The aim of this study is to investigate the NOx reduction activities of a Ag/Al_2O_3 catalyst in an NH_3-diesel dual fuel engine producing very low concentration of unburnt HC in the presence of NH_3 and H_2 mixture, while in parallel minimizing the amounts of THC and the NH_3 released into the atmosphere during the HC- and NH_3-SCR process. This was done by employing a DOC to reduce the amount of THC going into the SCR catalyst in a DOC+SCR aftertreatment configuration to represent exhaust condition similar to that of NH_3-diesel fuel combustion. It is envisaged that in a real situation: (1) the H_2 would be generated through a catalytic decomposition of liquid ammonia with some amount of ammonia left undissociated to support the activities of HC- and NH_3-SCR aftertreatment device and therefore, no need for separate hydrogen and ammonia storage; or (2) the unburnt ammonia resulting from an ammonia-diesel dual fuel engine, whilst the H_2 is being provided through onboard HC/NH_3 fuel reforming; or (3) NH_3-diesel dual fuel engine and the H_2 is generated in the combustion chamber from NH_3 reactions. Presented in Figure 5.1 is the schematic of the experimental setup with the catalysts' arrangements used for this research. The details of the engine test condition, and procedure are described in Section 5.2. Sections 5.3 presents the results and discussions of the effects of the presence of different concentrations of H_2 and NH_3 mixture

on NOx reduction, N_2O formation, HC and NH_3 conversions over Ag/Al_2O_3 catalyst. The overall results are summarised in Section 5.4.

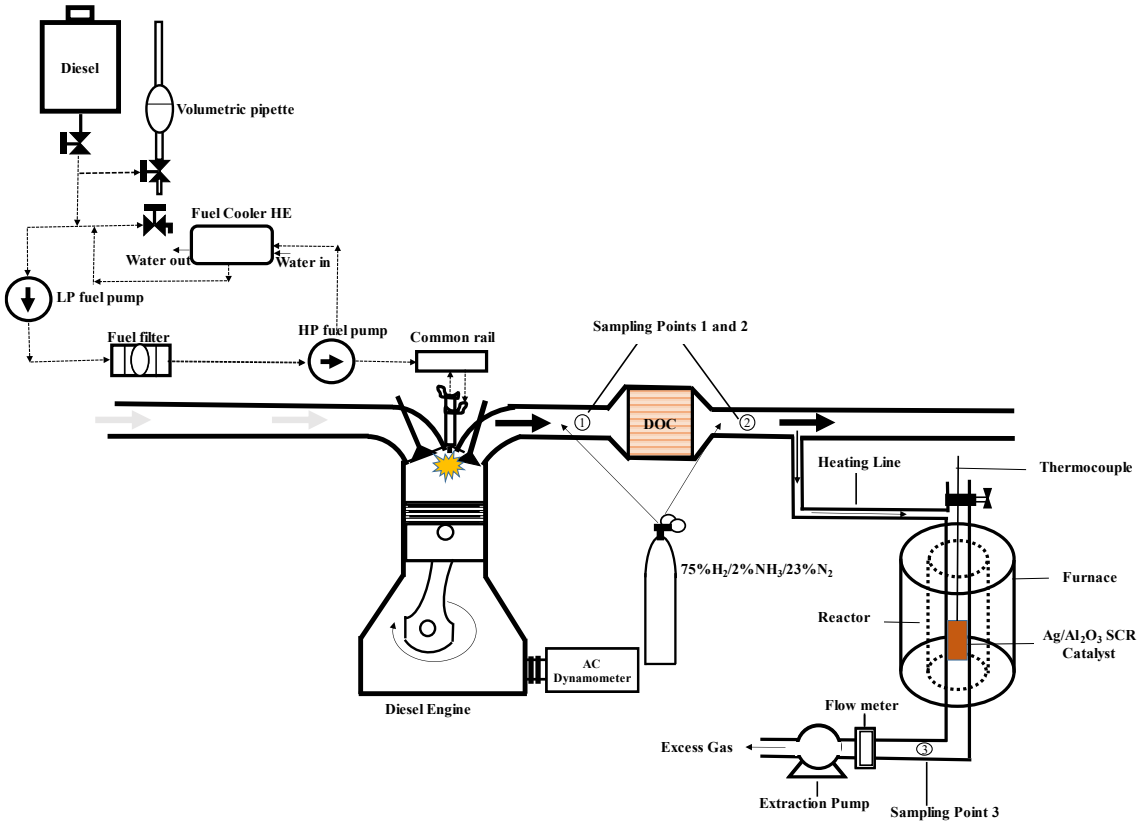


Figure 5. 1. Schematic of the experimental set-up.

5.2 Engine Test Conditions and Procedure

All experiments were carried out under steady state engine conditions of 1500 rpm speed and 2 bar indicated mean effective pressure (IMEP) whilst the fuel injection pressure was kept constant at 550 bar. As shown in Figure 5.1, the DOC temperature was dependent on the engine exhaust gas temperature and was maintained constant at 170 ^oC for the selected conditions. At 1500 rpm engine speed, the gas hourly space velocity (GHSV) for both, DOC and SCR catalyst was 35,000 h^{-1} and this was maintained constant throughout the experiment.

The SCR Ag/Al_2O_3 catalyst was placed in a reactor and a temperature-controlled tube was used to direct part of the exhaust gas to the catalyst (Figure 5.1). A tubular furnace was used to control the SCR reactor temperature. The reactor temperature was set to increase in four steps from 107, 189, 294 and 394 ^oC. It is important to state that in practical applications, an electrically heated catalyst (EHC) such as the one used by Moon et al. (2022) could be used to support catalyst temperatures higher than the exhaust gas temperature. For each test temperature, the catalyst temperature was allowed to stabilize before taking measurements at the specific inlet and outlet sampling points.

The tests were conducted with different concentrations of H_2 and NH_3 added upstream the catalysts with a 5-minute duration for each concentration. This was achieved using a simulated gas (i.e., 75% H_2, 2% NH_3 and 23% N_2) from a certified bottle. As shown from the measurements taken at sampling point 2 (Table 5.1), the H_2 and NH_3 level increased by introducing H_2 concentrations of 1000, 1500, 2000, 3000 and 5000 ppm and NH_3 ~ 28, 43, 55, 82 and 133 ppm also included. The flow rate was controlled by a digital flow meter connected to the engine exhaust line to be homogeneously mixed with the exhaust before going into the DOC and SCR Ag/Al_2O_3 catalysts.

Table 5. 1. Hydrogen concentrations and engine exhaust gas composition for H_2 and NH_3 injection upstream of SCR catalyst.

Sampling point 2						
H_2 (ppm)	0	1000	1500	2000	3000	5000
THC (ppm)	334	323	315	313	312	312
NO (ppm)	255	250	249	252	252	249
CO (ppm)	202	236	232	230	229	231
NO_2 (ppm)	38	37	37	36	35	38
N_2O (ppm)	1	1	1	1	1	1
NH_3 (ppm)	2	28	43	55	82	133
HC:NOx ratio	1.07	1.13	1.10	1.09	1.09	1.09

5.3 Results and Discussion

5.3.1 Effects of H_2 and NH_3 Mixture Addition before DOC

Figures 5.2 (a) and (b) show the concentrations of THC, CO, NO, NO_2 and N_2O sampled at points 1 and 2 (Figure 5.1), respectively, with or without H_2 and NH_3 injections before DOC. The oxidation of unburnt HC, CO and NO are the main reactions in the DOC catalysis process. However, the performance of the DOC is dependent on the exhaust gas temperature. At low temperature, the inability of the DOC to warm up to operating temperature (Boutikos, Žák, and Kočí 2019; Lefort, Herreros, and Tsolakis 2014) promotes the adsorption of HC and CO onto the catalyst active sites and consequently, reduces its efficiency. Addition of small amount of H_2 on the catalyst has been proven to be a solution to the low temperature performance. The presence of H_2 on the DOC promotes the conversions of all three of HC, CO and NO emissions at low temperatures.

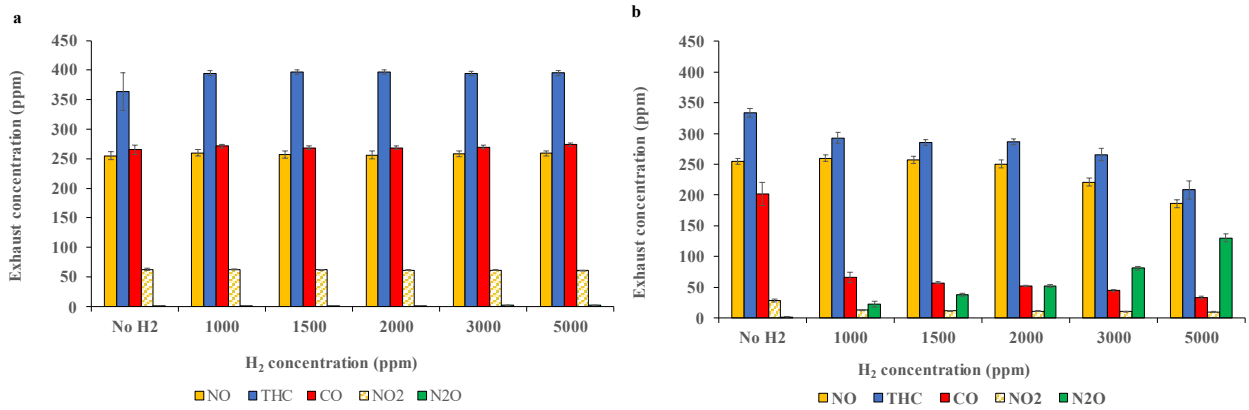


Figure 5. 2. NO, THC, NO_2 and CO concentrations at DOC: (a) inlet and (b) outlet for different concentrations of H_2 and NH_3 injection before DOC at 170 ^oC.

As it can be observed in the Figure 5.2, at this low catalyst temperature (i.e., 170 ^oC), the slightly but steadily decreasing trends in the levels of THC and CO could be ascribed solely to the effects of H_2 as it becomes more pronounced with increasing addition. The effects of H_2 on catalyst performance at low temperature were highlighted in previous study by Wang et al. (2015). According to the authors, H_2 enhanced the production of intermediate radicals (e.g., OH and HO_2), and increased the local temperature of the catalyst. The higher catalyst temperature enhances the desorption and oxidation of the adsorbed HC and CO and therefore, reduces their competition for catalyst active sites. In this case, while the observed reduction in both THC and CO could be attributed to oxidation promoted by the intermediate radicals, it seems that at this low temperature, significant amount of THC was still left unoxidized as evidenced in Figure 5.2 (b). This high amount of THC emission on the catalyst could limit NO access to the catalyst active sites. In a DOC, the amount of NO that is oxidized to NO_2 is dependent on the HC level and exhaust gas temperature (Theinnoi et al. 2013) as it is kinetically limited at lower temperature and thermodynamically limited at higher temperature. NO_2 being a very effective oxidant at low temperature is believed to have partly contributed to the oxidation of THC and CO and therefore, lower concentration of NO_2 was measured downstream of the catalyst (Figure 5.2 (b)).

Also, compared to THC, more of CO was reduced as the H_2 concentration increases, indicating higher reactivity of the latter compared to the former. On the other hand, while NO concentration decreases with increasing H_2 amount, evidence of its oxidation to NO_2 was not seen, rather a rapid increase in N_2O was recorded. It is known that N_2O is a by-product of NOx reduction in the presence of hydrocarbon at low temperature condition (Herreros et al. 2014a), but it has also been found to be promoted by both Pt and Pd being the main choices for commercial oxidation catalysts (Xie et al. 2018).

