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HC-SCR OF NO_x EMISSIONS OVER $Ag\text{-}Al_2O_3$ CATALYSTS USING DIESEL FUEL AS A REDUCTANT

by

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ABSTRACT

Hydrocarbon selective catalytic reduction (HC-SCR) of nitrogen oxides (NO_x) over silver-alumina ($Ag-Al_2O_3$) catalysts, in diesel exhaust gas, has been investigated and presented in this research thesis. The work involved the use of H_2 to activate diesel-type HC reductants. Numerous HC-SCR studies have been conducted (to date) by various authors and research groups in an effort to improve the low temperature (< 350 °C) NO_x reduction activity of the catalyst, but mainly at laboratory scale, using simulated diesel exhaust gases and the pelletized form of the catalyst. Conversely, the work presented and discussed herein is based on $Ag-Al_2O_3$ coated monolith substrates for the examination of the NO_x reduction efficiency when utilizing the full diesel exhaust gas.

The activity of the pelletized form of the catalyst and that of a coated monolith substrate could vary according to various characteristics, such as, the chemical (reaction kinetics) and physical (mass transfer, species filtration) processes. These effects were examined under ‘passive’ and ‘active’ operation of the respective catalysts. Diesel oxidation catalysts (DOCs) and unique prototype catalysts were also utilized in order to reduce possible poisoning species, which can lead to the deactivation of the Ag-based catalyst.

Furthermore, variations in exhaust gas temperature and composition, by continually changing engine load and speed, were explored and the effects on catalyst activity presented. It was suspected that the fluctuating temperature profiles of the exhaust gas could limit the amount of poison species accumulation onto the catalyst active surface and, as a result, could slow down the deactivation mechanisms.

Finally, fuel reforming of conventional diesel, RME and GTL fuels was conducted for the production of hydrogen (H_2). The produced H_2 could then be utilized in the combustion process itself or in a HC-SCR reactor, for reduced engine out or tailpipe emissions.

‘This thesis is dedicated to my mother,

***Chipo Siphiwe Sitshebo**,*

for her endless love and support.

A special dedication also goes to

my late father

***The Rt Rev. Wilson Timothy Sitshebo**,*

and my late sister,

***Nonceba Ivy Sitshebo**,*

with a lot of love and respect,

may both their souls rest in peace...’

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Simbarashe W.T. Sitshebo
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Symbol	**Unit**	
$\dot{m}_p$	kg/s	Mass flow rate of the combustion products
$\dot{m}_r$	kg/s	Mass flow rate of the combustion reactants
$\dot{V}_i$	cm^3/s	Measured intake air volumetric flow rate with EGR
$\dot{V}_o$	cm^3/s	Measured intake air volumetric flow rate without EGR
$\dot{m}_f$	kg/s	Mass flow rate of the combustion fuel
LCV_f	MJ/kg	Lower calorific value of the combustion fuel
LCV_p	MJ/kg	Lower calorific value of the products
LCV_r	MJ/kg	Lower calorific value of the reactants
P_b	kW	Engine brake power
PM_{10}	ppm	PM with an aerodynamic diameter of less than 10 µm
$PM_{2.5}$	ppm	PM with an aerodynamic diameter of less than 2.5 µm
P_{ref}	kW	Power input into the reformer
SV	h^{-1}	Space Velocity
T_b	Nm	Engine brake torque
T_{exh}	°C	Engine exhaust gas temperature
V_f	m^3/h	Volumetric gas flow rate
V_r	m^3	Reactor Catalyst Volume
η_c	%	Engine combustion efficiency
η_{ref}	%	Reforming reactor efficiency
η_{th}	%	Engine thermal efficiency
ω	rad/s	Engine Angular speed

LIST OF ABBREVIATIONS

A/F	Air to Fuel ratio
$Ag\text{-}Al_2O_3$	Silver-Alumina
ASTM	American Society for Testing and Materials
ATR	Auto-Thermal Reforming
BDC	Bottom Dead Centre
BOC	British Oxygen Company
BSFC	Brake Specific Fuel Consumption
BTL	Biomass-to-Liquid
C	Atomic Carbon
CAD	Crank Angle Degree
CCRT®	Catalysed Continuously Regenerating Trap
CFC	Chlorofluorocarbon
CI	Compression Ignition
CLD	Chemiluminescence
CN	Cetane Number
CO	Carbon Monoxide
$CO(NH_2)_2$	Urea
CO_2	Carbon Dioxide
CPSI	Cells Per Square Inch
CRT®	Continuously Regenerating Trap
CTL	Coal-to-Liquid
DOC	Diesel Oxidation Catalyst
DPF	Diesel Particulate Filter
ECU	Engine Control Unit
EGR	Exhaust Gas Recirculation
EOC	End of Combustion
EOI	End of Injection
FID	Flame Ionisation Dectection
FT	Fischer Tropsch
GC	Gas Chromatograph

GC-FID	Gas Chromatograph – Flame Ionisation Detector
GTL	Gas-to-Liquid
H_2	Hydrogen
$HC:NO_x$	Hydro-Carbon to NO_x ratio
HC-SCR	Hydro-Carbon Selective Catalytic Reduction
IC	Internal Combustion
KOH	Potassium Hydroxide
LSD	Low Sulphur Diesel
M	Storage Medium
MPD	Magneto-Pneumatic Detection
N_2O	Nitrous Oxide
NAC	NO_x Adsorber Catalyst
NaOH	Sodium Hydroxide
NDIR	Non-Dispersive Infra-Red
NH_3	Ammonia
NO	Nitric Oxide or Nitrogen Monoxide
NO_2	Nitrogen Dioxide
NO_x	Nitrogen Oxides
PGM	Platinum Group Metal
PM	Particulate Matter
PO_x	Partial Oxidation
PPM	Parts Per Million
RME	Rapeseed Methyl Ester
ROHR	Rate of Heat Release
SCR	Selective Catalytic Reduction
SI	Spark Ignition
SMPS	Scanning Mobility Particle Sizer
SO_2	Sulphur Dioxide
SOC	Start of Combustion
SOF	Soluble Organic Fraction
SOI	Start of Injection
SO_x	Sulphur Oxides

SR	Steam Reforming
TCD	Thermal Conductivity Detector
TWC	Three Way Catalyst
ULSD	Ultra Low Sulphur Diesel
US-EPA	United States Environmental Protection Agency
VOC	Volatile Organic Compound
WGS	Water Gas Shift

CHAPTER 1

INTRODUCTION

1.1. Diesel Engine and Operation

Diesel engines are essentially internal combustion (IC) engines which operate by utilizing the heat generated from the compression of an air charge to combust the air-fuel (A/F) mixture, in a process referred to as compression ignition (CI). A lot of investigative research has been devoted to these engines as they have significant advantages over their counterpart gasoline spark ignition (SI) engines; most notably, (i) enhanced fuel economy and high efficiency due to the absence of throttling, higher compression ratios and the overall lean mixture; and (ii) greater engine durability, as the engine has to be designed to withstand the high operating compression ratios (Heywood, 1988; Stone, 1999; Borman and Ragland, 1998). Furthermore, global warming concerns due to the increase in greenhouse gas emissions, particularly carbon dioxide (CO_2) from the automotive industry, is now one of the major driving forces towards the increasing popularity in diesel passenger vehicles, especially in Europe (~ 50 %), as they have a lower CO_2 footprint.

However, the after-treatment of other harmful emissions, such as nitrogen oxides (NO_x), from the diesel engine exhaust is still necessary and is not as straightforward as for SI engines, primarily due to diesel lean operation. Factors such as the fuel delivery system, the fuel delivery pressure, the amount of fuel delivered etc, all have an effect on the efficiency of a diesel engine and in turn its output exhaust gas emissions. Nowadays, diesel engines operate with a fully electronically controlled common rail direct injection system capable of extremely high injection pressures (> 1800 bar), with the latest technology using piezoelectric fuel injectors for greater spray precision into the combustion chamber, which can introduce multiple injections into a single cylinder in any one engine cycle. Better fuel economy, lower engine noise and reduced emissions are among the benefits compared to older models. Typical light-duty and heavy duty diesel engines operate on a 4-stroke cycle, which can be summarized as follows:

Induction: This is also referred to as the ‘intake’ stroke and generally consists of the induction of a fresh air charge into the cylinder as the piston moves down the chamber with the intake valve open. The intake valve closes just before the compression stroke begins from bottom dead centre (BDC).

Compression: The inducted air is compressed as the piston travels towards the top of the cylinder with both the intake and exhaust valves closed. This compression increases the pressure in the cylinder and consequently heats up the air charge to temperatures above which diesel fuel auto-ignites upon injection into the cylinder. Injection of the diesel fuel occurs towards top dead centre (TDC), i.e. towards the end of the compression stroke, where sufficient air charge temperatures are conducive for auto-ignition. The injected fuel is atomized into small droplets as it passes through the fuel injector nozzle tip. These fine fuel droplets then penetrate deep into the combustion chamber mixing with the preheated air and spontaneous ignition of portions of this mixture occur after a period of combustion delay, known as the ignition delay period. The ignition delay period is only a few crank angle degrees (CAD).

Expansion: The cylinder pressure increases as combustion of the A/F mixture progresses. The ignition delay of the fuel and air which have mixed to combustible limits is shortened due to the increasing temperatures in the cylinder and rapid combustion occurs. Fuel injection continues until the required amount of fuel has entered the cylinder and atomisation, vaporisation, A/F mixing and combustion continue until essentially all the fuel has passed through each process. The combustion cycle can be summarized as shown in Figure 1.1, where the different phases the fuel goes through are shown through the rate of heat release (ROHR).

The *'premixed combustion'* phase involves the burning of the A/F mixture which premixed to within flammability limits during the ignition delay period. There then follows the *'diffusion-controlled'* combustion phase where the burning rate is determined by the rate at which the A/F mixture becomes available for burning. Lastly, the *'late combustion'* phase is where any remaining fuel mixes with the already burning gases and is combusted in the process allowing for more complete combustion. The combustion phasing process leads to the expansion of the in-cylinder gases and the associated gradual decrease in heat release due to a fall in in-cylinder temperature as expansion progresses. This is known as the expansion stroke or the 'power stroke' of the diesel cycle as this is where mechanical power is extracted from the A/F mixture.

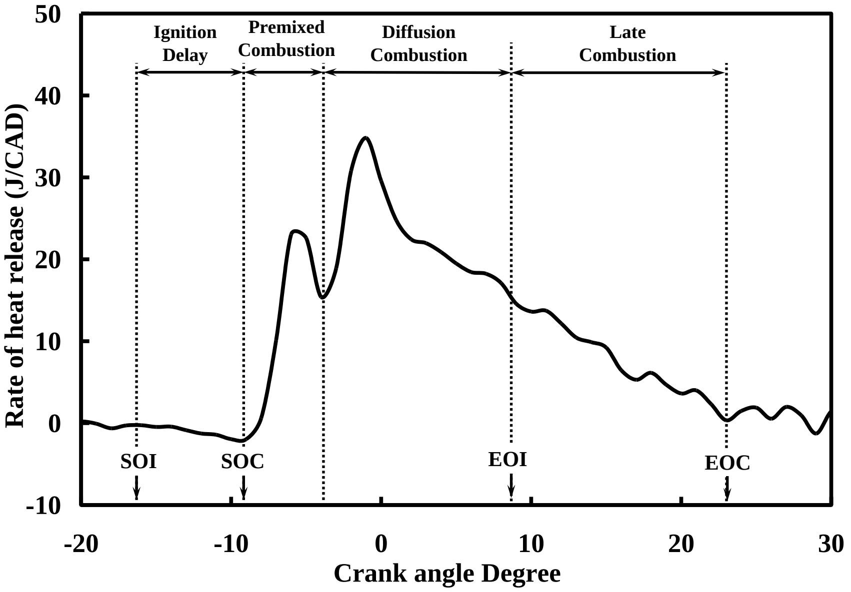


Figure 1.1: Combustion phasing of a single cylinder pump-line nozzle injection diesel engine showing the ignition delay, premixed combustion, mixing controlled (diffusion) and late combustion phases. Also shown are the start of injection (SOI), the start of combustion (SOC), the end of injection (EOI) and the end of combustion (EOC). (Theinnoi et al, 2009)

Exhaust: At BDC the exhaust stroke begins, whereby the burned gases are expelled from the combustion chamber through the open exhaust valve. However, due to the valve event timings, there are usually residual exhaust gases trapped in the combustion chamber which then mix in with the new fresh air charge at the beginning of the next induction stroke. The process is then repeated from the induction as the next engine cycle begins.

1.2. Diesel Emissions and Health Effects

The emissions produced from the diesel combustion process are very much dependant on the conditions during the combustion process, expansion process and especially prior to the exhaust valve opening. A/F mixing during the ignition delay period, fuel quality, combustion reactions at varying in-cylinder temperatures as well as the general engine design features, all play an important role in controlling or contributing to diesel emissions formation.

However, there is always a possibility for humans to be exposed to diesel emissions or their atmospheric transformation products in both ambient and occupational settings. As a result, some of the different diesel engine emissions and their effects are introduced below.

1.2.1. Hydrocarbons (HCs)

Hydrocarbon species are formed through the incomplete combustion of the A/F mixture which leads to unburned and partially decomposed fuel molecules or recombined intermediate compounds (Khair and Jääskeläinen, 2008). Additionally, lubricating oil on the cylinder walls is another contributing source of HCs but is considered minimal for engines in good condition. The HC emissions described here are those in the gaseous state; whereas those in the liquid/solid state are classed under ‘particulate matter’, which is discussed later.

For heavy duty engines, fuel dripping from the injector sac volume and lean mixtures formed during the ignition delay period are also contributing factors to the amount of HC species in the exhaust gas. Inclusive of these factors, other contributors in light duty engines include flame quenching within crevices, storage and release of fuel by deposits and/or oil layers (Ferguson, 1986) and an increased difficulty in achieving complete A/F mixing due to the overall richer ratios required to achieve high rated power density (Miles, 2007). As a result, HC emissions can be regarded as a measure of the combustion process inefficiency for a given engine operating mode.

There are several negative environmental effects associated with gaseous HC emissions, the main being that they are precursors of photochemical smog and ozone levels when they react with NO_x (Majewski and Khair, 2006).

1.2.2. Carbon Monoxide (CO)

Carbon monoxide is a colourless, odourless and poisonous gas formed due to the incomplete combustion of HC based fuel. It is part of the gaseous emission phase of diesel combustion that is highly toxic. Its formation is increased by the lack of oxidants (e.g. O_2 in air), temperature and residence time during the combustion process (Khair and Jääskeläinen, 2008). CO formation is an intermediate in hydrocarbon combustion and can be summarized as follows, with R denoting the HC radical (Bowman, 1975):

$$RH \rightarrow R \rightarrow RO_2 \rightarrow RCHO \rightarrow RCO \rightarrow CO \tag{1.1}$$

Fuel-rich mixtures normally produce the highest amounts of CO due to the lack of oxidant, but since diesel engines operate on a lean cycle, there is abundant amounts of air for the oxidation of CO to CO_2 through the mechanism shown in equation (1.2), hence the amount of CO emissions from diesel operation are generally low.

$$CO + OH \rightarrow CO_2 + H \tag{1.2}$$

If exposed to CO, it is absorbed into the bloodstream through the lungs and replaces oxygen by attaching chemically to haemoglobin forming carboxyhaemoglobin, a process which reduces the oxygen carrying capacity of the blood (Strauss et al., 2004). The symptoms of exposure depend on the degree of saturation of the haemoglobin with carbon monoxide, with greater risk of death as saturation increases. The level of haemoglobin saturation strongly depends on the concentrations of CO and the time of exposure, with increased concentrations requiring lesser exposure time for subsequent damage. Symptoms can vary from flu-like symptoms, headache, and nausea to impaired judgement, unconsciousness and ultimately death.

1.2.3. Carbon Dioxide (CO_2)

Carbon dioxide is a colourless and odourless gas which is generally harmless; however at high concentrations it has a sharp acidic odour and will act as an asphyxiant and an irritant. It is a by-product of the complete combustion of HC fuel. Equation 1.3 shows the complete combustion (oxidation) reaction of typical diesel-type fuel, producing CO_2 and water (H_2O) as products. Diesel engines typically produce lower CO_2 emissions per kilometre (km) compared to their counterpart gasoline engines, due to their higher combustion and volumetric efficiencies.

$$C_nH_{1.88n} + 1.47nO_2 \rightarrow nCO_2 + 0.94nH_2O \tag{1.3}$$

CO_2 gas is also one of the major contributors to the ‘greenhouse effect’ which is described in more detail later in this chapter. In terms of health effects, CO_2 amounts exceeding 10 000 parts per million (ppm), i.e. 1 % by vol., are considered harmful and those above 70 000 ppm, i.e. 7 % by vol., are considered very dangerous at exposures greater than a few minutes (Compressed Gas Association, 1990).

1.2.4. Nitrogen Oxides (NO_x)

Nitrogen oxides are generally a combination of nitric oxide (NO) and nitrogen dioxide (NO_2), with the former being the most abundant and constituting more than 70 – 90 % of the total NO_x. High temperatures and pressures occurring in the cylinder during the combustion process as well as flame conditions, residence time and concentrations of key reacting species, all contribute to the formation of NO_x in diesel engines. Obviously, the principal source for the formation of NO_x is the oxidation of atmospheric nitrogen (N_2). Additional sources of N_2 can be due to inherent amounts in the fuel or additives to the fuel. The mechanism of formation of the main product in NO_x i.e. NO, from molecular N_2 is governed by the extended Zeldovich mechanism, which is illustrated below:

$$O + N_2 \leftrightarrow NO + N \tag{1.4}$$

$$N + O_2 \leftrightarrow NO + O \tag{1.5}$$

$$N + OH \leftrightarrow NO + H \tag{1.6}$$

Chemical equilibrium considerations indicate that for burned gases at typical flame temperatures, NO_2/NO ratios should be negligibly small (Heywood, 1988). However in diesel engines, ratios as high as 30 % of the total oxides can be attributed to NO_2 emissions. Due to this, a mechanism has been proposed which explains the NO_2 formation process through reactions such as those shown below:

$$NO + HO_2 \rightarrow NO_2 + OH \tag{1.7}$$

Decay can also occur through the following reaction:

$$NO_2 + O \rightarrow NO + O_2 \tag{1.8}$$

Reaction (1.8) shows the conversion of NO_2 to NO occurring when the NO_2 produced is not quenched by mixing with cooler fluid in the combustion chamber. It has been reported that this mechanism is accurate with the highest NO_2 formation; occurring for engines operating at low engine load, hence lower peak combustion temperatures which allow for the quenching of the formed NO_2, thus preventing its decomposition accordingly.

Emissions of NO_x contribute to the greenhouse effect and are ground-level ozone precursors; therefore their reduction from the exhaust of diesel vehicles is paramount from an environmental and physiological perspective. Adverse effects on health are dependent on the level of exposure. For example, NO itself is not an irritant but it reacts with haemoglobin (in blood) yielding meta-haemoglobin which at high levels can be lethal, while NO_2 is an irritant gas and if breathed can cause severe damage to the lungs.

1.2.5. Particulate Matter (PM)

Particulate matter is defined as any matter in the exhaust gas that can be trapped on a sampling filter medium at 52 °C (125 °F) or less (Khair and Jääskeläinen, 2008). For example, the soluble organic fraction (i.e. high boiling hydrocarbons and their derivatives), soot (i.e. carbonaceous matter) particles, dust (in the inducted air) or inorganic material (in fuel or fuel additives), trace metals from engine wear and sulphate particles can all be classed under the aforementioned PM definition. Approximately over 90 % of all PM is fine particles which are in the respirable size range, these are commonly referred to as $PM_{2.5}$ i.e. particles less than 2.5 μm in aerodynamic diameter.

The breakdown of the particle size distribution in exhaust gas into its three main groupings is shown in Figure 1.2. The 'nuclei mode' particles are usually formed from volatile precursors as exhaust gas dilutes and cools, they range in diameter from 5 - 50 nm;

‘accumulation mode’ particles typically consist of carbonaceous agglomerates and adsorbed material and they range in diameter from 30 - 500 nm; ‘coarse mode’ particles consist of re-entrained accumulation mode particles which have been deposited on cylinder and exhaust system surfaces, these particles are normally larger than 1 μm (Kittelson, 1998). Also shown in Figure 1.2 are the definitions of atmospheric particle size distributions ranging from PM_{10} particles (particles smaller than 10 μm) to nanoparticles (defined as being smaller than 50 nm).

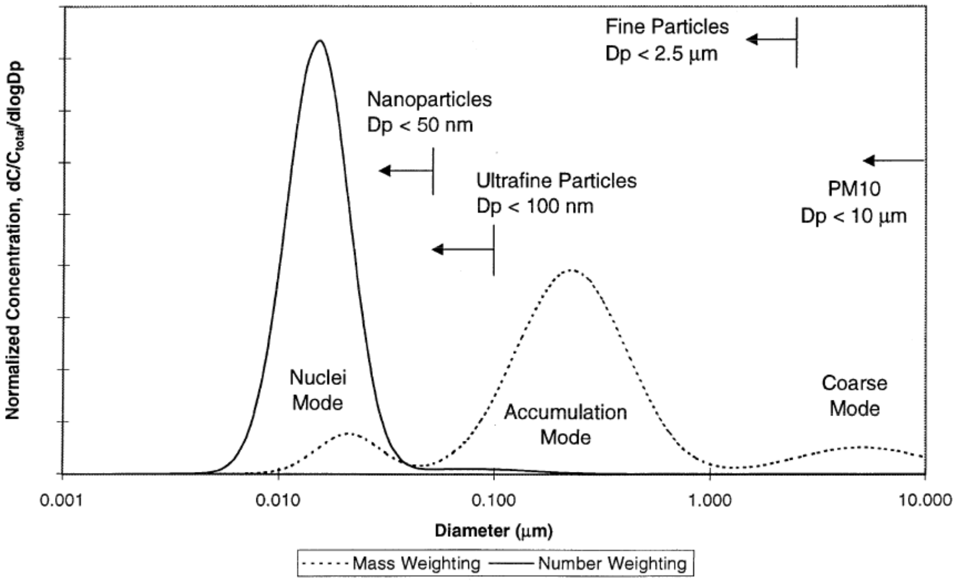


Figure 1.2: Typical engine exhaust particle size distribution by mass and number (Kittelson, 1998).

There are several health problems associated with the emission of PM which can include, but are not limited to, coughing, difficulty or painful breathing, aggravated asthma, bronchitis, emphysema, decreased lung function, weakening of the heart possibly leading to heart attacks and premature deaths in infants (Dockery et al. 1993). Exposure period is a major contributing factor to how severe the health risk suffered is, with prolonged exposure resulting in the most severe reported cases.

1.2.6. Volatile Organic Compounds (VOC)

Volatile organic compounds (VOCs) are compounds that have a high vapour pressure and low water solubility. They are often components of HC fuel and the dominating parameters to their formation are the degree of mixing in the combustion chamber and the combustion temperature. The type of fuel used e.g. diesel or biodiesel; give different VOC output compositions depending on high-temperature pyrolysis, mild thermal cracking, depolymerisation and mild oxidation processes occurring within the combustion chamber (Schulz et al., 1999).

Although ubiquitous in nature and modern industrial society, they may also be harmful or toxic. The extent and nature of health effects depends on many factors including the level of exposure, length of time exposed and type of compound exposed to. Some health effects can include eye, nose, and throat irritation; headaches, loss of coordination, nausea; damage to liver, kidney and central nervous system. Some organics can also cause cancer in animals with some suspected or known to cause cancer in humans (Environmental Protection Agency, 2009). For these reasons, some VOC emissions or subsets of these emissions are regulated.

1.2.7. Smoke

Smoke in diesel engines is a result of poor combustion which results from an over-rich A/F ratio or partially evaporated fuel during cold start conditions (Khair and Jääskeläinen, 2008). The smoke can be classified into two forms, namely, white smoke and black smoke. White smoke consists of fuel and lubricating oil particles in an unburned or partially burned state, more commonly referred to as liquid smoke or fog. Whereas, black smoke consists of solid carbon particles from complete combustion of the HC fuel, more commonly referred to as hot or solid smoke. There are also instances where the smoke is a shade of blue or grey which indicates that there is excessive lubrication oil consumption. The health risks of continued exposure to smoke emissions are essentially similar to those of PM emissions discussed above, as smoke is made up of very fine particles which are readily respirable.

1.3. Emissions Legislation and Environmental Concerns

Vehicular emissions have been the subject of continued interest for many decades due to environmental concerns. As a result, emissions legislation as stipulated by the relevant governing bodies has been becoming more and more stringent. Nowadays, diesel engines are cleaner than they were in the past and discussed below is some of the emissions legislation currently in place and that yet to be enforced in the near future, as well as the associated environmental concerns.

1.3.1. Emissions Legislation

The first emissions standards were introduced back in the 1970s in an effort to promote cleaner engines and reduce the potentially harmful emissions (as discussed above) from compression ignition engines. Ever since, the emissions governing legislation has been getting stricter to such an extent that at present, engine output emissions have become the major driving factor in diesel engine development. Due to these standards, diesel engine emission levels have decreased dramatically. Additionally, ever new and more stringent emission regulations and performance requirements imposed on modern diesel engines are strong motivators for new technology. A guide of the progression of the stringency of emission regulations is illustrated in Figure 1.3, below, where the two primary emissions of PM and NO_x are presented.

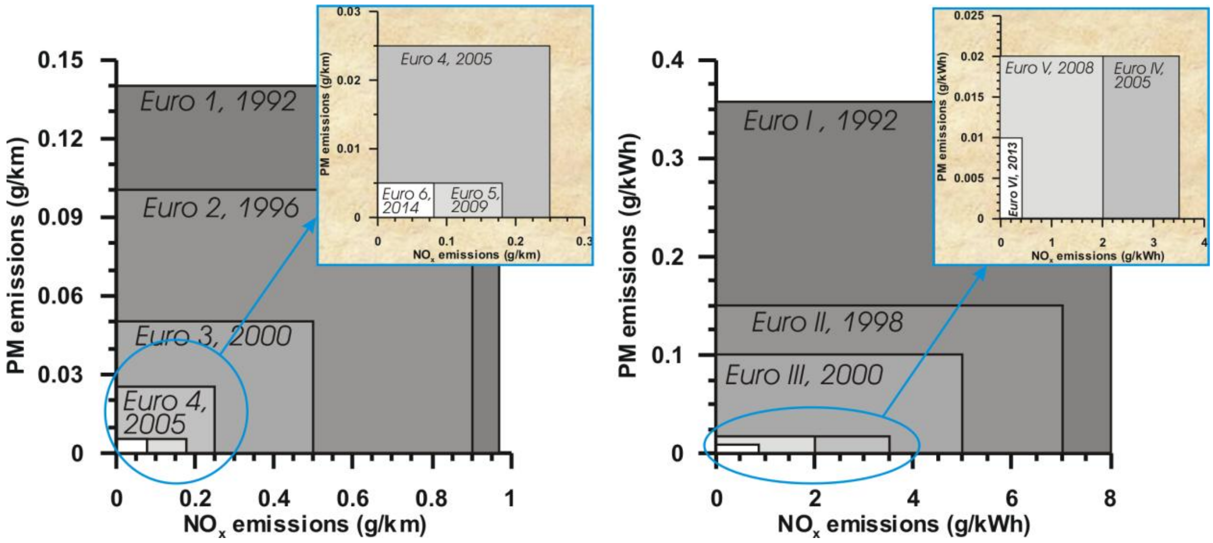


Figure 1.3: European PM and NO$_x$ emissions legislation for light duty diesel vehicles (g/km) and heavy duty applications (g/kWh).

From Figure 1.3, it is apparent that the legislation is going to get tougher and tougher to meet with time as the target emission levels get tighter and tighter. New technologies will be required to meet these new levels, with the cost effectiveness, efficiency and durability of the technology being the main driving forces. Fines are already in place for manufactures that produce vehicles that do not meet these set standards and there is even talk that in the near future the suspension of sales would be a more fitting punishment that will essentially force all manufactures to abide by the stipulated guidelines.

1.3.2. Environmental Concerns

Apart from the damage to humans, vehicular emissions are also associated with various environmental effects, some of which are discussed below:

Greenhouse Gases: These are gases that are emitted into the atmosphere that absorb and emit radiation within the thermal infrared range. Solar (short-wave) radiation from the sun is absorbed by the earth's surface, consequently warming it up. Infrared (long-wave) radiation is then emitted from the earth's surface upon which some of it is trapped and reemitted (back to earth) by the greenhouse gasses within the surface-troposphere. The direct effect of this cycle is the general warming of the earth's surface and the troposphere, more commonly referred to as global warming or 'the greenhouse effect' (Le Treut et al., 2007). The main contributors (in representative order) to the greenhouse effect are water vapour, carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O) and chlorofluorocarbons (CFCs).

Smog and Photochemical Smog: Standard smog is generally a combination of smoke and fog in the atmosphere. However, chemical reactions between certain components of diesel exhaust in the atmosphere can lead to photochemical smog. Ground-level ozone is the main component in photochemical smog and is formed by complex chemical reactions of VOCs and NO_x in the presence of heat and sunlight (An et al., 2008). Ozone forms readily in the lower atmosphere, usually during hot summer weather. Associated health impacts involve mainly the respiratory system leading to reduced lung functionality.

Acid rain: This is caused by emissions of sulphur dioxide (SO_2) and nitrogen oxides (NO_x) which become acids when they enter the atmosphere and react with water vapour. The resulting sulphuric and nitric acids can then fall as wet or dry depositions (Hook et al., 1994). Wet deposition is precipitation e.g. acid rain, snow, sleet or fog. Dry deposition falls as acidic particulates or gases. Effects range from acidification of lakes and streams which affects aquatic life, to forestry and buildings damage.

1.3.3. Emissions Reductions Techniques

A lot of research is going into finding ways to reduce the above mentioned emissions for the purpose of a cleaner environment. Various different methods are being explored for use in diesel engines and some of them are introduced briefly below.

Exhaust Gas Recirculation (EGR): This involves the recirculation of exhaust gas back into the combustion chamber by mixing it in with the air charge. The primary role of this technology is to reduce NO_x emissions. The NO_x emissions reduction is achieved by a reduction in peak in-cylinder temperature during combustion (through several effects) leading to the observed reduction in NO_x but at a cost of increased HC and PM emissions.

After-treatment Devices: Three-way catalytic (TWC) converters are used to effectively control NO_x, HC and CO emissions (> 85 % efficiency) in gasoline engines. They are designed for operation under stoichiometric operating conditions representative of spark ignition (SI) operation, but this is in contrast with a typical diesel engine which operates on a lean cycle i.e. in excess oxygen. Due to this, TWC technology cannot be utilized for cleansing the diesel exhaust gas as it is ineffective in a lean environment.

As a result, a lot of research work is on-going into effective after-treatment technology for diesel exhaust gas. Precious metals are used as catalysts as they are known to be very reactive. For example, platinum (Pt) and Palladium (Pd) are used in diesel oxidation catalysts (DOC) to reduce emissions of CO (> 90 % efficiency) and HCs (> 50 % efficiency), but do not reduce NO_x. Diesel particulate filters (DPF) are utilized for the reduction of PM emissions and are > 99 % efficient for solid matter but due to diesel PM having a non-solid portion the overall efficiency is > 90 %. Continuous operation of the DPF is aided by regeneration technology. DPFs also aid other after-treatment devices which would otherwise be hindered in the presence of increased particulates.

Silver (Ag), copper (Cu), cobalt (Co) and Iron (Fe) are among some catalyst metals being investigated for the reduction of NO_x through selective catalytic reduction (SCR). NO_x adsorbers are also being investigated based on their ability to trap NO_x at relatively low exhaust temperatures and then release and reduce it at high temperatures. These NO_x adsorber catalysts consist of an oxidation catalyst which is in front of an absorbing medium, which in turn is to the front of a reducing catalyst.

After-treatment devices, primarily Ag-based SCR catalysts as well as Pt oxidation and rhodium (Rh) fuel reforming catalysts are be the main subject of focus throughout this research thesis.

Combustion Fuels: Enhanced combustion fuels are of research interest based primarily on their quality and combustibility. Their associated superior combustion qualities have the ability to reduce engine-out emissions e.g. Fischer Tropsch gas-to-liquid (GTL), biomass-to-liquid (BTL) and other various bio-fuels. Other possibilities include the mixing of current conventional fuels with a certain percentage of bio-fuel to have synergistic benefits of the fuels or additives, e.g. to enhance the cetane number of the fuel, making it more combustible. Thus, the composition and properties of the fuel are of paramount importance for the reduction of diesel combustion emissions.

A more detailed discussion of the techniques for reduced diesel engine output emissions is offered in Chapter 2, which focuses on emissions reduction strategies, current and near future.

1.4. Research Objectives and Focus

This research work is based on monolithic silver-alumina (Ag-Al_2O_3) selective catalytic reduction (SCR) catalysts for the purpose of primarily reducing the amount of NO_x emissions from diesel engine exhaust. The work was to test a full catalyst system utilizing the whole diesel engine exhaust gas for analysis of the effectiveness of the monolith-type Ag-Al_2O_3 catalysts. The research objectives are summarized below.

1.4.1. Ag-Al_2O_3 Catalyst Activity Tests at Low Exhaust Gas Temperatures

The Ag loading as well as the catalyst preparation procedure affects the catalyst activity in reducing NO_x. Investigated herein is a catalyst with 2wt. % Ag on an alumina (Al_2O_3) support; a catalyst silver loading which has been reported and shown to have good SCR activity at high exhaust gas temperatures. The catalyst will be examined at low temperatures (< 350 °C), paying particular attention to the HC, NO_x and soot in the diesel exhaust gas. Optimization of these reactants can improve the selectivity of the SCR catalysts even at these low exhaust gas temperatures.

1.4.2. Low Temperature Ag-Al_2O_3 Catalyst Reductants

To test different reductant additions to the diesel exhaust gas during low temperature (< 350 °C) Ag-Al_2O_3 catalyst operation; typical of light-duty diesel engines. It has been reported in literature, mainly for powdered catalysts, that reductants such as H_2 and selective HC species into the exhaust gas stream can improve the NO_x reduction efficiency of the catalyst if a carefully regulated dosage is administered. Furthermore, associated poisoning mechanisms linked with Ag catalysis are negated or slowed down by the use of H_2 in the exhaust gas. Other catalysts could be used in conjunction with the Ag-SCR catalysts to cleanse the exhaust gas prior to the SCR catalysts and possibly help improve the reduction activity, for example, a diesel oxidation catalyst (DOC) to reduce the possible poisoning species.

1.4.3. Diesel Fuel-type Effects

To investigate the use of conventional ultra-low sulphur diesel (ULSD), bio-diesel (rapeseed methyl ester – RME) and Fischer Tropsch gas-to liquid (GTL) fuels and draw comparisons on the output of NO_x, PM and HC concentrations from the combustion of these fuels. These emission parameters are expected to have significant effects on the SCR catalyst's overall NO_x reduction activity.

1.4.4. Hydrogen from Fuel Reforming

To test the effect of simulated or actual reformer product gas (H_2, CO, CO_2, HC) on the activity of the SCR catalyst for improving NO_x reduction efficiency. ULSD, RME and GTL fuels will be reformed for H_2-rich gas production and due to the differences in fuel composition, the quantity of species produced from the process will vary accordingly. The quantity of H_2 and other species, e.g. the HC concentration, can improve or hinder the selectivity of the HC-SCR process, therefore regulation and control of the reformate feed into the SCR catalysts will be of importance.

1.5. Thesis Outline

An overview of diesel engine operation and the associated future emissions guidelines have been presented; nonetheless, the remainder of the thesis is categorized as follows:

Chapter 2: Literature Review: Emissions Reduction Strategies

Relevant technologies for the reduction of diesel emissions, mainly nitrogen oxides (NO_x) and particulate matter (PM) are presented and discussed.

Chapter 3: Experimental Setup

The experimental equipment used during the research work for this thesis is presented, from the bench diesel engine through to exhaust gas analysis equipment. Where appropriate, the measuring accuracy of the equipment used is detailed.

Chapter 4: Promoting HC-SCR of NO_x in diesel engine exhaust by hydrogen

Passive (no externally injected fuel) control of silver-Alumina ($Ag\text{-}Al_2O_3$) catalysts is investigated and discussed for the main purpose of removing NO_x emissions from the diesel exhaust gas with the help of externally added hydrogen (H_2). H_2 is a HC-SCR of NO_x mechanism enhancer but quantity of H_2 into the HC-SCR catalyst at different engine operating conditions is a key step in improving/maintaining good NO_x reductions.

Chapter 5: Improving the low temperature NO_x reduction activity of $Ag\text{-}Al_2O_3$

Quantity and selectivity of HC species can hinder or promote the NO_x reduction mechanism over $Ag\text{-}Al_2O_3$ catalysts. In this chapter, the effect of using a diesel oxidation catalyst (DOC) to treat exhaust gas prior to it passing through the SCR catalysts was studied for the purpose of trying to enhance the NO_x reduction reaction. Active (externally injected fuel) control was also investigated for the same purpose.

Chapter 6: Temperature dependence of $Ag\text{-}Al_2O_3$ catalysts during HC-SCR of NO_x

Due to the fact that urban driving is never steady, a fast steady-state cycle was devised to mimic a transient response cycle in order to observe the behaviour of the $Ag\text{-}Al_2O_3$ SCR catalysts under continually cycling engine speed-load conditions, thus varying exhaust gas temperatures. Several fuels were studied, namely, conventional ultra-low sulphur diesel

(ULSD), rapeseed methyl ester (RME) and Fisher-Tropsch gas-to-liquid (GTL) to look for any possible advantages, if any, one fuel had over the other.

Chapter 7: Partial oxidation and exhaust gas fuel reforming

Producing hydrogen on-board the vehicle has several infrastructural benefits associated with it and discussed in this chapter is the fuel reforming process (partial oxidation and exhaust gas fuel reforming) for the sole purpose of producing a H_2-rich gas using diesel-type fuel. The produced H_2 can then be utilized for different purposes including after-treatment and/or combustion. The viability of the technology and system setup is also examined for integrity.

Chapter 8: Conclusions

A summarization of all the research work undertaken including the key findings is presented. Future research recommendations and developments are also stated and clarified.

CHAPTER 2

LITERATURE REVIEW: EMISSIONS REDUCTION STRATEGIES

Emissions reduction strategies are now a necessary part for the reduction of engine out emissions to comply with the legislative directives being put in place by the environmental governing bodies, such as, the United States Environmental Protection Agency (US-EPA). Discussed in this chapter are the strategies that hold the most promise and have been shown to be able to reduce the overall output emissions from diesel engines, in particular, NO_x and PM. The strategies discussed mainly focus on combustion fuel technology, after-treatment of the lean exhaust gases and engine modifications.

2.1. Fuel Options

Due to the increasing fuel demand and reduced oil reserves coupled with the ever stringent emissions regulations from governing bodies, there is an increasing need to move towards cleaner, greener and more sustainable fuel sources. In this section, current and possible future trends in combustion fuel technology are discussed with a main focus on conventional ULSD, bio-diesel (mainly RME) and gas-to-liquid (GTL) fuels.

2.1.1. ULSD Fuels

Ultra-low sulphur diesel (ULSD) fuel was introduced as a replacement for low sulphur diesel (LSD) and it has been in use for light duty vehicles from 2005 and 2007 in European and US models respectively (Fanick, 2008). It contains very low levels of sulphur (< 15 ppm) compared to LSD which has a higher content (< 500 ppm). The introduction of this fuel was in conjunction with emissions regulations being stipulated for diesel engines, making advanced after-treatment systems a necessary component in the emissions reduction strategy (Fritz and Pitchon, 1997). Sulphur in the combustion fuel contributes to its natural lubricity, thus the lowering of fuel sulphur content yields a fuel with poor lubricity (Alleman and McCormick, 2003). However, additives are available that can improve the lubricity to commercially acceptable levels. Most after-treatment devices, such as diesel particulate filters (DPF), NO_x adsorber catalysts (NAC) and SCR technologies are very sensitive to the amount of sulphur content in the diesel fuel, with greater emissions reduction efficiencies being observed for fuels with virtually no sulphur (Tan et al., 2009; Thornton et al., 2006;).

With regards emissions, there is a general increase in the amount of PM emissions from the combustion of sulphur containing fuel (Kwon et al., 2001; Tan et al., 2009). This increase in PM is due to the formation of sulphur dioxide (SO_2) and sulphate particulates, which can also both bind with water to form sulphuric acid which also contributes to the total PM emissions (Fanick, 2008).

More fuel based technological advances are occurring with the main purpose of compliance with newer more efficient exhaust treating devices which lead to lower engine out emissions. Varying different parameters such as the cetane number, fuel density, viscosity, lubricity and aromatics content can influence qualities like the ignitability of the fuel through to the combustion product emissions, e.g. NO_x and PM (Majewski and Khair, 2006).

More and more research is now going into alternative fuels such as bio-fuels (e.g. RME) and synthetic fuels (e.g. GTL) which are supposed to potentially answer the sustainability and renewability questions in addition to possessing some favorable combustion qualities.

2.1.2. Bio-Diesel Fuels

Biodiesel is an alternative fuel consisting of alkyl monoesters of fatty acids from vegetable oils or animal fats (Monyem and Gerpen, 2001). These fuels are characterized by higher molecular weight and higher distillation temperatures compared to conventional diesel fuels e.g. ULSD. However, interest in biodiesel has increased over the years owing to pressures from governmental and environmental legislative bodies regarding the use of more sustainable and renewable fuel sources, which aid emissions reduction (Basha et al., 2009; Lapuerta et al., 2008).

Almost all biodiesel is produced using base catalyzed transesterification as it is the most economical process, with very high yields (> 98 %) (Schuchardt et al., 1998; Zhou and Boocock, 2006). The transesterification process involves the converting of triglyceride (fats/oils) into a biodiesel. The nature of the fats can in turn affect the characteristics of the end biodiesel. Alcohol is used to react with the triglyceride in the presence of a base catalyst such as potassium (KOH) or sodium (NaOH) hydroxide producing the biodiesel and glycerol (Cvengros and Považanec, 1995).

The process can be surmised by the following reaction:

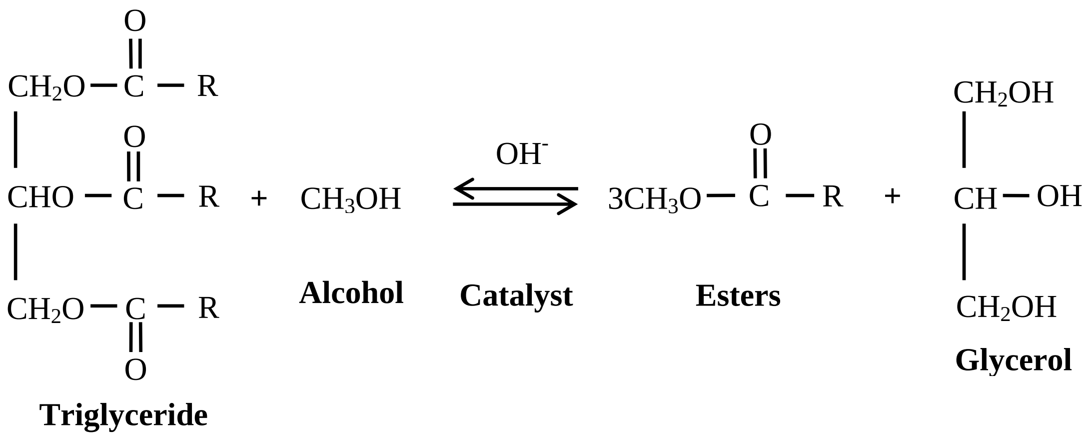


Figure 2.1: The transesterification process of triglyceride into esters showing the main components of reaction and the output products.

The benefits of the transesterification process include the fact that the resulting fuel has a maintained cetane number, lowered viscosity, boiling point, flash point and the glycerides are completely removed; making it more suitable as a combustion fuel. RME is the most common type of biodiesel in Europe and its formation comes from the reaction of rapeseed oil with methanol in the presence of a NaOH catalyst to produce rapeseed 'methyl ester' as a product.

Many researchers have reported benefits from biodiesel combustion to include lower CO, unburned HCs, and PM compared to ULSD fuels (Chuepeng et al., 2007; Szybist et al., 2005; Tsolakis et al., 2007b; Graboski and McCormick, 1998). These associated advantages are primarily due to the chemical composition, most notably, the inherent O_2 content (e.g. as high as 10wt. %). As a result, biodiesel is more combustible and due to its higher bulk modulus, advances injection timing compared to conventional diesel e.g. ULSD, but at the expense of an increase in the NO_x emissions from the combustion process. Combustion of biodiesel fuel results in advanced combustion, reduced ignition delay and increased heat release rate in the initial uncontrolled premixed combustion phase leading to increased in-cylinder pressure and temperature which are conducive for NO_x formation (Chuepeng et al., 2007; Tsolakis et al., 2007b). These increased NO_x emissions can be reduced by the use of EGR in the exhaust system as discussed later. Another method to reduce the NO_x emission increases is by use of blends of biodiesel and conventional diesel, to try and get synergistic benefits from both fuels. For example, work by Theinnoi et al. (2009) reported that blends of synthetic diesel and bio-diesel (RME), 50% by volume, allowed for reductions in emissions of CO, HC, smoke and NO_x while maintaining combustion characteristics typical of conventional diesel fuel.

2.1.3. Fischer-Tropsch Fuels

The Fischer-Tropsch (FT) process converts a mixture of hydrogen and carbon monoxide derived from coal, methane or biomass to liquid fuels. The technologies are aptly named coal to liquids (CTL), gas to liquids (GTL) and biomass to liquids (BTL), respectively. The process of producing these fuels consists of three steps as discussed below (Alleman and McCormick, 2003; Forrest and Muzzell, 2005; Johnson et al., 2001).

Syngas generation: This can be formed from any carbonaceous material, for example, natural gas (methane), coal or biomass. The production of syngas has been reported by Dry (2002) to account for 60 – 70 % of all capital and running costs of a typical production plant. In the production of syngas from natural gas, reforming processes are employed, e.g. steam reforming, autothermal reforming or partial oxidation (Dry, 1999 and 2002). However, in syngas production from coal or biomass a gasification process is employed, wherein the feedstock is reacted with steam and oxygen (Alleman and McCormick, 2003). Comparatively methane reforming is much cheaper (~ 30 %) and is therefore favoured over the other processes.

Fischer-Tropsch synthesis: The synthesis process involves the conversion of the syngas into HC fuels characterized by a) low temperature (200 – 240 °C) synthesis (catalyzed by iron or cobalt based catalysts) producing heavier molecular weight HCs, e.g. diesel fuel and b) high temperature (300 – 350 °C) synthesis (catalyzed by iron based catalysts) producing gasoline and light olefins (Alleman McCormick, 2003; Dry, 2002).

Post processing: This last step involves the processing by hydro-cracking, hydro-treating or distillation of the fuels to meet commercial specifications, such as the cetane number and lubricity (Dry, 1999).

As aforementioned, the most popular process is that involving the conversion of methane to form GTL. As with all FT process fuels, GTL is a virtually pure paraffinic hydrocarbon fuel with excellent combustion properties and burns with a smooth controlled flame (Shell Gas and Power, 2009). Furthermore, it is practically free of sulphur and aromatics, with a high cetane number (i.e. it has a short ignition delay) and as a result has emissions reductions associated with its use as a combustion fuel, which include; lower PM, NO_x, un-burnt HC and CO (Dry, 1999; Larsen et al., 2007). These characteristics are favourable in lean after-treatment devices, as lower impurities in the engine exhaust gas generally lead to better NO_x reduction efficiency over specific catalysts e.g. in HC-SCR and NO_x adsorbers (Houel et al.,2007b; Theinnoi et al., 2008b; Johnson et al., 2001; Takeuchi and Matsumoto, 2004).

2.2. After-treatment Technology

Older diesel engines were considered heavy, noisy, expensive and dirty (Borman and Ragland, 1998), however current technological advances show that these problems are being eliminated while maintaining the benefits of diesel combustion such as the higher efficiency and better fuel economy. Nonetheless, with ever more stringent emission regulations being enforced by the environmental governing bodies with regards the emissions from automobiles; diesel after-treatment is now a necessary component in the emissions reduction strategy. PM and NO_x emissions legislation, particularly regarding diesel engines, is getting ever more stringent owing to increased environmental concerns, e.g. in Europe, Euro 5 as of late 2009 and Euro 6 as of late 2014, for light duty diesels. Research into more innovative, cheaper and better solutions and also into improvement of current systems for better emissions reduction efficiency is an ongoing effort.

2.2.1. Lean NO_x Catalysis

This refers to catalysis which deals with catalysts that are designed for use in oxygen rich environments (lean); typical of those found in diesel engine exhaust gas since the engine operates on a lean cycle. Lean NO_x catalysts can be noble metal, zeolite or metal oxide based as summarized below.

***Noble metal catalysts*:** these are catalysts made up of platinum group metals (PGM) e.g. platinum-alumina ($Pt\text{-}Al_2O_3$). PGMs consist of platinum (Pt), iridium (Ir), osmium (Os), palladium (Pd), rhodium (Rh) and ruthenium (Ru). The catalysts are stable and highly active for NO_x removal, but suffer from a narrow active temperature range and poor selectivity for NO_x reduction to N_2, yielding considerable amounts of N_2O (Kim and Nam, 2004; Ozturk and Senkan, 2002; Twigg, 2007).

***Zeolite catalysts*:** zeolites are microporous, aluminosilicate materials that are used as commercial adsorbents. Catalysts made up of zeolite material are active and selective in NO_x reduction, but are hydrothermally unstable (Houel et al., 2005). An example of a zeolite catalyst formulation would be Cu-ZSM-5.

***Metal oxide catalysts*:** These are highly selective and stable catalysts with flexible formulations which are relatively durable and inexpensive, however, they are moderately active and reductant sensitive (Iliopoulou et al., 2004). An example of a metal oxide catalyst formulation would be silver-alumina ($Ag\text{-}Al_2O_3$).

The latest after-treatment technologies are discussed herein, focusing primarily on PM and NO_x eradication from diesel engine exhaust.

2.2.1.1. Ammonia and Urea SCR

Pure anhydrous ammonia and aqueous ammonia are generally the options available for ammonia-SCR (NH_3-SCR). However, anhydrous ammonia is hazardous, toxic and has a high vapor pressure, making it challenging to store safely. On the other hand, aqueous ammonia is less hazardous making it easier to handle. Since the majority of the NO_x in diesel exhaust is in the form of NO, the main reaction in NH_3-SCR is (Majewski and Khair, 2006; Koebel et al., 2000; Chatterjee et al., 2008):

$$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O \qquad (2.1)$$

There is also the reaction of NO and NH_3 which occurs at a much slower rate and consumes no O_2

$$4NH_3 + 6NO \rightarrow 5N_2 + 6H_2O \qquad (2.2)$$

A reaction mechanism faster than the main reaction (2.1) involves the equimolar reaction of NO and NO_2

$$4NH_3 + 2NO + 2NO_2 \rightarrow 4N_2 + 6H_2O \qquad (2.3)$$

NO_2 can react with NH_3 through a reaction mechanism that is slower than (2.1) and (2.3) as follows

$$8NH_3 + 6NO_2 \rightarrow 7N_2 + 12H_2O \qquad (2.4)$$

At elevated temperatures, undesired reactions which can consume NH_3 and form other emissions can also take place resulting in the loss of NO_x reduction activity. An example is the formation of nitrous oxide (N_2O) according to

$$4NH_3 + 4NO + 3O_2 \rightarrow 4N_2O + 6H_2O \qquad (2.5)$$

Other reactions can involve the oxidation of NH_3 forming NO, thus limiting the maximum NO_x conversion activity.

Aqueous urea $CO(NH_2)_2$ is the preferred selective reducing agent for automotive SCR applications (Koebel et al., 2000) as it provides a safer non-toxic delivery mechanism of ammonia (Chi, 2009). When injected into the hot exhaust gases, NH_3 acts as the reducing agent over the SCR catalyst but initially the NH_3 gas has to be formed. The first step is the evaporation of the water from the aqueous urea according to

$$CO(NH_2)_2\ (l) \rightarrow CO(NH_2)_2\ (s) + xH_2O\ (g) \tag{2.6}$$

Thermal decomposition of the urea then occurs, yielding NH_3 and isocyanic acid in gaseous form

$$CO(NH_2)_2\ (s) \rightarrow NH_3\ (g) + HNCO\ (g) \tag{2.7}$$

The isocyanic acid then hydrolyzes over the SCR catalyst forming more NH_3 and CO_2

$$HNCO\ (g) + H_2O\ (g) \rightarrow NH_3(g) + CO_2\ (g) \tag{2.8}$$

With the formation of NH_3 (reactions (2.7) and (2.8)) in the exhaust gas the SCR reactions can commence and proceed according to reactions (2.1) through to (2.5).

SCR catalyst formulations include vanadium (e.g. V_2O_5-TiO_2-WO_3), Cu-Zeolite and Fe-Zeolite.The difference in NO_x reduction performance of these catalysts formulations lies in their ammonia storage capabilities and resistance to elevated temperatures (Chi, 2009). Furthermore, the exhaust gas temperature has to be above 200°C to avoid the formation of explosive ammonium nitrate (NH_4NO_3), nevertheless, temperatures below 250°C can cause catalyst fouling through the formation of ammonium sulphate ($(NH_4)_2SO_4$) but this deactivation is reversible if the catalyst is operated again at higher temperatures.

Ammonia slip is another associated problem with this technology, though generally avoided or minimized by the precise injection of urea based on the required ammonia for the SCR reaction. As can be seen from reaction (2.1), stoichiometry occurs at an NH_3/NO_x ratio of approximately 1 and in practice, the ratios used are between 0.9 and 1 to minimize NH_3-

slip (Majewski and Khair, 2006). Additionally, NH_3-slip can be minimized further through the adsorption capacity (for NH_3) of the SCR catalysts, due to their strongly acidic surface properties; especially at low exhaust gas temperatures (Kleemann et al., 2000; Koebel et al., 2000). However, ammonia slip increases at higher NH_3/NO_x ratios although it decreases with increasing temperatures.

Urea-SCR is now in production given its proven track record as a durable solution for the abatement of NO_x emissions from diesel exhaust gas with NO_x reductions consistently above 80% having been demonstrated (Shimizu and Satsuma, 2007). Furthermore, the infrastructure for urea delivery is taking shape with more and more refilling stations being established. Although urea-SCR offers superior NO_x reduction activity, other advanced after-treatment technologies are still being researched owing to their possible simplicity and comparable efficiency, as discussed in the following sections.

2.2.1.2. HC-SCR

In this process, SCR catalysts are used to selectively reduce the NO_x emissions in diesel engine exhaust. In HC-SCR of NO_x a variety of reductants (HC-based fuels) can be used in relation to what catalyst is being employed. This technology is one of the simpler solutions for NO_x abatement provided that the proposed catalysts are able to operate both in the high temperature regions (> 350 °C) and low temperature regions (< 350 °C). In catalytic HC-SCR, firstly the NO is activated into NO_2 (reaction 2.9) and the HC reductant is activated into a HC-oxygenate. The HC-oxygenate then reacts with NO_2 to form N_2, CO_2 and H_2O (reaction 2.10) according to the simplified reactions:

$$NO + O_2 \rightarrow NO_2 \tag{2.9}$$

$$C_xH_yO_z + NO_2 \rightarrow N_2 + CO_2 + H_2O \tag{2.10}$$

The addition of H_2 to the exhaust gas stream aids in the faster kinetics of reaction 2.9 and 2.10 over the SCR catalyst; nevertheless, there are a lot of intermediate reactions taking place at the same time. Generally accepted is the fact that the NO + O_2 reaction also leads to the production of surface nitrate species (NO_3^-), while the interaction between HC and O_2 leads to the formation of acetate species ($CH_3CO_2^-$), both whose kinetic rates are increased by the addition or presence of H_2 gas into the exhaust gas stream. The reaction between the surface nitrates and acetate yields nitrogen (N_2) via isocyanate (NCO) and cyanide (CN) species (Lee et al., 2001; Shibata et al., 2003, Shimizu et al., 1999). The more complete mechanism (showing the intermediate reactions) of the reduction of NO_x using hydrocarbons is illustrated in Figure 2.1, below.

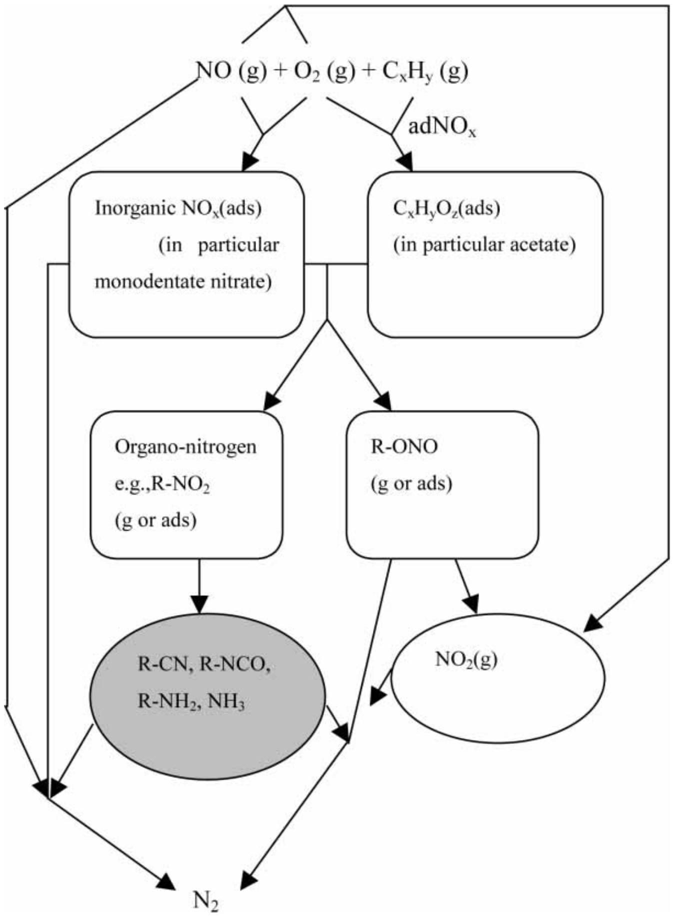


Figure 2.2: Reaction scheme of the oxidation-reduction mechanism of NO_x in HC-SCR (Meunier et al., 2000)

However, the competitive non-selective oxidation of HCs can also occur through the reaction pathway

$$HC + O_2 \rightarrow CO_2 + H_2O \tag{2.11}$$

Thus the selectivity of the SCR catalysts for NO_x is important as the amount reduced can be seen to be dependent on the amount of available reductant, thus equation (2.11) is undesirable.

Among the various SCR catalysts available, it is generally accepted that the Ag-Al_2O_3 catalyst with a 2 wt. % Ag loading is the most promising catalyst for the reduction of NO_x due to its high activity and selectivity (Burch et al., 2002; Masuda et al., 1996). This high activity and selectivity for the SCR of NO_x is observed when various HCs and oxygenated HCs are used as reductants in lean diesel exhaust (Satokawa, 2000; Thomas et al., 2005; Zhang et al., 2007a; Zhang et al., 2007b). However, its associated low temperature limitations need to be resolved for it to become a commercially viable NO_x abatement option in diesel vehicles (Kim and Nam, 2004; Lindfors et al., 2004).

The quality of the HC reductant used is an important parameter for improved NO_x reduction activity over the silver based catalyst. In the case of diesel engines, the primary HC is diesel fuel but other HCs can be injected into the exhaust stream to aid in the reduction of NO_x. For example, ethanol (C_2H_5OH) has been reported to be extremely effective for the SCR of NO_x over Ag-Al_2O_3 catalysts (Yu et al., 2004; Zhang et al., 2007a). Various other HC species, particularly alkanes, such as propane (Satokawa, 2000), octane, decane and dodecane (Houel et al., 2007a; Houel et al., 2007b), to name but a few, have all been shown to be active in the reduction of NO_x over Ag-Al_2O_3 catalysts. Although long chain alkanes such as diesel and synthetic diesel fuels can improve the catalyst low temperature (< 350 °C) NO_x reduction activity, the catalyst is sensitive to poisoning by carbonaceous species deposits (Theinnoi et al., 2007; Houel et al., 2007b). It has been shown by other researchers that the poisoning mechanism of Ag-Al_2O_3 catalysts at low temperatures is not only limited to the deposition of C-containing species but is also due to nitrate formation and accumulation. For example, it has been reported that the deactivation of Ag-Al_2O_3 is due the accumulation of the nitrate species NO_3^+ (Creaser et al., 2009). Creaser et al. (2009) concluded in their study using octane as a reductant that NO_3^+ accumulates on the catalyst surface in the absence of hydrogen through the reaction of NO_2^+ and O^+ free radicals. When diesel type fuels (long chain HCs) are used for the reduction of NO_x emissions, both deactivation mechanisms (i.e. C-species & nitrate accumulation) can occur consecutively leading to Ag-Al_2O_3 catalyst activity decay.

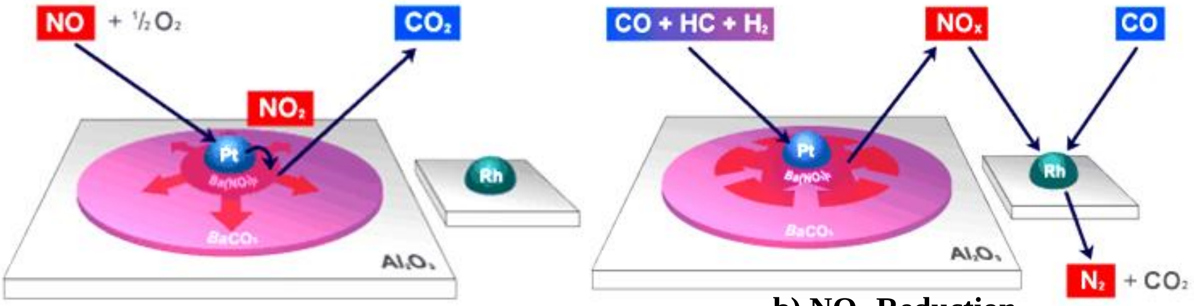
However, hydrogen addition into the exhaust gas upstream the SCR catalyst in the presence of unburned or injected HCs improves the low temperature NO_x conversion activity by preventing catalyst poison accumulation (Houel et al., 2007a; Satokawa et al., 2007; Shimizu et al., 2007). There is also general agreement about the positive effect of hydrogen on activating various hydrocarbons and on the overall rate of the HC-SCR of NO_x reduction reaction (Breen and Burch, 2006; Satokawa et al., 2003; Zhang et al., 2007b). Eränen et al. (2004) found that H_2 has two main functions, namely, contributing to improved oxidation of a wide variety of different surface species, resulting in faster production of key intermediates, and aiding in the formation of activated NO_x species for the gas-phase reactions.

Reactant ratios also play an important role in the NO_x conversion selectivity of the Ag-Al_2O_3 catalysts e.g. excessively high HC:NO_x ratios tend to deactivate the catalyst by coking (Houel et al., 2007b, Theinnoi et al., 2008a), whereas ratios which are too low will not be enough for good NO_x reduction activity given the lack of reductant. The reductant quantity strongly depends on the exhaust gas temperature, since at elevated temperatures reductant oxidation may be more prevalent and as a result higher volumes will be required to sustain the NO_x reduction efficiency.

As with all other advanced after-treatment devices, sulphur content in the combustion fuel leads to the SCR catalyst used being poisoned by the formed sulphur compounds; which then accumulate on the catalyst active sites, in turn leading to the loss of NO_x selectivity and reduction efficiency (Shimizu et al., 2007; Shimizu and Satsuma, 2007). Nonetheless, this effect is reversible through the thermal decomposition of the sulphate species at increased exhaust gas temperatures (circa 450 °C or higher).

2.2.1.3. NO_x Adsorbers or Traps

A NO_x adsorber catalyst (NAC) is an alternative after-treatment device designed for use in lean burn exhaust gas. The design was devised to counter problems experienced in other after-treatment devices such as the need for a continued reductant supply to maintain a given C_1:NO_x ratio in SCR (Mital et al., 2003).



a) NO_x Trapping **b) NO_x Reduction**

Figure 2.3: Schematic showing the NAC process under, a) lean exhaust gas operation (trapping) and b) rich exhaust gas operation (regeneration). (Courtesy of Johnson Matthey Plc)

The principle chemical workings of the system have been well documented since the early work by Miyoshi et al., 1995 and Brogan et al., 1998. Generally, the process involves the adsorption of NO_x under lean operation and then its subsequent release and reduction under rich operation. The NAC wash-coat consists of three main components, namely, (i) an oxidizing catalyst e.g. Pt, (ii) storage medium e.g. barium carbonate ($BaCO_3$) and (iii) a reducing catalyst e.g. Rh. Illustrated in Figure 2.3 is the general principle workings of a $Pt/BaCO_3/Al_2O_3$ NAC with a Rh-based reducing catalyst.

The key reaction steps are summarized as follows (Gill et al., 2004): firstly during the lean operation phase (Figure 2.3a), the NO_x which is primarily NO is oxidized into NO_2 through the reaction

$$2NO + O_2 \rightarrow 2NO_2 \tag{2.12}$$

The formed NO_2 is then stored by the storage medium (M), in this case in the form of barium nitrate. MCO_3 is the stable form of the adsorbing material and the formed $M(NO_3)_2$ is the stable NO_x containing compound

$$MCO_3 + 2NO_2 + \frac{1}{2}O_2 \rightarrow M(NO_3)_2 + CO_2 \tag{2.13}$$

When the adsorber catalyst becomes saturated with NO_x elevated exhaust gas temperatures are required for regeneration (Figure 2.3b). Induced rich conditions in the exhaust gas increase the temperature causing the stored nitrate species to become thermodynamically unstable and desorb from the adsorber forming NO and NO_2 according to

$$M(NO_3)_2 + 2CO \rightarrow MCO_3 + NO + NO_2 + CO_2 \tag{2.14}$$

This is the regeneration stage of the storage catalyst, ready for the next lean operation phase. The released NO_x is then reduced over the reducing catalyst in the presence of CO, HC and H_2 to form N_2 through reaction pathways such as

$$NO_2 + CO \rightarrow NO + CO_2 \tag{2.15}$$

$$NO + CO/HC \rightarrow \frac{1}{2}N_2 + CO_2/H_2O \tag{2.16}$$

Current NACs consist of an alkaline earth, primarily barium-based adsorbers or combined systems of Ba and an alkali metal (e.g. potassium (K), sodium (Na), lithium (Li)); with Ba + alkali metal adsorbers providing the better NO_x conversion (Dou et al., 2002; Majewski and Khair, 2006).

Overall NO_x reduction efficiencies are high (> 80%), for both fresh and aged catalysts over a typical diesel cycle. However, some problems may still exist, for example, Mital et al., (2003) reported in their NAC study for light duty engines that NH_3 formation was proportional to the HC injection quantity but surmised that if the control strategy is well defined to avoid over injection, NH_3 formation may not be a problem. Also, sensitivity to sulphur oxides remains a challenge for NACs. Sulphur oxides (SO_x) are almost exclusively sulphur dioxide (SO_2) and react with the catalyst in the same way as NO_x (Gill et al., 2004; Majewski and Khair, 2006; Takeuchi and Matsumoto, 2004). The typical reactions are as follows:

$$2SO_2 + O_2 \rightarrow 2SO_3 \qquad (2.17)$$

$$BaO + SO_3 \rightarrow BaSO_4 \qquad (2.18)$$

Matsumoto et al., 2000 and Takeuchi and Matsumoto, 2004 identified two types of sulfur poisoning mechanisms on a NO_x-adsorber catalyst with the components as shown in figure 2.3, above: (i) the SO_2 is oxidized on the precious metal and reacts with the alumina (γ-Al_2O_3) to form aluminium sulphate ($Al_2(SO_4)_3$ which plugs the micro-pores of γ-Al_2O_3, and (ii) the SO_x reacts with the NO_x storage components to form barium sulphate ($BaSO_4$, see reaction (2.17) and (2.18)) and since sulphates are more stable than nitrates, once the storage compound forms the sulphate, NO_2 storage is no longer possible and the catalyst gradually loses its activity. Temperatures as high as 700 °C have been reported for efficient desulphurization of the NAC while those required for NO_x regeneration are lower than 500 °C

(Blakeman et al., 2003; Molinier, 2001). Research is ongoing with regards investigating sulphur resistant oxides for use in NACs and among them TiO_2-ZrO_2 complex oxides are accepted as generally possessing better physical and chemical properties in addition to tolerance to sulphur poisoning (Ito et al., 2007; Liu et al., 2008; Takahashi et al., 2006).