However, in this study, it could be suggested that the NH_3 inlet to the DOC is the main contributor to the N_2O formation. As seen in equation 5.1 (Shan et al. 2021), the drop in NO is believed to be a result of the reaction of NO with NH_3 in the presence of an oxidizing medium (DOC) to generate the N_2O. Therefore, it is concluded that in the presence of NH_3 in the exhaust stream, H_2 could still promote the conversion of THC and CO over the DOC in the presence of low exhaust temperatures. However, this could come with the penalty of increase engine out N_2O emission and therefore, it is not a good strategy.

$$4NH_3 + 4NO + 3O_2 \rightarrow 4N_2O + 6H_2O \qquad 5.1$$

5.3.2 Effects of H_2 and NH_3 Addition before DOC on the NOx Reduction Activities of Ag/Al_2O_3 Catalyst

The trends in Figure 5.3 represent the effects of H_2 on the levels of NO, NO_2, NH_3 and N_2O concentrations measured downstream of the Ag/Al_2O_3 catalyst as a function of time for all four catalyst temperatures (i.e., 107, 189, 294 and 394 ^oC) with the different H_2 and NH_3 mixtures addition upstream of the DOC. As it can be observed, there was no significant evidence of H_2 consumption as the concentrations measured at the inlet of the SCR catalyst were almost the same

as those measured at the outlet. The trend is almost similar in all cases except with the slight changes seen with increasing catalyst temperature which could be a result H_2 oxidation. This is because as the H_2 was injected upstream the DOC, greater amount was utilized and as a result much was not made available for the activity of the downstream Ag/Al_2O_3 catalyst. In previous studies, it has been shown that both HC and NH_3 can simultaneously contribute to the reduction of NOx in the SCR mechanism over Ag/Al_2O_3 catalyst in the presence of H_2 (Xu et al. 2019). Therefore, both were considered as reductants in this study.

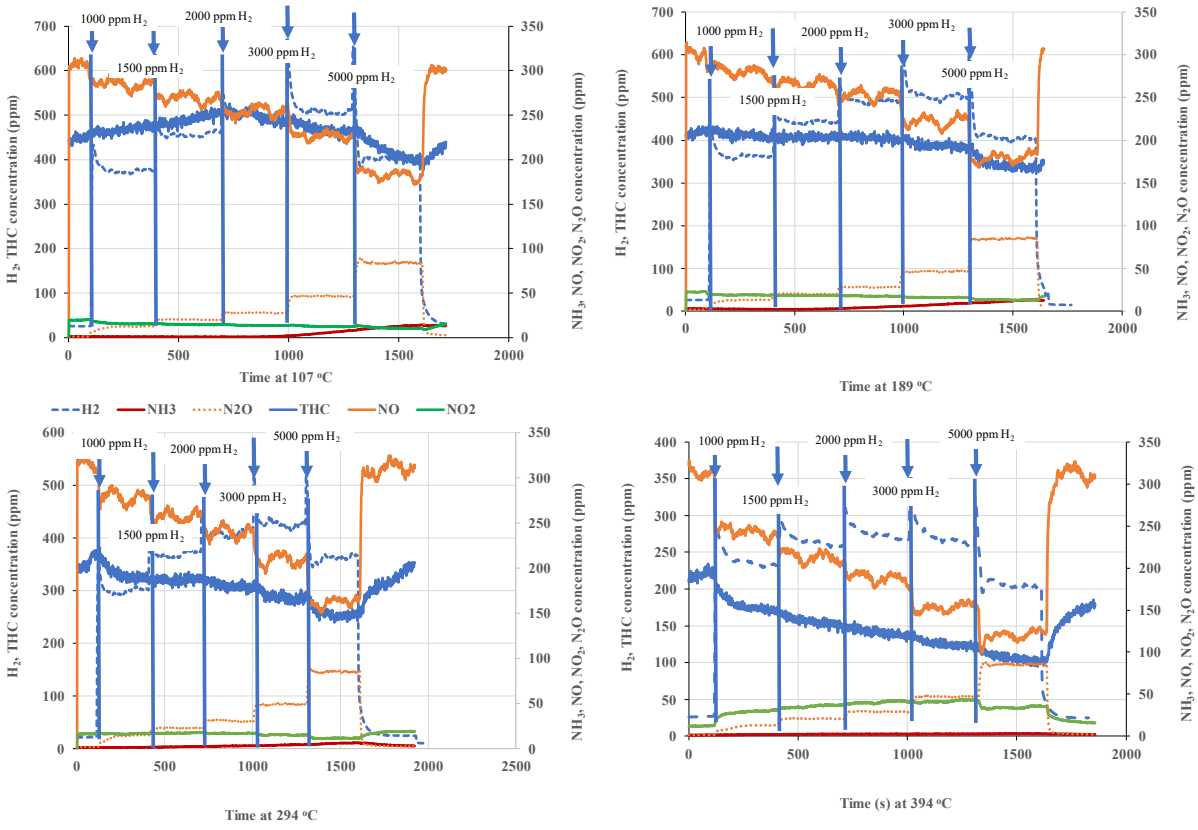


Figure 5. 3. SCR outlet concentrations of H_2, NH_3, N_2O, THC, NO, NO_2 at SCR catalyst temperatures of 107, 189, 294 and 394 °C for H_2 and NH_3 mixture addition before DOC.

As it can be seen in Figure 5.3, whilst the H_2 concentration upstream and downstream of the SCR catalyst remained almost constant, a very low level of NH_3 that levelled out regardless

the H_2 and NH_3 concentrations and catalyst temperature was recorded. It was expected that the addition of H_2 and NH_3 before and the presence of DOC would result to an increase in the amount of NO_2 being fed to the SCR. However, while in the absence of H_2 and NH_3 mixture, the temperature of 170 ^oC is thought to be too low to activate the oxidation of significant amounts of NO to NO_2, the catalyst temperature as shown in Figure 5.4 (b) became lower as 23% of N_2 gas was added as part of H_2 and NH_3 mixture with reference to Figure 5.1. This is important because when H_2 is added to enhance the performance of a HC-SCR catalyst, the catalyst bed temperature usually increases due to exothermic reaction that occurs (Abu-Jrai, Tsolakis, and Megaritis 2007). The higher temperature resulting from the H_2 addition also contributes to enhance the performance of the catalyst. Therefore, it is likely that the reductions in the temperatures due to the addition of 75%H_2/2%NH_3/23%N_2 mixture partly contributed to the low level of NOx reduction activity of the catalyst.

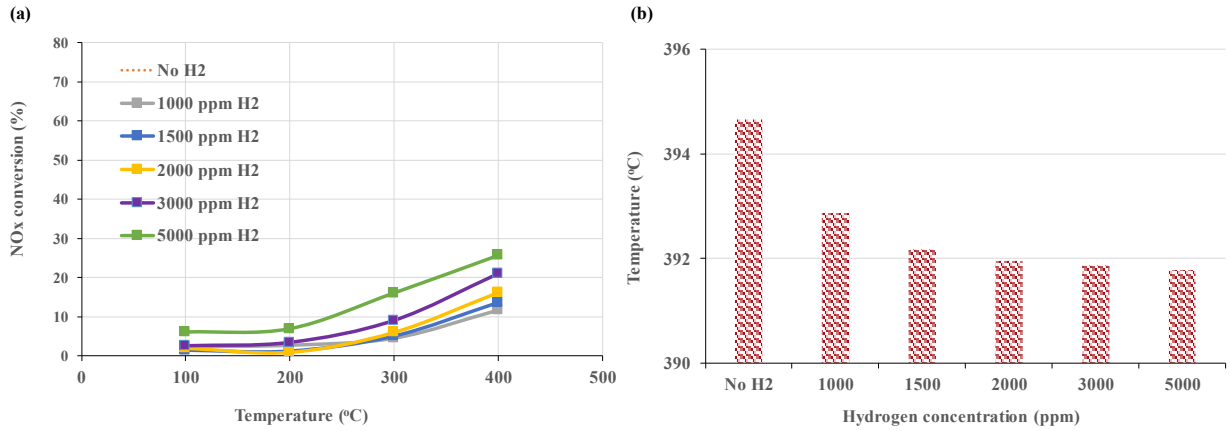


Figure 5. 4. Effects of varying H_2 and NH_3 injections before DOC on: (a) NOx conversion efficiencies and (b) catalyst maximum temperature.

Furthermore, it was observed that whilst the concentration of THC was not affected significantly by the DOC, greater amount of NH_3 was consumed as the H_2 and NH_3 mixture was injected before the DOC. This means that the main reductant available for the downstream SCR reaction in this case was the unburnt HC. Furthermore, as more H_2 was also consumed over the

DOC, less of it was left available for the downstream HC-SCR activities and consequently, the NOx reduction activity is obviously very low, only achieving a maximum efficiency of 25% as shown in Figure 5.4 (a) because both HC-, and NH_3-SCRs were not activated. We may attribute this low NOx conversion efficiency to a number of factors, including insufficient reductants, deficit in H_2 concentration (Fogel and Gabrielsson 2014), preferential production of N_2O over the DOC.

5.3.3 Effects of H_2 and NH_3 Addition before Ag/Al_2O_3 Catalyst on NOx Conversion

The concentrations of exhaust gas species measured upstream the SCR catalyst (sampling point 2) in the absence and presence of different concentrations of H_2 and NH_3 mixture injections are presented in Table 5.1. These were measured to show how much of these species are being sent into the SCR catalyst to participate in the NOx reduction activity. Similarly, the outlet concentrations of H_2, NH_3, N_2O, THC, NO, NO_2 against time over the SCR catalyst at all four temperatures points are presented in Figure 5.5. It can be observed that irrespective of the amount of H_2 and NH_3 addition, at the low temperature regions, between 107 and 189 ^oC there is no clear evidence of H_2 consumption over the catalyst as the concentrations injected upstream of the SCR catalyst were almost the same or slightly higher than those that were measured downstream and thus, indicating that H_2 was not utilized over the catalyst. However, as the catalyst temperature was increased, the NO emission became lower, and the maximum reduction was achieved at 394 ^oC. It is important to note the trends of NO and NH_3 emissions with increase in the catalyst temperature as well. It can be observed that the temperature at which NO reduction became significant, the lowest concentration of NH_3 was also measured. This may be attributed to the activities of NH_3-SCR over the catalyst in the presence of H_2.

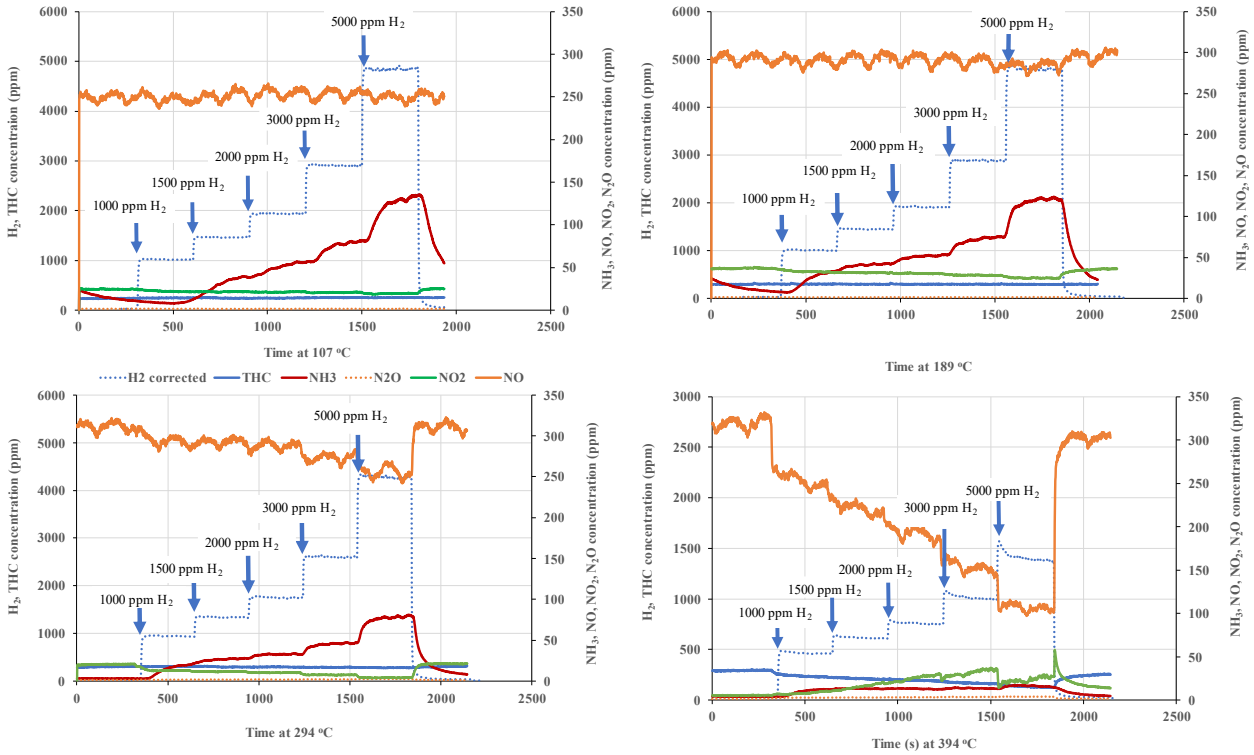


Figure 5. 5. SCR outlet concentrations of H_2, NH_3, N_2O, THC, NO, NO_2 at SCR catalyst temperatures of 107, 189,294 and 394 ^oC for H_2 and NH_3 mixture addition before SCR catalyst.