The activity window of NACs is fairly wide extending from ~ 200 – 500 °C, with the low temperature region determined by the catalyst activity regards the oxidation of NO to NO_2 as well as NO_x release and reduction, while the upper temperature is dependent on the nitrates thermodynamic stability, as they tend to undergo thermal decomposition even in the lean phase at high temperatures (Majewski and Khair, 2006). The ability to widen the temperature window of the NAC either individually or in combination with other systems, as shown by Blakeman et al., 2003, allows for greater flexibility for the designers of future diesel emissions control systems. As a result, the NAC is a well suited candidate for diesel NO_x after-treatment.

2.2.2. Oxidation and Filtration Devices

NO_x reduction activity is currently interdependent on other technologies, such as diesel particulate filters (DPFs) and diesel oxidation catalysts (DOCs). The DPF and DOC technology's primary role is to reduce emissions of CO, HCs and PM, which are harmful components present in diesel engine exhaust gas. At the same time, the reduction of these has another important benefit, since cleaner exhaust gas at the inlet of after-treatment devices e.g. NAC and SCR catalysts (located downstream of the DOC/DPF in a typical configuration), can improve durability and NO_x reduction efficiency.

2.2.2.1. Diesel Oxidation Catalyst (DOC)

A common DOC is designed to continuously oxidize carbon monoxide, gas phase HCs, and the soluble organic fraction (SOF) of PM to carbon dioxide (CO_2) and water (H_2O), at relatively low exhaust gas temperatures typical of those from diesel engine operation (< 350 °C). Thus by so doing, a DOC reduces the total PM number and mass in the exhaust. Pt-based catalysts, with the Pt in a very highly dispersed form for thermal stability, are used to oxidize CO and HC. To improve cold start DOC efficiency, zeolites are now being incorporated into the formulation for the purpose of trapping HCs at low temperatures and then releasing them at the DOC operating temperature, thus improving efficiency (Andersson et al., 2007; Farrauto and Voss, 1996; Twigg, 2007). Since the diesel engine operates on a lean burn cycle, there is sufficient oxygen (O_2) necessary for the oxidation reactions. The main reactions over a DOC follow these reaction pathways

$$2CO + O_2 \rightarrow 2CO_2 \tag{2.19}$$

$$[HC] + O_2 \rightarrow CO_2 + H_2O \tag{2.20}$$

Work by Nakane et al. (2005) in their aging study of a DOC showed that long term operation only resulted in worse light-off temperatures but the reduction efficiency is maintained to levels similar to those achieved with a fresh catalyst. However, significant deactivation can occur under certain critical conditions as reported by Andersson et al. (2007), who in their study on the deactivation of DOCs established three modes of deactivation, namely, that (i) high temperature and presence of water (H_2O) caused significant HC storage capacity loss, (ii) low temperature, generally in combination with H_2O, facilitated the adsorption of sulphur species on the washcoat and (iii) loss of low temperature performance was due to accumulation of catalyst poisons and degradation from high temperature aging.

Due to the reactions over the DOC being highly exothermic, small increases in NO_x are not uncommon. On the other hand, there is a reduction in the overall PM in diesel exhaust due to the oxidative atmosphere which can aid the oxidation of some soot. In practical diesel exhaust applications, total PM reductions (number and mass) over a DOC depend on the engine operating conditions, as this influences the exhaust gas temperature and composition, as well as the size and structure of inherent PM or organic compounds (Lakkireddy et al., 2006a).

In terms of solid particulate (soot) reduction, the early work by Neeft et al. (1997) on catalysts for the oxidation of soot from diesel exhaust, reported that surface interaction of the soot with a catalyzed monolith channel is still the major problem with regards soot reduction efficiency limitations. This is due to the ‘loose contact’ between the catalyst and soot in an open channel catalyst-coated monolith. Wall flow filters which physically trap soot have since been developed and at present are catalyzed so as to continuously trap and regenerate (oxidize) soot, for continued filtration.

It is therefore not surprising that DOCs are used in several after-treatment devices, for example, in DPF regeneration through increased inlet exhaust gas temperatures (during active operation); and in SCR systems allowing for more selective and reactive reductant species to be added or injected upstream the SCR catalysts.

2.2.2.2. Diesel Particulate Filter (DPF)

A DPF is designed to trap and periodically or continuously burn off the accumulated particulate matter (PM) in engine exhaust gas. The soot accumulated in the DPF has to be kept below a balanced threshold so as not to cause undesirable back pressures in the exhaust tailpipe (Lakkireddy et al., 2006b; Watanabe et al., 2007) which could reduce the fuel economy and engine durability. In simple terms, the DPF has to satisfy this simple equation during its operation

$$PM\ combustion\ rate \geq PM\ accumulation\ rate \tag{2.21}$$

There exist several forms of the DPF, ranging from the simple type to the more complicated, more efficient, modern type. A diesel vehicle equipped with a functioning filter will emit no visible smoke from its exhaust tailpipe. The most common types and configurations of diesel particulate filters will now be discussed.

Wall-Flow Filter: These filters are usually made from cordierite or silicon carbide. They are monolithic substrates that consist of alternately plugged channel ends to force exhaust gas through porous walls, thus trapping any solid matter (Figure 2.4). Efficiencies in these filter traps are high (> 90 %), but in their simplest form, there is no regeneration method, meaning that once they are fully loaded with soot they have to be specially emptied or replaced by new ones.

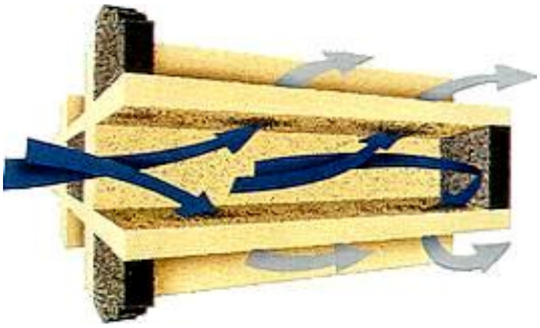


Figure 2.4: A typical wall-flow monolithic filter schematic showing how the exhaust gas is forced to flow through the porous walls and consequently filtered. (Courtesy of Corning Inc)

Wall-flow filters are essentially the building block of the latest and more innovative regenerative diesel filters.

Continuously Regenerating Trap (CRT$^{®}$): The setup consists of a DOC placed in front of a particulate filter, which is a wall-flow filter (Figure 2.5). The purpose of the DOC is to oxidize the HC and CO in the exhaust (as described in the DOC section above) and also to convert some of the NO emissions from the engine into NO_2 according to the reaction

$$2NO + O_2 \rightarrow 2NO_2 \tag{2.22}$$

The NO_2 then reacts with the accumulated PM in the filter trap oxidizing it to CO_2 and NO. The reaction is as follows

$$[C] + 2NO_2 \rightarrow CO_2 + 2NO \tag{2.23}$$

This filter is one of the most widely used filters in the world but there are several conditions to be met for continued efficiency e.g. the exhaust gas temperature has to be maintained above 250 °C for approximately 50 % of the time with a NO_x:PM ratio of 20:1 or greater (Sumiya and Yokota, 2004).

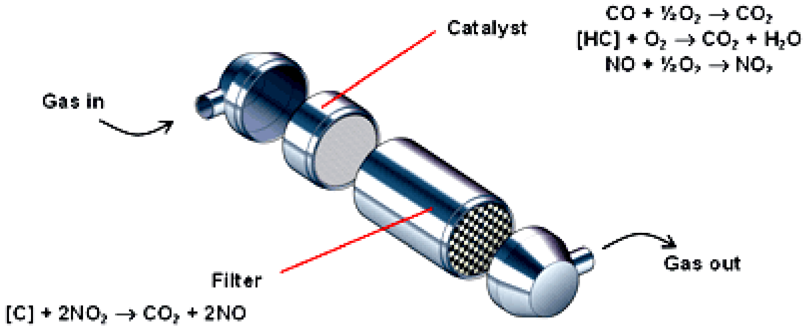


Figure 2.5: A schematic showing the operation of a continuously regenerating trap (CRT®) and the reactions over the respective components. (Courtesy of Johnson Matthey Plc)

There is another similar design with comparable efficiencies which has the DOC formulation on the DPF itself, called the catalyzed DPF (CDPF) or the catalyzed soot filter (CSF). In this system, there is no DOC at the front and the working principle is the same as that of the CRT®, but with all the reactions taking place on the catalyzed filter.

Catalyzed Continuously Regenerating Trap (CCRT®): This filter is a catalyzed version of the CRT® and the reactions taking place are essentially the same (Figure 2.6). On the other hand, due to the catalyzed wall-flow filter, when NO is formed in the filter after the initial regeneration, some of it is converted back to NO_2 and with it more PM is oxidized. Efficiency is the same as that of the non-catalyzed CRT®. Catalysis of the DPF allows for the filter to be used under lower exhaust gas temperatures than those for the CRT® and also at lower NO_x:PM ratios.

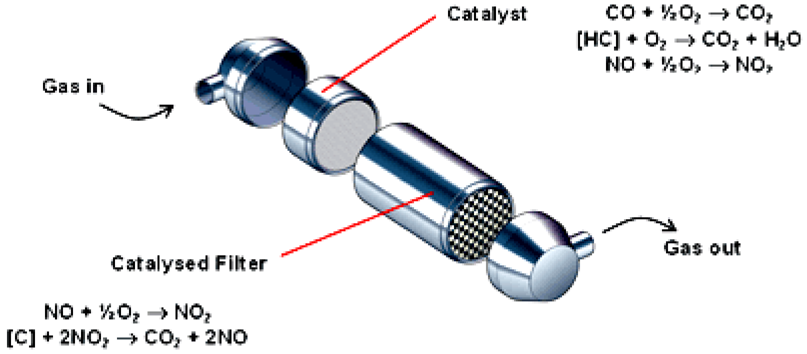


Figure 2.6: A schematic showing the operation of a catalyzed continuously regenerating trap (CCRT®) and the reactions over the respective components. (Courtesy of Johnson Matthey Plc)

2.2.3. Fuel Reforming

There is growing interest in the possibility of on-board fuel reforming to produce H_2-rich synthetic gas for different applications such as fuel cells, IC engines and after-treatment systems. In these systems, H_2 is the active gas for either assisting or enhancing their operation or efficiency. Unfortunately, H_2 gas is not available as a primary source of energy such as hydrocarbon fuel used in the automotive , aerospace and other industrial sectors, but has to be produced through the conversion of hydrogen-rich energy carriers, such as natural gas, petroleum derived hydrocarbons, methanol and coal (Naidja et al., 2003). To produce the hydrogen gas, fuel reforming techniques are used and the process essentially involves the catalytic cracking of the source feed into synthesis gas (H_2 + CO).

There are several methods that could provide the H_2-rich gas for the different applications it could be used for, and the most common techniques are partial oxidation (PO_x), steam reforming (SR) and auto-thermal reforming (ATR). These processes involve the reformation of primary (natural gas, gasoline and diesel) fuels and secondary (methane and methanol) fuels (Naidja et al., 2003; Tsolakis and Golunski, 2006).

Partial Oxidation (PO_x): this reaction is highly exothermic in nature and involves the 'partial' oxidation of the HC source fuel into CO and H_2 in the presence of air, according to reaction 2.24. The O_2 content has to be regulated so as to provide the best process efficiency for H_2 production, with the overall best efficiency being observed as the O/C ratio approaches 1 (Tsolakis and Megaritis, 2004; Tsolakis and Golunski, 2006). The reaction is self-sustaining once initiated and the initiation itself is achieved by completely combusting part of the fuel according to reaction 2.25. Nevertheless, PO_x is not usually considered to be an attractive technology in terms of efficiency because it is an exothermic process and the resulting H_2-containing reformate gas has a lower calorific value than that of the original feedstock (Houseman and Hoehn, 1974).

$$C_xH_yO_z + \left(\frac{x}{2} - \frac{z}{2}\right) O_2 \rightarrow xCO + \frac{y}{2} H_2 \tag{2.24}$$

$$C_xH_yO_z + \left(x + \frac{y}{4} - \frac{z}{2}\right) O_2 \rightarrow xCO_2 + \frac{y}{2} H_2O \tag{2.25}$$

Steam Reforming (SR): the reaction takes place at high temperatures (> 800 °C) and involves the interaction of superheated water vapour and HC fuel to produce synthesis gas. This reaction is endothermic and follows the reaction pathway

$$C_xH_yO_z + xH_2O \rightarrow xCO + \left(x + \frac{y}{2}\right) H_2 \tag{2.26}$$

Commercially, steam reforming of natural gas is the most common method of hydrogen mass-production. It is the most cost effective method and has maximum hydrogen production efficiencies of approximately 75 %.

Auto-thermal Reforming (ATR): utilizes the heat from the exothermic reactions taking place after the initiation, for use in the sustenance of the endothermic reactions as they require a continued heat supply (Trimm et al., 2004). The exothermic reactions involve the fuel combustion and partial oxidation while the endothermic reactions include the SR (discussed above) as well as the dry reforming (DR) and the water gas shift (WGS) reactions. DR involves the reaction of the HC with CO_2 to yield the syngas (reaction 2.27); the reaction normally occurs at temperatures above 800°C, similar to those for the SR reaction. On the other hand, the WGS takes place at temperatures between 550 – 750 °C, and involves the reaction of CO and H_2O to yield H_2 and CO_2 (reaction 2.28). The overall process efficiency of auto-thermal reforming is generally lower than that of steam reforming, however, an auto-thermal reforming plant is cheaper to build compared to a steam reforming plant.

$$C_xH_yO_z + xCO_2 \rightarrow 2xCO + \frac{y}{2}H_2 \tag{2.27}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \tag{2.28}$$

All the aforementioned reactions take place at specific temperature profiles across the reforming catalyst as shown in Figure 2.7. This figure shows that the oxidation reactions i.e. PO_x and combustion, instigate the rise in temperature near the frontal face of the monolithic reforming catalyst and when the appropriate temperatures have been reached the DR and SR reactions start. Since the DR and SR reactions are endothermic in nature, their initiation requires the highest temperatures, and once started, heat is absorbed from the system leading to the gradual loss as depicted (Figure 2.7). As the temperature drops, the WGS reaction is instigated. The WGS reaction is a reversible reaction which occurs within a certain temperature range above which the reverse reaction is favoured over H_2 yield. This reaction takes place at the lowest temperatures and towards the back end of the reforming catalyst.

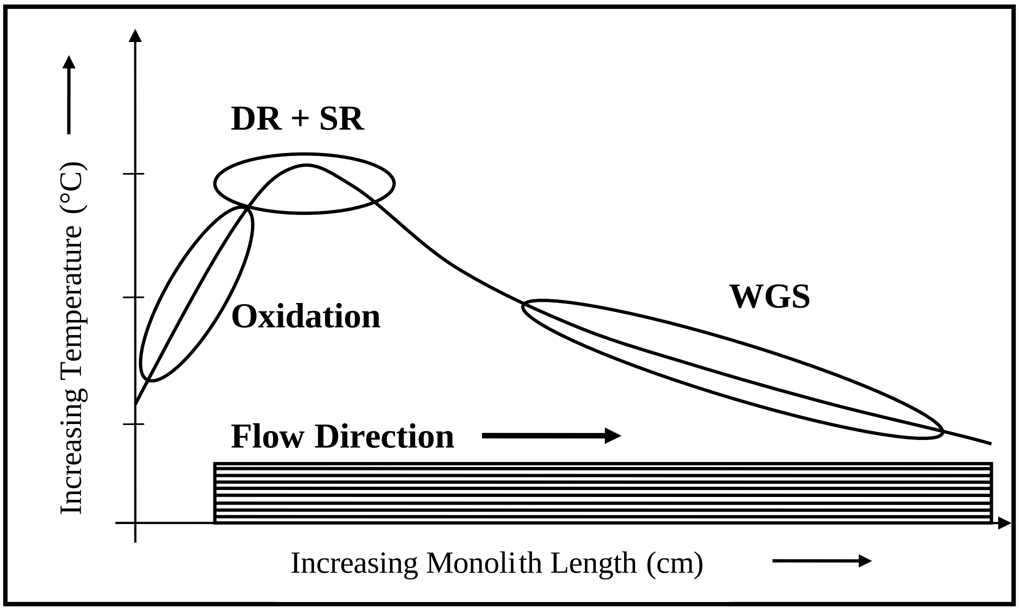


Figure 2.7: The typical temperature profile over a reforming catalyst, showing the different processes that can take place with the correct amount of reactants in the feed gas.

Since the focus of this research thesis is on diesel emissions, the primary focus for fuel reforming will be H_2 production for after-treatment devices. After-treatment devices have been shown to be positively responsive to the addition of H_2 into the exhaust feed, especially at low temperatures. For example, the H_2 effect on lean NO_x catalysts has been extensively investigated for application into urea selective catalytic reduction (urea-SCR) and hydrocarbon selective catalytic reduction (HC-SCR) for the purposes of enhancing the low temperature NO_x activity of the respective after-treatment methods (Satokawa, 2003; Shimizu et al., 2007; Shimizu and Satsuma, 2007).

One of the major obstacles at the present time is how to store H_2 onboard the vehicle for on-demand supply as of when its required. Thus, a hydrogen source is required and instead of having an external hydrogen storage tank on-board the vehicle, fuel reforming techniques could be applied for on-board hydrogen production. Exhaust gas fuel reforming could be utilized, whereby part of the engine exhaust gas is used for the reforming of HC fuel, thus retaining some of the heat from the combustion process to help light-off the reformer catalyst.

Exhaust gas fuel reforming has been reported to be similar in nature to that of ATR (Tsolakis and Golunski, 2006). However, for on-board fuel reforming systems to be considered, minimization and optimization of the system would be necessary.

Fuel reforming catalyst formulations are generally a closely guarded secret in the automotive sector for commercial reasons. However, they mainly consist of precious metals e.g. PGMs supported on metal oxides. They are designed to be thermally durable to high temperature limits since the reforming processes are highly exothermic in nature, with temperatures regularly exceeding 800°C.

2.3. Engine modifications

There have been numerous developments and improvements to diesel engine design, but the amount of NO_x and PM reductions from these modifications is not going to be enough to meet the future emissions legislation (e.g. Euro 6, for light duty diesels from 2014). As a result, engine modifications coupled with after-treatment technology will be essential in the NO_x and PM reduction strategy. Some popular engine modifications are discussed below.

2.3.1. Injection timing

Injection timing refers to when in the diesel cycle the fuel is injected relative to the crankshaft during the compression stroke and is generally defined by crank angle degrees (CAD) before TDC. Two methods exist that can be used for the purpose of improving various aspects associated with diesel combustion e.g. emissions and/or brake specific fuel consumption (bsfc); these are, advanced injection and retarded injection. The processes including their advantages and disadvantages are discussed below.

Advancing Injection Timing: involves the start of injection (SOI) being earlier than the original standard timing. Injection timing advance has a tendency to increase unburned HC emissions, through the extension of the ignition delay period which leads to a wider lean flame-out region (Majewski and Khair, 2006). Another cause for HC increase is due to the fuel being injected into a lower pressure medium with lower temperatures which can increase fuel impingement in the combustion chamber (Khan and Grigg, 1971). Furthermore, the longer the ignition delay period the greater the portion of fuel injected during this period, leading to an increase in the premixing of the A/F mixture prior to ignition. Since NO_x formation is related to the duration of the premixed combustion phase, advancing the injection timing has a tendency to increase the premixed fuel portion and as a result, increases the NO_x output from the combustion process.

Retarding Injection Timing: is when the SOI of fuel is later in the compression cycle than the original standard setting. The ignition delay period tends to be shorter with retarded injection and consequently the premixing of the A/F mixture is reduced. This has the effect of reducing the combustion chamber peak temperatures and ultimately leads to lower NO_x formations. Sayin et al. (2009) noted that the retardation of injection timing shifted the whole combustion process further into the expansion stroke, which influences the progression of combustion and formation of emissions as more fuel burns after TDC. Due to the benefit of reducing NO_x with retarded injection timing, this technique is utilized for this purpose in diesel engines (Majewski and Khair, 2006).

There is however a trade-off when retarding injection timing, namely, the favourable decrease in NO_x emissions is accompanied by an increase in the brake specific fuel consumption and PM emissions of the engine. To reduce the fuel economy, measures such as higher compression ratios and injection pressures have been adopted, such as common rail systems.

Injection pressure: increasing the injection pressure leads to an increase in fuel economy, due to better fuel spray, atomization and spray penetration. Common rail fuel injection systems are now common place and are designed with increased injector holes coupled with finer hole geometries. In the common rail system, the generation of the injection pressure is separate from the injection itself. Using a high-pressure pump, pressures greater than 1800 bar (determined by the engine control unit - ECU), can be achieved in the accumulator or ‘rail’ independent of engine operating speed and fuel injected. The fuel is then fed into the injectors which inject the precise amount of fuel in a fine spray into the combustion chambers. Parameters such as the rail pressure, injection timing and duration are all controlled electronically for greater precision.

In their study on the effect of injection pressure on a V6 engine, Abdullah et al. (2009) noted that the use of increased injection pressures led to significant improvement in engine performance and emissions for almost all engine conditions tested with only the NO_x emissions increased. Other advantages associated with the use of these systems include the following (Khair, 2003):

- Fuel pressure does not depend on the engine speed and load conditions allowing for flexibility in controlling both the injection rates and timing.
- High injection pressures and good spray preparation are possible even at low engine speeds and loads.
- Capability to deliver stable, small pilot injections can be used for decreased NO_x emissions and noise. Up to 5 – 7 injections a cycle are now achievable.

- Option for a post injection may be used together with such emission control technologies as particulate filters, lean NO_x catalysts, or NO_x adsorbers.
- For most engines, common rail systems can replace conventional injection systems without requiring major engine modifications.

2.3.2. Exhaust Gas Re-circulation (EGR)

The principle behind EGR is that a portion of the exhaust gas from the combustion process is re-circulated into the combustion chamber via the inlet system e.g. Figure 2.8. EGR is applied for the purpose of reducing NO_x emissions from the combustion process (Heywood, 1988). EGR is not a new technology; it has been utilized in gasoline passenger vehicles since the mid-1970s and was later introduced to diesel passenger vehicles, but only recently (from early 2000s), has it been introduced into heavy-duty diesel vehicles (Hawley et al., 1999).

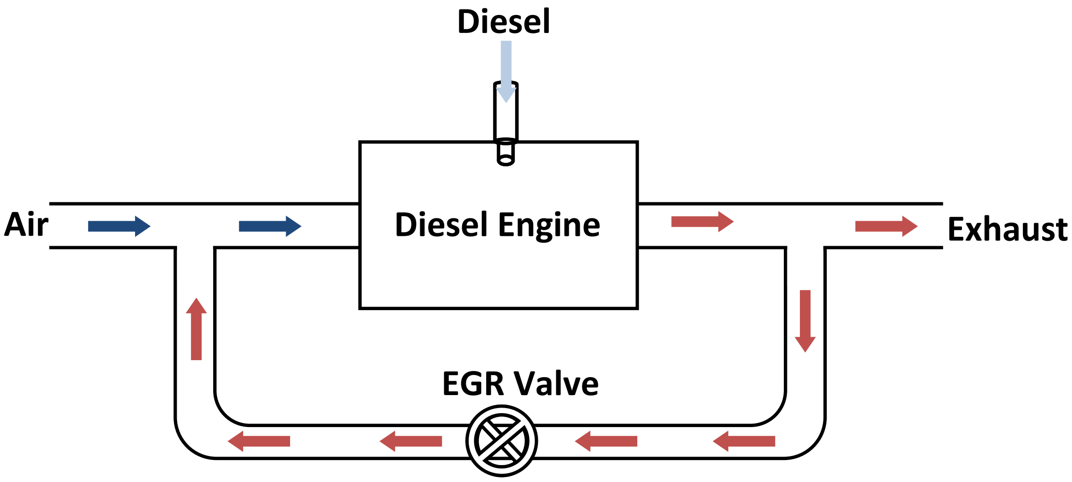


Figure 2.8: A schematic showing the principle of exhaust gas re-circulation (EGR).

The introduction of EGR influences diesel engine combustion through three main effects, i.e. thermal, chemical and dilution, as identified and discussed by Ladommatos et al. (1996, 1997):

Thermal effect: is related to the increase in specific heat capacity of the inlet charge given that the exhaust gas consists mostly of H_2O and CO_2 which have significantly higher specific heat capacities than air; findings reverberated by Khair (2006) and Zheng et al. (2004). There could also be an increase in the inlet charge temperature if ‘hot’ EGR is used, however, this would affect the volumetric efficiency of the engine; a phenomenon also referred to as thermal throttling as reported by Hountalas et al. (2008).

Chemical Effect: this effect involves the diluent (EGR) gases dissociating or actively participating in chemical reactions during the combustion process. Heat is consumed through these highly endothermic reactions such as those of the dissociation of CO_2 and H_2O, leading to the reduction in the peak in-cylinder temperature.

Dilution Effect: is related to the dilution of the inlet charge with inert exhaust gas which results in lower peak flame temperatures, through the added mass of non-reacting gas in the combustion zone absorbing heat and therefore lowering the temperature. Experimental work has shown that reduction in oxygen concentration resulted in reduced NO_x with increased PM and HC as confirmed by Shiozaki et al. (1996) and Ropke et al. (1995). Additionally, the mass fraction of oxygen (O_2) available for the reactions associated with the formation of NO_x is reduced, leading to reduced NO_x formation rate, but this is far less important compared to the lowering of the flame temperature.

In another study on EGR effects on diesel combustion heat release, Ladommatos et al. (1998) explained that the overall NO_x output is decreased due to the charge gas having a higher specific heat capacity, which has a corresponding increase in the ignition delay period in the combustion phasing of an engine running with EGR, resulting in the products of combustion spending shorter periods at high temperatures. However, the EGR temperature and method of application has significant influence. For example, in their review of diesel engine exhaust gas re-circulation, Zheng et al., (2004) showed that NO_x reductions greater than 70 % are possible with enhanced cooled EGR, whereas with the use of hot EGR only 25 % reductions were observed at best.

Hot EGR: consists of external EGR without the use of a heat exchanger mechanism (to cool the re-circulated exhaust) or it can be internal residual exhaust gas trapped via valve overlapping (Schwoerer et al., 2004).

Cool EGR: is administered by external piping fitted with a control valve and a heat exchanger to cool (extract heat from) the exhaust gas before mixing with the fresh air charge. By cooling the EGR, the heat absorbing capacity of the inlet charge increases and in turn lowers the peak in-cylinder temperature more which further reduces NO_x emissions.

External EGR consists of ‘external’ piping for the EGR feed (as in Figure 2.8). On the other hand, ‘internal’ EGR consists of trapping residual exhaust gas inside the combustion chamber ready for mixing with the next fresh air charge and is achieved by valve timing events. However, the former method allows for more EGR concentrations to be administered compared to the latter and consequently, the former is the most common method for EGR applications. EGR rate (by volume) can be defined based on the CO_2 content as follows

$$\%EGR = 100 \times \frac{CO_{2,intake} - CO_{2,air}}{CO_{2,exhaust} - CO_{2,air}} \tag{2.29}$$

or through the reduction of the volumetric flow rate of air into the engine by

$$\%EGR = 100 \times \frac{\dot{V}_o - \dot{V}_i}{\dot{V}_o} \tag{2.30}$$

where $\dot{V}_o$ and $\dot{V}_i$ are the measured intake air volumetric flow rates ‘without’ and ‘with’ EGR, respectively.

There is however, a trade-off with EGR use. The more EGR used within an engine, the more the NO_x emissions are reduced during combustion, but at the expense of increased PM emissions, which are regulated. This physical characteristic is more commonly referred to as the NO_x/PM trade-off. The increase in PM emissions is attributed to the prevailing incomplete combustion. Due to the fact that the EGR is diluting the fresh air charge and displacing the O_2 in the cylinder, the soot oxidation rate drops leading to higher concentrations of carbonaceous PM species. Ladommatos et al. (1998) also commented on how the increased ignition delay led to a shift in the combustion process towards the expansion stroke resulting in earlier flame quenching and yielding the increased incomplete combustion products i.e. PM and HC, in the exhaust gases. It is therefore apparent that the continued increase in the amount of EGR concentration will eventually lead to unstable combustion and prolonged use is suspected of compromising engine durability (Dennis et al., 1999; Majewski and Khair, 2006).

EGR amounts as high as 50 % have been reported for diesel engines at idle conditions where there is excess O_2 content in the exhaust gas. Diesel engines normally produce an exhaust stream that contains oxygen from 5 % at full load to 20 % during idle conditions (Zheng et al., 2004). The higher the engine load the more CO_2 and H_2O is produced, and if EGR is being employed, leads to higher specific heat capacities of the inlet charge, thus at low loads high EGR can be applied while lower EGR at high loads is sufficient.

In addition to the increased PM, the brake specific fuel consumption (bsfc) of the engine increases with increasing EGR amounts due to the lower combustion efficiency. With respect to emissions legislation and the discussed pros and cons of EGR, it is apparent that its application for future emissions legislation, especially in diesel engines, will have to be in conjunction with advanced engine modifications, precise control strategies and after-treatment devices.

CHAPTER 3

EXPERIMENTAL SETUP

The equipment that was used during the experimental stage of this research thesis is introduced in this chapter. This included the diesel bench engine, the lean catalysts and associated reactors as well as the exhaust gas analyzers. A concise description is offered as well as details of how the equipment was set up during the experiments to obtain the required measurements.

3.1. Test Bench Engine

The bench engine used in the experiments for this research thesis was a Lister Petter TR1 diesel engine. It is a direct injection, naturally aspirated, air cooled single cylinder diesel engine (Figure 3.1). A Thrige Titan direct current (DC) electric dynamometer with a load cell and a thyristor-controlled Shackleton System Drive was used to load and motor the engine. The engine specifications are detailed in Table 3.1.

The engine was equipped with standard test rig equipment for analysis purposes, which included K-type thermocouples with a range of 0 to 1250 °C and accurate to ± 2.2 °C (or 0.75 %) for measurement of the charge air inlet temperature, exhaust gas temperatures and oil temperature. The emissions measurement equipment was calibrated daily, before any recording of data, by automatically purging with air to provide a ‘zero’ reading and then supplying with a ‘span’ gas of known concentrations to assess whether the equipment was within acceptable error limits (~ 5 %). If the values measured by the emissions analyzer for the span gas were out by a certain factor, an auto calibration was done to compensate for the apparent error for that particular day. Finally, another ‘zero’ purge with air was done to ensure that the analyzer returned to zero values.

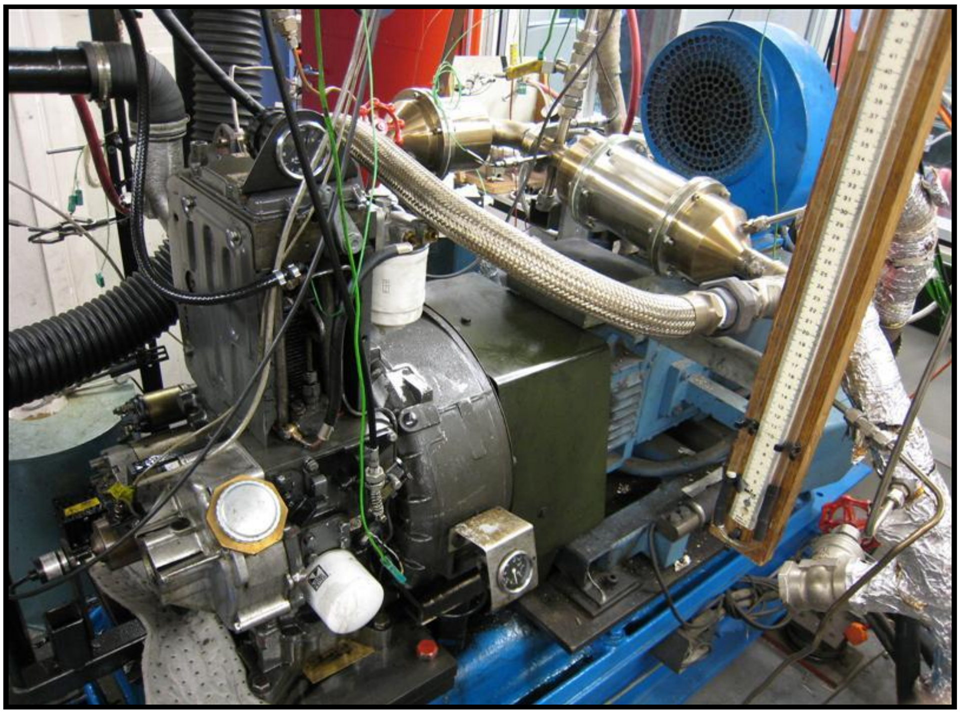


Figure 3.1: The single cylinder Lister Petter TR1 diesel engine used during the experimental work of this research thesis. The exhaust system with the catalyst reactors is also shown.

Table 3.1: Test bench engine specification

Engine Parameter	**Value**
Bore (mm)	98.4
Stroke (mm)	101.6
Displacement Volume (cm^3)	773
Compression Ratio	15.5
Maximum Power (kW)	8.6 @ 2500 rpm
Maximum Torque (Nm)	39.2 @ 1800 rpm
Standard Injection (°CA)	22

An engine oil check and exhaust tailpipe leak test was also conducted, after which the engine was warmed up before each set of tests were conducted in order to negate the effect of engine emissions fluctuations usually associated with cold-start operation. Atmospheric conditions such as the temperature and pressure within the test cell were also monitored during engine testing.

3.1.1. Diesel Engine Exhaust System

The engine exhaust system consisted of three stainless steel reactors into which various monolithic catalysts could be inserted for experimental purposes. During the warm-up period of engine operation, the ‘by-pass’ was utilized to minimize catalyst fouling before the required operational condition was reached, thus by-pass valve 2 was open while by-pass valve 1 remained closed (Figure 3.2). This was to allow the majority of the exhaust gas to ‘by-pass’ the catalysts. When the required engine operating condition was reached, all of the exhaust gas was allowed to flow through the catalysts by opening by-pass valve 1 and closing by-pass valve 2.

The catalysts tested varied in composition and application; for that reason different measuring points were required for the sampling of exhaust gas before and after each particular set of catalysts, as shown in Figure 3.2. Exhaust gas temperatures were also measured and recorded as after-treatment catalysts are well-known to be very temperature dependant for particular chemical reactions e.g. HC-SCR of NO_x.

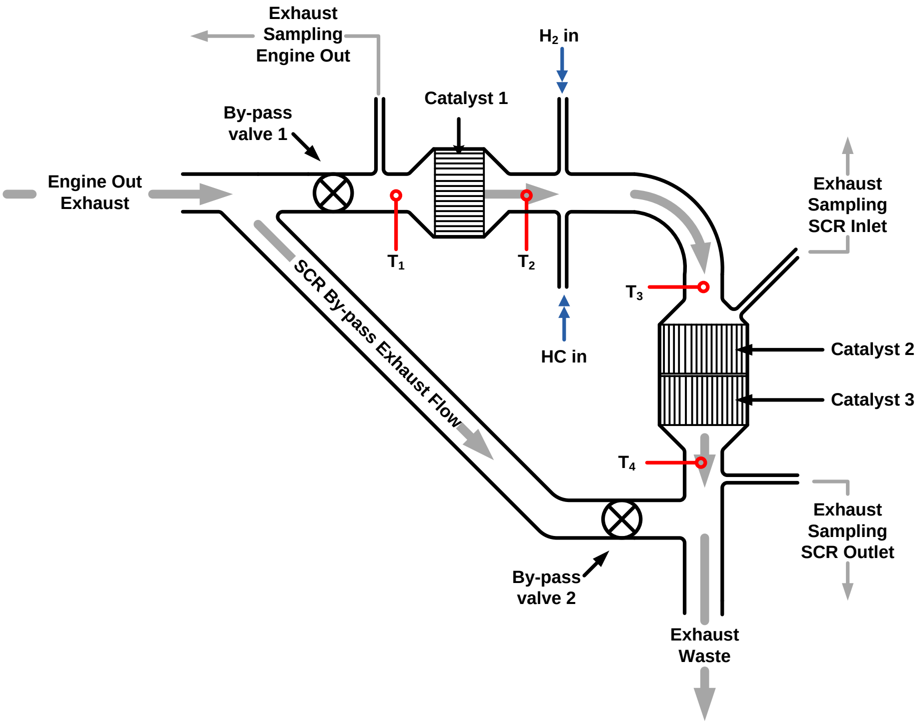


Figure 3.2: The diesel engine exhaust system schematic diagram, showing the monolith catalyst reactors and also the exhaust sampling and reductant addition points.

3.1.2. Pelletized Powder HC-SCR Reactor

The SCR powder reactor was heated by a tubular furnace, the temperature of which was controlled by means of a thermocouple positioned at the inlet of the reactor, 5 mm upstream of the catalyst bed (Figure 3.3).

The precise amount of exhaust gas required for testing was drawn into the powder reactor by means of a pump located downstream of the SCR powder outlet. The use of the pump also allowed for the SV over the catalyst to be controlled accordingly. A by-pass was incorporated into the powder reactor so as to allow excess exhaust gas entering to escape, as only a specified amount was being drawn through the powder Ag-Al_2O_3 catalysts (Figure 3.3).

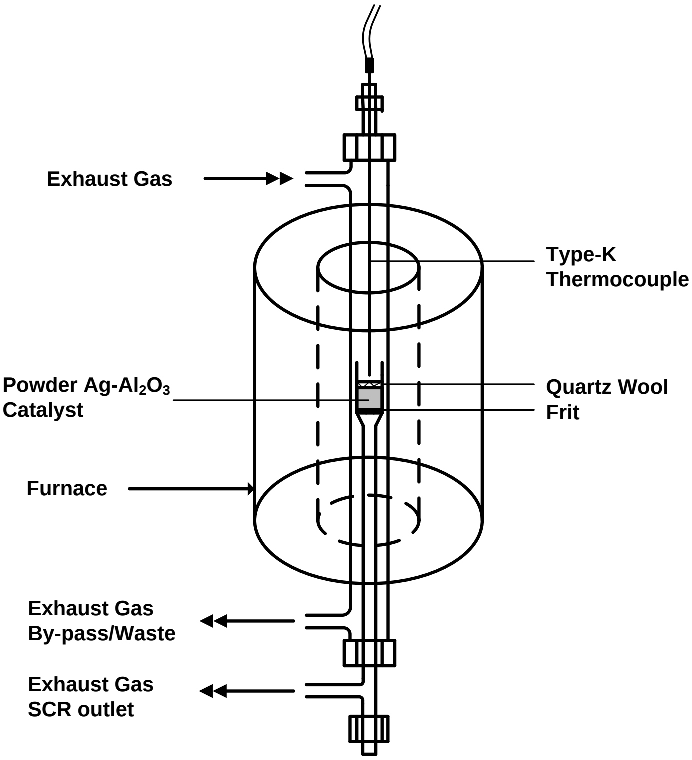


Figure 3.3: The powder Ag-Al_2O_3 catalyst reactor showing the main components of the system.

3.1.3. Fuel Reforming Reactor

The fuel reforming reactor used in this research involved a three-phase operation: solid (catalyst), liquid (fuel) and gas (air or exhaust gas), as illustrated in Figure 3.4. The reactor was placed into a tubular furnace whose temperature was controlled by means of a temperature controller. The reforming catalyst temperature under operation was monitored using a K-type moveable thermocouple.

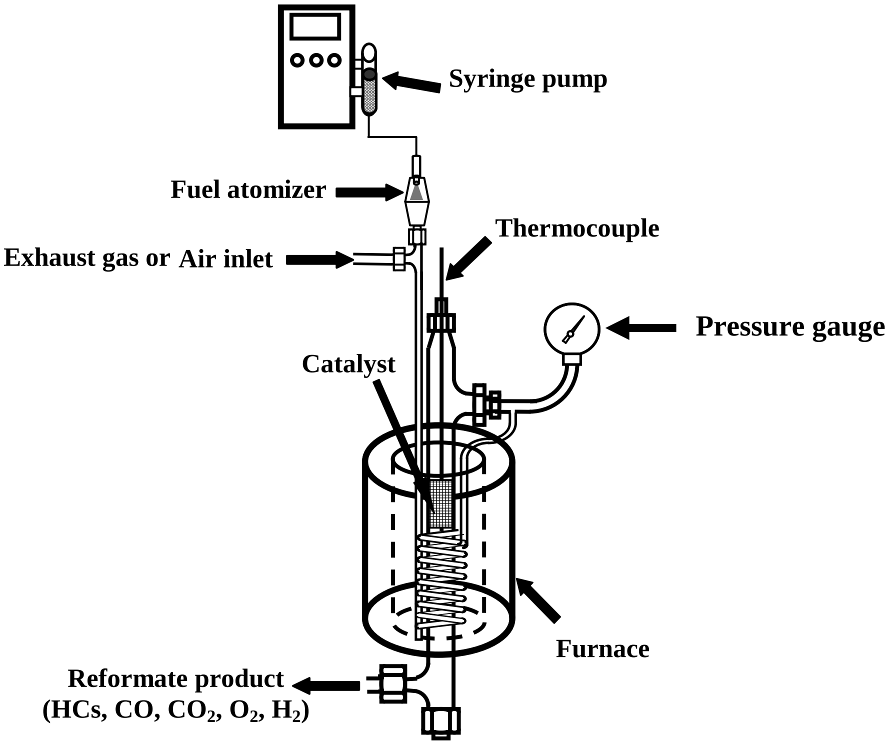


Figure 3.4: The reforming reactor setup schematic for partial oxidation or exhaust gas fuel reforming.

Air or exhaust gas was supplied into the reactor at a controlled flow rate using a flow meter and a heated pump. The pressure of the supplied gas was also monitored by use of a pressure gauge. Fuel was supplied through the use of an electronic syringe pump, which also regulated the flow rate. The fuel was passed through a fuel atomizer to allow for better mixing with the incoming air or exhaust gas feed. The mixture then proceeded towards a preheating coil, in which thorough mixing was achieved before chemical reactions commenced on reaching the reforming catalyst surface. When air was used as the fuel carrier gas, the reforming process was referred to as partial oxidation (PO_x) fuel reforming, whereas when exhaust gas was used as the fuel carrier gas, the system was operating in exhaust gas fuel reforming mode (discussed in chapter 2). At the reformer output, reformed gas (or syngas) was filtered using a condenser and a water-trap filter to remove the water content; allowing for analysis of the gaseous dry fraction.

3.2. Catalysts

Discussed here are the main catalysts that were used during the research i.e. the silver-based HC-SCR catalysts and the rhodium-based fuel reforming catalysts, which were provided by Johnson Matthey Plc.

3.2.1. HC-SCR Catalysts

The HC-SCR catalysts were generic silver catalysts (2 wt.%) on an alumina (Al_2O_3) support. They were prepared by impregnating γ-alumina (surface area ~150 m^2/g) with aqueous silver nitrate ($AgNO_3$), before drying and calcining in air for 2 hrs at a temperature of 500 °C. The catalyst was made into an aqueous suspension, which was then uniformly coated onto ceramic monolith substrates (Ø = 115 mm, L = 75 mm) with a high cell density (600 cpsi).

Catalyst coated monolith substrates are commonly used for full exhaust system purposes due to them leading to reduced exhaust back pressures. On the other hand, powder catalysts, in their pelletized form, are commonly used in low flow rate tests typical of laboratory sized experiments. Both these types of catalysts are shown in Figure 3.5, where the pelletized powder and honeycomb monolith substrates are illustrated.

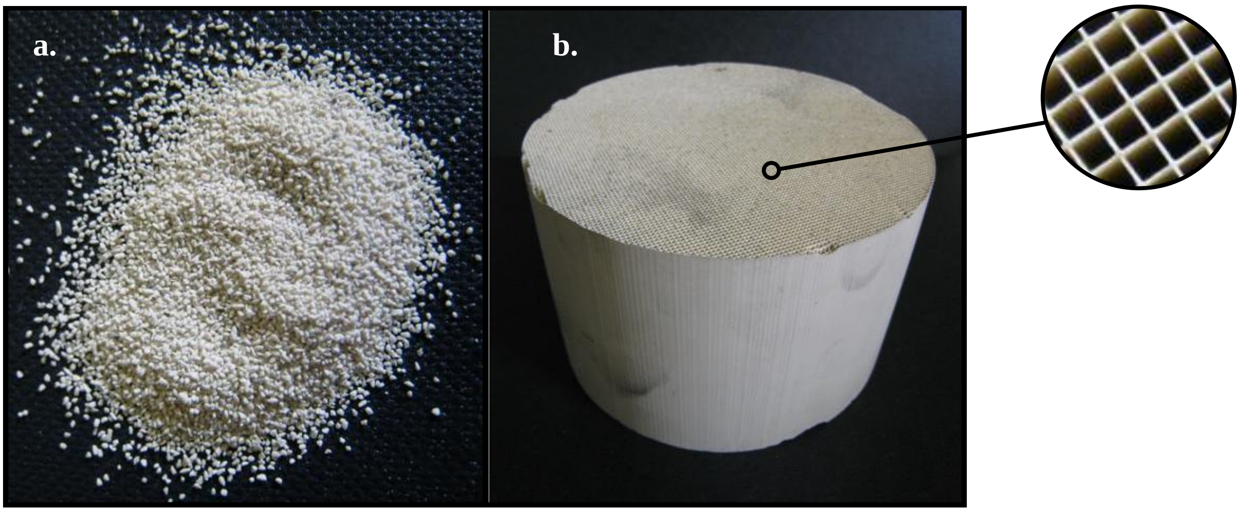


Figure 3.5: a) The pelletized powder form of the Ag-Al_2O_3 catalyst and b) a monolith substrate onto which the catalyst formulation is coated onto the micro-channel walls (inset).

3.2.2. Diesel Oxidation Catalysts

The catalysts comprised of a prototype precious metal formulation developed by Johnson Matthey Plc, which had a dual purpose: i) to adsorb hydrocarbons and oxidize CO at low exhaust temperatures and ii) to release hydrocarbons and/or oxidize C-containing species (i.e. CO, PM and some HC species) at high exhaust gas temperatures. Diesel oxidation catalysts usually consist of precious metal catalysts supported on metal oxides and they now incorporate zeolites for the purpose of trapping HCs at temperatures below the optimal operating temperature of the DOC. Figure 3.6 shows one of the DOCs used in this research study coated with the prototype formulation, supplied by Johnson Matthey Plc.

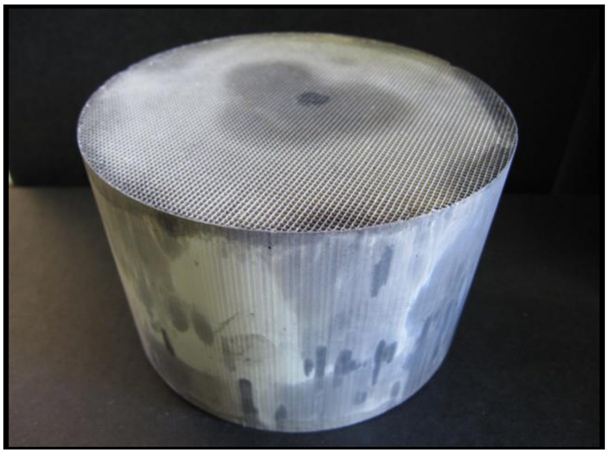


Figure 3.6: Showing a catalyst-coated monolith DOC with a high cell density.

3.2.3. Reforming Catalysts

A reforming catalyst with a nominal composition of 1 wt.%Rh/CeO_2-ZrO_2 was prepared by impregnating 50 g of 50:50 (mole basis) ceria-zirconia (CeO_2-ZrO_2) powder with 30 cm^3 of an aqueous solution of rhodium nitrate ($Rh(NO_3)_3$) containing 0.5 g rhodium (Rh). The impregnated powder formed a slurry, which was dried at 120 °C for 8 hours, before being calcined in static air at 500 °C for 2 hours. The reforming catalyst was made into an aqueous suspension, which was uniformly coated onto ceramic monolith substrates with a high cell density (900 cpsi).

The reforming catalysts do not necessarily need to be of a large size as the H_2-rich gas product (reformate) required for significant improvement in combustion or after-treatment performance is relatively low. The reforming catalysts used in this research thesis were originally made from monolith substrates with a big diameter and length, from which the required size of reforming catalyst was then cored (as in Figure 3.7). The coring of the catalysts was done using a specially designed coring drill. The catalysts shown in Figure 3.7 have been previously used and central holes which run along the lengths of the catalysts represent the moveable thermocouple positioning during experiments, which allowed for temperature profiles along the length of the catalysts to be monitored.

Figure 3.7: Typical monolith fuel reforming catalysts after coring and sizing. The diameter of the catalysts shown here is ~25.4mm.

3.3. Fuels

The experimental work for this thesis was conducted using mainly three combustion fuels, namely, ultra low sulphur diesel (ULSD), rapeseed methyl ester (RME) and Fischer Tropsch gas-to-liquid (GTL), all supplied by Shell Global Solutions UK. The fuel specifications of the respective fuels are presented in Table 3.2.

Table 3.2: The respective properties of the combustion fuels.

Fuel Properties	Method	Diesel	RME	GTL/SD
Cetane Number	ASTM D613	54.1	54.7	80
Density @ 15°C (kg m^{-3})	ASTM D4052	833.3	883.3	784.6
50% Distillation (°C)	ASTM D86	278	335	295.2
95% Distillation (°C)	ASTM D86	340.4	342	353
Viscosity @ 40°C (cSt)	ASTM D 445	2.83	4.478	3.497
LCV(MJ kg $^{-1}$)		42.7	39	43.9
Carbon (wt. %)		85.3	77.2	85
Hydrogen (wt. %)		13.9	12.0	15
Oxygen (wt. %		-	10.8	-
Aromatics (wt. %)		25.6		~0
Sulphur (mg/kg)	ASTM D2622	7	5	-

3.4. Exhaust Gas Analysis and Measuring Equipment

The catalyst activity was measured based on the reduction of particular emissions, for example, when using the HC-SCR catalysts, the main parameter was selectivity towards the reduction of NO_x from the exhaust gas. Each gaseous component was measured using a special technique incorporated conveniently into multi-gas analyzers or specialist analyzers only used for the detection of a particular gaseous component. The exhaust gas analyzers used in the experimental work are presented below detailing the components they were used to measure.

3.4.1. Horiba and AVL Emissions Analyzers

A Horiba Mexa 7100DEGR analyzer was used to measure the concentrations of NO_x ($NO + NO_2$) by heated vacuum-type chemiluminescence detection (CLD); CO and CO_2 by non-dispersive infrared (NDIR); O_2 by a magneto-pneumatic detection (MPD) method and C_1 hydrocarbons (HCs) by flame ionization detection (FID). For the measuring range, resolution and accuracy of the equipment, refer to Appendix A: Table A.1 and A.1.2.

An AVL DiGas 440 analyzer had similar detection capabilities as the Horiba but was used mainly during the reforming experimental work. This was to avoid contamination between sampling engine exhaust gas and sampling the reformate gas, due to possible condensed HCs in the sampling line. For the measuring range, resolution and accuracy of the equipment, refer to Appendix A: Table A.2.

3.4.2. Gas Chromatograph (GC)

Hydrogen Measurement: A Hewlett-Packard (HP) gas chromatograph equipped with a thermal conductivity detector (TCD) was used for measurement of the hydrogen concentration either in the exhaust gas or from the reformer outlet. A double-column arrangement was used for this analysis. The first column was 1 m long with a 1/8-in. diameter Haysep Q, 80 - 100 mesh. The second column was a 2 m long 1/8-in. diameter Molesieve 5Å (MS5A). Higher TCD sensitivity to hydrogen was achieved by using argon as the carrier gas since argon's thermal conductivity is less similar to that of hydrogen compared with other typical carrier gases such as helium and nitrogen. The H_2 chromatogram area was measured using a HP 3395 integrator.

To determine the amount of H_2 gas in the exhaust gas, the apparatus was first calibrated using a certified gas composed of 30 % H_2 in N_2. This gave an area plot from the integrator that was representative of 300 000 ppm H_2 (i.e. 30 % by volume). On sampling the actual exhaust gas, another area plot representative of the H_2 peak was obtained and from this the actual H_2-ppm in the exhaust gas could be calculated by extrapolation from the known certified calibration gas. For all tests, several samples were taken of which the average calculated value of hydrogen was used.

3.4.3. Gas Chromatograph – Flame Ionization Detector (GC-FID)

Hydrocarbon Analysis: Quantitative hydrocarbon analysis (C_1 – C_7) at the inlet of the SCR catalysts was performed on a Hewlett Packard Model 5890 Gas Chromatograph - FID equipped with a 25-meter x 0.32 mm i.d. capillary column with a 10 µm film thickness PoraPLOT Q. The gas samples were introduced into a gas-sampling valve outfitted with a 1 ml sample loop. To calibrate the GC-FID for hydrocarbon species (i.e. qualitative and quantitative) analysis, several standard mixtures of paraffins and olefins (containing 15 hydrocarbon components) from C_1 to C_7 with known concentrations, were used. The calibration gas was certified and supplied by the British Oxygen Company (BOC).

The GC-FID run time was 28.5 minutes (for total analysis of a sample of exhaust gas) and the hydrocarbon species were identified through their retention times (Table 3.3). The GC retention time scale was calibrated daily by the use of the certified sample gas. The areas of the peaks in the chromatogram were proportional to the concentration of the specific HC compound associated with that peak. Flame Ionisation Detection was used as the HC detector and Agilent Chem-station (ver.3.08b) software was used to acquire and integrate the basic gas-chromatograph data.

Table 3.3: The retention times of different HC compounds in the GC-FID.

Peak No.	Compound	Retention Time - RT (min)
1	Methane	0.845
2	Ethylene	1.353
3	Propylene	3.861
4	Propane	4.141
5	iso-Butene	7.638
6	1-Butene	8.066
7	1,3-Butadiene	8.395
8	n-Butane	8.556
9	iso-Pentane	12.271
10	1-Pentene	12.613
11	n-Pentane	12.944
12	n-Hexane	16.732
13	Benzene	17.253
14	n-Heptane	20.197
15	Toluene	20.930

3.4.4. Scanning Mobility Particle Sizer (SMPS)

Particulate Matter Sampling: The particulate matter sampling system used a Scanning Mobility Particle Sizer (SMPS) Spectrometer manufactured by TSI. It comprised of an electrostatic classifier series 3080, a 3081 Differential Mobility Analyzer (DMA) and a model 3775 Condensation Particle Counter (CPC). The exhaust gas dilution ratio was preset to 100:1 (using a properly calibrated dilutor) and particle distributions were measured in the 10 – 500 nm range. Some of the other parameters used for particulate matter sampling are shown in Table 3.4. Exhaust samples were taken from the same position in the exhaust manifold for both the SMPS and the exhaust gas analyzers. For a broader specification, see Appendix A: Table A.3.

Table 3.4: SMPS particulate matter measuring parameters.

Parameter	Value
Sheath Flow Rate (l/min)	5.00
Aerosol Flow Rate (l/min)	0.50
Lower Size (nm)	10.746
Upper Size (nm)	486.968
D_{50} (nm)	978.876
Scan Time (sec)	120

CHAPTER 4

PROMOTING HC-SCR OF NO_X IN DIESEL ENGINE EXHAUST BY HYDROGEN

4.1. Introduction

In this chapter, hydrocarbon selective catalytic reduction (HC-SCR) over Ag-Al_2O_3 monolith catalysts was investigated for NO_x emissions control in a diesel engine. The work was based on ongoing laboratory experiments, catalyst research and process development. Despite the large quantity of experimental studies on the effect of H_2 addition on HC-SCR of NO_x over Ag-Al_2O_3 catalysts at laboratory scale using powdered silver catalysts, there are only a limited number of studies using full scale engine exhaust gas with catalysts coated on a monolith substrate (e.g. Klingstedt et al., 2004; He and Yu, 2005; Zhang et al., 2007a). This study represents a step towards the design of a full scale Ag-Al_2O_3 HC-SCR catalyst system for reducing NO_x emissions under standard diesel engine exhaust gas conditions (i.e. real exhaust gas temperatures and compositions) and provides a basis to optimize the design of the exhaust gas after-treatment system.

The effects of hydrogen addition (0, 700, 1500, 3000 and 5000 ppm) were examined at twelve steady state engine operating conditions (speed-load), as shown in Table 4.1. The added hydrogen was from a bottled source of a high purity (99.9 %), supplied by the British Oxygen Company (BOC). The engine exhaust catalyst setup and the exhaust gas sampling points were as shown in Figure 4.1, with the catalyst inlet exhaust gas temperature being recorded just prior to the HC-SCR reactor.

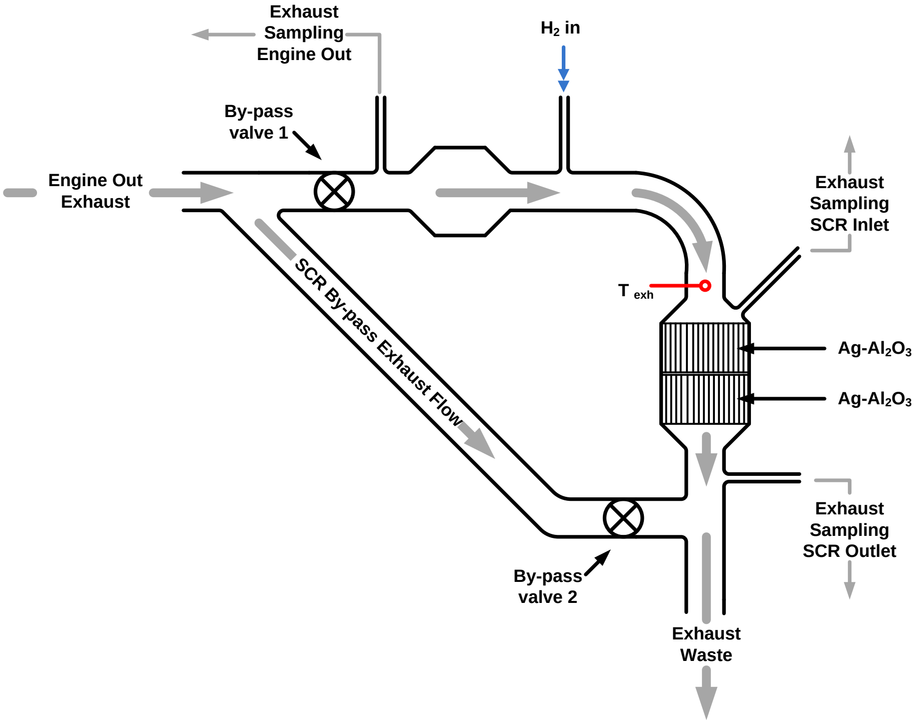


Figure 4.1: The full scale HC-SCR catalyst arrangement on the Lister Petter TR1 engine exhaust.

Three engine speeds of 1200, 1500 and 1800 rpm were selected in order to also investigate the effect of the space velocity (SV) on the SCR catalyst activity for NO$_x$ reduction. The SV is defined as the volume of gas, measured at standard temperature and pressure, per unit time per unit volume of the reactor catalyst, as follows (Hayes and Kolaczkowski, 1997; Majewski and Khair, 2006):

$$SV = V_f / V_r \tag{4.1}$$

where V_f is the volumetric gas flow rate (m^3/h), and V_r is the volume of the catalyst in the reactor (m^3). As a result the unit for SV is the reciprocal of time i.e. more commonly expressed as h^{-1}.

Also investigated were the effects of exhaust gas temperature and exhaust gas composition, at four different engine loads (12, 25, 50 and 75 % of the maximum engine load at each speed) under similar SV (constant engine speed). Engine load was measured using a dynamometer in the form of brake torque (T) with units of Nm and defined as:

$$T_b = P_b/\omega \tag{4.2}$$

where P_b is the brake power delivered by the engine (kW) and ω is the angular speed of the engine (rad/s).

At each engine operating condition the measured NO_x, HC, HC:NO_x ratio, O_2 and exhaust gas temperature at the inlet of the SCR catalyst were recorded and are shown in Table 4.1. In practice, the exhaust gases of an internal combustion engine (ICE) consists of incomplete combustion products (e.g. CO, unburned HCs, soot) and complete combustion products (e.g. CO_2 and H_2O). However, in a lean combustion engine the incomplete combustion products are small. Given that not all the supplied fuel is being utilized in the combustion process it is useful to define the term combustion efficiency (η_c). It is defined as the actual heat produced by combustion as a fraction of the total heat potential of the fuel consumed

$$\eta_c = (\dot{m}_r LCV_r - \dot{m}_p LCV_p)/(\dot{m}_r LCV_r) \tag{4.3}$$

where $\dot{m}_r$ and $\dot{m}_p$ represent the mass flow rate of the reactants (fuel) and products, respectively; while LCV_r and LCV_p representing the lower calorific values of the reactants and products (MJ/kg), respectively.

For diesel engines which always operate lean, the combustion efficiency is generally very high and typically above 98 % (Heywood, 1988). The missing proportion is that which makes up the unburned HCs and CO emissions from the combustion process of a particular fuel.

Table 4.1: Output parameters at different engine speeds and loads.

1800rpm **SV=25k h^{-1}**	**Engine Load (%)**	**12**	**25**	**50**	**75**
	NO$_x$ (ppm)	388	494	806	1089
	HC (ppm)	367	390	422	465
	HC:NO$_x$ ratio	0.95	0.79	0.52	0.43
	O$_2$ (%)	16.5	15.87	13.85	11.74
	Exhaust Temp. (°C)	165	224	285	327
1500rpm **SV=20k h^{-1}**	**Engine Load (%)**	**12**	**25**	**50**	**75**
	NO$_x$ (ppm)	373	523	815	1064
	HC (ppm)	343	349	396	425
	HC:NO$_x$ ratio	0.92	0.67	0.49	0.40
	O$_2$ (%)	17.02	16.15	14.1	11.77
	Exhaust Temp. (°C)	159	197	240	306
1200rpm **SV=15k h^{-1}**	**Engine Load (%)**	**12**	**25**	**50**	**75**
	NO$_x$ (ppm)	361	457	668	993
	HC (ppm)	333	364	380	480
	HC:NO$_x$ ratio	0.92	0.80	0.57	0.48
	O$_2$ (%)	17.03	15.98	13.57	10.68
	Exhaust Temp. (°C)	137	177	237	297

The engine brake thermal efficiency is another important parameter of an engine as it is defined as a measure of how much of the heat energy input (from fuel injection) is converted into mechanical work. It is defined by the equation

$$\eta_{th} = P_b/(\dot{m}_f LCV_f) \qquad (4.4)$$

where P_b and $\dot{m}_f$ represent the brake power delivered by the engine (kW) and the mass flow rate of fuel into the engine (kg/s), respectively, while LCV_f is the lower calorific value of the fed fuel. As a result, the greater the thermal efficiency of an engine is, the more power the engine can deliver for a specified amount of fuel flow rate.

Nonetheless, in the experimental results presented in this chapter, emphasis is on the output emissions from the engine and how efficient an Ag-Al_2O_3 after-treatment catalyst was at reducing diesel engine exhaust gas emissions at full-scale.

4.2. Passive HC-SCR under Different Engine Loads

The trend for varying hydrogen additions at different engine loads and exhaust gas temperatures on the NO_x reduction activity over Ag-Al_2O_3 monolith catalysts, under passive conditions (no externally injected fuels) followed similar trends for the respective engine speeds investigated and only results from the engine speed of 1200 rpm (SV = 15k h^{-1}) are presented (Figure 4.2). At low temperatures (i.e. low loads) the catalyst activity (reading taken after 10 min) in reducing NO_x was improved with increased H_2 addition as compared to the higher engine loads (i.e. high temperature), where a limit was reached after which there was no further improvement with increased H_2 addition. This observation is in agreement with the work that was reported by Richter et al. (2004) who showed that the activation energy of the overall NO_x reduction reaction is significantly lowered in the presence of H_2. It was concluded from their studies that, 'H_2 has the ability to activate the silver oxide (Ag_2O) formed on the catalyst surface into zero-valent silver (Ag^0) which promotes a dissociation pathway of NO_x conversion', at low operating temperatures. At the low engine loads, corresponding to low exhaust gas temperatures (< 250 °C) the HC-SCR of NO_x reaction was predominant over the HC oxidation reaction, besides this, the lower NO_x concentration per catalyst active site further improved the NO_x reduction, as illustrated in Figure 4.2.

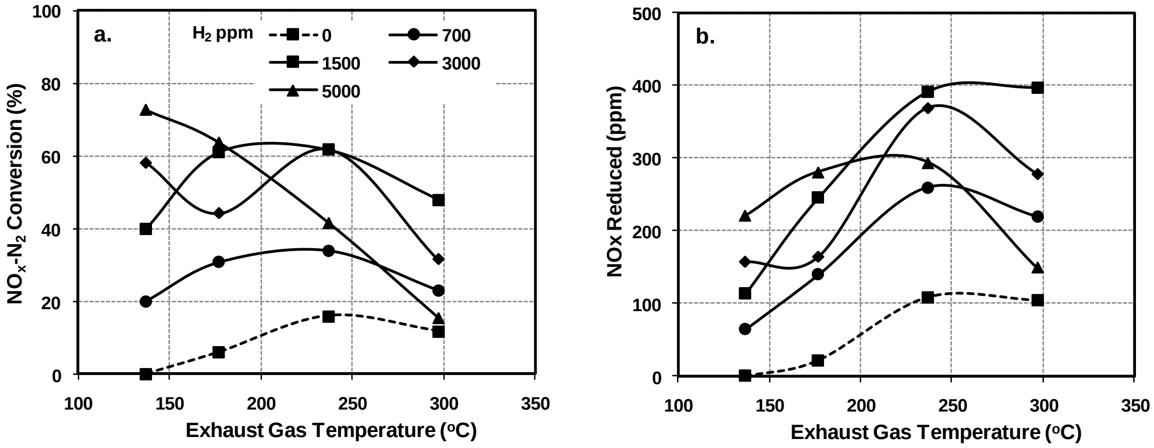


Figure 4.2: Effect of hydrogen (ppm) addition on the NO_x to N_2 reduction activity a) as a percentage and b) in ppm, over Ag-Al_2O_3 monolith catalysts at different engine exhaust gas temperatures (i.e. different engine loads). Engine speed 1200 rpm, SV = 15k h^{-1}.

At higher engine loads, hence higher temperatures (> 250 °C) the peak NO_x conversion and number of NO_x - ppm reduced were achieved with significantly less H_2 (~ 1500 ppm) addition. Addition of higher H_2 amounts (3000 - 5000 ppm) produced a noticeable decay in the Ag-Al_2O_3 catalyst NO_x conversion activity. This is thought to be due to reductant (hydrocarbon) oxidation, promoted by the presence of excess hydrogen. As a result there are less HC species available for the HC-SCR reaction, due to the increased NO_x production from the engine at these particular conditions.

Satokawa (2000) and Satokawa et al. (2003 and 2007) have previously reported that the ability of hydrogen to improve the NO_x reduction activity of Ag-Al_2O_3 catalysts at relatively low temperatures (the 'H_2-effect') occurred for short chain alkanes (e.g. ethane, propane and iso-butane) and alkenes (e.g. ethene and propene). Further studies for possible NO_x reductants over Ag-Al_2O_3 catalysts now also include oxygenated HCs e.g. extensive work with ethanol by Zhang et al. (2007b) and Yu et al. (2004). Under 'passive' HC-SCR mode, i.e. where no diesel fuel is injected into the engine exhaust gas, a large percentage of the HCs in the exhaust gas are short chain species, products of the diesel fuel combustion (Lanning et al., 2000; Maricq, 2007). Thus, H_2 is able to activate these shorter chain HCs into more reactive species for NO_x reduction at relatively low exhaust gas temperatures.

At high engine loads, which are associated with high exhaust gas temperatures and NO_x concentrations, external fuel injection (active control) into the engine exhaust gas will be required to increase the HC:NO_x ratio and thus enhance the HC-SCR of NO_x reaction. Similarly, the incorporation of EGR technology can increase the HC:NO_x ratio by increasing HCs and by significantly reducing NO_x concentration in the engine exhaust gas.

The implication of the presented experimental findings is that there has to be an optimized HC:NO_x ratio, specific to any given engine condition (i.e. exhaust gas temperature) under passive mode SCR, which would help achieve the highest NO_x conversion activity in the presence of H_2. In agreement with these findings is Houel et al. (2007a) who found that the NO_x activity was very much dependant on the HC:NO_x ratio and that as the exhaust gas temperature increased so did the corresponding ratio. Further investigation is still required in order to understand the full mechanistic role of hydrogen in the NO_x reduction activity over Ag-Al_2O_3 catalysts, taking into account the exhaust gas temperature, hydrocarbon concentration and speciation of real diesel engine exhaust gas.