Shown in Figure 5.6 (a) is the NOx conversion efficiencies at the different catalyst temperatures in the presence and absence of H_2 additions. At temperatures <200 ^oC, there was no clear evidence of NOx reductions other than when the H_2 concentration was increased to 5000 ppm. However, as the temperature was increased, the NOx conversion began to be increasing with respect to H_2 concentrations. This is an indication that the NOx reduction activities of both HC- and NH_3-SCRs depend on H_2 concentration. Because the H_2 and NH_3 were injected as a mixture, an increase in H_2 concentration provided the $Ag/Al_2/O_3$ catalyst with more NH_3 reductant to participate in the NH_3-SCR process. As a result, both the HC- and NH_3-SCR activities were simultaneously promoted to increase the efficiency up to 62%. This could be an indication of a synergy between HC and NH_3 in enhancing the NOx reduction activity. Kim et al. (2012) reported increased NOx reduction efficiency over Ag/Al_2O_3 catalyst in the presence of HC and ammonia

reductants in the exhaust feed. According to the authors, this was as a result of efficient production of reactive intermediates due to the synergistic effects of both reductants.

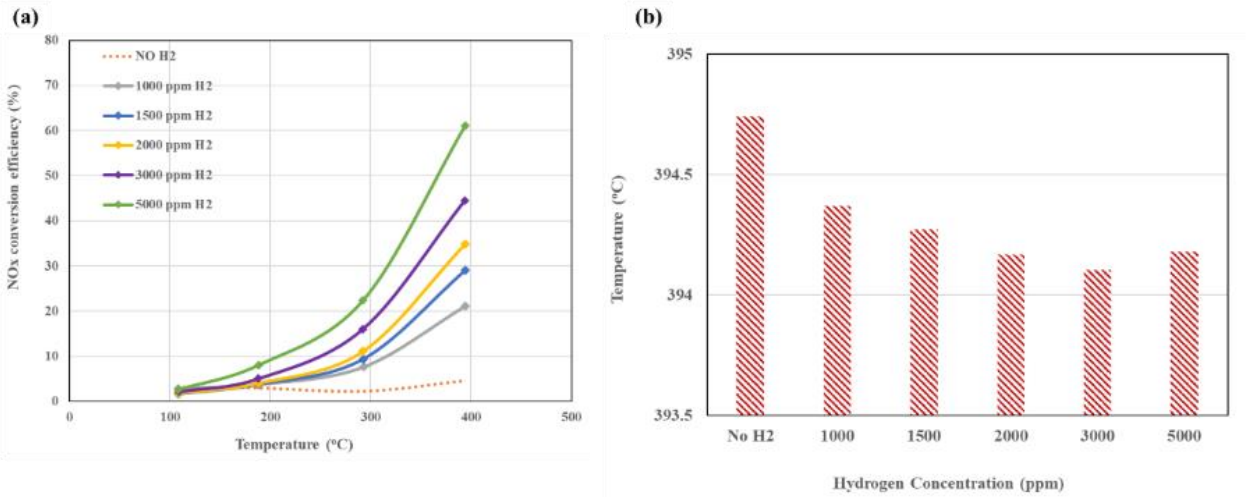


Figure 5. 6. Effects of varying H_2 and NH_3 concentrations before SCR catalyst on: (a) NOx conversion and (b) maximum catalyst temperature.

However, with respect to earlier studies where 1% (10, 000 ppm) H_2 was used to promote HC-SCR and NH_3-SCR to achieve higher efficiencies at lower temperatures (Arve et al. 2006; Richter, Fricke, and Eckelt 2004), in this case maximum efficiencies were only achieved at 394 ^oC when H_2 concentration was increased to 5000 ppm. Although, the reason for this is not too clear, but it has been shown in earlier study that NOx reduction activity is more reliant upon H_2 concentration (Arve et al. 2006). For the results presented here, the H_2 effects became more beneficial as the NH_3 concentration was increased 126 ppm. At lower temperature and in the presence of enough reductant, H_2 is believed to enhance the formation of reactive species over the catalyst (Herreros et al. 2014a). However, due to the very low amount of reductant available, it is thought that more H_2 is required to activate the HC (i.e., partially oxidize the HC) (Gunnarsson et al. 2017) to provide the reactive intermediate radicals required to enhance the NOx reduction activity (Lee et al. 2021).

For SCR, besides the reduction of NO, oxidation of the reducing agent also occurs. At higher temperature, there is a possibility of HC evaporation (Sitshebo, Tsolakis, and Theinnoi 2009), and preferential oxidation by molecular oxygen over the Ag/Al_2O_3 catalyst (Arve et al. 2009; Dimaggio et al. 2009; Gunnarsson et al. 2017) to further decrease the amount of HC reductant required for NOx reduction activity. The HC-SCR of NOx over Ag/Al_2O_3 catalyst depends on the HC/NOx ratio (Lindfors et al. 2004), amount of H_2 concentration used and the reducing agent (Arve et al. 2009; Sitshebo et al. 2010). When both HC and NH_3 are involved in the NOx reduction process, it becomes quite difficult to isolate their individual contribution as the NOx reduction activity of the Ag/Al_2O_3 catalyst is believed to be a consequence of the overlapping effects from the two reducing agents (Abu-Jrai and Tsolakis 2007) to promote both HC- and NH_3-SCR reactions. With respect to the role of the individual influence of HC and NH_3 on NOx conversion, it is likely that the low level of HC/NOx as shown in Table 5.1, could be reduced further as HC would be oxidized in the high temperature region. This means less HC reductant will be made available for the HC-SCR reaction. However, it can be observed in Figure 5.6 (a) that the NOx conversion increases as the NH_3 concentration measured upstream the Ag/Al_2O_3 catalyst increases. Therefore, the main drawback observed with application of H_2 and NH_3 mixture in this study is the very low concentrations of NH_3 reductant available for NOx reduction activity. This is pertinent when considering the practical application of H_2 and NH_3, as it shows the need for a careful optimization of NH_3 in the mixture to promote the NOx reduction activity. Due to the very low amount of reductants (e.g., HC and NH_3) available, lack of NO_2 needed to promote fast SCR, increased NOx conversion efficiency was only achieved at higher temperature.

As it can be observed in Figure 5.6 (b), the gas temperatures at the catalyst surface continues to decrease as H_2 and NH_3 concentrations were increased, except for the slight increase

in 5000 ppm H_2. This means that the application of $75H_2/2\%NH_3$ /23% N_2 mixture as a reductant and promoter of the Ag/Al_2O_3 catalyst did not favour the usual exothermic reaction following the addition of H_2 on the catalyst. The decrease in temperature could be attributed to the activities of $23\%N_2$ and NH_3 on the Ag/Al_2O_3 catalyst. As the mixture was injected into the catalyst, it is believed that the 23% N_2 content, although it is an inert gas, but with its high specific heat capacity as well as the conversion of NH_3 being an endothermic reaction (Gill et al. 2012), the combined effects were able to suppress the thermal effect resulting from H_2 addition. This loss in exotherm therefore, led to decrease in the oxidation of the adsorbed THC activity. Therefore, it could be concluded that due to the low HC:NOx ratio and the temperature prevailing at the catalyst surface, higher concentration of H_2 was required to activate both NO and HC to surface-bound NOx and partially oxidized the HC species that would initiate the first reaction steps of HC-SCR process (Korhonen et al. 2011).

Furthermore, accumulation of C- and N- containing species on Ag/Al_2O_3 catalyst is known to be associated with diesel-type fuels (Sitshebo, Tsolakis, and Theinnoi 2009). In a previous study, H_2 was reported to have negligible effects on the accumulation of C-containing species where the reductant involved is a long chain multi-component fuel (e.g., conventional and synthetic diesel) at high HC:NOx ratio (Houel et al. 2007; Sawatmongkhon et al. 2010). Hence, because the HC reductant was from the product of diesel combustion, it is believed that these accumulated species were only removed from the catalyst surface when the H_2 concentration was increased to 5000 ppm. And in the presence of NH_3, the very low amount of NO_2 recorded compared to NO suggest the activity of standard SCR (i.e., $4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O$) being the main NH_3-SCR reaction that was promoted by the H_2. In addition, it appears the higher NOx conversion achieved in this case can be attributed to H_2 chemical effect (Dimaggio et al.

2009) as the NOx reduction only responded to increasing H_2 concentration irrespective of catalyst temperatures.

It has been suggested that co-feeding H_2 with various reductants promotes the removal of reaction inhibitors (Hernández-Terán and Fuentes 2014). This is made possible as the addition of H_2 enhances the catalyst bed temperature through exothermic reactions (Abu-Jrai, Tsolakis, and Megaritis 2007) (thermal effect), and (2) promotes the formation of reactive species and oxidation of NO to NO_2 over the catalyst (Herreros et al., 2014a; Gu, Chun, and Song 2015) (chemical effects). These species participate in the SCR reactions and consequently, support the NOx reduction process at lower temperature. Thus, as the exothermic reaction was not observed due to the decreasing trends in the catalyst bed temperatures (Figure 5.6 (b)) as H_2 was added, it could be speculated that NOx conversion was mainly promoted through the chemical effect.

5.3.4 Effects of H_2 and NH_3 Additions and N_2O Concentrations over Ag/Al_2O_3 Catalyst

Nitrous oxide (N_2O) yield during the SCR activities when the H_2 and NH_3 mixture was added before and after DOC were analysed and presented as shown in Figure 5.7. Figure 5.7 (a) shows higher concentration of N_2O since the bulk of it was produced in the DOC but was carried over to the downstream SCR catalyst. However, when the injection point was moved upstream the SCR catalyst, the maximum N_2O emission measured became 4 ppm which could be seen as low and permissible when the H_2 concentration was increased to 5000 ppm. Although, for now there is no defined limit for N_2O emission in the EU emissions standard (Xu et al. 2021). However, N_2O from an environmental point of view is a harmful greenhouse gas with a global warming potential (GWP) that is ~300 times higher than CO_2 (Kamasamudram et al. 2012; Wiebenga 2014). Furthermore, it is widely reported that N_2O would become regulated under the new EURO VII

standard. Therefore, it is undesirable and N_2O emission will not be a challenge to the application of H_2 and NH_3 when it is injected before Ag/Al_2O_3 catalyst.

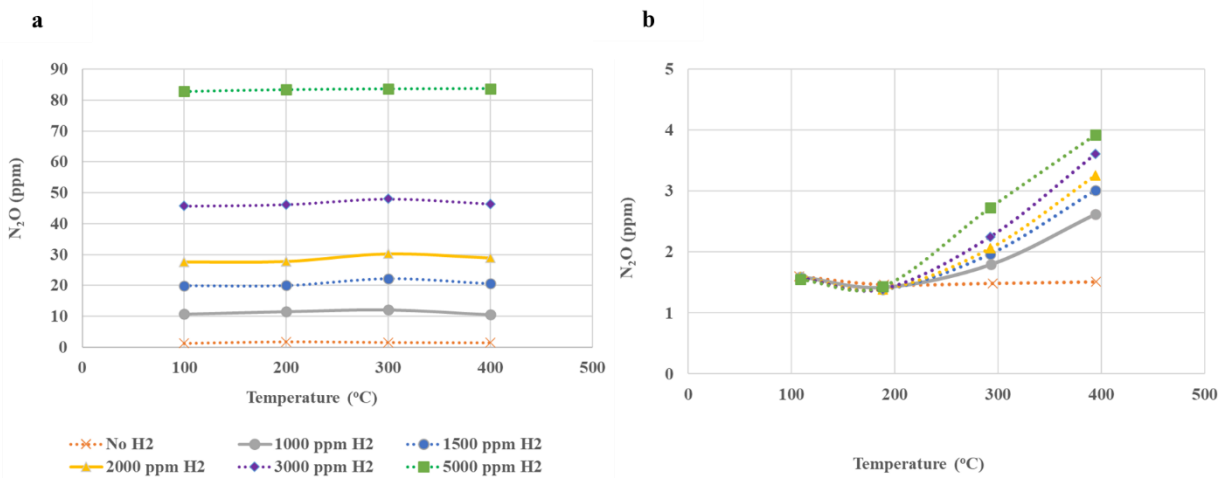


Figure 5. 7. N_2O concentrations at Ag/Al_2O_3 SCR catalyst outlet at different operating temperatures for H_2 and NH_3 mixture injections before: (a) DOC and (b) SCR.

5.3.6 Effects of H_2 Concentrations on THC and NH_3 Conversions over Ag/Al_2O_3 Catalyst

The conversions of NH_3 and THC in the absence and presence of different H_2 concentrations are shown in Figure 5.8. At lower temperatures and in the absence of H_2, some amounts of THC conversion were achieved. However, NH_3 conversion efficiency was negative (not shown on the graph), which is an indication of NH_3 production in HC-SCR process (Gunnarsson et al. 2017; Thomas et al. 2005) over Ag/Al_2O_3 catalyst. Can et al. (2011) showed that NH_3 generated during NOx SCR process is due to the alumina support that produced isocyanate species (NCO) as a precursor to NH_3 formation. Macleod and Lambert (2003) reported that the NH_3 formed most likely through the hydrolysis reaction $HNCO + H_2O \rightarrow NH_3 + CO_2$, could only take place in the presence of CO through $NO + CO \rightarrow NCO$. This suggests the inactivity of NH_3-SCR over Ag/Al_2O_3 in the absence of H_2 (Xu et al. 2021).

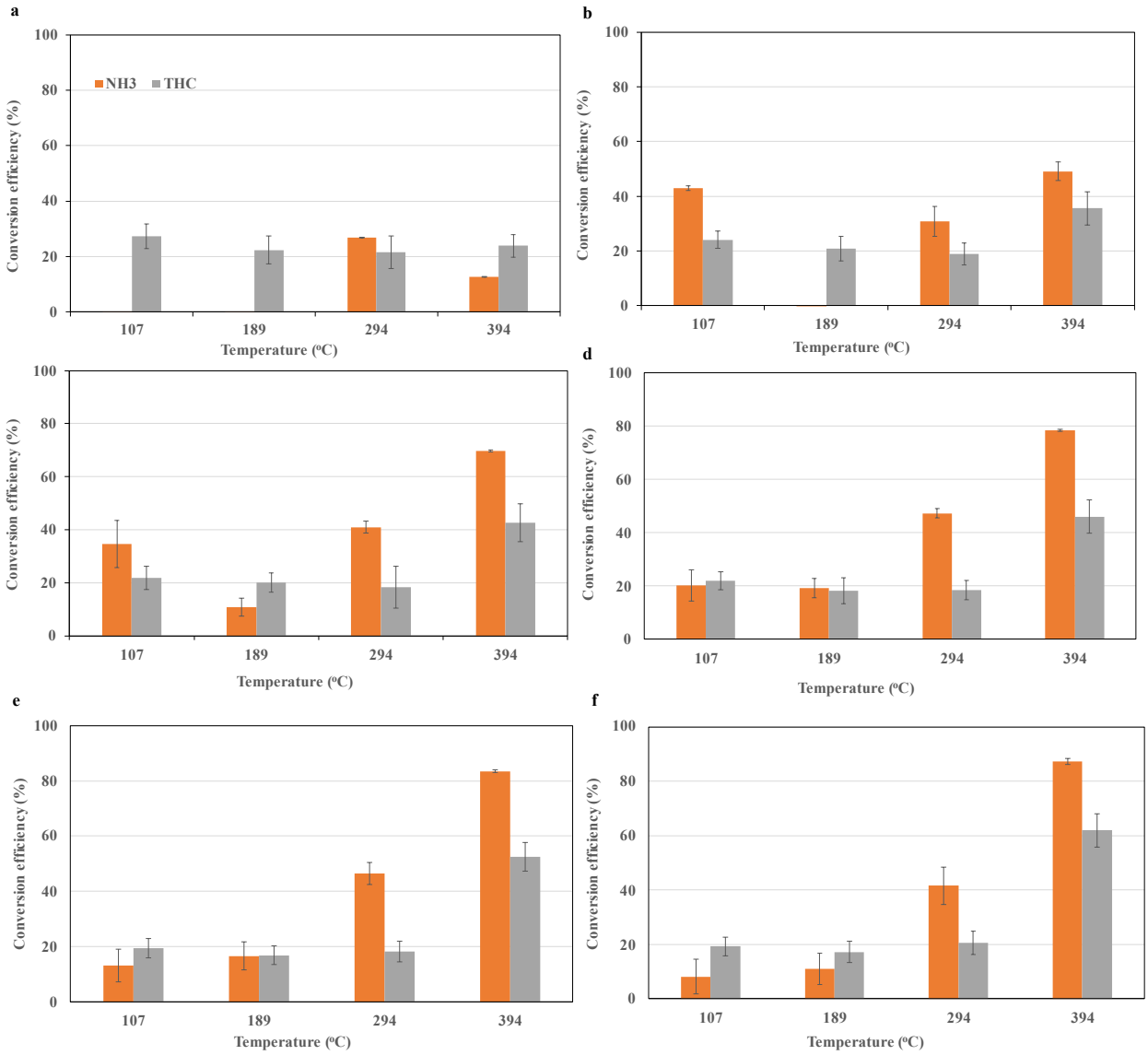


Figure 5. 8. NH_3 and THC conversions efficiencies over the Ag/Al_2O_3 catalyst in the presence of: (a) no H_2, (b) 1000 ppm of H_2, (c) 1500 ppm of H_2, (d) 2000 ppm of H_2, (e) 3000 ppm of H_2 and (f) 5000 ppm of H_2 at different catalyst temperatures.

It can be observed that as the H_2 concentration increases, both the NH_3 and HC conversions increased accordingly over the Ag/Al_2O_3 catalyst. However, it seems as the NH_3 concentration increases, it becomes more reactive with H_2 over the catalyst compared to the THC. As the exhaust gas contains various HC components in varying amounts, it is likely that the lower HC conversion compared to NH_3 could be an indication of the presence of low reactive HC species with strong

adsorption effect on the catalyst sites. Similarly, it is thought that due to the decreased catalyst temperature because of N_2 and NH_3 as well as the strong HC adsorption on the catalyst sites, significant level of NO reduction and HC oxidation were only achieved at higher temperatures.

In the presence of NH_3 and under lean exhaust condition, H_2 is believed to facilitate the conversion of molecular oxygen to reactive oxygen species (O_2^-) over Ag/Al_2O_3, which participates to activate the oxidation of NO and NH_3 to NO_2 and NHx ($x \leq 2$) that react to form N_2 (Kondratenko et al. 2006; Shimizu and Satsuma 2007). As observed in the NH_3 profile, the high conversions of NH_3 seen at the low temperature region (<200 ^oC) could be the result of NH_3 storage rather than actual conversion. At low catalyst temperatures, while HC coking effects (accumulation of carbonaceous species on the catalyst surface) have been attributed to the low performance of HC-SCR over Ag/Al_2O_3 (Theinnoi et al. 2007), storage of NH_3 on catalytic sites seems to appear as a valid reason for this seemingly high conversion at low temperature compared to THC. Fogel and Gabrielsson (2014) in their study of the effect of H_2 assisted NH_3 over Ag/Al_2O_3, reported significant amount of stored NH_3 on Ag/Al_2O_3 catalyst surface which was subsequently released as the temperature was increased. Therefore, at the lower temperatures, it is believed that NH_3 was not actually converted, but rather it was temporarily stored on the catalyst and as a result, low concentration of NH_3 was measured at the downstream of the SCR catalyst. However, as the temperature was increased, the stored NH_3 was desorbed to react with NOx at the catalyst active sites.

5.4 Summary

This chapter investigated the effects of different concentrations of H_2 and NH_3 mixture on the NOx conversion activities of Ag/Al_2O_3 catalyst. In doing that, a combination of DOC and SCR aftertreatment arrangement was employed to investigate the effects of H_2 and NH_3 mixture injection on the NOx reduction activity over Ag/Al_2O_3 catalyst. The study was carried out by firstly, injecting the H_2 and NH_3 mixture before the DOC to investigate the activity of the catalyst in converting THC, CO and NO. However, in injecting the H_2 and NH_3 mixture upstream the DOC, even though some level of conversions of THC and CO were seen, both H_2 and NH_3 were almost consumed in the DOC with the latter reacting with NO in the presence of O_2 to produce N_2O emission. Therefore, this approach was discontinued because it was not good due to the production of N_2O emission. Thereafter, the injection of the mixture was moved upstream of the SCR catalyst. The findings showed maximum NOx reduction efficiency of 62% at 394 ^oC which was due to the increase in H_2 and NH_3 concentrations that were injected before the SCR catalyst. It was suggested that due to the low HC:NOx ratio available for the HC-SCR activity, reduction in the NO_2:NO ratio needed for fast SCR and decrease in catalyst temperature due to the presence of cool gases (i.e., N_2 and NH_3), higher amount of H_2 was utilized to promote the HC-SCR reaction and also activate the standard SCR. It is believed that these reasons were responsible for the increase in NOx conversion at the high temperature region. The findings from this work highlight the potential benefits of NH_3 and H_2 onboard vehicles. This is significant as the NOx reduction activities of Ag/Al_2O_3 catalyst can be supported with the unburnt NH_3 in the exhaust of diesel-NH_3 fuel engine. Furthermore, while NH_3 as part of the engine fuel leads to lower C-based emissions, NOx is also controlled using less expensive catalyst.

CHAPTER 6

ENHANCING THE NOx REDUCTION ACTIVITY OF Ag/Al_2O_3 CATALYST WITH PROPANE AND H_2/NH_3 MIXTURE.

6.1 Introduction

NOx reduction over silver on alumina (Ag/Al_2O_3) catalysts has been extensively studied with varieties of reductants under excess air environment (Herreros et al. 2014a; Houel et al. 2007; Theinnoi et al. 2010; Tamm 2013). This is because the reductant type is an important parameter for the removal of NOx over Ag/Al_2O_3 catalyst (Iliopoulou et al. 2004), as it inhibits or promotes the performance of the aftertreatment system. In this regard, the application of cleaner, low to zero carbon fuel such as propane, hydrogen and ammonia in the transportation sector would ensure a better and more efficient aftertreatment system.

Although the combustion of gaseous fuels in compression ignition engines in dual fuel modes can reduce the level of NO emissions, during part load operations, it can generate high level of unburnt HC and NO_2 as well. Whilst the unburnt HC is useful to further reduce the remaining NO where a HC-SCR catalyst is fitted at the exhaust, the NO_2 is also beneficial as it can support the cleaning of the catalyst by oxidizing adsorbed soluble fractions of HC and soot and consequently accelerates the reduction of NOx (Azis et al. 2015; Fayad et al. 2018; Theinnoi et al. 2010).

In chapters 4 and 5, combustion and emissions of diesel-propane dual fuel engine and application of H_2/NH_3 mixture in diesel engine SCR aftertreatment were investigated respectively.

Whilst the combustion of propane as part of the engine fuels led to the reduction of engine out NO emission, significantly high level of THC and NO_2 emissions were produced at the exhaust. As regards to the SCR aftertreatment, the application of H_2/NH_3 mixture in addition to the unburnt HC at the exhaust provided the catalyst with additional reductant to support the performance of Ag/Al_2O_3 SCR catalyst. It has been shown that both HC and NH_3 are very effective reductants for NOx removal in lean burn engines in the presence of H_2 where a Ag/Al_2O_3 SCR catalyst is fitted at the exhaust (Barreau et al. 2018; Tamm 2013; Shimizu and Satsuma 2007). Furthermore, Gill et al. (2012) have studied the feasibility of diesel-H_2 and NH_3 tri-fuel compression ignition engine with the option of providing the H_2 and NH_3 mixture onboard the vehicle through the catalytic dissociation of gaseous NH_3.

In this chapter, the effects of a diesel-propane dual fuel engine on the NOx reduction activity over a Ag/Al_2O_3 SCR catalyst were investigated. The aim was to investigate the NOx reduction activities of the Ag/Al_2O_3 SCR catalyst, utilizing the unburnt HC from a diesel-propane fuelled engine in the presence and absence of H_2 and NH_3 mixtures in the exhaust. It is believed that this study would provide a better understanding of exhaust compositions typical of a propane-diesel dual fuel engine combustion and their individual impacts on NOx reduction activity over the Ag/Al_2O_3 catalyst in the presence and absence of H_2 and NH_3 mixture. In a practical point of view, propane and liquid NH_3 can be stored onboard and used as engine fuels and reducing agent to reduce the NOx emission at the exhaust. The NH_3 in liquid phase can be converted into NH_3 gas using the exhaust heat which would be supported by an electric heating element. The gaseous NH_3 is thereafter, transported to a catalytic reformer which is also fitted onboard to generate the H_2 and NH_3 mixture.