4.3. Passive HC-SCR under Different Space Velocities

The space velocity (SV) i.e. 15, 20 and 25k h^{-1} (representative of 1200, 1500, 1800 rpm) had varied influence on the NO_x conversion over the Ag-Al_2O_3 SCR catalyst when 1500 and 3000 ppm hydrogen were added, across the tested engine load range. The H_2 additions of

1500 and 3000 ppm were chosen as they showed the highest NO_x reduction activity over the Ag-Al_2O_3 catalysts (Figure 4.2).

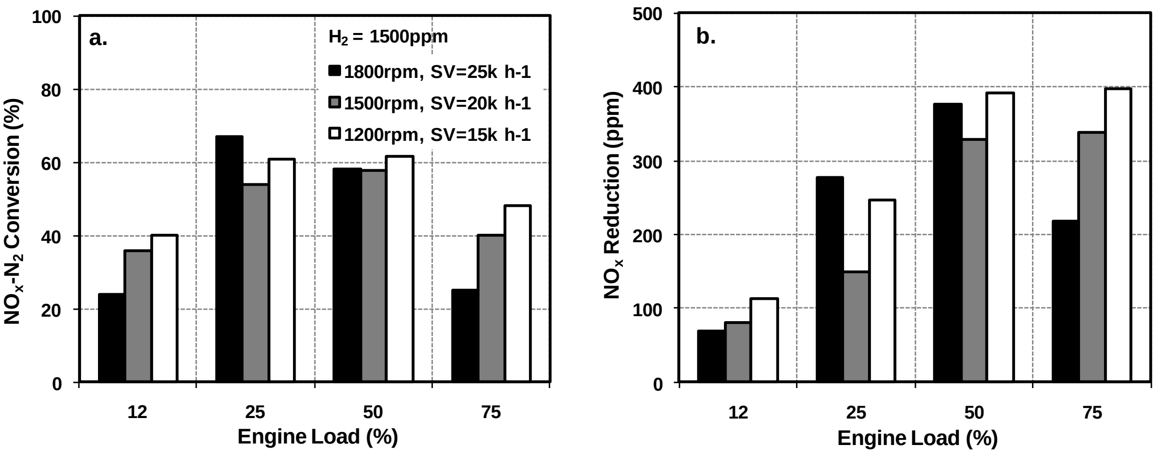


Figure 4.3: a) NO_x-N_2 conversion (%) and b) reduction (ppm) after H_2 additions of 1500ppm.

The most notable SV influence was observed at the low engine load (12 %) and the high engine load (75 %), where a significant drop in the catalyst activity was observed with increasing SV (Figures 4.3 and 4.4).

Under the same engine load condition i.e. 12, 25, 50 and 75 %, the HC:NO_x ratios were similar (Table 4.1) and were not noticeably affected (with the small exception at 1500rpm and 25% load) by the differences in the engine speed (i.e. space velocity). However, some influence on the catalyst activity in reducing NO_x can also be attributed to the small differences in HCs. Furthermore, HC concentration variation at each operating condition will also result in the variation of the specific reactivity of the respective HC species for NO_x over the Ag-Al_2O_3 catalysts, e.g. Figure 4.3a at 25 % load, the best NO_x conversion was observed for the highest speed of 1800 rpm.

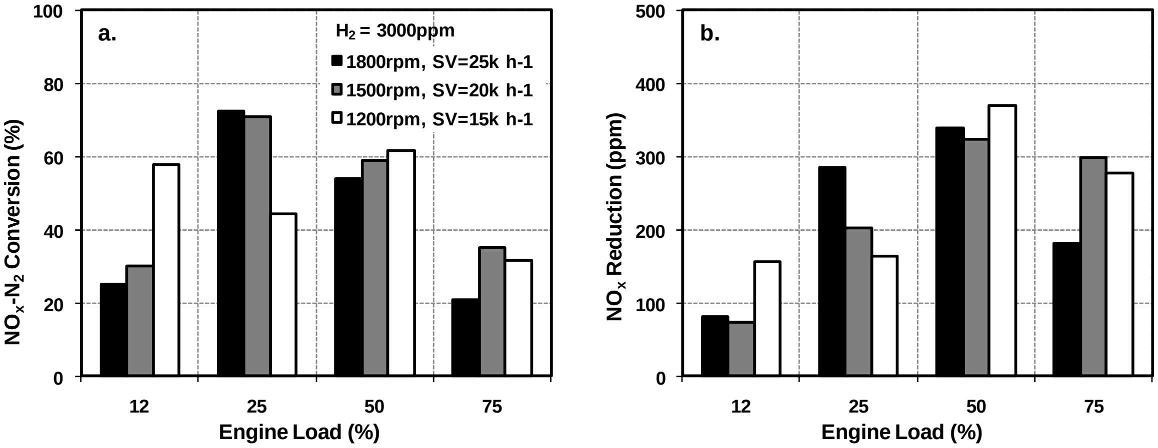


Figure 4.4: a) NO_x-N_2 conversion (%) and b) reduction (ppm), after H_2 additions of 3000ppm

Increasing the SV lowers the residence time and hence the time for reaction over the catalyst surface, resulting in possible loss of catalyst NO_x reduction activity. Apart from the heterogeneous reactions; gas phase reactions in the HC-SCR process of the Ag-alumina catalyst can also be affected by changes in SV, especially at low exhaust gas temperature (e.g. 170 °C at an engine load of 12 %), as shown in Figures 4.3 and 4.4. This is in agreement with several authors (Masuda et al., 1996; Klingstedt et al., 2004; Theinnoi et al., 2008a; Eränen et al., 2000; Trimm, 1983) who have investigated the SV effect as part of on-going work on NO_x reduction over Ag-Al_2O_3 catalysts; reporting that if the SV is too high the catalytic reactions may not go to completion hence limit the catalyst activity. However, this effect was not observed at the engine load of 25 % where similar (with the exception of 1200 rpm) values were obtained for the respective speeds. This is most likely due to the difference in HC speciation between the operating speeds or the rate of oxidation of the reductant.

At 25 and 50 % engine load the increase in the SV seems to have an insignificant effect on the catalyst activity but as the engine load was further increased to 75% the NO_x conversion over the catalyst was reduced with the increase of the SV. This is a result of the significantly increased NO_x concentration from the engine combustion process. Additionally, at this engine load, the HC:NO_x ratios were at their lowest (Table 4.1), as a result, more reductant would be required for improved NO_x activity over the SCR catalyst. With fresh catalysts or minimally aged catalysts, the experimental repeatability of the data was high (results not shown), but durability of the Ag-Al_2O_3 catalysts was low, hence after long periods of testing, the catalyst activity got poorer. This phenomenon is maybe due to the lack of poisons reduction from the catalyst surface with time due to stronger adsorption chemistry onto the active sites.

For maximum NO_x conversion, parameters such as the space velocity, HC:NO_x ratio, HC and H_2 content need to be optimized, for each particular exhaust gas composition and temperature. An understanding of the process characteristics through further experimental work is needed for the optimization of each parameter before any possible road worthy prototype system can be considered.

4.4. Active Mode HC-SCR (Powders and Monoliths).

The quality and quantity of the hydrocarbons present in the engine exhaust gas determines the Ag-Al_2O_3 catalyst performance in reducing NO_x (e.g. Thomas et al. 2005; Lindfors et al. 2004; Theinnoi et al., 2007; Breen and Burch, 2006). This is also in accordance with earlier work by Eränen et al. (2000) who reported that the HC:NO_x ratio had significant influence on the amount of NO_x reduced over the Ag-Al_2O_3 SCR catalyst, in their engine bench tests; with increased NO_x conversion being observed at higher HC:NO_x ratios and exhaust gas temperatures above 375 °C. Although there was no apparent evidence of monolith catalyst deactivation and loss of activity over time in this particular study, excess hydrocarbons can deactivate the catalyst. At higher engine loads and corresponding temperatures (> 300 ^oC), the results suggest that additional HCs (i.e. diesel fuel) are required in order to further improve the NO_x conversion activity.

To examine the effects of the diesel fuel quantity in the presence of H_2, further tests were devised with selective HC (diesel fuel) injections (i.e. active control) into the exhaust gas, up-stream of the SCR catalysts. The catalyst activity was assessed using catalyst coated monoliths and powdered catalysts. The latter was placed in a powder catalyst reactor which was supplied with only 3 l/min of diesel exhaust gas. The engine - catalyst development system comprised of a diesel fuel atomizer for HC atomization and improved mixing.

Under active mode HC-SCR, carbonaceous deposits on the catalyst can include high molecular weight polycyclic aromatics and carbon (which may be formed in the gas phase or on the catalyst surface) as well as catalytic carbons (the formation of which can occur in the presence of a suitable catalyst). Trimm (1977 and 1983) described three major processes of catalyst coking, namely (i) gas phase free radical intermediates, (ii) surface intermediates and (iii) catalytic intermediates which are said to lead to gas phase tars and gas phase carbon, non-catalytic surface tars and surface carbon, and catalytic carbon respectively.

From the present results, it seems that there is a trade-off between catalyst activity and deactivation when comparing pelletized powder and coated monolith catalysts. The powder catalyst initially provides higher NO_x conversion but there is noticeable deactivation with time, signified by the loss in NO_x reduction activity. There are several reasons that can explain this effect, such as, the pressure drop along the catalyst or the fact that powders can more effectively capture (filter) C-containing species (i.e. soot and HCs) including those species that can initially be used for NO_x reduction, but also accelerate catalyst fouling and deactivation (Figure 4.5).

Moreover, even if the global conditions in the SCR catalyst are lean, with O_2 percentage in the range of 10 - 20 % (e.g. Table 4.1), part of the catalyst surface is in an oxygen free environment (i.e. saturated by hydrocarbons); conditions that can also reduce the amount of Ag^+ and Ag^o active sites in the SCR of NO_x at high and low temperatures, respectively. This is in agreement with Shimizu et al. (2001) who reported that the Ag^+ ions are responsible for the SCR of NO_x while the Ag_n clusters are responsible for the HC combustion and N_2O formation. Thus at low temperatures, with the addition of H_2 can aid the reduction of excess HC which would otherwise cause catalyst deactivation through coking. Furthermore, it is generally thought that hydrogen causes the formation of Ag clusters, however their role in the improvement of SCR activity of the catalyst are debatable. For example, Sazama and Wichterlová (2005) in their study of Ag-Al_2O_3 catalysts using hydrogen peroxide as a reductant, suggested that a hydroperoxy species is the important intermediate for the hydrogen promoted HC-SCR over Ag-Al_2O_3 catalysts. However, loss in Ag-Al_2O_3 NO_x reduction activity can also be due to some isolated species that strongly interact with the Al_2O_3 support and are difficult to reduce, especially at higher NO_x concentrations or low exhaust gas temperatures (Shimizu et al., 2001).

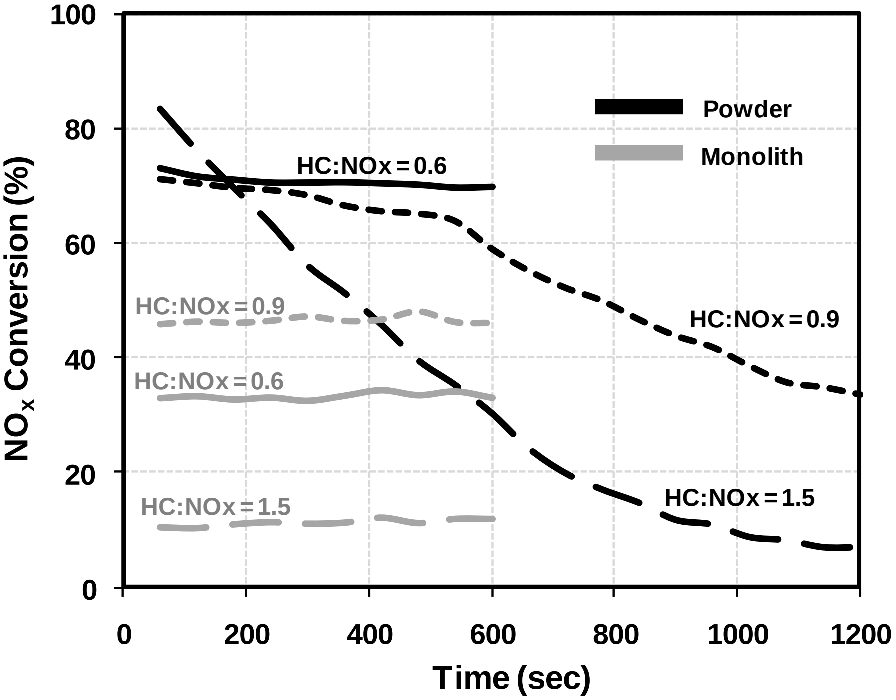


Figure 4.5: Effect of HC:NO_x ratio (fuel injection of 0 ml/h - HC:NO_x = 0.6, 25 ml/h - HC:NO_x = 0.9 and 50 ml/h – HC:NO_x = 1.5) on the SCR catalyst NO_x conversion (%) over the powder (**black lines**) and the monolith (**grey lines**) catalysts, H_2 = 3000 ppm. Engine speed = 1500 rpm, SV = 20k h^{-1}, $T_{exh.}$~320 °C.

Catalyst type, the reactions involved, the exhaust gas conditions and composition can greatly influence the catalyst activity. From the powder vs. monolith catalyst comparison, given the high exhaust gas temperature (~ 320 °C); at HC:NO_x = 0.6 (passive control) the NO_x reduction activity between the monolith and the powder catalysts was very different during the test period (Figure 4.5). This can be attributed to the different mechanistic reactions over the respective catalysts (e.g. diffusion limitations, mass transfer effects, and total active catalyst surface area). Physical deposition of high molecular C-containing species on the Ag-Al_2O_3 catalyst surface decreases the available catalyst active surface area and blocks access to the pores. In effect, there are less available active sites for NO_x reduction with simultaneously increased diffusional resistance in the pores. Under real engine exhaust gas conditions and active mode control, there are significant differences between the physical deposition of the C-containing species on powders and monoliths. The main one being that monoliths lack species filtration capabilities and as result will not suffer from pressure drops across their length and can therefore maintain catalyst activity for longer without deactivating.

The poisoning (fouling) mechanism of powdered catalysts tested in our mini-reactor possessed similar characteristics to those shown in Figure 4.6 after the 1st, 5th and 10th minute of testing. This was indicated by a progressive darkening of the powder catalyst granules, which is an effect that is reversible but exhaust temperatures exceeding 350 °C are required.

Despite keeping H_2 addition constant and increasing the HC:NO_x ratio to 1.5, the monolith catalyst NO_x reduction activity dropped to around 10 % when compared to lower ratios (Figure 4.5). It is suspected that, in this particular instance, the catalyst coated onto the monolith substrate channels was saturated with HC fuel and as a result was not fully active for NO_x reduction. On the other hand, the fresh powdered catalyst showed the maximum recorded NO_x conversion activity at the start of the experiment for a HC:NO_x ratio of 1.5 but after a short period of time (20 minutes) the NO_x reduction activity had dropped to the same level as that of the monolith.

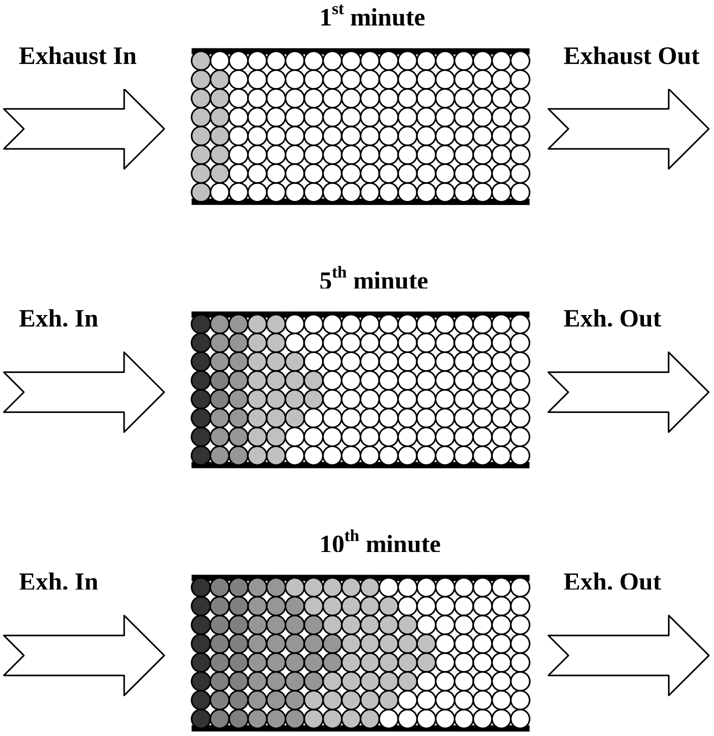


Figure 4.6: Powder catalyst gradual poisoning mechanism, whereby the active catalyst acts as a filter for poisoning species from the front to the back when exposed to the exhaust stream gas for a significant period of time.

Table 4.2: Effect of diesel fuel injection on the engine fuel penalty at 1500 rpm.

Engine Load (Nm)	External HC Injection (l/hr)	Fuel Penalty (%)
30	0.000	0.00
	0.025	1.71
	0.050	3.42

The amount of H_2 and HC concentrations required for the SCR of NO_x are dependent on the exhaust gas temperature (i.e. engine load) and NO_x concentration. Under the same engine and SCR catalyst conditions, the optimum HC:NO_x ratios for maximum NO_x conversion were 0.9 for the monoliths and 0.6 for the powders. In the case of powders there is no requirement for HC injection, however in the case of the monolith, fuel injection upstream of the catalysts is required and this increased the engine fuel consumption by 1.7 % for a flow rate of 25 ml/hr (Table 4.2). Further increase in HC concentration upstream of the SCR catalyst, apart from worsening the fuel consumption, also reduces the catalyst activity.

4.5. Summary

Hydrocarbon-SCR technology over wash-coated monoliths has been shown to require a reasonable quantity of hydrocarbons (in the presence of H_2) to provide satisfactory reduction of NO_x emissions at low temperatures. Small quantities of hydrogen can also significantly reduce the requirements of hydrocarbons in the SCR reactor, as specific hydrogen amounts have been shown to be able to activate the HC concentrations in the exhaust gas and provide good NO_x reduction under lean conditions. During the experimental passive control tests conducted utilizing the whole diesel engine exhaust gas, H_2 addition improved the NO_x conversion over the catalyst in the temperature range of $130\ ^{\circ}C < T < 330\ ^{\circ}C$, which falls into the typical operational range of a light-duty diesel engine. In this temperature window, hydrogen optimization for maximum NO_x reduction will be dictated mainly by the hydrocarbon concentration and the exhaust gas temperature. These findings surpass most laboratory studies which show substantial NO_x reduction during operating temperatures exceeding 300 °C.

At high engine loads (i.e. high temperatures), the oxidation reaction is more predominant, hence external HC injection will be required. At low engine loads (i.e. low temperature), it seems the relatively high HC:NO_x ratios may result in the poisoning (by coke or nitrates accumulation) of the Ag-Al_2O_3 catalyst. One way to counter this effect is by the addition of increased amounts of H_2 into the exhaust feed. An alternative way would be to reduce the HC concentration in order to avoid catalyst poisoning and be more selective with the quality and quantity of the HC species. Overall, the hydrogen and HC quantities have been shown to be key factors in obtaining high NO_x conversion and the application of the Ag-Al_2O_3 – SCR reactor will require adaptive optimization for different engine operating conditions to achieve greater effectiveness over a wider temperature range.

CHAPTER 5

IMPROVING THE LOW TEMPERATURE NO_X REDUCTION ACTIVITY OF $Ag-Al_2O_3$

5.1. Introduction

After-treatment of diesel exhaust emissions relies on various components designed to reduce and/or remove specific emissions from the diesel exhaust, such as, diesel particulate filters (DPFs) and diesel oxidation catalysts (DOCs). The primary role of DPFs and DOCs is to reduce emissions of CO, HCs and PM from diesel exhaust gas, as these are harmful to both humans and the environment, as discussed in Chapter 1. At the same time, the reduction of these emissions has another important benefit, since less impurities (e.g. excess/un-reactive HCs) in the exhaust gas at the inlet of a selective catalytic reduction (SCR) catalyst (located downstream of the DOC or DPF, in a typical configuration) improves durability and efficiency at reducing NO_x emissions (Watanabe et al., 2007). In this chapter, the promotional effect of H_2 for full-scale diesel engine exhaust utilizing a prototype diesel oxidation catalyst (PC) and $Ag-Al_2O_3$ SCR catalysts was studied and is discussed herein. The results presented show how the activity and/or durability of $Ag-Al_2O_3$ catalysts can be possibly improved for NO_x reduction in real diesel engine exhaust gas streams.

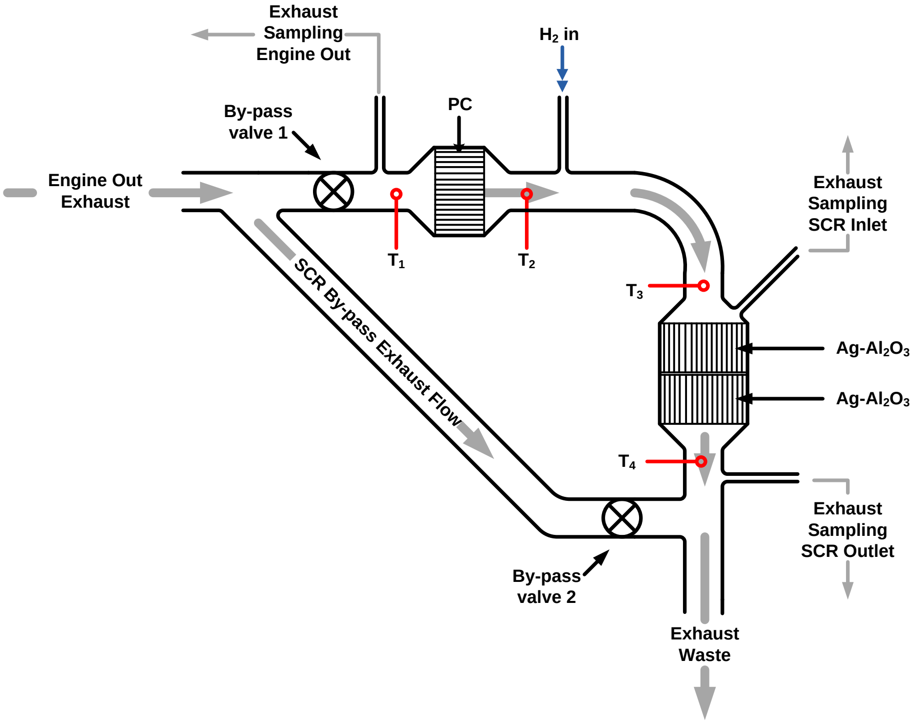


Figure 5.1: The catalyst arrangements in the diesel engine exhaust tailpipe.

The PC was placed upstream of the SCR catalysts, in a reactor connected to the exhaust as shown in Figure 5.1. The catalyst comprised of a formulation developed by Johnson Matthey Plc, whose main purpose was to (i) absorb hydrocarbons and oxidize CO at low exhaust gas temperatures, and (ii) to release hydrocarbons and/or oxidize C-containing species (i.e. HC, CO, PM) at high exhaust gas temperatures.

The effect of the PC on the Ag-Al_2O_3 catalyst activity with hydrogen addition (0, 700, 1500, 3000 and 5000 ppm) from a certified bottled source (including ~ 50 - 100 ppm from the combustion process itself), was examined for twelve steady-state engine operating conditions (speed-load). Additionally, in order to investigate the effect of the space velocity over the Ag-Al_2O_3 catalysts, engine speeds of 1800, 1500 and 1200 rpm were tested, resulting in space velocities of 25, 20 and 15 k h^{-1}, respectively.

Table 5.1: SCR catalyst inlet parameters **without** the use of the PC.

1800 rpm SV=25k h^{-1}	**Engine Load (%)**	**12**	**25**	**50**	**75**
	NO_x (ppm)	388	494	806	1089
	CO (ppm)	174	126	111	257
	HC (ppm)	367	390	422	465
	HC:NO_x ratio	0.95	0.79	0.52	0.43
	O_2 (%)	16.5	15.87	13.85	11.74
	T_3 (°C)	165	224	285	327
1500 rpm SV=20k h^{-1}	**Engine Load (%)**	**12**	**25**	**50**	**75**
	NO_x (ppm)	373	523	815	1064
	CO (ppm)	187	164	133	153
	HC (ppm)	343	349	396	425
	HC:NO_x ratio	0.92	0.67	0.49	0.40
	O_2 (%)	17.02	16.15	14.1	11.77
	T_3 (°C)	159	197	240	306
1200 rpm SV=15k h^{-1}	**Engine Load (%)**	**12**	**25**	**50**	**75**
	NO_x (ppm)	361	457	668	993
	CO (ppm)	288	230	251	1261
	HC (ppm)	333	364	380	480
	HC:NO_x ratio	0.92	0.80	0.57	0.48
	O_2 (%)	17.03	15.98	13.57	10.68
	T_3 (°C)	137	177	237	297

Table 5.2: SCR catalyst inlet parameters **with** the use of the PC.

1800 rpm **SV=25k h^{-1}**	**Engine Load (%)**	**12**	**25**	**50**	**75**
	NO_x (ppm)	341	406	687	1035
	CO (ppm)	0	0	0	5
	HC (ppm)	228	234	267	292
	HC:NO_x ratio	0.67	0.58	0.39	0.28
	O_2 (%)	16.91	15.74	13.52	11.1
	T_3 (°C)	190	231	299	342
1500 rpm **SV=20k h^{-1}**	**Engine Load (%)**	**12**	**25**	**50**	**75**
	NO_x (ppm)	356	480	660	837
	CO (ppm)	1	1	1	4
	HC (ppm)	289	276	217	189
	HC:NO_x ratio	0.81	0.58	0.33	0.23
	O_2 (%)	16.79	15.75	13.70	11.32
	T_3 (°C)	171	207	273	335
1200 rpm **SV=15k h^{-1}**	**Engine Load (%)**	**12**	**25**	**50**	**75**
	NO_x (ppm)	341	443	544	840
	CO (ppm)	2	0	1	5
	HC (ppm)	211	227	157	222
	HC:NO_x ratio	0.62	0.51	0.29	0.27
	O_2 (%)	17.00	15.88	13.10	9.94
	T_3 (°C)	152	183	260	340

At each engine speed, the effect of exhaust gas temperature and composition were investigated through various engine loads (12, 25, 50 and 75 %). Engine load was defined as the percentage of the maximum torque achievable at each engine speed, running the engine with the same fuel. The NO_x, CO, HC, HC:NO_x ratio, O_2 and exhaust gas temperature at the inlet of the $Ag-Al_2O_3$ catalysts were recorded and are shown in Tables 5.1 and 5.2.

5.2. PC Effect on Engine Exhaust Emissions

The primary design role of the PC was to reduce C-species such as HCs, CO and part of the PM (soluble fraction) from diesel engine exhaust gas which typically has relatively low NO_x reduction efficiencies at low operating temperatures over Ag-based SCR catalysts. Its effectiveness at lowering these particular emissions is illustrated in Figure 5.2. The catalyst HC reduction efficiency is dependent on the engine exhaust gas temperature. As indicated from the HC conversion under the same SV (i.e. engine speed), the PC achieved its light-off (50 % reduction) temperature only at high engine loads (i.e. 50 and 75 %), representative of exhaust gas temperatures exceeding 225 °C.

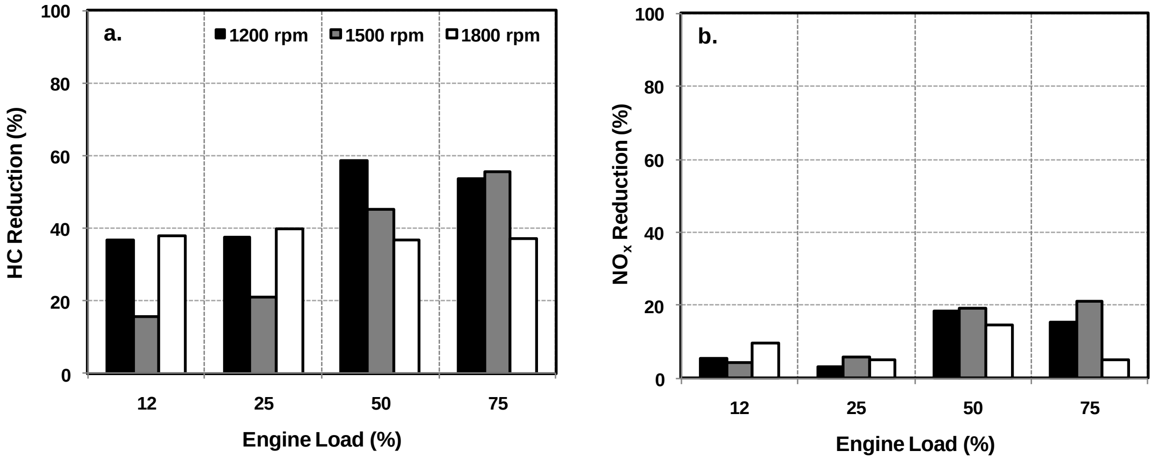


Figure 5.2: Effect of the PC on the a) HC and b) NO_x emissions in the diesel exhaust gas.

The CO reduction efficiency was very high (> 98 %) across all tested engine conditions (Tables 5.1 and 5.2) due to the formulation of the PC which allowed for the reduction of CO over a wider temperature range, when compared to HC molecules. On the other hand, the NO_x reduction activity of the PC was relatively low as Figure 5.2b illustrates, with reductions of only ~ 20 % being achieved at the higher temperatures in the engine load operating range of 50 and 75 % (> 225 °C). This means that the decline in the concentration of HCs is partially due to the NO_x-reducing reactions taking place over the PC. In the lower temperature region (< 225 °C), corresponding to 12 and 25% engine loading, there was less than ~10 % NO_x reduction.

For all the tested engine load conditions, the space velocity over the PC seemed not to significantly affect its performance for the reductions of CO, HC and NO_x emissions. Overall, it could be concluded that the PC only needs to reach light-off temperature to maintain its effectiveness across a wide range of operating temperature conditions.

5.3. PC effect on Particle Size Distribution and HC emissions

Particulate matter, especially the soluble fraction may have negating effects on the overall NO_x reduction activity of a $Ag\text{-}Al_2O_3$ catalyst, through adsorption onto active sites, leading to reduced NO_x reduction efficiency (Creaser et al., 2009). The work done by Sumiya and Yokota (2004), showed that an oxidation catalyst can effectively reduce the SOF of PM as well as both regulated and unregulated HC species from the exhaust of a diesel engine.

5.3.1. PC effect on Particle Size Distribution

In the present study, the particle size distribution of the different engine speed-load conditions yielded different results, but from our experimental findings the characteristics observed followed a similar trend, therefore, only the results of the highest and lowest engine speeds of 1800 and 1200 rpm at 50 % load respectively, are presented (Figure 5.3). From the particle number distribution analysis (Figure 5.3), it was generally found that the particle number concentration, in almost all the particle diameter range measured, was reduced after the PC. This is attributed mainly to the oxidation of the SOF of PM and also the un-burnt HC molecules within the exhaust gas.

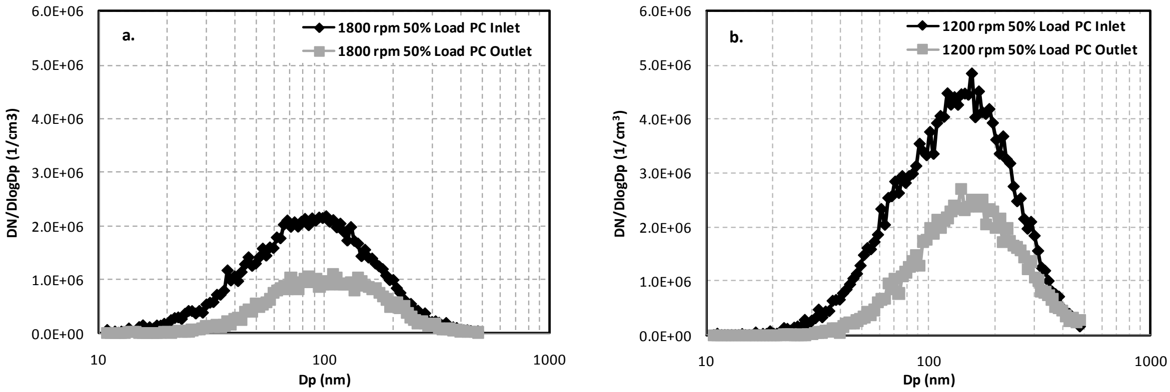


Figure 5.3: The total particle number distribution of the diesel engine exhaust gas with and without the prototype catalyst for: a) 1800 rpm and 50 % load, b) 1200 rpm and 50 % load.

Furthermore, through a mass analysis, the PC can be seen to effectively reduce the total particle mass and total particle number from the diesel exhaust gas, particularly as the engine load was increased (Figures 5.4 and 5.5). It was also observed that the reduction in particle number over the PC was, in general, higher than the reduction in mass. This indicates that the PC was more effective in removing the smaller particles, which are formed (totally or in a high proportion) by hydrocarbons. It is well known that hydrocarbons are more easily trapped or oxidized compared to soot, over a typical purpose built catalyst.

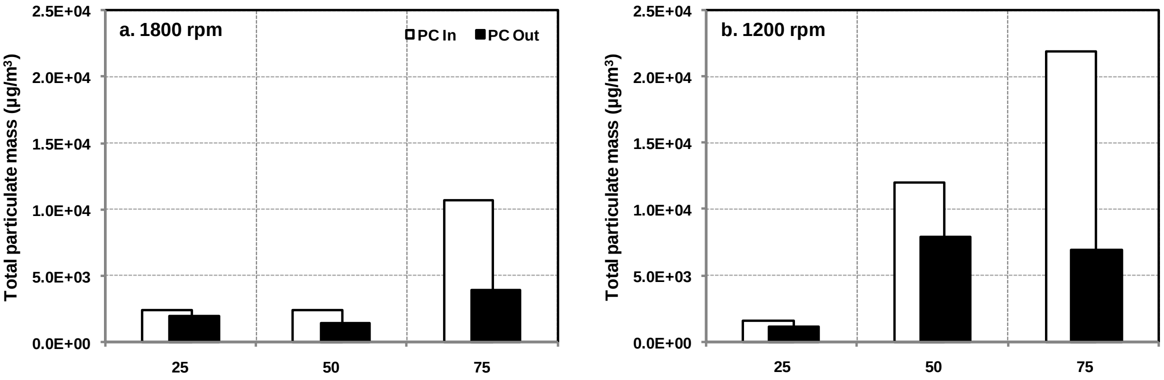


Figure 5.4: Total particulate mass concentration in the exhaust gas before (PC In) and after (PC Out) the prototype catalyst for, **a)** 1800 rpm and **b)** 1200 rpm.