Figure 6.1 is the schematic of the experimental setup with the SCR catalyst and fuel arrangements used for this research. The details of the engine test condition, and procedure are described in section 6.2. The results and discussions of the effects of unburnt THC and other exhaust gaseous species in the absence and presence of low and medium concentrations of 1000 ppm and 3000 ppm of H_2 including 28 ppm and 82 ppm of NH_3 concentrations measured at sampling point 2 are presented and explained in section 6.3. With respect to chapter 5 where different concentrations of the H_2/NH_3 mixtures were investigated in the presence of low concentration of HC reductant, this chapter only consider the lowest and medium concentration due to the considerable amount of unburnt HC reductant available at the exhaust of diesel-propane dual fuel combustion. The overall results are summarized in section 6.4.

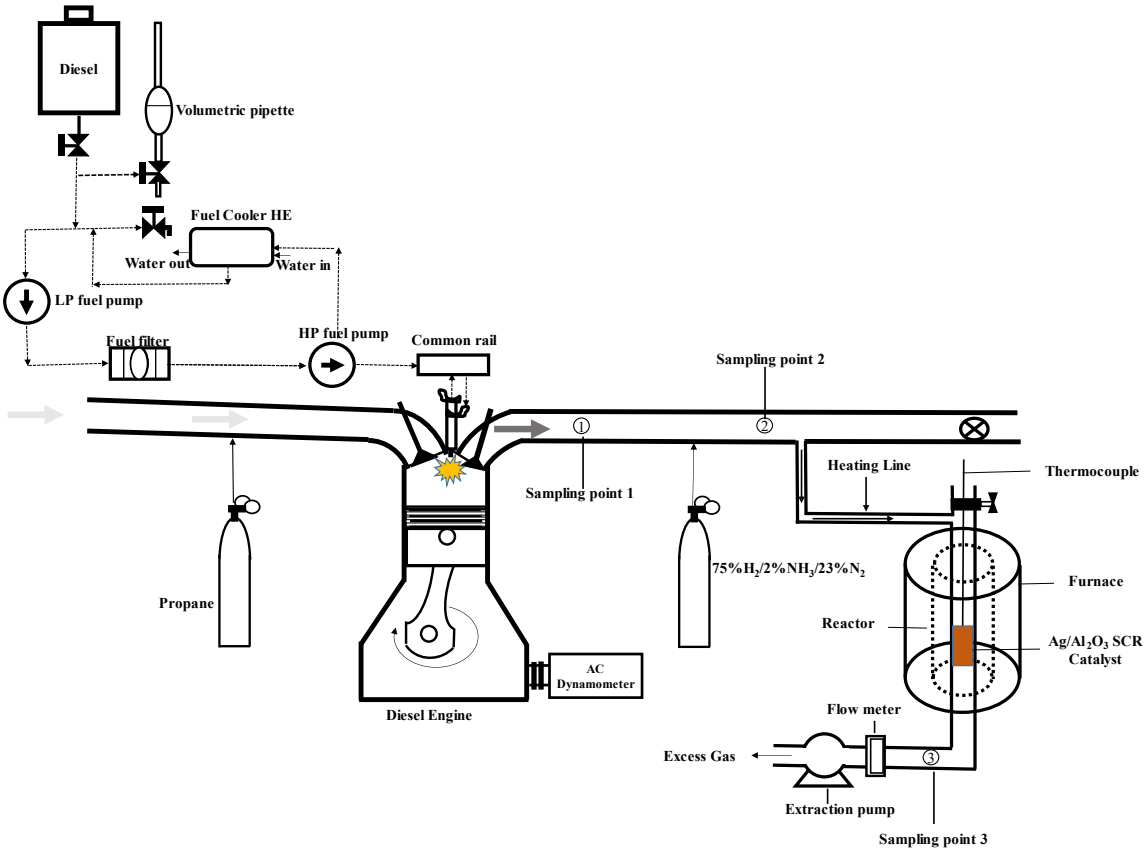


Figure 6. 1. Schematic of the experimental set-up.

6.2 Engine Test Conditions and Procedure

The engine was run with ultra-low Sulphur diesel fuel (ULSD) and propane gas supplied from a gas bottle. Whilst the diesel fuel was supplied through the normal engine fuelling system, propane was injected into the engine intake manifold. The purpose of this chapter is to enhance the performance of Ag/Al_2O_3 SCR of NOx with considerable amount of exhaust HC. Therefore, based on the two percentages of propane that were used in chapter 4, the 25% of propane in the diesel-propane dual fuelled combustion produced the higher concentration of HC at the exhaust. Furthermore, considering the environmental benefits of propane fuel compared to diesel fuel and the inconsequential difference in BTEs between 15% and 25% of propane in diesel (Figure 4.7), it is obvious that the 25% represents a favourable choice for further study. All experiments were carried out under steady state engine conditions of 1500 rpm speed and 2 bar indicated mean effective pressure (IMEP). The diesel fuel injection pressure was maintained constant at 550 bar and diesel fuel injection timing of D18-8 was chosen as this condition provided the lower NO emission compared to D21-11. The study was carried out with SCR Ag/Al_2O_3 catalyst placed in a reactor and a temperature-controlled tube was used to direct part of the exhaust gas to the catalyst. A gas hourly space velocity (GHSV) of 35,000 h^{-1} for the SCR was maintained constant throughout the experiment. A tubular furnace was used to control the SCR reactor temperature. The thermocouples were properly connected to ensure that the temperature readings are stable, however, due to variations in temperature values, the Ag/Al_2O_3 catalyst was investigated at 115, 196, 287 and 400 ^oC which are slightly higher than those in chapter 5. For each test temperature, the catalyst temperature was allowed to stabilize before injecting 1000 ppm and 3000 ppm of hydrogen concentration, respectively in a cyclic pattern upstream the catalyst. The H_2 injection was carried out in a sequence of five minutes 'H_2 off', followed by five minutes 'H_2 on' and five

minutes 'H_2 off' in a symmetric injection cycle with the 1000 ppm and 3000 ppm of H_2 concentration before the SCR catalyst. The "H_2 off" was done to allow NH_3 and H_2 from previous injection to be fully utilized over the catalyst and consequently, minimizing the amount that would be stored and released for subsequent cycle. These were done to examine NOx reduction activities of Ag/Al_2O_3 catalyst with exhaust HC in the presence and absence of low and medium concentrations of H_2 and NH_3. This was achieved by using simulated gas (i.e., 75% H_2, 2% NH_3 and 23% N_2) from a certified bottle. The H_2 and NH_3 level increased by introducing H_2 concentrations of 1000 and 3000 and NH_3 concentrations of ~ 28 and 82 as shown in Table 6.2. The flow rate was controlled by a digital flow meter to the engine exhaust line where it homogeneously mixed with the exhaust before going into the SCR catalyst.

Table 6. 1. Hydrogen concentrations and engine exhaust gas composition for H_2 and NH_3 injection upstream of SCR catalyst.

Fuel type	Diesel			Diesel-propane		
Sampling point 2						
H_2 (ppm)	0	1000	3000	0	1000	3000
THC (ppm)	279	309	328	1683	1691	1674
NO (ppm)	258	254	246	104	107	109
NO_2 (ppm)	60	59	56	206	201	199
NO/NO_2	4.3	4.3	4.4	0.50	0.53	0.55
NH_3 (ppm)	2	28	82	2	28	82
CO (ppm)	247	246	247	1311	1289	1289
HC:NOx ratio	1.06	0.99	1.09	5.43	5.49	5.44

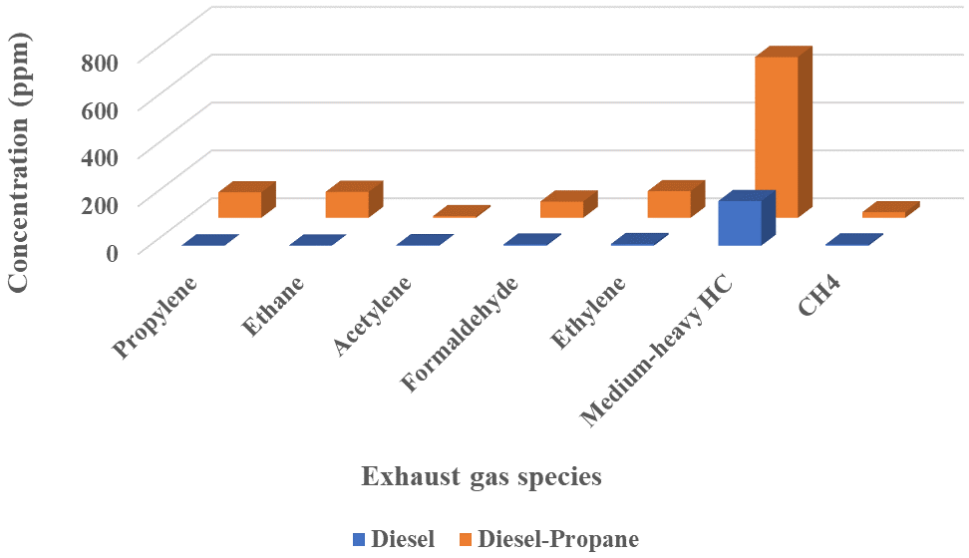


Figure 6. 2. Engine out hydrocarbon species from diesel and propane fuel combustion.

6.3 Results and Discussions

6.3.1 Influence of Diesel-Propane Fuel and Exhaust Gas Composition

Compared to when the engine was fuelled with only diesel, the combustion of diesel-propane fuel decreases NO concentration but increases the concentration of NO_2. The increase in NO_2 emission is common to combustion in gas-liquid dual fuel engines and it has been attributed to the production of peroxyl radicals (HO_2 and RO_2) during low temperature combustion (Li et al. 2018). THC and CO emissions increase significantly for the diesel-propane combustion. This again is expected with dual fuel engines operation at part load engine condition as it is an indication of low combustion efficiency. However, with this level of THC in the exhaust, the need for additional fuel injection and control systems are eliminated as it would be beneficial for NOx removal where a HC-SCR catalyst is fitted at the exhaust.

Similarly, for the individual exhaust HC species as shown in Figure 6.2, all the HC components analysed were increased with propane-diesel fuel combustion. For the medium-heavy HC, even though these hydrocarbons are produced from the combustion of diesel fuel (Lefort, Herreros, and Tsolakis 2014), it is obvious that the combustion of diesel-propane fuel increases their concentrations at the exhaust. This could be attributed to the low in-cylinder combustion temperature facilitated by the presence propane. Furthermore, longer ID could lead to decrease in the local equivalence ratio of some regions in the combustion chamber as well. The low cylinder temperature reduces the combustion efficiencies of both the diesel and propane fuels and therefore, increases the heavy-medium and short chain HC species.

Shown in Figures 6.3 (a and b) are the NOx conversions efficiencies under single diesel and propane-diesel dual fuel combustion with or without H_2/NH_3 addition. Several studies have shown that NOx conversion efficiency is strongly dependent on the nature of reductant and HC:NOx ratio, as higher amount of hydrocarbon in the exhaust favours the conversion of NOx. As it can be seen on Table 6.2, the exhaust from single diesel combustion provided HC:NOx ratio of ~1, which is believed to have led to the lower level of NOx conversion efficiency in Figure 6.3 (a) compared to Figure 6.3 (b) in the absence of H_2 and NH_3 mixture.

To enhance the performance of Ag/Al_2O_3 HC-SCR of NOx, reasonable amount of HC is required in the exhaust gas. However, this is not the case when the engine is running under lean burn condition and therefore, addition HC reductant is required at the exhaust (Lindfors et al. 2014). Previous works have employed in-cylinder post fuel injection (Serhan et al. 2019), EGR (Theinnoi et al. 2010) and external fuel injections (Herreros et al. 2014a) to increase the HC:NOx ratio in engines running on diesel fuels. It is known that at low engine load operations, the combustion efficiency of gas-diesel dual fuel engines is usually low. Therefore, when propane was

used to displace 25% of the diesel fuel under the same engine conditions, the exhaust HC:NOx ratio was increased to about 5, as can be seen in Table 6.2. Based on Figure 6.3, when the NOx conversion efficiencies of (a) and (b) in the absence of H_2 and NH_3 mixture are compared, the differences between them indicate the importance of higher HC concentrations. This perhaps suggests the necessity to further investigate other percentages of propane that would provide the optimum HC:NOx ratio. However, it is important to note that the NOx conversion activity of the Ag/Al_2O_3 SCR catalyst is contingent on the catalyst temperature (Kim et al. 2013). At low temperature, due to masking of the catalyst surface by aromatic and unsaturated hydrocarbon contents of the conventional ULSD fuel, or low reactivity of short chain alkanes (e.g., methane and propane), the HC/NOx ratio becomes immaterial. It is also important to mention that at high temperature, the HC/NOx ratio can be lower as the HC is preferentially oxidized by directly reacting with oxygen.

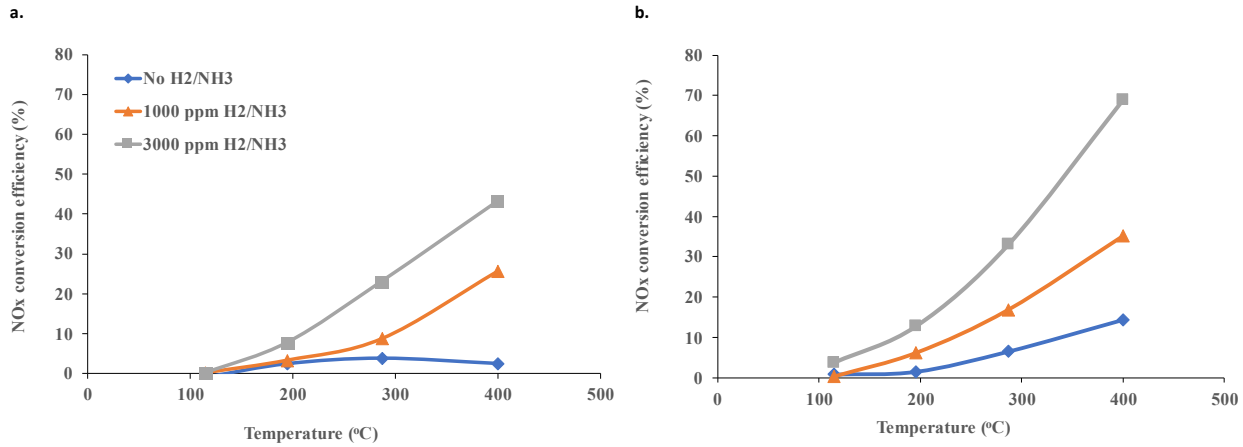


Figure 6. 3. NOx conversions under: (a) diesel fuel and (b) diesel-propane dual fuel conditions in the presence and absence of H_2 and NH_3 mixtures at different catalyst temperatures.

At higher temperatures and in the absence of H_2 and NH_3 mixture, there is a clear difference in the NOx conversion trends of Figures 6.3 (a) and (b). The NOx conversion efficiency for diesel fuel is seen to have declined at higher temperature. This could be explained by hydrocarbon oxidation at higher temperatures that further reduced HC:NOx ratio required for HC-SCR for the

diesel operated engine. On the other hand, under diesel-propane fuel condition, NOx conversion efficiency increases with temperature. This maybe an indication of the benefit of a dual fuel engine in terms of NOx conversion, as it is capable of providing higher HC:NOx ratio with a variety of unburnt HC and low carbon species as reductants for HC-SCR of NOx.

Therefore, it is likely that under diesel-propane dual fuel operation, besides the higher amount of unburnt HC, the increase in NOx conversion efficiency could be attributed to production of more hydrocarbon species that can easily participate in the HC-SCR in gaseous phase due to their low boiling point as shown in Figure 6.3. Furthermore, the higher amount of NO_2 and lower amount of NO compared to single diesel operation could also contribute to the increase in NOx conversion. In this case, NO_2 can promote the NOx reduction performance through two ways: (1) as an oxidizer, it can clean the catalyst by removing adsorbed HC species and consequently, reduces species competition and allow NO to diffuse faster to active sites; (2) the presence of NH_3 in the exhaust can also support the reduction of NOx through the fast NH_3-SCR reaction (equation 2.20) that needs an optimum NO_2:NO. It is also likely that some of the unburnt HC species due to their stable nature, could have survived to higher temperature regions to participate in HC-SCR activities and consequently, caused the NOx conversion efficiency for (b) to be higher with respect to (a).

In the presence of H_2 and NH_3, NOx conversion efficiency was increased for Figures 6.3 (a) and (b) with increasing catalyst temperature. This becomes more pronounced for the diesel-propane fuel combustion as more of the unburnt HCs were made available at the exhaust stream. Although, the level of unused HCs sampled downstream of the catalyst during the test is obviously high, the slight increase in NOx conversion efficiencies at the lower temperature region (100-200 ^oC) is believed to be a consequence of both HC- and NH_3-SCRs activities promoted by the presence

of H_2. However, in a previous study involving HC and NH_3 reductants, Tamm (2013) reported higher NOx conversion over Ag/Al_2O_3 catalyst in the presence of NH_3 and H_2 at low catalyst temperature. At low catalyst temperature, adsorption of carbonaceous and nitrate species as well as the presence of other stable exhaust species impede the reduction of NOx. However, as the catalyst temperature was increased, the adsorbed HC and nitrates were desorbed and more of the HCs were also converted to reactive radicals which in turn participated in the HC-SCR of NOx. Therefore, it could be concluded that due to the preponderance of stable and low reactive HC species in the exhaust of a diesel-propane dual fuel engine, high level of NOx conversion was only achieved at temperature above 350 ^oC, when the unburnt hydrocarbon was utilized to reduce NOx over Ag/Al_2O_3 catalyst.

6.3.2 Influence of H_2 on THC and CO over the Ag/Al_2O_3 Catalyst

Figure 6.4 shows the plots of THC and CO emissions measured downstream of the SCR catalyst in the presence and absence of H_2 at the different catalyst temperatures for diesel and diesel-propane dual fuelled combustion. At the lower temperature regions, H_2 seems not to have any effect on THC as decrease in its concentration as well as the effect of H_2 on it can only be seen as the temperature was increased to 400 ^oC. The increase in THC concentration which has been explained earlier is a consequence of the unburnt propane and other light HC species in the combustion chamber that escaped to the exhaust. These HCs are mostly short chain and saturated, and their reactivity is low as well. Therefore, they need higher temperature to be converted. The high THC emissions could be that the H_2 concentrations used were too low to have any significant effect on propane and other gaseous HC products at lower temperature regions (Schmieg, Blint, and Deng 2009).

Carbon monoxide on the other hand exhibits a rather different trend, showing lower concentrations at low temperature and then increased in-between before decreasing at high temperatures. As CO is a product of partial oxidation, the low concentration could be an indication of the HC low reactivity which led to lower amount of CO measured downstream of the catalyst. As the temperature was increased (between 196 and 187 ^{o}C), partial oxidization of part of the HC led to the production of more CO. However, as the catalyst temperature was increased further to 400 ^{o}C, oxidation of HC and CO to CO_2 which was further promoted by the presence of H_2 led to the reduction in CO emissions sampled downstream the catalyst.

Although, the main purpose of this investigation was to promote the HC-SCR of NOx by utilizing the unburnt THC contained in the exhaust of diesel-propane dual fuel combustion, the engine conditions did not favour the efficient utilization of the fuel and therefore, produced high concentration of CO at the exhaust. With this amount of CO in the exhaust going to the SCR catalyst, the NOx conversion achieved could be a consequence of competitive adsorption between CO and HC that limited NOx access to catalyst active sites. Therefore, it is likely that under the same engine conditions, the application of DOC before the SCR catalyst to oxidize part of the CO would reduce its impacts and enhances the conversion efficiency of NOx.

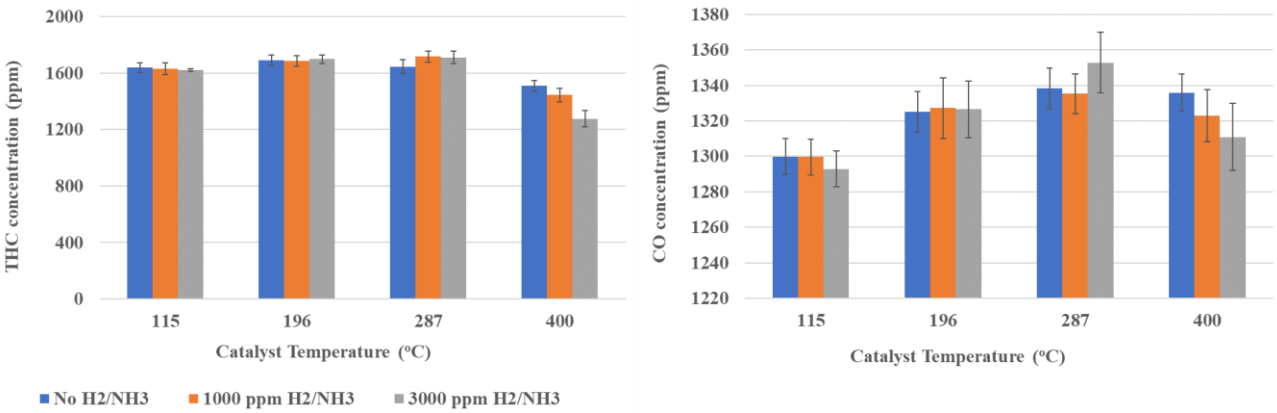


Figure 6. 4. THC and CO emissions measured after SCR catalyst in the presence and absence of H_2 and NH_3 mixtures at different catalyst temperature and dual fuelling.

6.3.3 Effects of H_2 and NH_3 Cycle on NO, NO_2, THC at Different Catalyst Temperatures

To investigate the influence of H_2 and NH_3 on NO, NO_2 and THC activities, 1000 ppm and 3000 ppm of H_2 which also included 28 ppm and 82 ppm of NH_3 were injected upstream the catalyst. As it was explained in section 6.2, the injection sequence was modified slightly to allow the H_2 and NH_3 from the previous cycle to be fully converted before increasing the concentration. This was carried out in a cyclic 5 minutes 'H_2 off', followed by 5 minutes 'H_2 on' in a symmetric sequence with 1000 ppm and 3000 ppm of H_2 concentrations.

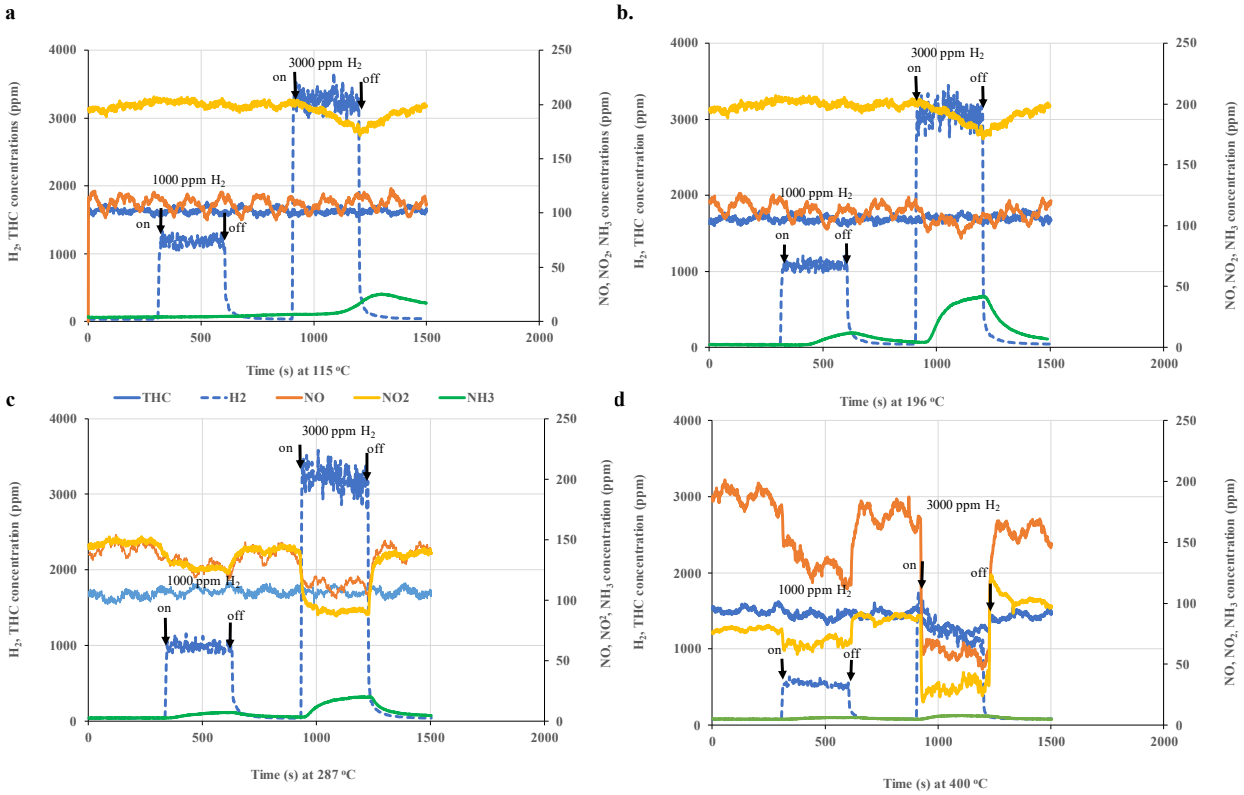


Figure 6. 5. Effects of on and off injections of H_2 and NH_3 mixtures on NO, NO_2 and THC performance sampled at SCR outlet for: (a) 115 °C, (b) 196 °C, (c) 287 °C and (d) 400 °C catalyst temperatures.