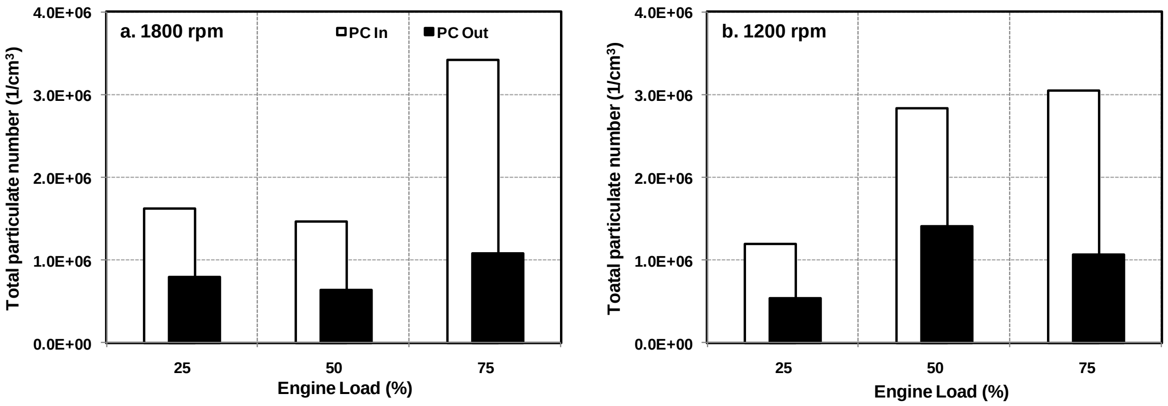


Figure 5.5: Total particulate number concentration in the exhaust gas before (PC In) and after (PC Out) the prototype catalyst for **a)** 1800 rpm and **b)** 1200 rpm.

By reducing both the total particulate mass and number in the diesel exhaust, the NO_x reduction mechanism over $Ag\text{-}Al_2O_3$ catalysts could be improved, possibly leading to better efficiencies, due to lower impurities.

5.3.2. PC effect on HC emissions (C_1 - C_7)

Analysis of the HC species from the combustion process itself was carried out for short chain species (C_1 – C_7). The HCs shown in Tables 5.1 and 5.2 are representative of the total C_1 count and since the experimental study was focusing on 'passive' HC-SCR over $Ag\text{-}Al_2O_3$ catalysts, speciation was a necessary component for trend analysis during NO_x catalysis. For trend analysis, the engine conditions chosen for this part of the study were the highest speed of 1800 rpm and the lowest speed of 1200 rpm both at engine loads of 25 and 75 %.

Varying engine speed at low engine load (25 %) showed only a slight effect on the C_1 – C_7 HC species distribution pattern and magnitude (Figure 5.6). The HC species distribution was predominantly of the order toluene > ethylene > methane > propylene in both conditions. At 1200 rpm in particular (Figure 5.6a), the poor toluene reduction of 15 % reflects the difficulty of oxidization of this aromatic HC compound. This can be attributed to the combined effects of exhaust gas temperature and the reduced SV, which lowers the effective heat transfer towards an exothermic reaction.

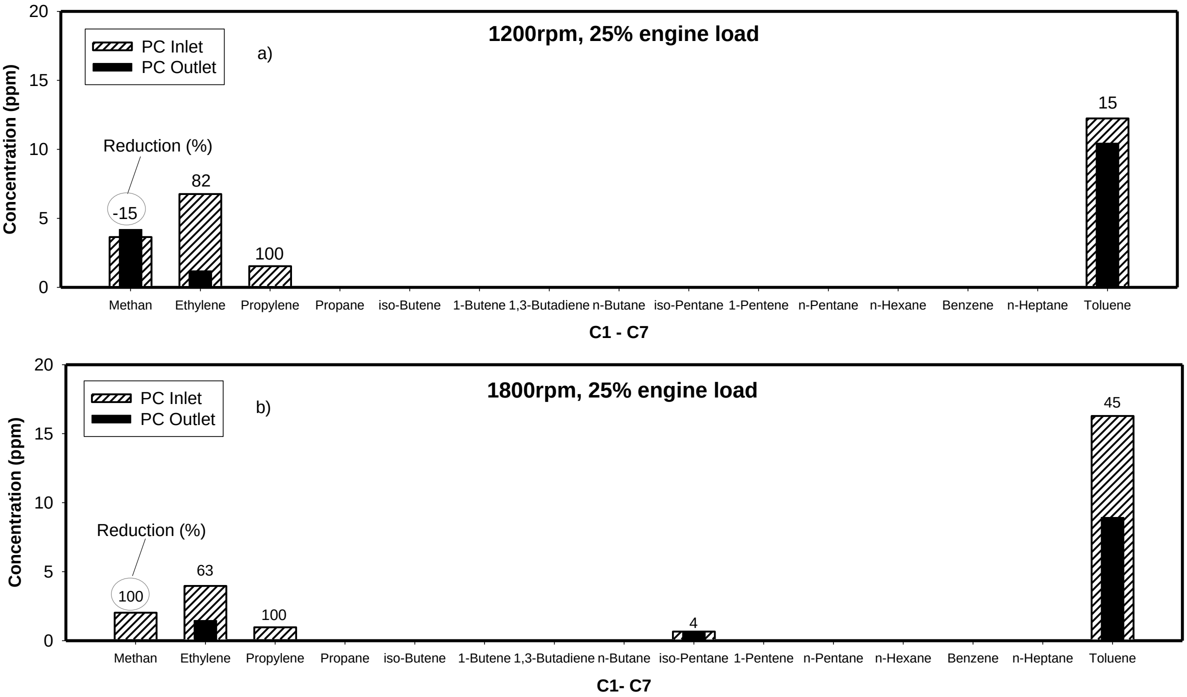


Figure 5.6: Comparison of the variation in short chain (C_1 – C_7) HC species at the engine speed of 1200 and 1800 rpm operating at an engine load of 25 %.

At the higher engine load of 75 % (Figure 5.7), greater variation is observed in the inlet HC species especially at 1200 rpm. At this condition, low toluene output from the engine was measured but with an increase in the other light species. Included in the other light HC constituents was the photo-chemically reactive compound of 1,3-butadiene, which is a known carcinogen according to the United States Environmental Protection Agency (US-EPA). In contrast, at 1800 rpm a significantly higher toluene concentration was observed before the PC, along with a reduced amount of light alkanes and alkenes, suggesting a less complete combustion for each engine cycle. This combustion completeness discrepancy between the HC species emissions from the engine could be attributed to the difference in residual time inside the combustion chamber due to the difference in engine speed. The rest of the undetected HC species making the total C_1 count (Table 5.1 and 5.2) are representative of the heavier HCs (i.e. greater than C_7).

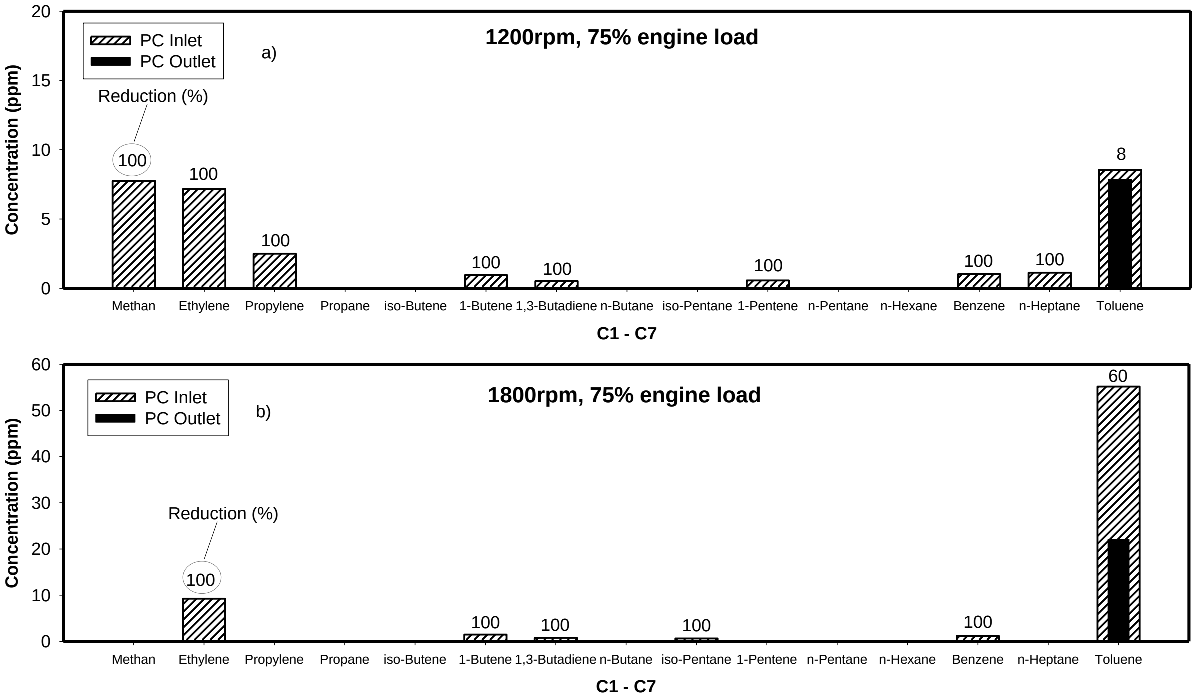


Figure 5.7: A comparison of the variation in short chain (C_1 – C_7) HC species at the engine speed of 1200 and 1800 rpm operating at an engine load of 75 %.

From analysis of the engine out and PC out emissions (Figure 5.6 and Figure 5.7), it can be observed that the PC was very effective at removing the small amounts of light HCs which have been reported to be un-reactive at low exhaust gas temperature in $Ag-Al_2O_3$ NO_x catalysis (Houel et al., 2007a). Comparatively, of the HC species characterized, toluene (an aromatic HC) seems to be the major output product from the combustion process of ULSD, before and after the PC. Other small chain HCs can be present but only in small quantities. Arve et al. (2005a) in their study on a cascade concept system involving Ag/alumina and a Cu-ZSM-5 catalyst found that toluene was not very good as a reductant over the Ag catalyst. They found that the addition of toluene into the exhaust gas stream into the Ag catalyst resulted in an increase in the temperature for initial NO catalytic activity. These findings are in agreement with Breen et al (2007b) who in their study on the sulphur tolerance of Ag/γ-

Al_2O_3 catalysts, found that the addition of toluene to the exhaust stream had a negating effect on the temperature at which the Ag catalyst showed significant NO_x activity. It can therefore be surmised that the presence of aromatics in the exhaust gas during the HC-SCR of NO_x is a major disadvantage for $Ag\text{-}Al_2O_3$ catalysts.

As a result, a study of the NO_x activity over $Ag\text{-}Al_2O_3$ catalysts was necessary in order to conclusively show that the activity of the catalysts could be improved through the use of the PC by limiting the amount of possible poisoning species (in the diesel exhaust gas) leading to reduced deactivation mechanisms.

5.4. H_2-Effect on HC-SCR of NO_x with PC use

The PC was used in conjunction with H_2 addition (700 – 5000 ppm) in order to study its effectiveness on SCR of NO_x over $Ag\text{-}Al_2O_3$ with reduced impurities. This was to check whether there was any notable improvement in the NO_x reduction activity of the $Ag\text{-}Al_2O_3$ catalysts as compared to a similar study in Chapter 4 (Sitshebo et al., 2009) involving no PC use, where there was suspicion of SCR catalyst deactivation due to excess C-species or nitrate adsorption at low exhaust gas temperatures. A simplified mechanism of the HC-SCR reaction involves the activation of NO to NO_2 and then the reaction of this NO_2 with activated/oxygenated HC's to form nitrogen (N_2), carbon dioxide (CO_2) and water (H_2O), as follows:

$$2NO + O_2 \rightarrow 2NO_2 \tag{5.1}$$

$$(CH_2) + \frac{3}{2}NO_2 \rightarrow \frac{3}{4}N_2 + CO_2 + H_2O \tag{5.2}$$

where, (CH_2) is representative of a typical hydrocarbon combustion fuel with a H:C ratio of ~ 2.

It can be surmised (on a molar basis) that the HC amount (ppm) can reduce the equivalent of 1.5 times the NO_x (ppm), since the NO and NO_2 in reaction are 1:1 equivalent (reaction 5.1 and 5.2). It is generally accepted that there are intermediate reactions that occur between reaction 5.1 and 5.2 which form the critical path of reaction for the reduction of NO_x (Chapter 2; Figure 2.2). This simplified NO_x reduction mechanism shows that the reaction of HC and NO_x does not have to be at 1:1 or higher, to achieve complete NO_x reduction in diesel exhaust gas.

To illustrate the effect of hydrogen addition on the SCR catalysts, the results for the engine speed of 1500 rpm have been chosen for representation since this engine speed led to a notable increase in the NO_x reduction efficiency over the $Ag\text{-}Al_2O_3$ catalyst. Without the addition of H_2 to the exhaust gas, there was no significant NO_x reduction observed across the whole engine speed-load range for both cases, i.e. with and without the use of the PC (Figure 5.8). However, an increase in hydrogen addition to the diesel exhaust gas upstream the Ag SCR catalysts had a corresponding positive effect on the NO_x reduction, but predominantly in the low temperature (low load) regions, where higher HC:NO_x ratios were observed. With higher engine temperature, the HC:NO_x ratios and NO_x conversion activity were reduced; with the peak NO_x conversions being observed for lower H_2 additions at these particular conditions. This highlights the necessity to optimize the H_2 content depending on the exhaust gas temperature and the HC:NO_x ratio, based on the reactive fraction of HC species. The low HC:NO_x ratios observed were due to the higher engine-out NO_x emissions as the engine load was increased. Furthermore, the presence of toluene in the exhaust gas does not aid the HC-SCR reaction over Ag-based catalysts (Arve et al., 2005a). The reduced maximum NO_x conversion and HC:NO_x ratios (at higher loads) is in agreement with several authors (Eränen et al., 2000; Theinnoi et al., 2009; Houel et al., 2007a; Eränen et al., 2004), who have reported that the HC:NO_x ratio has significant influence on the amount of NO_x reduced over the $Ag-Al_2O_3$ SCR catalyst; with increased NO_x conversion being observed at increased HC:NO_x ratios primarily dependant on the operating temperature i.e. lower ratios being required at lower temperatures.

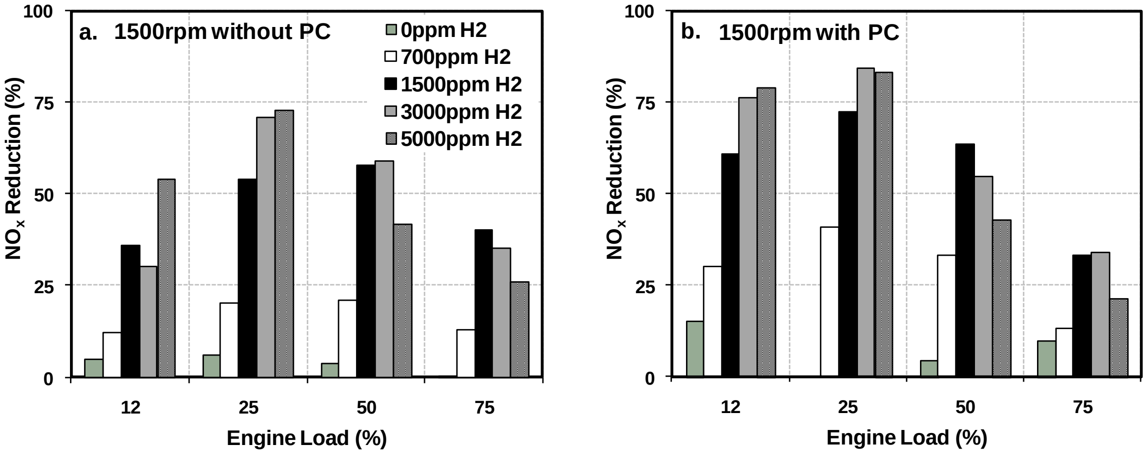


Figure 5.8: Effect of varied H_2 addition on $Ag-Al_2O_3$ NO_x reduction activity: a) without PC use and b) with PC use, at an engine speed of 1500 rpm.

An important reported key step in low temperature NO_x reduction activity lies in hydrogen's reductive activation of molecular oxygen (O_2^-) species involved in the oxidative activation of HCs (Satokawa et al., 2007; Eränen et al., 2004; Arve et al., 2005b). The improvement in overall NO_x conversion with the use of the PC for the 1500 rpm engine speed (Figure 5.8b), was possibly due to higher chain HC activation over the PC surface, coupled with the H_2 activation effect of HCs after the PC, making them more reactive. However, according to the results herein, the most probable explanation lies in the reduction of poisoning species e.g. un-reactive HCs, soot particles etc, as illustrated and discussed in the above sections. Thus, despite the fact that the HC:NO_x ratio was reduced by using the PC, it has been proven that the same or even better NO_x reduction can be achieved over the SCR catalyst if it is fed with either less poisoning species or more active HCs, especially in the low temperature (< 225 °C) regions (12 and 25 % engine load). However, the space velocity (SV) seemed to play an important role in the effectiveness of the PC at improving NO_x reduction at all conditions as discussed in the following section.

When using the PC, the best NO_x conversion peaked at ~ 82 % at low engine load conditions and at an engine speed of 1500 rpm. Exhaust gas temperature, HC:NO_x ratio and SV are all among the influential factors in NO_x reduction activity and given the peak conversion occurring at the 25 % engine load; near optimum values of the influential parameters may have been attained here. While at the higher engine loads (higher temperatures), there was not enough active HCs after the PC for NO_x selectivity over the Ag-Al_2O_3 SCR catalysts, which may have resulted in the lower NO_x conversions obtained. Consequently, external selective injection of HCs will need to be administered if there is to be a notable improvement in NO_x reduction activity in the high load (i.e. high temperature) region for any engine speed.

5.5. Space Velocity Effect

Given that the respective speeds of 1800, 1500 and 1200 rpm yielded varying SVs over the Ag-catalyst, its ability to maintain NO_x reduction was assessed. The residence time (i.e. time spent by exhaust gas over the catalyst) increases with decreasing engine speed and may lead to increased NO_x reduction activity (Adams et al., 1996). The SV effect is illustrated in Figure 5.9, where the NO_x conversion with and without the PC over the same engine load range is shown. It was observed that the PC increased the SCR inlet temperature (by approximately 10 - 40 °C) in all three engine speed representations. The increase in temperature was due to the oxidative catalytic activity over the PC and the associated temperature gradient in the direction of exhaust gas flow after the catalyst (Hayes and Kolaczkowski, 1997).

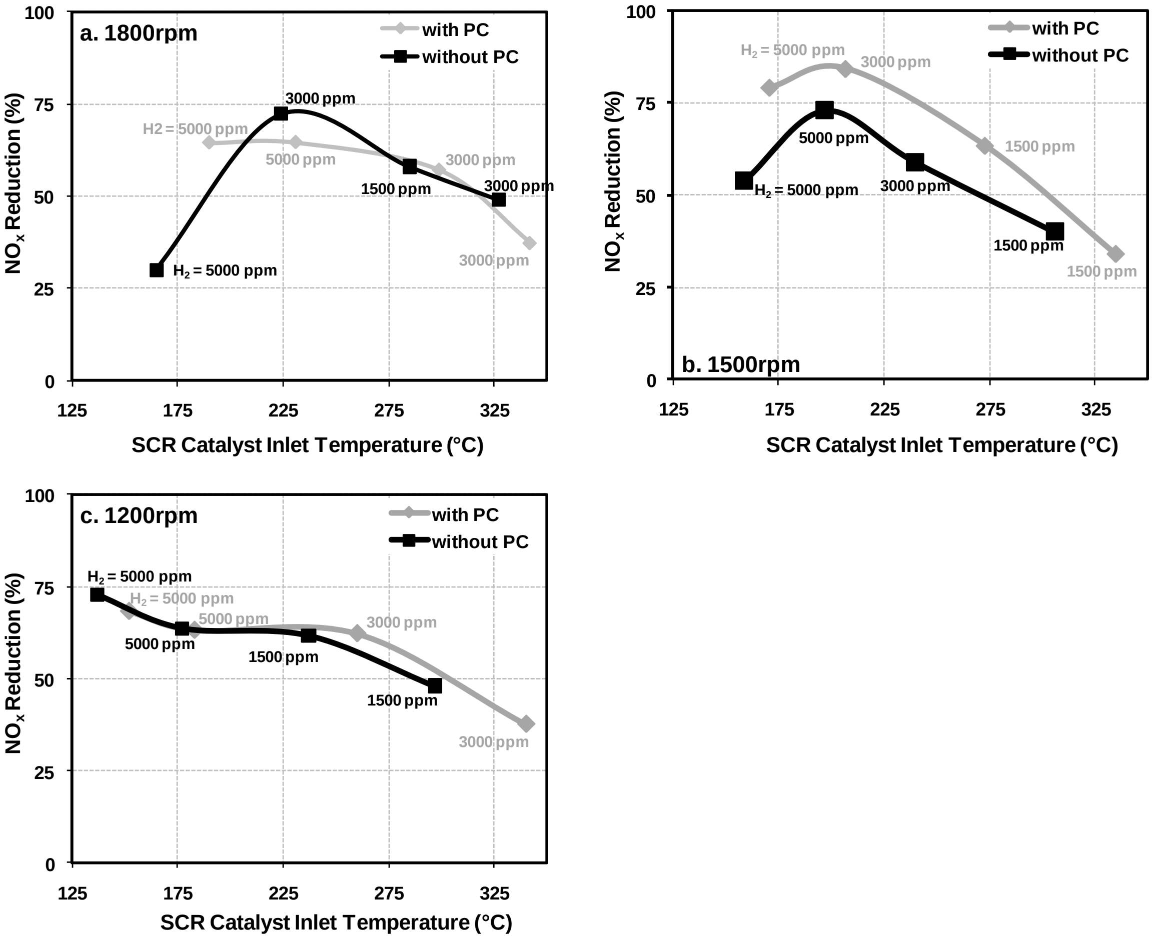


Figure 5.9: The maximum NO_x conversion with H_2 addition and PC use for, a) 1800 rpm, b) 1500 rpm and c) 1200 rpm, for varying SCR inlet exhaust gas temperatures (corresponding to 12, 25, 50 and 75 % engine load, respectively).

At the SV of 25k h^{-1} (1800 rpm) the residence time between the catalyst reactive surface and the exhaust gas was the shortest (compared with the SV of 15 and 20 kh^{-1} respectively); but increased temperatures at the high speed conditions resulted in relatively good NO_x reduction activity for temperatures above 190°C, due to the advanced PC and Ag-Al_2O_3 catalyst light-off at these particular conditions (Figure 5.9a). Due to the constant HC conversion observed over the PC prior to the Ag-Al_2O_3 SCR catalysts (Figure 5.2a), less SCR catalyst surface species accumulation and improved inlet temperatures were observed (Hayes and Kolaczkowski, 1997; Nagashima et al., 2004). The PC initiated Ag-Al_2O_3 catalyst light off earlier than without its use, especially at lower engine load. Confirmation of this characteristic was also observed at the SV of 20k h^{-1}, where the PC helped maintain a NO_x conversion rate that was higher than that without the use of the PC (Figure 5.9b). This lower SV may have been near optimum for the Ag-Al_2O_3 SCR catalysts used at this specific engine speed-load range. At the even lower SV of 15k h^{-1} (Figure 5.9c), it was noticed that the PC had no significant influence on the NO_x reduction activity compared to the results with no PC use, yielding results similar to those observed at 25k h^{-1}, whereby there was no significant overall improvement in NO_x reduction with PC use. Possible explanations at these particular conditions can be due to i) the reactive reductant in the exhaust gas composition requiring either lesser or greater residence time over the SCR catalyst surface for improved NO_x reactivity or ii) the homogeneous gas phase reactions having become significant prior the PC; reaching a point where they were much greater than the catalytic reactions over the PC and as result the PC may not have been required in the diesel exhaust system prior to the Ag-Al_2O_3 SCR catalysts (Adams et al., 1996).

5.6. Summary

A prototype diesel oxidation catalyst has been shown to effectively reduce the light hydrocarbons, carbon monoxide and particulate matter from diesel engine exhaust gas; which in turn helps enhance Ag-Al_2O_3 low temperature NO_x reduction activity at specific operating conditions. It is suspected that at low temperatures the prototype catalyst activates the more reactive long chain HC species, which aid the NO_x reduction reaction.

At high temperatures the PC readily oxidizes the PM and light HCs from the engine exhaust gas which when coupled with the low HC:NO_x ratios observed, leads to lower NO_x reduction activity over the Ag-Al_2O_3 catalysts. At these conditions, an external hydrocarbon injection source will be required to achieve reasonably good reactant ratios (in the presence of

H_2) and thus possibly improve the NO_x reduction activity over the $Ag-Al_2O_3$ SCR catalysts. During the short chain HC species analysis, toluene was found to be the most abundant species after the combustion process. Due to its lack of NO_x reactivity as a reductant over $Ag-Al_2O_3$ catalysts, it can easily be deduced that introducing a HC reductant both qualitatively and quantitatively into the exhaust gas could yield better NO_x reductions. Thus, the PC can be used at every operating condition in a proposed full system, supplemented by HC dosing as of when it is required.

SV has to be carefully controlled for the prototype oxidation catalyst to have any positive effect on passive $Ag-Al_2O_3$ catalyst performance for NO_x reduction. Furthermore, optimized H_2:HC and HC:NO_x ratios would be required to maximize the NO_x reduction performance of the SCR catalysts at specific operating conditions, since it was found that the lower the HC:NO_x ratio the lower the H_2 required for the maximum possible NO_x conversion at particular exhaust gas compositions.

CHAPTER 6

TEMPERATURE DEPENDENCE OF $Ag\text{-}Al_2O_3$ CATALYSTS DURING HC-SCR OF NO_x

6.1. Introduction

Many researchers have published investigative studies showing the H_2-effect (at low temperatures) for lean exhaust gas over $Ag\text{-}Al_2O_3$ catalysts mainly based on steady-state simulated diesel engine exhaust gas conditions (e.g. Burch et al., 2004; Houel et al., 2007a). Nevertheless, road vehicles rarely operate at steady-state conditions as they tend to be consistently accelerating and decelerating, especially under real world driving conditions (Giakoumis and Alafouzos, 2010). Thus, simulated transient test cycles are better suited for the assessment of the behaviour of vehicular emissions as they represent the true output.

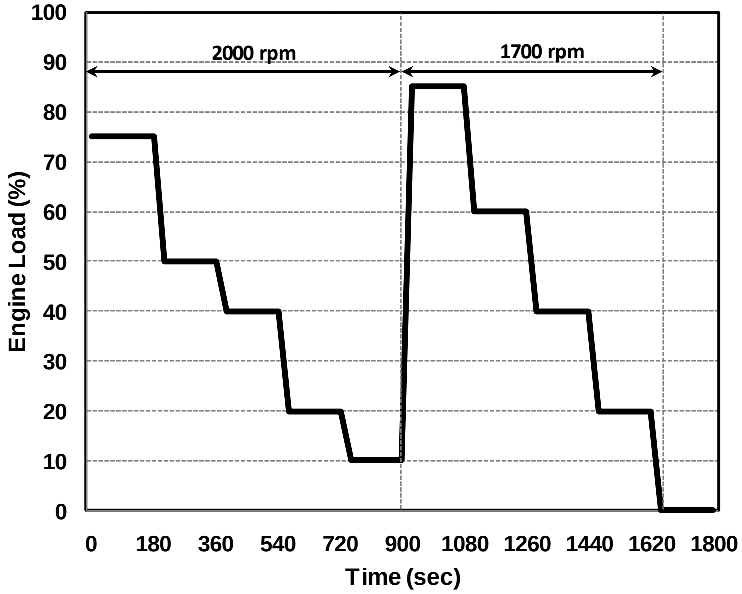


Figure 6.1: The fast steady-state ramp cycle test as a function of time. At the ‘zero’ load condition the engine was running at 900 rpm.

The Ag-Al_2O_3 catalyst is well known to suffer from poor low temperature (< 350 °C) NO_x reduction activity (Theinnoi et al., 2008a), which is associated with the accumulation of poisoning species (Creaser et al., 2009; Shibata et al., 2003). During transient operation, the exhaust gas temperature is not constant, resulting in fluctuating exhaust gas temperature profiles; therefore, there may not be sufficient time for C-species and/or nitrate species accumulation, possibly leading to reduced deactivation mechanisms, primarily during low temperature lean operation of Ag-Al_2O_3 catalysts. The addition of H_2 into the exhaust gas has already been shown in the previous chapters to aid the NO_x reduction reaction; hence its use with fluctuating exhaust temperatures may produce favourable results.

This Chapter explores the HC-SCR of NO_x over Ag-Al_2O_3 lean NO_x catalysts during a series of fast steady-state ramps (see Figure 6.1), to try and mimic a transient cycle operation. A variety of fuels, namely, ULSD, RME and GTL were assessed for NO_x production from the combustion process through to the SCR of NO_x over the Ag-Al_2O_3 catalysts. The engine was run at each specified engine speed-load condition for only a short period of time which allowed for the sampling of the exhaust gas emissions. Once the emission data had been recorded, the next test condition was set and the process repeated. The experimental catalyst setup in the engine exhaust was the same as that illustrated in Chapter 5 (Figure 5.1), whereby a PC was placed upstream of the SCR catalysts, in a reactor connected to the exhaust. This study is a continuation of that work, but now exploring the temperature dependence of the Ag-Al_2O_3 catalysts during the HC-SCR of NO_x, utilizing several combustion fuels.

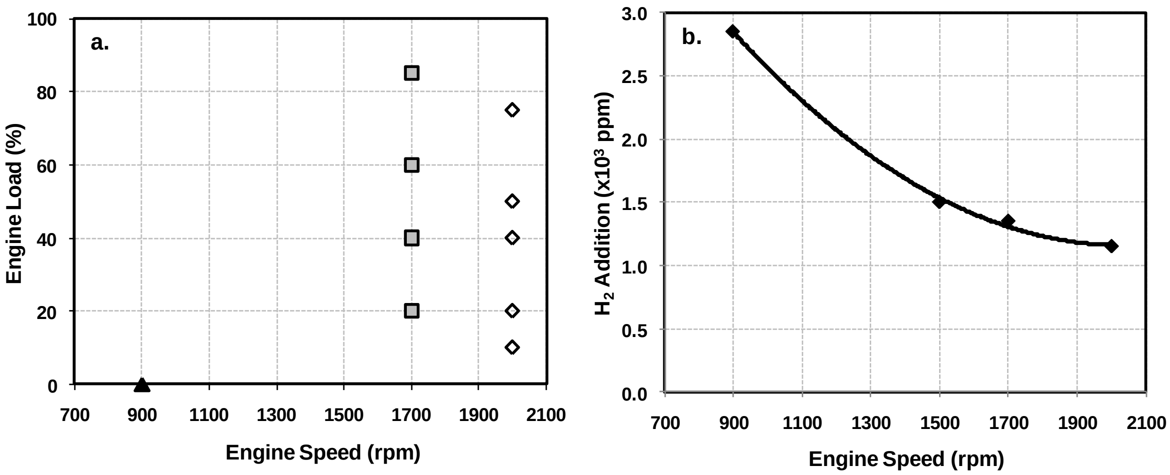


Figure 6.2: a) The fast steady-state diesel engine test cycle conditions and b) the variation of hydrogen (ppm) addition with engine speed (rpm), for the conditions tested in relation to the reference 1500 ppm at an engine speed of 1500 rpm.

Table 6.1: The engine test parameters and SCR inlet emissions.

Engine Speed (rpm)	Engine Load (%)	NOx (ppm)			HC (ppm)			HC:NOx			CO (ppm)		
		ULSD	GTL	RME	ULSD	GTL	RME	ULSD	GTL	RME	ULSD	GTL	RME
2000	**75**	911	917	1010	290	248	196	0.32	0.27	0.19	4	9	7
	50	609	541	705	220	238	170	0.36	0.44	0.24	2	4	3
	40	511	425	577	215	250	173	0.42	0.59	0.30	1	1	1
	20	372	347	479	215	242	172	0.58	0.70	0.36	0	1	0
	10	328	296	412	290	230	170	0.88	0.78	0.41	0	1	0
1700	**85**	1050	968	1105	250	268	197	0.24	0.28	0.18	4	5	5
	60	671	589	693	245	240	177	0.36	0.41	0.26	3	1	1
	40	487	440	576	250	229	165	0.51	0.52	0.29	0	0	0
	20	418	307	520	235	230	150	0.56	0.75	0.29	0	0	0
900	**0**	240	223	308	202	249	155	0.84	1.12	0.50	3	0	1

For this particular study, three engine speeds of 2000, 1700 and 900 rpm were selected in conjunction with various engine loads to represent the experimental test cycle conditions.

The emissions measured at the SCR inlet and the temperature profiles of the three combustion fuels are shown in Table 6.1 and 6.2, respectively. The engine tests were conducted from high load (i.e. high temperature) to low load (i.e. low temperature), starting from the high engine speed of 2000 rpm; the specific conditions are shown in Figure 6.2a.

Hydrogen gas (calibrated at an engine speed of 1500 rpm) was also added to the engine exhaust gas, from a certified bottled source at 1500 ppm. As a result, due to varying air flow rates into the combustion chamber at different engine speeds, the H_2 being added to the exhaust gas stream was decreased from the reference 1500 ppm for the higher engine speeds (i.e. 1700 and 2000 rpm). At the engine speed of 900 rpm, the H_2 amount added was more than the reference 1500 ppm (Figure 6.2b).

Table 6.2: The temperatures of the respective engine speed-load conditions.

Engine Speed (rpm)	**Engine Load (%)**	**Temperature (°C)**		
		Diesel	**GTL**	**RME**
2000	**75**	403	410	414
	50	366	369	379
	40	330	321	332
	20	271	246	253
	10	223	203	225
1700	**85**	368	362	379
	60	320	316	327
	40	272	268	286
	20	226	231	234
900	**0**	142	148	157

6.2. PC Effect on CO, HC and NO_x Emissions

The effectiveness of the PC at removing diesel combustion associated emissions, i.e. CO, HC and NO_x emissions, was studied during the fast steady-state test ramps for the three respective combustion fuels. The findings are presented and discussed below.

6.2.1. PC Effect during ULSD Combustion

The fuel used here was a conventional fossil derived ULSD fuel with a sulphur content of less than 10 ppm (Chapter 3, Table 3.2 for more detail). The fast steady-state ramp for ULSD combustion is shown in Figure 6.3, and it can be observed that the PC was very effective at reducing the HC emissions from the diesel exhaust gas at all the engine test conditions tested, especially at the high engine operating speed of 2000 rpm. The operating speed of 2000 rpm possessed the highest exhaust gas temperatures of all the respective operating conditions (Table 6.2), and in turn would have helped increase the overall HC reduction efficiency over the PC when compared to previous values e.g. those attained and presented in Chapter 5. In addition, NO_x reduction over the PC remained minimal, reaching a maximum of only ~ 25 %, at best (Figure 6.3, 1700 rpm 40 % engine load).

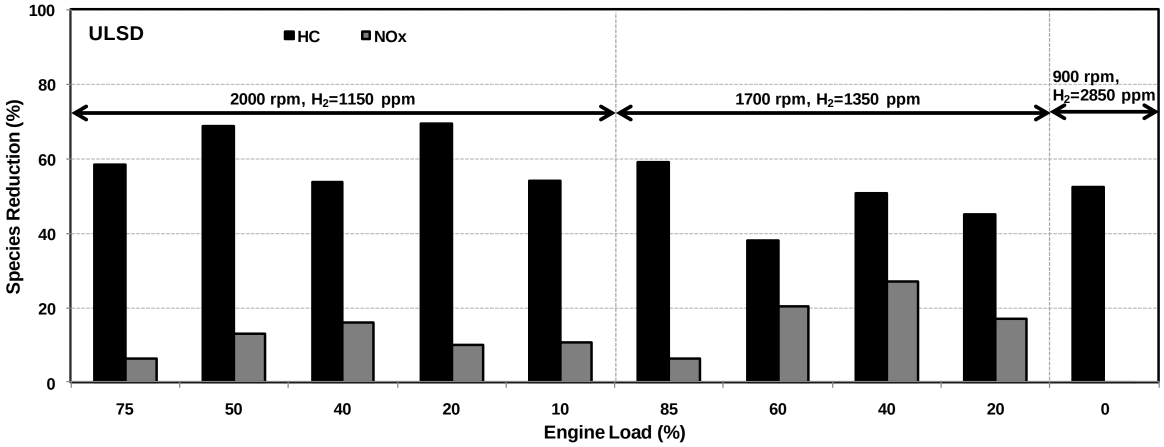


Figure 6.3: PC effect on the HC and NO_x emissions at engine speeds of 2000, 1700 and 900 rpm, which is representative of the fast steady-state test ramp for ULSD combustion.

Moreover, HC species present in the exhaust gas were suspected, in earlier work (Theinnoi et al., 2008a; Sitshebo et al., 2009), of causing SCR catalyst deactivation through adsorption (of C-species or nitrates) onto the SCR catalyst surface. The PC has also been shown, in Chapter 5, to be able to reduce the SOF of PM. Thus, by reducing the overall C-containing compounds into the SCR catalysts, the accumulation mechanism of the deactivating species is lessened and a positive effect can be seen for the HC-SCR of NO_x over Ag-Al_2O_3 catalysts. Theinnoi et al. (2008b), in their study of a different prototype diesel oxidation catalyst also confirmed that their catalyst was able to significantly reduce the PM fraction and the overall HC emissions dependent on the engine operating conditions. They went on to speculate in their investigation that the observed reductions in PM (total number and mass) could help improve after-treatment device efficiency by helping reduce deactivating species, therefore reducing SCR catalyst poisoning mechanisms.

6.2.2. PC Effect during GTL Combustion

The GTL fuel tested here was a derivative from natural gas and a virtually pure paraffinic hydrocarbon with excellent combustion properties. Gas-to-Liquid fuels are now more commonly referred to as next generation or 2^nd^ generation bio-fuels. Characteristic of these fuels is their paraffinic nature and lack of sulphur and their advantages include a reduction in soot emissions while power output and fuel consumption are comparable to conventional fuels (Oguma et al., 2002 and 2004). Additionally, GTL has virtually no aromatic content, the presence of which is linked to the increase of NO_x and PM emissions as reported by Ullman et al. (1994). The lack of sulphur in the fuel is therefore very favourable, since newer more advanced after-treatment devices, which are highly sensitive to sulphur are introduced to meet future emission legislation guidelines (Fanick, 2008; Houel et al., 2007b; Takeuchi and Matsumoto, 2004).

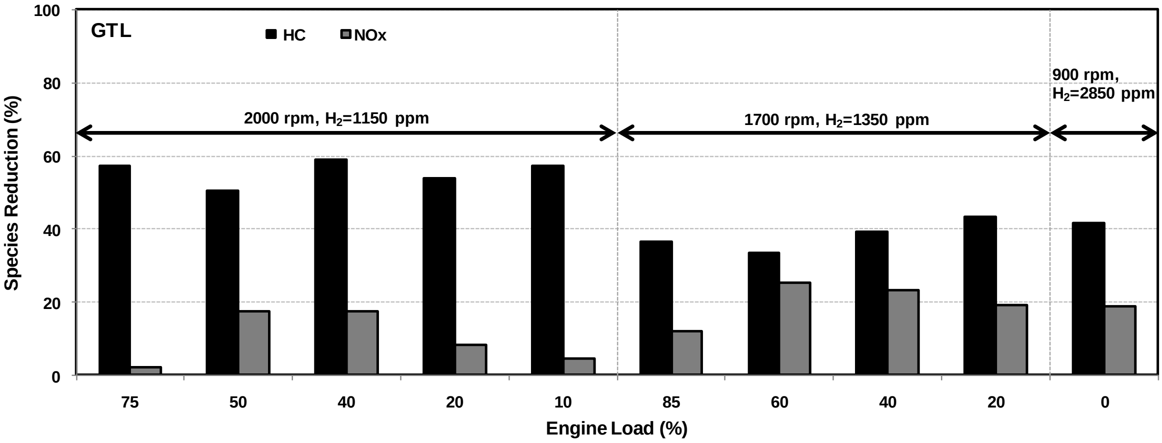


Figure 6.4: PC effect on the HC and NO_x emissions at 2000, 1700 and 900 rpm, which is representative of the fast steady-state test ramp for GTL combustion.

Analysis of the PC reduction activity during GTL combustion yielded results that were unexpectedly lower on average compared to those for ULSD fuelling. Being a cleaner fuel and having lower inherent impurities seemed not to have a beneficial effect on the HC reduction efficiency of the fuel, especially when the lower engine speeds were tested (Figure 6.4, 1700 and 900 rpm). However, the PC was considerably successful at reducing the overall HC emissions from the exhaust gas of GTL combustion across the engine speed-load range of the fast steady-state test cycle. Similar reductions in overall NO_x emissions reduction over the PC were obtained when compared to ULSD fuelling, reaching a maximum of only ~ 25 % (Figure 6.4, 1700 rpm 60 % engine load).

6.2.3. PC effect during RME Combustion

Biodiesel fuels are characterized by higher molecular weight and higher distillation temperatures compared to conventional diesel fuels e.g. ULSD. They also increase the emission of heavy hydrocarbons and the soluble organic fraction (SOF) of particulate matter

(Lapuerta et al., 2008). Atomisation and vaporisation of bio-diesel fuels in the combustion chamber is predicted to be relatively poor in comparison to ULSD and GTL fuelling, due to the fuel properties. As a result, an increase in fuel injection pressure with smaller nozzle hole diameter would be appropriate for good air-fuel mixture formation (Kawano et al., 2006). Furthermore, the inherent oxygen content (~ 10 wt.% for RME) in their structural formulation, aids in the combustibility of the fuel and thus higher combustion temperatures are obtained. The higher bulk modulus of biodiesel tends to promote premixed-combustion through the advancement of fuel injection timing, which when coupled with the inherent O_2 in the fuel, leads to the higher in-cylinder temperatures (due to more complete combustion) and the associated increase in NO_x emissions (Eränen et al., 2004; Kawano et al., 2007; Zheng et al., 2008).

In a study on a light duty RME fuelled vehicle, Karavalakis et al. (2009) found that the NO_x, HC and PM emissions were lower than those from ULSD combustion during specific drive cycles. However, in the current study, only a reduction in HC emissions was observed with a significant increase in NO_x emissions, which is more in agreement with Zheng et al. (2008), who reported lower soot, CO and un-burnt HCs during biodiesel combustion, with a notable increase in NO_x emissions.

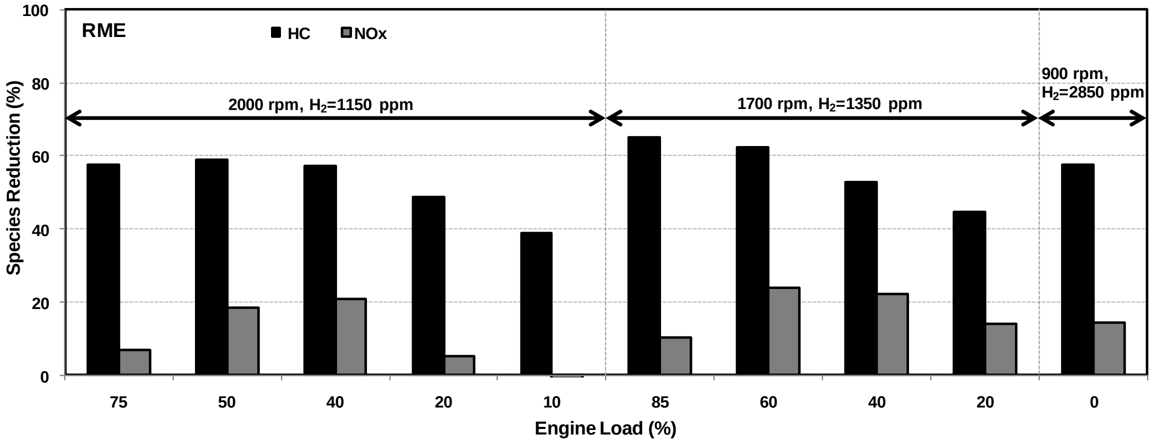


Figure 6.5: PC effect on the HC and NO_x emissions at 2000, 1700 and 900 rpm, which is representative of the fast steady-state test ramp for RME combustion.

From Figure 6.5, it can be observed that the PC reduced HC emissions effectively at the high temperature regions, with a loss of reduction as the exhaust gas temperature lowered. However, NO_x emissions were not significantly reduced over the PC, with a peak of only ~ 23 % (Figure 6.5, 1700 rpm 60 % engine load). Considering the fact that RME produced the least HC emissions output (Table 6.1) from its combustion process, the relative HC (%) reduction over the PC catalyst is testament to the greater heavy HC content from RME combustion. The heavy HCs may have been broken down into smaller chains and not necessarily oxidized over the PC, leading to the low overall HC-ppm reduction.

In general, for all the combustion fuels, the reduction efficiency of CO emissions over the PC was very high (> 96 %) across the whole operating engine speed-load range of the fast steady-state test ramps.

6.3. PC effect on HC-SCR of NO_x over Ag-Al_2O_3

The overall HC reduction activity of the PC for all the combustion fuels used has been reported to be beneficial to the Ag-Al_2O_3 catalysts used in this experimental study (refer to Chapter 5), especially at low exhaust gas temperatures. However, the correct conditions have to be satisfied for the improvement to be observed. During these particular tests with a variety of combustion fuels, a significant improvement in the NO_x reduction activity of the Ag-Al_2O_3 catalyst was expected primarily at the low load (low temperature) operating range, where catalyst deactivation due to HC accumulation was suspected. Discussed herein is the NO_x reduction activity of the Ag-based SCR catalyst for the respective combustion fuels.

6.3.1. ULSD Fast Steady-State Ramp

From the results, there was evidence of the suspected improvement in NO_x activity due to cleaner exhaust gas flowing through the SCR catalysts. This was illustrated by the NO_x reduction activity over the Ag-Al_2O_3 SCR catalysts being relatively low ‘without’ (w/o) when compared to ‘with’ (w) PC use in the exhaust gas (Figure 6.6). Additionally, it was confirmed from these results that the HCs produced from ULSD combustion are, to a certain extent, active in the HC-SCR of NO_x in ‘passive’ mode i.e. with no externally injected HCs.

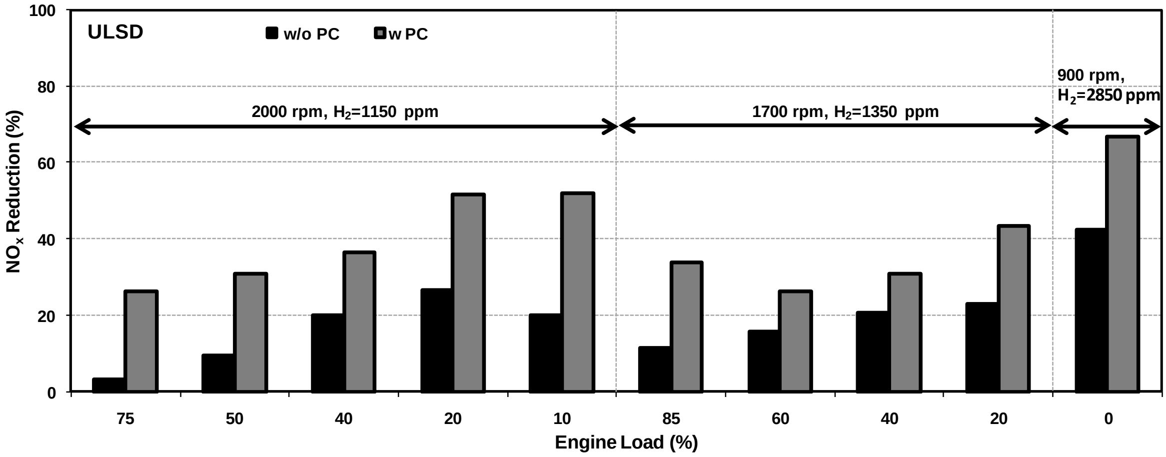


Figure 6.6: PC effect on the Ag-Al_2O_3 HC-SCR of NO_x at 2000, 1700 and 900 rpm, which is representative of the fast steady-state test ramp for ULSD combustion.

The reduced activity without a PC (Figure 6.6) is believed to be due to the accumulation of deactivating species (present in untreated diesel exhaust gas) onto the SCR catalyst active sites, leading to poor NO_x reduction activity (Burch et al., 2004; Creaser et al., 2009; Furusawa et al., 2003). Furthermore, the improvement in NO_x reduction with the use of the PC could lie in the fact that there was a temperature gradient over the PC in the direction of exhaust gas flow due to the oxidative exothermic reactions taking place over the catalyst surface (Hayes and Kolaczkowski, 1997). The oxidation reactions over the PC reduce the PM species and could also partially oxidize the un-burnt HCs from the engine combustion process into more reactive species for the NO_x reduction reaction (Viola, 2008); which would enhance the activity of the HC-SCR reactions over the Ag-Al_2O_3 catalysts by slowing down or inhibiting surface species adsorption.

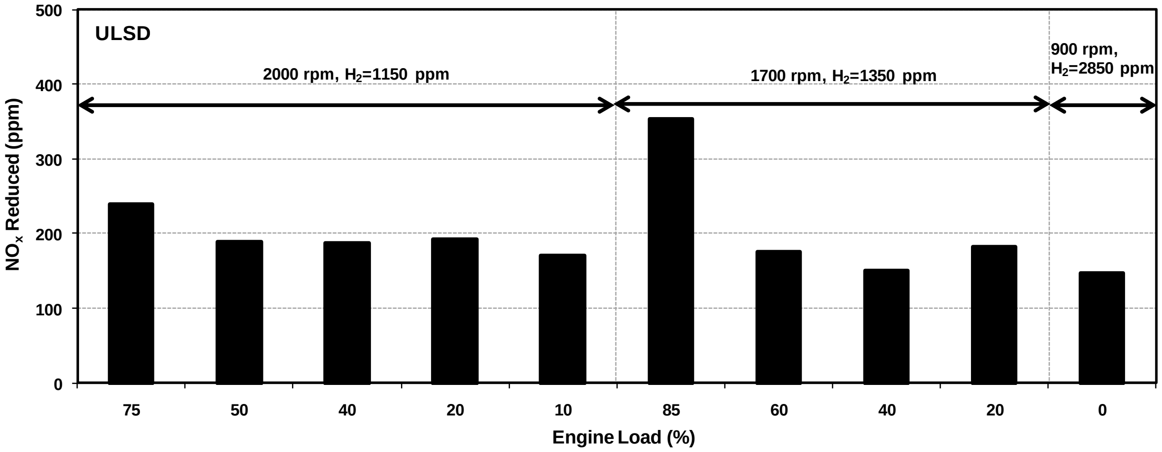


Figure 6.7: The NO_x (ppm) reduced over the Ag-Al_2O_3 catalysts for 2000, 1700 and 900 rpm, representative of the fast steady-state test ramp for ULSD combustion with the use of the PC.

The average NO_x-ppm reduced over the SCR catalysts was approximately constant at the highest operating engine speed of 2000 rpm (Figure 6.7, 2000 rpm), suggesting that at these particular operating conditions there was no considerable accumulation of surface species over the catalyst. However, when the engine speed was lowered to 1700 rpm; the initial NO_x-ppm converted was higher but then subsequently dropped for the remainder of the test cycle (Figure 6.7, 1700 rpm). This suggests that there was catalyst surface species accumulation through the adsorption of inhibiting species onto the SCR catalyst surface, which led to the loss in NO_x-ppm reduction. However, the overall NO_x reduction (%) was not drastically affected owing to the NO_x output from the diesel engine at the respective load conditions. At the lowest speed of 900 rpm, the NO_x output from the engine was at its lowest, but the NO_x-ppm reduced over the catalyst was still relatively high (compared to the whole speed-load range), hence the overall NO_x reduction at this engine operating condition was the highest (Figure 6.7 and Figure 6.6, 900 rpm).

6.3.2. GTL Fast Steady-State Ramp

Given the combustion cleanliness which is related to GTL fuel, it was expected that the NO_x reduction activity would be better than that of ULSD fuel. At the engine speed of 2000 rpm, the overall NO_x reduction (%) increased with reducing engine load for GTL fuelling (Figure 6.8). However, comparatively (with ULSD), improved NO_x reduction (%) was only observed at engine loads below 50 % (Figure 6.8a and Figure 6.6).

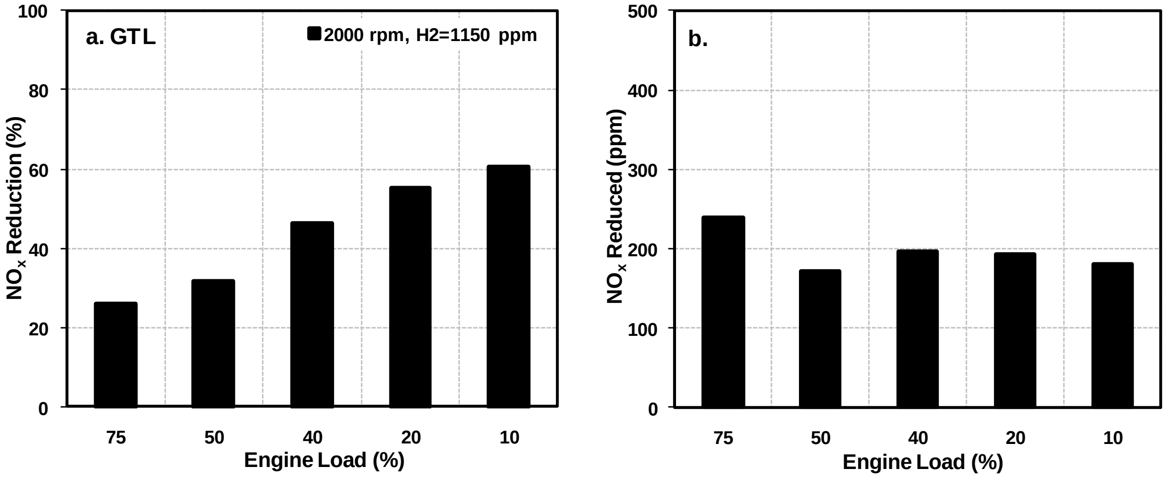


Figure 6.8: NO_x reduction over the Ag-Al_2O_3 catalysts during GTL combustion, represented as a) a percentage (%) and b) parts per million (ppm), for the engine speed of 2000 rpm.

With respect to the overall NO_x activity improvement, the inherent un-burnt HC species present in the exhaust gas were being consistently utilized for the HC-SCR of NO_x reaction. As Figure 6.8b shows, the NO_x-ppm reduced over the Ag-Al_2O_3 catalysts showed a difference of only ~ 70 ppm across the load range for the engine speed of 2000 rpm. Additionally, the HC:NO_x ratios at 2000 rpm for GTL combustion were comparable to those for ULSD combustion. Therefore, due to the continued NO_x-ppm reduction consistency, the overall NO_x (%) reduction was improved as the NO_x-ppm output from the diesel engine reduced with load, again suggesting no apparent catalyst deactivation.

The presence of H_2 to the system (1150 ppm) must have had an influential effect on the overall NO_x conversion. With reducing load i.e. temperature, the HC:NO_x ratios became more favourable (increased) for improved HC-SCR of NO_x and given the activation effect H_2 has on the $Ag-Al_2O_3$ catalysts (Arve et al., 2005b, Houel et al., 2007a; Satokawa et al, 2007), better NO_x conversions were thus to be expected. In their investigation of a NO_x reducing catalyst by thermo-gravmetric analysis, Rodríguez-Fernández et al. (2009) found that the accumulation of surface species (associated with deactivation) on the catalyst was more pronounced at low temperatures; however, with GTL fuelling, a decreased amount of accumulated species was observed. A characteristic which in the presence of hydrogen should lead to improved NO_x reduction efficiencies.

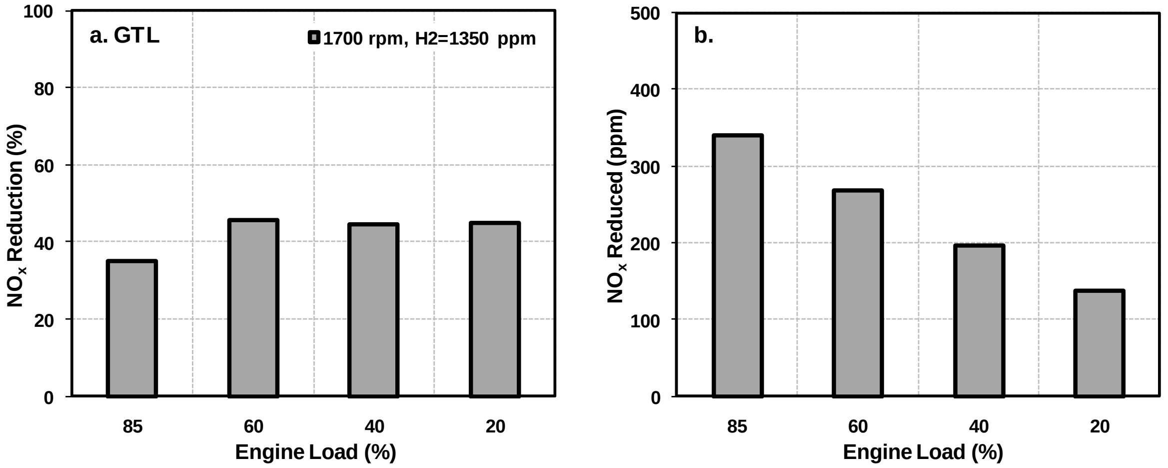


Figure 6.9: NO_x reduction over the $Ag-Al_2O_3$ catalysts during GTL combustion, represented as a) a percentage (%) and b) parts per million (ppm), for the engine speed of 1700 rpm.

When the engine speed was reduced to 1700 rpm, the overall NO_x reduction (%) was averaging ~ 40 % (Figure 6.9a). This consistency in NO_x reduction was however not representative of the trend in the amount of NO_x-ppm reduced over the SCR catalysts (Figure 6.9b). From the high load region, the amount of NO_x-ppm that was reduced was relatively high but was not maintained through to the lower loads. Exhaust gas temperature decrease with lowering engine load may have made it easier for poison-species to accumulate on the SCR catalyst, especially in the case where the exhaust gas temperature was below that of 50% distillation of the fuel. At this operating speed (1700 rpm), the H_2 in the exhaust gas increased slightly to ~ 1350 ppm, which theoretically should have led to better NO_x conversions over the SCR catalysts, provided there was enough reductant. However, although the HC:NO_x ratios observed at this engine speed were similar to those at 2000 rpm, the overall NO_x conversion was on average lower. Possible explanations range from the lack of reactive reductant, given the clean combustion of GTL, to SCR catalyst saturation with species which can accelerate the deactivation of the Ag-Al_2O_3 catalyst such as surface carbon (Houel et al., 2007b; Theinnoi et al., 2008a) or nitrates (Breen et al., 2006; Creaser et al., 2009; Richter et al., 2004; Shibata et al., 2003).

At the even lower engine operating speed of 900 rpm, where the engine was operated with no load, the NO_x-ppm output from the engine was at its lowest. Consequently the overall NO_x reduction was relatively high although only ~150 ppm of NO_x was being reduced over the Ag-Al_2O_3 catalysts (results not shown). The H_2 addition at this engine condition was calculated at ~ 2850 ppm, the highest of any condition. With the HC:NO_x ratio being recorded at ~ 1.1, additional H_2 must have had a positive influence on the HC-SCR reaction, yielding the best overall NO_x reduction of ~ 65 %, over the SCR catalysts.

6.3.3. RME Fast Steady-State Ramp

Characteristic of bio-fuel combustion, as aforementioned, is the increased heavy HC emissions and increased NO_x output emissions. At the engine speed of 2000 rpm, the overall NO_x reduction at high load was relatively poor when compared to the other operating engine loads (Figure 6.10a). The highest overall reduction was observed at 40 % engine load, which coincidentally was also the condition at which the highest NO_x-ppm was reduced over the SCR catalyst (Figure 6.10b). However, with lowering engine load the NO_x-ppm reduction was greatly decreased which is in relation to the overall NO_x reduction.

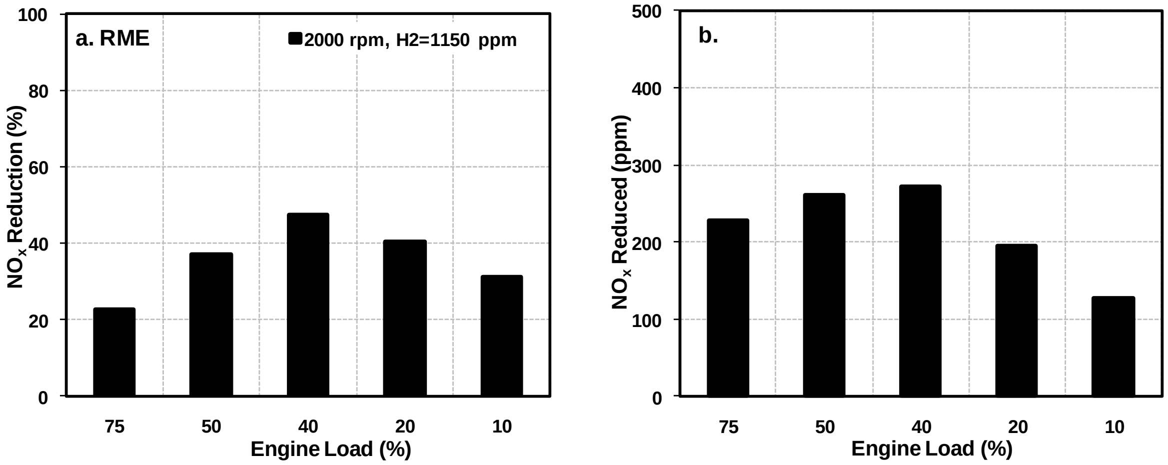


Figure 6.10: NO_x reduction over the Ag-Al_2O_3 catalysts during RME combustion, represented as a) a percentage (%) and b) parts per million (ppm), for the engine speed of 2000 rpm.

The amount of H_2 (1150 ppm) present in the exhaust gas should have played an important role, in that, its presence should have improved the HC-SCR reaction for NO_x, given that RME yielded the highest exhaust gas temperatures. Nevertheless, if the HCs present in the exhaust gas were not of a very reactive nature, as attributed to bio-fuels, there would be no significant improvement in the overall NO_x reduction activity. From Figure 6.10b, it can easily be noted that there was a significant loss in catalytic activity after 40 % engine load, signified by the rapid loss in NO_x-ppm reduced.

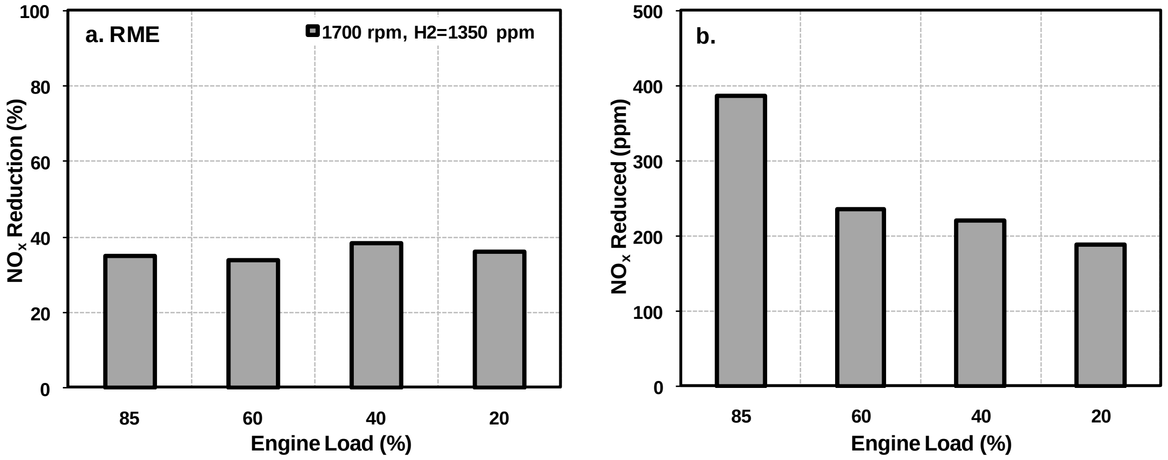


Figure 6.11: NO_x reduction over the Ag-Al_2O_3 catalysts during RME combustion, represented as a) a percentage (%) and b) parts per million (ppm), for the engine speed of 1700 rpm.

When the added H_2 amount increased to 1350 ppm through the decrease of the engine speed to 1700 rpm, the observed NO_x reduction was expected to increase, but was unexpectedly similar to that observed at 2000 rpm, where only 1150 ppm H_2 was present. Interestingly, although the overall NO_x reduction was consistent across all the engine loads (Figure 6.11a), the NO_x-ppm that was actually being reduced over the SCR catalysts was initially high, but then decreased with engine load (Figure 6.11b). Heavy un-reactive HC presence (and possible deposition) was suspected of causing the lack of improved catalyst activity given the increased H_2. This notion can be supported by the amount of NO_x-ppm reduction over the SCR catalysts, which was seen to drop drastically with decreasing engine load (from 85 – 60 %), then more gradually from 60 – 20 % engine load, as illustrated in Figure 6.11b.

With the even higher H_2 amount of 2850 ppm into the SCR catalysts attained at the operating engine speed of 900 rpm, there was no notable improvement in the overall NO_x reduction activity of the Ag-Al_2O_3 catalyst, which remained at ~ 40 % (results not shown). Also, the NO_x-ppm reduced over the SCR catalysts continued to fall with decreasing engine load and was recorded at ~ 120 ppm reduced at 900 rpm.

In general, more selective HCs are required for a notable improvement in NO_x activity performance over the SCR catalysts, especially with the use of RME as a combustion fuel, due to its apparent un-burnt HCs lacking HC-SCR reactivity for NO_x reduction in ‘passive’ mode operation.

6.4. Space Velocity Effect with Temperature

The space velocity associated with the respective engine speeds may have played an important role in the NO_x reduction efficiency of the SCR catalysts. SV influences the reaction contact time between the exhaust gas and the catalyst active sites and therefore can limit or hinder the full progression of particular reactions e.g. the NO_x reduction reaction (Hayes and Kolaczkowski, 1997). Some reactions require a short residence time because they occur very quickly over the catalysts surface while in contrast, others may require longer times for reaction completion. Eränen et al. (2004) noted in their study that SV played an important role in the NO_x conversion reaction over Ag-Al_2O_3 catalysts. They reported that the strong dependency of the NO_x reduction activity on SV was due to the extremely slow reaction of NO and HC activation, considered a key step in the formation of important intermediates. Therefore, a long residence time would be required for the reaction mechanism to reach completion.

However, the presence of H_2 is said to enhance this reaction; hence allows for better NO_x conversions with higher SV. It is apparent that catalyst volume plays an important role in regulating the SV in the exhaust tailpipe of an engine. Schmieg et al. (2006) also confirmed that as the SV increased, the temperature required for Ag-Al_2O_3 catalyst light-off (i.e. the temperature to achieve 50 % NO_x conversion) increased. However, these findings are in contrast to the results from this investigation from which it was observed that the higher SV exhibited slightly better NO_x conversions over the SCR catalysts across the majority temperature range (Figure 6.12). The SVs used in this investigation were approximately 26k, 22k and 10k h^{-1}, representative of the engine speeds of 2000, 1700 and 900 rpm, respectively.