As shown in the Figures 6.5 (a-d), at catalyst temperature <196 ^{o}C, except with the slight reduction seen in NO_2 when the H_2 concentration was increased to 3000 ppm, it seems H_2 does not have any effect on THC and NO. At 115 ^{o}C temperature, the NH_3 concentration detected downstream the catalyst at this temperature was very low regardless of the amount injected upstream the catalyst. This is believed to be a result of NH_3 storage in the catalyst at low temperature as was explained in chapter 5. However, the NH_3 concentration increases as the catalyst temperature was increased to 196 ^{o}C. It seems at this temperature, NH_3 contribution to NOx removal through the NH_3-SCR reaction was not significant as more NH_3 slipped through the catalyst unconverted. When the catalyst temperature was increased as in (c), the THC concentration was not affected regardless of the amount of H_2. On the other hand, both NO and NO_2 decreased with H_2 injection and then were restored after five minutes as H_2 was switched off. At (d) when the catalyst temperature was increased further, NO, NO_2 were decreased and then increased when alternating the on and off H_2 injections. The THC was only affected as the hydrogen concentration was increased to 3000 ppm.

At temperatures of 287 ^{o}C and 400 ^{o}C, it can be speculated that in the presence of 1000 and 3000 ppm H_2, the catalyst promoted the conversion of NOx through the reactions in equations 2.20 and 2.21. For HC-SCR of NOx over Ag/Al_2O_3 catalyst, activation of the hydrocarbon is an important step needed to provide partially oxidized HC intermediates that would react with NOx and reduce it to nitrogen. At low catalyst temperatures, both C- and N- containing species can easily deposit on the catalyst surface. One of the roles of H_2 in the HC-SCR reaction is to activate the hydrocarbon species. However, the bulk of the exhaust HC is believed to be unburnt propane and other low reactive HC species. The conclusion is that, whilst these species of HC are difficult to activate at low temperature region, at higher temperature they need more of the H_2 to promote

their activation. And therefore, suggesting that the H_2 concentration that is required to promote the conversion of NOx through NH_3-SCR reaction could be lower than the amount needed for HC-SCR reaction where propane is used as the reductant.

6.3.4 Unregulated Emissions

The exhaust gas from diesel combustion contains several hydrocarbon species, including the short chain, aromatic and longer chain hydrocarbons which to some extent also influence the NOx conversion activities. Furthermore, because these hydrocarbon species are dependent on the physical and chemical properties of the fuel used for combustion (Theinnoi et al. 2010), for a diesel-propane dual fuel combustion, both the gaseous and liquid fuels have strong influence on the exhaust HC compositions (García et al. 2019). In this regard, increase in concentrations of THC and other light hydrocarbon species have been reported in the exhaust from diesel-propane dual fuel engine (Lefort, Herreros, and Tsolakis 2014). As the efficiency of HC-SCR of NOx is dependent on the type of reductant, it would be of great interest to investigate and understand how some of these exhaust species are affected by the Ag/Al_2O_3 catalyst due to the presence and absence of H_2 and NH_3.

Shown in Figure 6.6 (a-d) are the different exhaust species from diesel-propane dual fuel combustion measured downstream of the catalyst at the sampling point 3 in Figure 6.1.

Methane and Ethane are saturated hydrocarbons, and due to the stability of their molecular structure, they are difficult to activate especially at low catalyst temperature. As it can be noticed, they are not affected by the presence of H_2 even as the temperature was increased to 400 ^oC. This, therefore, suggests the low reactivity of these HC species over the Ag/Al_2O_3 catalyst.

Ethylene and Propylene are unsaturated hydrocarbons. Compared to the saturated HCs, these are more reactive and the mean dissociation energy to break the H-C bond of unsaturated HC is lower. As expected, even though the amount of ethylene and propylene entering the catalyst are quite high, the results presented show evidence of slight reduction especially in propylene as the H_2 concentration was increased to 3000 ppm.

Acetylene (C_2H_2) is also an unsaturated hydrocarbon and is highly reactive due to it C-C triple bond. As shown in Figure 6.6 (a-c), whilst it is not affected by the presence of H_2 it was completely oxidized as the temperature was increased to 400 ^oC.

Formaldehyde (HCHO) is a gaseous pollutant capable of causing great damage to human health can be produced from transport. As it can be observed, decrease in formaldehyde only occurs at higher temperature and then it declined further as H_2 concentration was increased. Although, Ag-based catalysts have shown high catalytic activities for HCHO oxidation at low temperature (Zhang et al. 2020), it seems the decrease in HCHO concentration is more likely due to thermal decomposition taking place at high temperature in the presence of oxygen. Also, evidence of NO_2 reaction with HCHO to produce NO and CO as shown in equation 6.1 has been reported by (Ngo et al. 2020). Therefore, it is difficult to draw a conclusion as to the cause of the decrease in HCHO concentration as it might be caused by several reasons as stated.

$$NO_2 + HCHO \rightarrow NO + CO + H_2O \qquad 6.1$$

Ammonia concentration at the exhaust gas from diesel and dual fuel combustion is low. However, as H_2 was injected at the exhaust along with NH_3, when the H_2 concentration was increased from 1000 ppm to 3000 ppm, more of the NH_3 was also supplied to the catalyst. Although, evidence of NH_3 production can be seen in Figure 6.6 (a), with the amount of NH_3 that

was injected along with 1000 ppm and 3000 ppm of H_2 as shown on Table 6.1, it is evident that NH_3 was utilized over the catalyst and is believed to have partly contributed to the NOx conversion efficiency. Due to the level of NO_2 produced from diesel-propane combustion, it could be speculated that at higher catalyst temperature, part of the NH_3 was involved in NO_2/SCR of NOx as presented in equation 2.21.

Medium-heavy hydrocarbon species are also presented in Figure 6.6 (d). It can be observed that these HCs are only oxidized as the catalyst temperature was increased to 400 ^oC and were further reduced in the presence of H_2. While the HC was partially oxidized at a higher temperature, it seems that HC-SCR was also enhanced by the presence of H_2. It is known that the mean dissociation energy for medium and heavy HCs is lower compared to those of the short chain HCs (Gu, Chun, and Song 2015). Therefore, the addition of H_2 is believed to have enhanced the breaking of the long chain H-C and C-C bonds of these HCs. From Figure 6.6 (a-d), it could be concluded that under similar engine conditions and fuelling system, the medium-heavy HCs would be more beneficial for the HC-SCR of NOx than the light HCs.

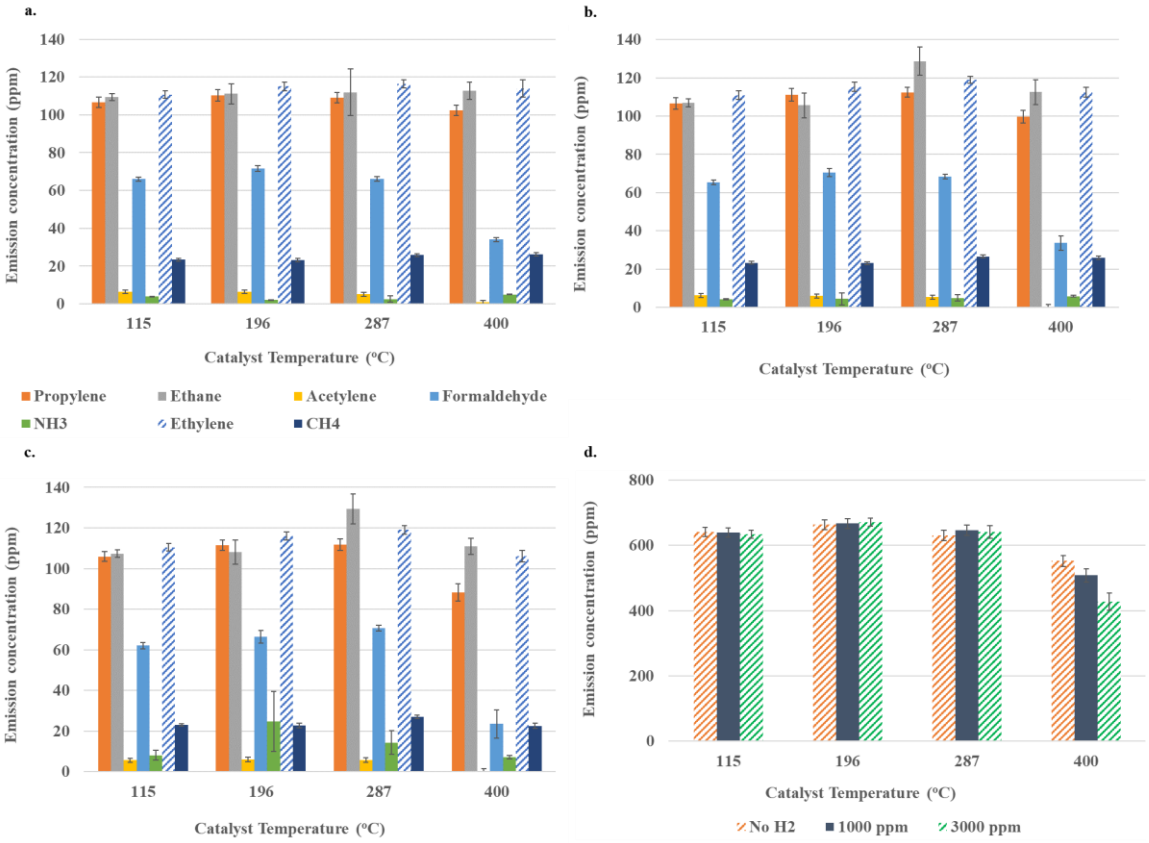


Figure 6. 6. Exhaust species at catalyst outlet in the presence and absence of H_2 at different catalyst temperatures for: (a) no H_2, (b) 1000 ppm of H_2, (c) 3000 ppm of H_2 and (d) medium-heavy hydrocarbon species.

Nitrous Oxide (N_2O) is an undesired gas and a by-product of both HC-, and NH_3-SCR reactions. Therefore, it is also analysed as shown in Figure 6.7. As it can be observed, N_2O emissions decreases at temperature of 196 °C irrespective of the H_2/NH_3 level. However, as the catalyst temperature was increased, the N_2O level also increases up to about 4.5 ppm when 3000 ppm of H_2 and 82 ppm NH_3 mixture were added at 400 °C. Based on the result, it is clear that N_2O emission is dependent more on the catalyst temperature. However, it could be suggested that the application of Ag/Al_2O_3 catalyst in diesel exhaust system, using propane as the reductant in the presence of NH_3 and H_2 can be a promising NOx reduction strategy with low level of N_2O production.

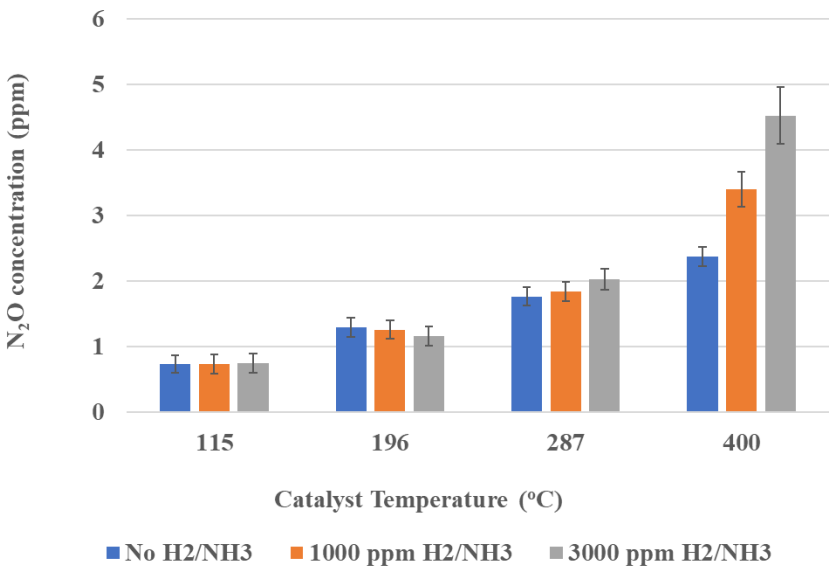


Figure 6. 7. N_2O concentration measured downstream SCR catalyst in the absence and presence of H_2 and NH_3 mixture at different catalyst temperatures under diesel-propane fuel combustion.

6.4 Summary

To achieve significant amount of NOx conversion efficiency in HC-SCR over Ag/Al_2O_3, the exhaust must contain reasonable amount of HC fuel which ordinarily is not available in conventional diesel engine exhaust. Besides the known methods of increasing the exhaust HCs such as in-cylinder post fuel injection, EGR and external fuel injection, the high level of HC in diesel-gas dual fuel engines can also provide the HC reductant. This is important in anticipation of future emission standards and the progressing research in the decarbonization of the IC engines, as the applications of low to zero carbon fuels in ICEs would provide the environmental benefits.

Consequently, with diesel-propane dual fuel engine capable of providing lower NO and PM emissions, it also generates substantial amount of unburnt HC which became an advantage as it provided the needed reductant for HC-SCR of NOx. However, the application of the exhaust HC from diesel-propane dual combustion as reductant of HC-SCR of NOx in the presence and absence

of H_2 and NH_3 mixture resulted to maximum NOx conversion efficiency of 70% at higher temperature.

Analysis of the exhaust species showed that the application of propane constituting 25% of the engine fuel produced high level of medium-heavy HCs and low reactive light HC species at the exhaust stream. The light HC species and medium-heavy HCs in the exhaust due to the presence of propane were left almost unconverted as they transited through the catalyst in the presence and absence of H_2.

Therefore, it was concluded that owing to the low reactivity of the HC species generated from the combustion of diesel-propane, higher temperature and higher H_2 concentration were required to activate these HCs for HC-SCR. Also, it was found that in the presence of H_2 and NH_3, decrease in concentrations of the medium-heavy hydrocarbon species were recorded. The important points from this work are that: (1) propane and NH_3 can be used onboard as engine fuel and NOx reductants, and (2) with the application of diesel-propane dual fuel engine, more hydrocarbon reductants with low boiling point are provided to participate in the gaseous phase of HC-SCR. However, due to low reactivity of most of these HC which is attributed to the stability of their molecular structures, higher catalyst temperature is required to achieve a significant level of NOx reduction in the presence of H_2 and NH_3.

CHAPTER 7

CONCLUSIONS AND FURTHER WORK

7.1 Concluding Remarks

Propane was used as part an engine fuels for a diesel engine running on a dual fuel mode at low load condition. The study was carried out using 15 and 25 % of propane to displace diesel fuel, whilst the diesel fuel injection timings were fixed at pre-18, main-8; and pre-21, main 11, respectively. Subsequently, the engine was run on only diesel fuel with H_2 and NH_3 mixture injected upstream SCR Ag/Al_2O_3 catalyst. This was done to study the effects of H_2 and NH_3 on NOx conversion in the presence of low exhaust HC concentrations, which was used to represent typical exhaust condition for a diesel-NH_3 dual fuel engine. A follow-up study was carried out to investigate the effects of high concentrations of exhaust HC on the performance of same catalyst in the presence and absence of H_2 and NH_3 mixture. The motive for this was to investigate the effects of exhaust HC, enriched with propane and other gaseous species from diesel-propane dual fuel engine combustion and to understand their individual contribution to NOx conversion over SCR Ag/Al_2O_3 catalyst. The main findings of this research are summarized below.

7.1.1 Combustion, Performance and Emissions Characteristics of a Diesel-Propane Dual Fuel Engine.

The experimental results revealed that under low engine load condition, the diesel fuel injection timing is important for a diesel-propane dual fuel engine. A well-planned injection timing helps in controlling the premixed combustion phase and therefore, favours the engine performance. The effects of injection timing became significant especially when higher fraction of the diesel

fuel was displaced by propane. Thus, suggesting that the injection timing of the HRF could be used to fix the proportion of propane in a diesel-propane dual fuel engine.

The combustion of diesel-propane dual fuel decreases the BTE slightly by about 0.3% and increases the CO and THC level due to low combustion efficiency associated with low load dual fuel combustion. However, while the advance diesel fuel injection timing increases NO emissions in diesel fuel combustion, under diesel-propane fuel condition, the decrease in NO emissions also increases the concentration of NO_2. With advance injection timing, more diesel fuel is injected and combusted in the cylinder and as a result caused the pressure and temperature to increase. However, the high specific heat capacity of propane suppressed the effects of advance injection timing and thus, decreased the rate of NO formation. The results suggest that with well optimized diesel fuel injection timing, propane can be used to displace substantial amount of the diesel fuel even under low engine load condition without adversely affecting the engine performance and NO emissions. However, because this strategy results to increase in NO_2, CO and THC emissions, DOC may be required in practice to eliminate THC, CO and provide optimum amount of NO_2 for downstream aftertreatment devices.

7.1.2 The Effects of H_2 and NH_3 Mixture on NOx Reduction Activity over Ag/Al_2O_3 Catalyst.

The THC concentration in the exhaust of a diesel fuel engine was reduced with a DOC and fed to a SCR Ag/Al_2O_3 catalyst. Different concentrations of H_2 and NH_3 mixture were injected before and after the DOC. This is aimed at simulating an exhaust gas composition similar to that of a diesel-NH_3 dual fuel engine. Thereafter, the effects of H_2 and NH_3 mixtures on the NOx reduction activity over the SCR Ag/Al_2O_3 catalyst were investigated.

The addition of H_2 and NH_3 mixture before the DOC consumed significant amount of H_2 and NH_3 and generated high level of N_2O and therefore, this strategy is not beneficial for the performance of Ag/Al_2O_3 catalyst. When the injection point was moved to before the SCR catalyst, additional reductant was provided through the H_2 and NH_3 mixture that led to NOx conversion efficiency of 60%. However, due to the low amount of reductant and NO_2, 60% NOx conversion efficiency was mainly achieved at higher temperature when the H_2 concentration was increased to 5000 ppm.

The H_2 and NH_3 were injected as a mixture and therefore, increase in the H_2 concentration to 5000 ppm also increased the level of NH_3 going into the SCR Ag/Al_2O_3 catalyst. With 75%H_2 and 2%NH_3 in 23%N_2 used for this research, increase in H_2 concentration supplied the catalyst with more NH_3 and N_2. Whilst the H_2 enhanced the catalyst temperature through H_2 chemical effects, exothermic reaction was not promoted due to NH_3 and N_2 effects and therefore, the reduction in the catalyst surface temperature also caused the performance of the catalyst to decrease. The role of the DOC was to eliminate or reduce the THC in the exhaust and provides more NO_2 for the downstream SCR catalyst. However, it was clear that with the low engine load condition used for this research, the 170 ^oC exhaust temperature did not favour the activities of the DOC in reducing the HC concentration prior to the SCR catalyst.

7.1.3 The Effects of H_2 and NH_3 Mixture on NOx Reduction Activity over Ag/Al_2O_3 Catalyst with Diesel-Propane Fuel Engine.

HC-SCR of NOx was investigated by feeding SCR Ag/Al_2O_3 catalyst with the exhaust gas produced from a diesel-propane dual fuel engine operating under low engine load condition. The NOx reduction activity was investigated in the presence and absence of H_2 and NH_3 mixture

addition before the Ag/Al_2O_3 catalyst. The effects of the catalyst on the THC, CO and other exhaust species in the presence and absence of H_2 and NH_3 were also investigated.

In low engine load condition, diesel-propane dual fuel engine generates high amount of unburnt propane and other low and medium-high carbon exhaust gas species which escaped to the exhaust. These caused the THC in the exhaust to increase significantly and alter the concentrations of other gaseous species such as propylene, ethane, and formaldehyde. The high amount of THC increased the NOx conversion efficiency slightly. However, the addition of 3000 ppm H_2 and 82 ppm NH_3 led to significant increase in NOx conversion efficiency. Analysis of the THC, CO and other gaseous products downstream the catalyst showed there was no evidence of conversion at low temperature.

Although, the diesel-propane dual fuel engine provided more HC reductants for the catalyst, the stability of these HC reductants shifted their conversions to higher catalyst temperatures. The high level of CO is believed to have deteriorated the NOx reduction further through species competition to access catalyst active sites. The results revealed that reducing the amount of diesel fuel with a low carbon fuel, capable of supplying the Ag/Al_2O_3 catalyst with low amount of PM, higher NOx conversion efficiency was achieved under diesel-propane dual fuel condition compared to diesel fuel engine under same engine conditions.

7.2 Future Work

7.2.1 Higher Diesel Fuel Replacement with Propane

In chapter 4, diesel fuel was replaced with 15 and 25% of propane. In view of the need to drastically reduce CO_2, NO and PM in the transportation sector, this level of propane is considered too low. Therefore, it is necessary to investigate higher fractions of propane that would truly represent low carbon fuel engine. However, this must be done with regards to the injection timing of the HRF in order to arrive at an optimum condition.

7.2.2 Effects of NO_2 and Different H_2 and NH_3 Mixtures on Ag/Al_2O_3 in the Presence of Low HC Concentration

NH_3-SCR of NOx requires high level of NO_2 to achieve NO:NO_2 ratio of 1 that would provide significant level of NOx conversion at low catalyst temperature. The engine was run on low load and therefore, the catalyst temperature was also low. In the future, a DOC heater needs to be considered to enhance the NO_2 production. Furthermore, the H_2 and NH_3 mixture used for this study were fixed at 75%H_2 and 2%NH_3. It is also necessary to investigate the mixtures with higher percentages of NH_3.

7.2.3 Diesel-Propane with Diesel Oxidation Catalyst

In this chapter, exhaust gas from the diesel-propane dual fuel engine was fed directly to the SCR Ag/Al_2O_3 catalyst. In this way, the high level of CO from the engine exhaust goes directly to the SCR where part of the CO masked the surface of the catalyst, and the rest is released directly into the atmosphere. A further study is required to investigate the effects of very low concentration

of CO in the exhaust and its effects on the SCR in the presence and absence of H_2 and NH_3. This can be done by passing the exhaust gas through DOC before the SCR catalyst.

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APPENDIX

LIST OF PUBLICATIONS

1. Poku, R., Doustdar, O. Brinklow, G., Zeraati-Rezaei, S., Tsolakis, A., Herreros, J. M. The effects of diesel-propane dual fuel system and H_2 and NH_3 mixture on NOx reduction activity over Ag/Al_2O_3 catalyst. Prepared ready for submission.

2. Poku, R**.,** K. X. Kallis, J. Singh, A. Tsolakis, J. M. Herreros, E. Price, A. P. E. York. Low PGM loading aftertreatment systems design for improved cold start and low load emissions of modern GDI engine. Prepared and is being corrected for publication.

3. Andrade Torres, F., Doustdar, O., Herreros, J. M., Li, R., Poku, R**.,** Tsolakis, A., Martins, J., Vieira de Melo, S. A. B. A Comparative Study of Biofuels and Fischer-Tropsch Diesel Blends on the Engine Combustion Performance for Reducing Exhaust Gaseous and Particulate Emissions. *Energies 2021, 14, 1538.*

4. Andrade Torres, F., Doustdar, O., Herreros, J., M., Li, R., Poku, R**.,** Tsolakis, A., Martins, J., Vieira de Melo, S. A. B. Fischer-Tropsch Diesel and Biofuels Exergy and Energy Analysis for Low Emissions vehicles. *Appl. Sci. 2021, 11, 5958.*