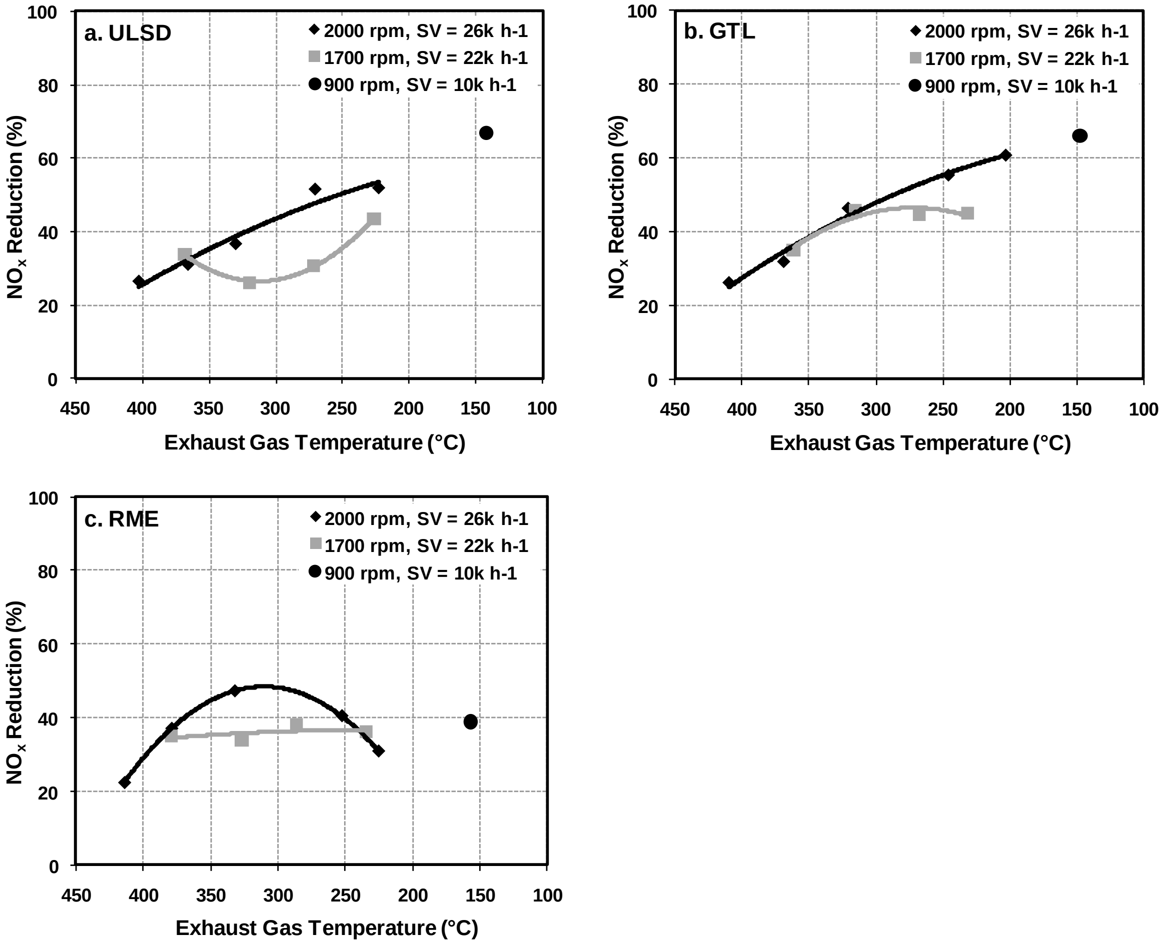


Figure 6.12: The SV effect on NO_x reduction over the Ag-Al_2O_3 catalysts for a) ULSD, b) GTL and **c)** RME fuel combustion, presented as a function of varying exhaust gas temperature across the test cycle.

In comparison, the ULSD results for NO_x reduction are similar to those for RME in that the overall NO_x conversion was generally higher for the SV of 26k h^{-1} as opposed to that for 22k h^{-1} (Figure 6.12a and Figure 6.12c). Overall, the HC:NO_x ratios from the combustion of RME were generally lower than those of ULSD and GTL (Table 6.1) and consequently the NO_x efficiency of this particular fuel was lower on average. At the lowest engine speed of 900 rpm (SV = 10k h^{-1}), NO_x conversion for RME combustion was not at its highest, as was the case for the other respective combustion fuels. This was due to the presence and/or accumulation of partially un-reactive HCs (and other C-species) from the combustion of RME, which in turn significantly reduced the NO_x reduction activity, especially at lower exhaust gas operating temperatures. At high exhaust gas temperatures (> 300 °C), GTL was the only combustion fuel to yield results that were similar for the SV of 26 and 22k h^{-1} (Figure 6.12b).

Due to the reactants in the exhaust gas of all the combustion fuels not being optimized for each of the respective speed-load conditions i.e. H_2 amount and HC species/amount, a loss in NO_x reduction is observed at the lower SV of 22k h^{-1}, possibly due to the lack of reactive HC species or due to carbon species deposits and/or other poisons contributing to the lack of activity, given the increased residence time over the catalyst (Burch et al., 2004; Creaser et al., 2009, Richter et al., 2004). Conversely, the best NO_x reduction activity was observed at 900 rpm for ULSD and GTL fuelling, a condition at which the residence time was highest. The increased NO_x activity was most likely due to the greatly increased H_2 in the exhaust gas (~ 2850 ppm) and the presence of more reactive inherent HC species for these particular combustion fuels.

It can therefore be appreciated that the increased amount of H_2 at the near idle conditions could have resulted in the oxidation of some of the excess HCs in the exhaust gas and possibly activation of others (Viola, 2008), both of which could have helped in maintaining a cleaner more reactive catalyst surface (through lesser accumulating species) leading to improved NO_x reductions.

6.5. Active Operation of Ag-Al_2O_3

During the fast steady-state ramps discussed above, it became apparent that the behaviour of the Ag-Al_2O_3 catalysts was not only dependant on the H_2 and HC amount in the exhaust gas, but also the engine operating temperature and SV. As a result of these observations, a series of tests with only the conventional ULSD fuel were devised to establish whether the PC was a necessary component at all engine operating conditions.

For this particular investigation, the same engine operating conditions were used (Figure 6.2a), with hydrogen addition now increased to 3000 ppm for the reference engine speed of 1500 rpm. The respective amounts present at each of the other test conditions were as illustrated in Figure 6.13a.

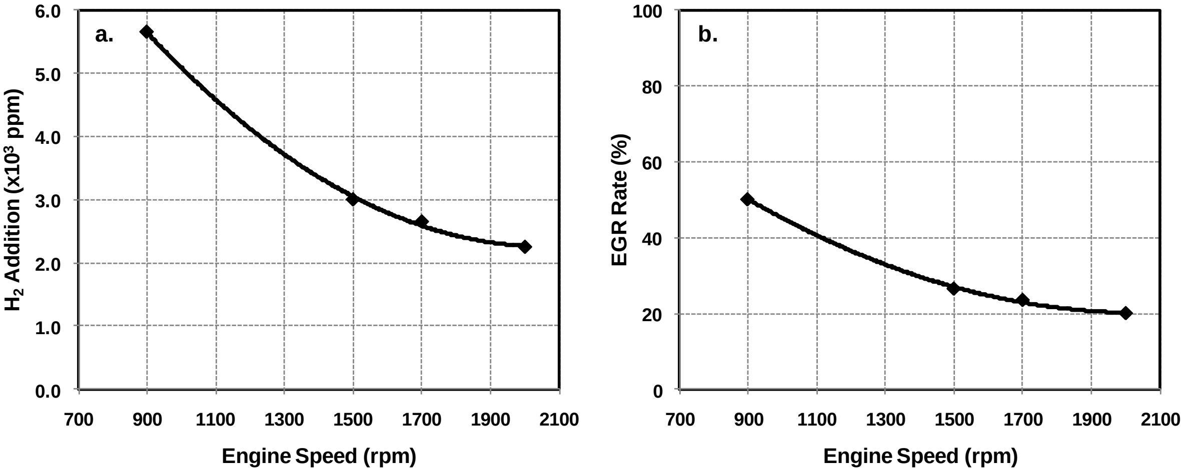


Figure 6.13: The variation of a) hydrogen (ppm) addition and b) the EGR rate (%), with engine speed (rpm), for the conditions tested in relation to the reference of 3000 ppm at an engine speed of 1500 rpm.

The engine was operated with 20 % EGR at a reference of 2000 rpm. Thus, as the engine speed was lowered the EGR rate was increasing. The rate of the increase was as illustrated in Figure 6.13b. At the near idle operating speed, the engine was operating with approximately 50 % EGR. The SCR catalyst input parameters are shown in Table 6.3. The exhaust system was slightly modified for this part of the investigation to allow for the addition of H_2 at two respective points, since different catalyst configurations were to be studied (Figure 6.14). The activity of the SCR catalysts at respective conditions would then be assessed and the relevance of the PC evaluated.

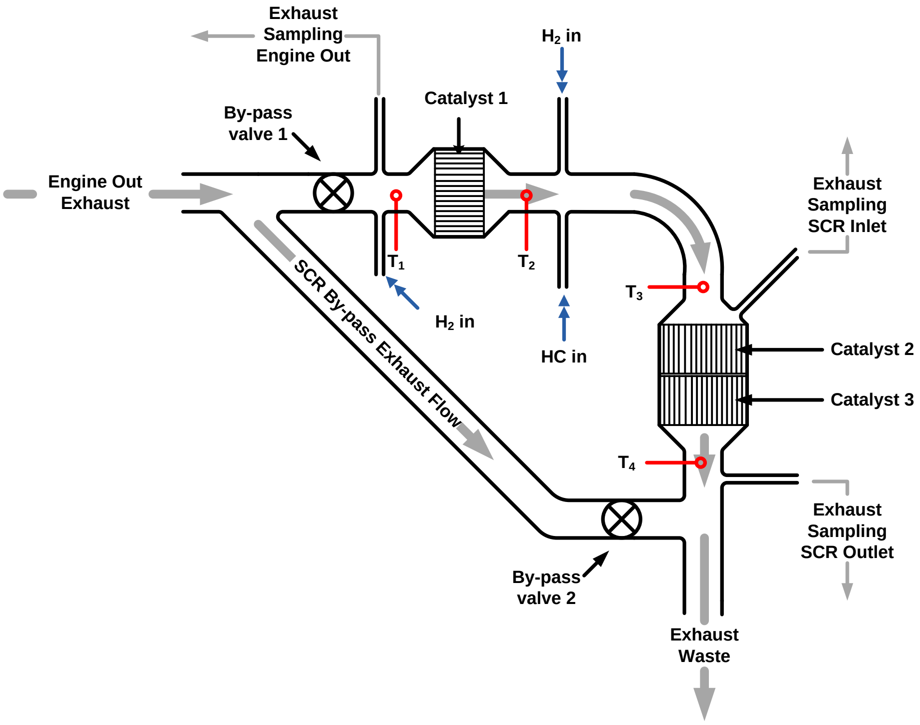


Figure 6.14: Schematic showing the modified engine exhaust system with an additional H_2 input point in front of the first monolith catalyst brick.

It was observed from the tests above, that the use of a PC at low temperature was aiding the HC-SCR of NO_x reaction at low engine load (low temperature) by the removal of excess reductants and other species. However, at the higher engine loads (higher temperatures) the PC was suspected of minimizing the available reductant and as a result inhibiting the NO_x reduction reaction over the SCR catalysts. To investigate this effect, if at all, two different catalyst arrangements were examined in the exhaust of the diesel engine, namely, PC-Ag-Ag and Ag-Ag-PC. In both instances, the H_2 was added to the Ag catalysts inlet and not to the PC input as it would have been oxidized prior to reaching the SCR catalysts. Among a number of catalysts, Ag-Al_2O_3 catalysts exhibit high activity for NO_x reduction with alcohols or higher hydrocarbons (Chafik et al., 2000; Shimizu et al., 2001). For this particular experiment, the latter reductant was explored, i.e. long chain HC injection in the form of ULSD.

Table 6.3: The engine test parameters and SCR catalyst input parameters

Engine Speed (rpm)	**Engine Load (%)**	**T (°C)**	**20 % EGR, PC-Ag-Ag**			**20% EGR, Ag-Ag-PC**			**25 ml/hr ULSD**	
			HC	**NOx**	**HC:NOx**	**HC**	**NOx**	**HC:NOx**	**HC**	**HC:NOx**
2000	**75**	415	400	376	1.06	962	402	2.4	1187	3.0
	50	374	330	393	0.84	1060	453	2.3	1285	2.8
	40	340	325	335	0.97	700	398	1.8	925	2.3
	20	278	325	323	1.01	1058	358	3.0	1283	3.6
	10	224	360	266	1.35	785	298	2.6	1010	3.4
1700	**85**	375	340	444	0.77	833	475	1.8	1098	2.3
	60	341	335	389	0.86	542	488	1.1	807	1.7
	40	290	340	320	1.06	693	438	1.6	958	2.2
	20	237	325	273	1.19	593	329	1.8	858	2.6
900	**0**	150	300	190	1.57	632	193	3.3	1197	6.2

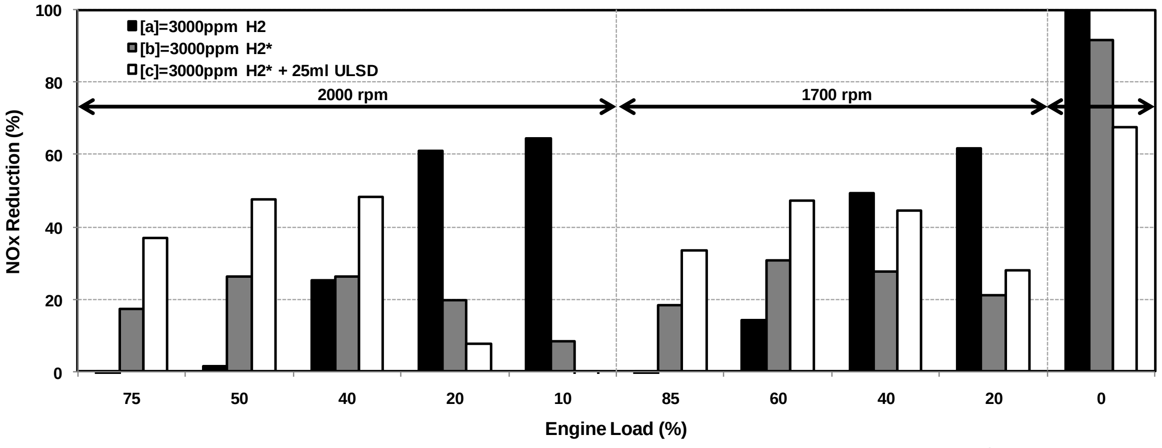


Figure 6.15: NO_x reduction over Ag-Al_2O_3 catalysts during the test cycle for arrangements **[a]** PC-Ag-Ag, **[b]** Ag-Ag-PC and **[c]** Ag-Ag-PC + 25 ml/hr ULSD. H_2 shown is with reference to 1500 rpm engine speed, see Figure 6.12. (* 50/50 H_2 split into both Ag bricks).

The relevance of the PC is illustrated in Figure 6.15, where it can be seen that the PC is not necessarily needed at all the operating conditions. With the use of the PC at the front of the SCR Ag catalysts (case **[a]**), the NO_x reduction is very low and in some instances zero. It is suspected that this effect is due to the PC oxidizing the remaining reactive HC species in the exhaust gas and only allowing some of the non-reactive species to pass through it. This effect seems more prominent at higher engine loads (higher exhaust temperature) conditions. Consequently, there seems to be no need for a PC at high temperature conditions as the overall NO_x reduction is generally low (Figure 6.15, 2000 and 1700 rpm). However, with a change in the tailpipe arrangement by putting the Ag catalysts in front of the PC (case **[b]**); the high load operation NO_x reduction improved. In this respect, it is apparent that the PC is not required under high temperature operation. Furthermore, in case **[b]**, the low temperature NO_x reduction efficiency of the SCR catalysts was getting progressively lower with decreasing engine load, thus temperature.

To confirm the fact that the PC was reducing the reactive HC species from the exhaust gas, a study with the injection of 25 ml/hr of conventional ULSD fuel was devised (case **[c]**). The arrangement of the catalyst was the same as that in case (b). As expected, at the high engine load (high temperature) operating conditions, the NO_x reduction efficiency was further improved by nearly 100% across all engine loads of above 20 %. Interestingly, at the near idle operating condition the NO_x reduction was not as drastically affected as the other low load operating conditions (e.g. Figure 6.15: 2000 rpm at 20 and 10 % load), in that although similar trends were observed, the efficiency was above 60 % for all the three case studies with no engine load.

It can therefore be concluded that the temperature and composition of the exhaust gas is very influential to the use of a PC. Generally, the HC:NO_x ratio of the exhaust gas is highest at the lower load and the best NO_x reduction can also be observed at these conditions. Consequently, a PC is a necessary component at low engine operating temperatures but is not required at the higher operating temperature conditions.

6.6. Summary

From the fast steady-state test ramps studied here; the results show that in a transient-like mode (as tested) the NO_x-N_2 reduction is dependent on the exhaust gas temperature, the space velocity (SV) and the exhaust gas composition. Given that the tests were conducted in the order ‘high speed-high load’ to ‘low speed-low load’, poisoning characteristics normally associated with the Ag-Al_2O_3 catalysts at low temperatures were minimized leading to the observed increase in overall NO_x reduction activity for ULSD and GTL fuelling. It is therefore suspected that, when tested at the lower engine loads, the SCR catalysts were relatively free of adsorbed species. However, selective HC injection will be required to further improve the SCR catalyst NO_x efficiency, especially at higher temperatures (> 250 °C) where the HC:NO_x ratio is relatively low.

The prototype diesel oxidation catalyst effect has also been shown, in that, its use upstream the SCR catalysts has an improving effect on the HC-SCR reaction mechanism at specific operating conditions. The improvement is possibly due to the removal of poisoning species by oxidation reactions over the PC surface and by the maintenance of high exhaust gas temperatures (through these oxidation reactions), which then aid in maintaining/improving the SCR of NO_x reaction over Ag-Al_2O_3 catalysts.

SV plays an important role in the NO_x activity efficiency of the Ag-Al_2O_3 catalyst; the higher the SV, the lower the residence time over the SCR catalyst surface, therefore the shorter the subsequent time of reaction for NO_x reduction. However, the higher NO_x reduction activity was observed at the higher SV for all the three combustion fuels tested. This phenomenon is attributed to the lack of selectivity of HC species in the exhaust gas (from the combustion process) that could hinder the HC-SCR reaction for NO_x. Interestingly, throughout all the experiments, the highest NO_x conversion was always observed for the near idle condition. Due to these particular conditions possessing the least NO_x emissions and the most H_2 amount; any small reduction of NO_x-ppm over the SCR catalyst led to significant overall NO_x reductions.

Lastly, through the different catalyst arrangement study with EGR, it was found that the PC is only a necessary component at low engine load (low temperature) conditions, while at the high engine loads (high operating temperatures), only selective HC injection is required. A solution would be to always use the PC at the front of the SCR catalysts and then selectively inject HC species (in the presence of H_2) as of when they are required, into the inlet of the SCR catalysts, taking into account the exhaust gas compositions.

CHAPTER 7

PARTIAL OXIDATION AND EXHAUST GAS FUEL REFORMING

7.1. Introduction

In this Chapter, H_2 and low chain HCs (C_1 - C_6) production from the PO_x of diesel (ULSD), GTL and RME with air, is examined and discussed, with reformer operation under the same input power. The reaction associated with PO_x has already been described by reaction 2.24 (Chapter 2). The reformer reactor and catalyst are described in greater detail in Chapter 3. Air and fuel ratios into the reformer were selected to provide a range of reformer operating conditions e.g. input power, space velocity and O/C ratios (Table 7.1). The power (P_{ref}) from the heat release due to the combustion of a specific fuel in a reforming reactor is defined as

$$P_{ref} = \dot{m}_f LCV_f \tag{7.1}$$

where $\dot{m}_f$ (kg/s) is the mass flow rate of the fuel fed into the reactor and LCV_f (MJ/kg) is the lower calorific value of the fuel. The input power (P_{in}) into the reformer reactor was determined by taking into account mass flow rate and lower calorific value (MJ/kg) of the ULSD, RME and GTL fuels respectively, as defined in reaction (7.1).

From this definition, the reforming process efficiency (η_{ref}) can be determined as the fraction of the chemical power (kW) of the H_2 and CO produced divided by the chemical power of the fuel fed into the reforming reactor, as follows:

$$\eta_{ref} = (\dot{m}_p LCV_p)/(\dot{m}_f LCV_f) \tag{7.2}$$

where $\dot{m}_p$ and LCV_p are the mass flow rate and the lower calorific value (LCV) of the product gas (CO and H_2).

Throughout all the tests conducted, the furnace was maintained at a temperature value of ~ 200 ^oC, for the purpose of preheating the catalyst to operating (light-off) temperature. The temperature was chosen because it is typical of diesel engine exhaust gas when operating at low loading. It provides evidence that the reforming catalyst can be activated by diesel exhaust gas at relatively low temperatures, therefore, could possibly be incorporated into the exhaust system without the need for an external heating source.

A comparison is also made between the PO_x and exhaust gas fuel reforming processes when an Ag-Al_2O_3 SCR catalyst is used for NO_x after-treatment purposes (Figure 7.1). Exhaust gas fuel reforming is similar in nature to the PO_x reaction but is inclusive of water (H_2O), CO_2, CO, un-burnt HC and soot particles. The main idea behind examining the two processes was to find out if the exhaust gas reforming process gave results that were similar in nature, to those produced by PO_x reforming, both in terms of H_2 yield and NO_x conversion efficiency.

Optimization of process parameters e.g. space velocity and O/C ratios is essential to get the best H_2 yield from the reforming process due to sensitivity of the process to the feedstock conditions. The findings herein provide a basis for the future development of a PO_x diesel-type fuel reformer for possible on-board H_2-rich gas production and show that this technology is viable and could be successfully implemented into a diesel HC-SCR after-treatment system with moderate ease . Furthermore, Tsolakis et al., (2003) have shown that reforming can be used as a way to lower combustion emissions such as smoke, PM and NO_x by feeding the reformate (i.e. the reformed product gas) into the cylinder through mixing with the inlet charge air. Apart from emissions benefits, Alvarez-Galvan et al., (2008) also suggested that fuel reforming could be used as a source of fuel for fuel cell applications in their investigation of Pt-based catalysts supported on Al_2O_3. Such studies just add emphasis to the versatility of fuel reforming technology.

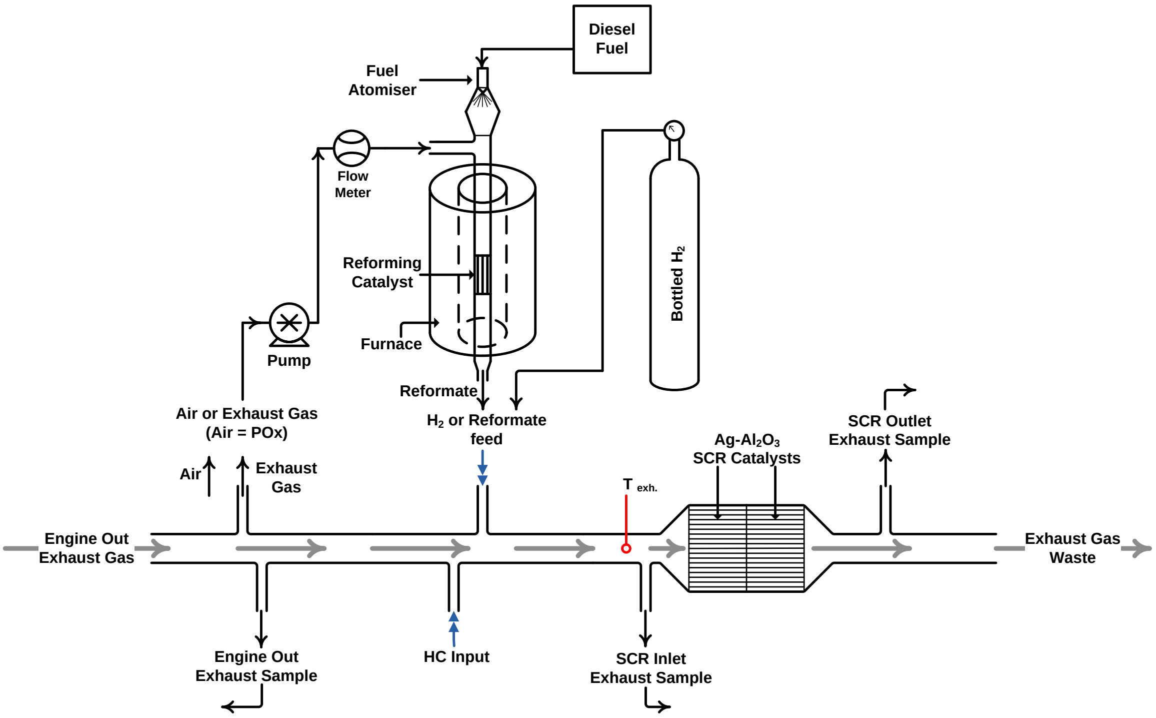


Figure 7.1: Simplified schematic showing the reforming reactor connected to the diesel engine exhaust, operating either in PO_x mode or in Exhaust gas fuel reforming mode.

Table 7.1: PO_x reforming conditions, Air flow = 4 $Lmin^{-1}$, SV = ~ 35k h^{-1}.

P_{in} (kW)	**ULSD Flow ($mL\ h^{-1}$)**	**ULSD Flow ($g\ h^{-1}$)**	**RME Flow ($mL\ h^{-1}$)**	**RME Flow ($g\ h^{-1}$)**	**GTL Flow ($mL\ h^{-1}$)**	**GTL Flow ($g\ h^{-1}$)**
0.34	34.6	28.83	35.5	31.37	35.5	27.85
0.39	39.6	33.00	40.6	35.88	40.6	31.85
0.45	46.0	38.33	47.1	41.62	47.1	36.95

7.2. Reformer Performance under the same Input Power

Under similar reformer space velocities (constant air flow rate) operation and in order to have the same reformer input power operation the volumetric fuel flow rate into the reformer was adjusted for each fuel (Table 7.1). So by increasing the fuel flow rate the input power was also increased (Figure 7.2). Therefore, varied fuel flow rates were used to achieve the required input powers, which also resulted in different peak temperatures and temperature profiles. The Gas hourly space velocity (SV) was kept at a constant value of 35k h^{-1} for this part of the investigation so as to only observe the effect of the input power into the reforming reactor. Partial oxidation reforming is an exothermic process resulting in the reaction temperature rising to values higher than 800 °C and is producing self-sustaining reactions if the heating source (i.e. furnace) was to be turned off (Kopasz et al., 2005).

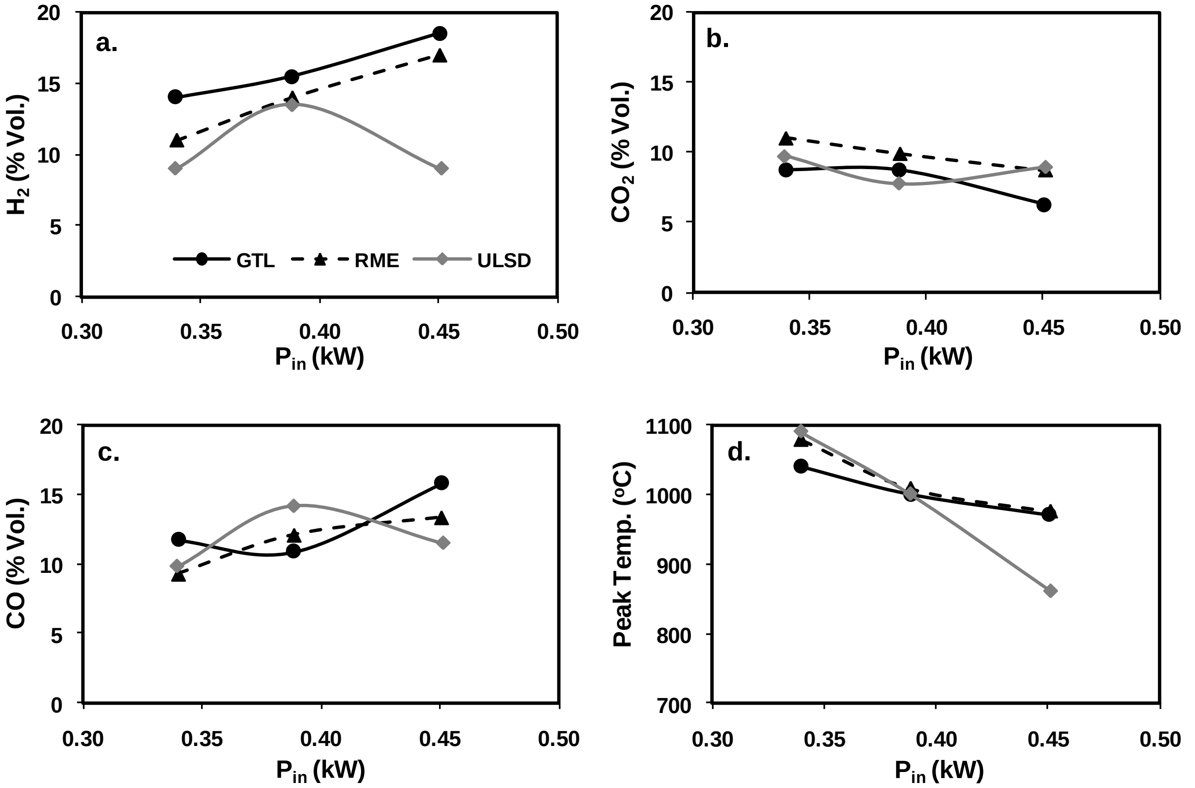


Figure 7.2: Effect of the input power (P_{in}) on the PO_x reformate gas for a) H_2 yield, b) CO_2 yield, c) CO yield and d) peak reactor temperature.

Hydrogen yield at similar input powers followed the trend GTL > RME > ULSD throughout the entire test conditions (Figure 7.2), which unexpectedly is similar to the O/C trends (Figure 7.3).

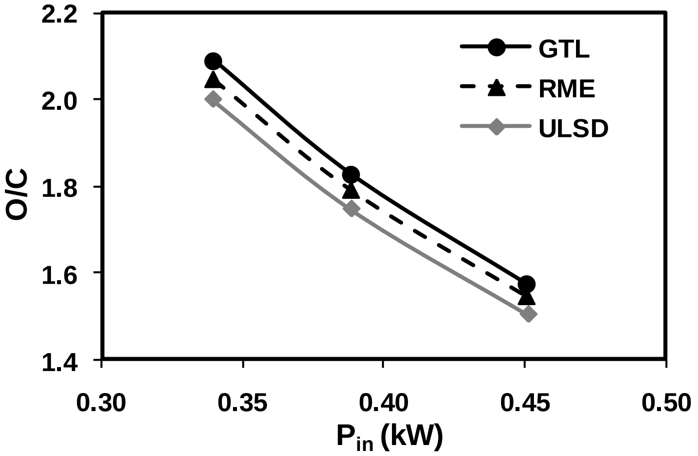


Figure 7.3: Effect of the input power on the O/C ratio.

Under the same input power the fuel flow rate (by mass) into the reformer in the case of GTL (higher calorific value fuel) is slightly lower than ULSD and significantly lower than that of RME. It was estimated that the fuel power used in the complete oxidation reaction during the reforming of ULSD, GTL and RME was 0.231 kW, 0.226 kW and 0.281 kW, respectively. Under the same input power; the available fuel mass of GTL for the endothermic reactions (i.e. steam and dry reforming) is estimated to be approximately 1.1, 1.4 and 1.9 % (wt.) lower than the corresponding mass of ULSD, and 13.6, 15.6 and 18.1 % (wt) higher than RME for the reformer input powers of 0.34, 0.39 and 0.45 kW, respectively. Parameters that can explain the higher H_2 production in the case of GTL compared to RME reforming as the extra GTL fuel amount was utilized in the endothermic reactions (i.e. steam and dry reforming) as revealed by the increased production of H_2 and CO. Furthermore, only in the case of GTL this extra fuel was utilized as reflected by the improved GTL reforming process efficiency and on the consumed CO_2 (Figure 7.2).

The higher H:C ratio of the GTL fuel and its superior qualities as compared to ULSD and RME fuels can also attribute to the increased H_2 production. For example, the higher cetane number associated with GTL fuel aids faster light-off resulting in faster kinetics during the reforming process. Also, the lack of sulphur and virtually zero aromatics content within the fuel helps by not promoting catalyst deactivation by coking or sulphur poisoning, especially during the initial light off period. On the other hand, the ULSD fuel used in this study contained the highest amount of aromatics and due to this, may have deactivated the reforming catalyst through carbon deposition. Reforming catalysts are less prone to deactivation by coking with synthetic (mainly paraffinic) derived diesel fuels; such as Gas-to-Liquid (GTL) compared to crude oil derived diesel fuels.

In general, C-C bond energies of aromatics are stronger than those of paraffins, which decreases the reaction rate and leads to higher reforming temperatures being required (Cracknell et al., 2004).This is also in agreement with Kopasz et al. (2005) who reported that when reforming simple hydrocarbons e.g. dodecane, there is an increase in complex aromatic species formation which suggests the initial steps in carbon deposition, through the formation of large complex ring systems. As a result, the inherent aromatics in ULSD fuel aid in the formation of these more complex catalyst poisoning species. This phenomenon was more apparent in this investigation at the higher reformer input powers (higher fuel flow rates), as signified by the sudden loss in H_2 yield, with a corresponding significant peak temperature drop (Figure 7.2a and 7.2d). In order to improve ULSD fuel reforming, higher reaction temperatures are required and can be achieved by optimizing the reactants (i.e. air to fuel ratio) or the space velocity (Tsolakis et al., 2007a).

From Figures 7.2b and 7.2c, it is apparent that apart from the partial oxidation reaction, other reactions were also taking place as illustrated by the CO_2 output in the reformate. This CO_2 could be from the complete oxidation of HCs over the catalyst, leading to the production of small amounts of water. The steam reforming reaction (SRR) could then take place through the reaction of the water vapour and hydrocarbons to produce CO and H_2. The dry reforming reaction (DRR) could consecutively take place, thus consuming some of the CO_2 produced from the other reactions over the reforming catalyst surface to produce more CO and H_2. Furthermore, it is during SRR and DRR (reactions 2.26 and 2.27, respectively) that the peak reformer temperatures are observed for any particular test condition and these reactions usually occur towards the front of the catalyst bed were the fuel mixture is introduced. This increase in temperature is associated with the rapid decline in gas-phase O_2, indicating the sudden oxidation of the fuel when it came into contact with the reforming catalyst bed (Tsolakis and Golunski, 2006).

As the input power was increased by the addition of more fuel into the reformer, there was a corresponding decrease in the peak reformer temperature due to the promotion of endothermic nature reactions. Maximum H_2 yields observed were 19, 17 and 14 % for GTL, RME and ULSD respectively. Apart from the peak for ULSD fuel, those for GTL and RME occurred at the higher reactor input powers.

From equilibrium calculations, it is generally accepted that the highest amount of H_2 will be produced at O/C = 1; which complements our findings as the O/C ratio approached 1 there was an increase in H_2 output from the reforming process for each of the respective fuels (Figure 7.2a and Figure 7.3), except that of ULSD fuel, as explained earlier. With more fuel being added to the reformer reactor, the O/C ratio decreased but the fuel penalty, for better H_2 yield, increased. If the reformer system is to be implemented into a diesel engine for commercial use, the fuel penalty resulting from the use of the reformer would be a major consideration factor.

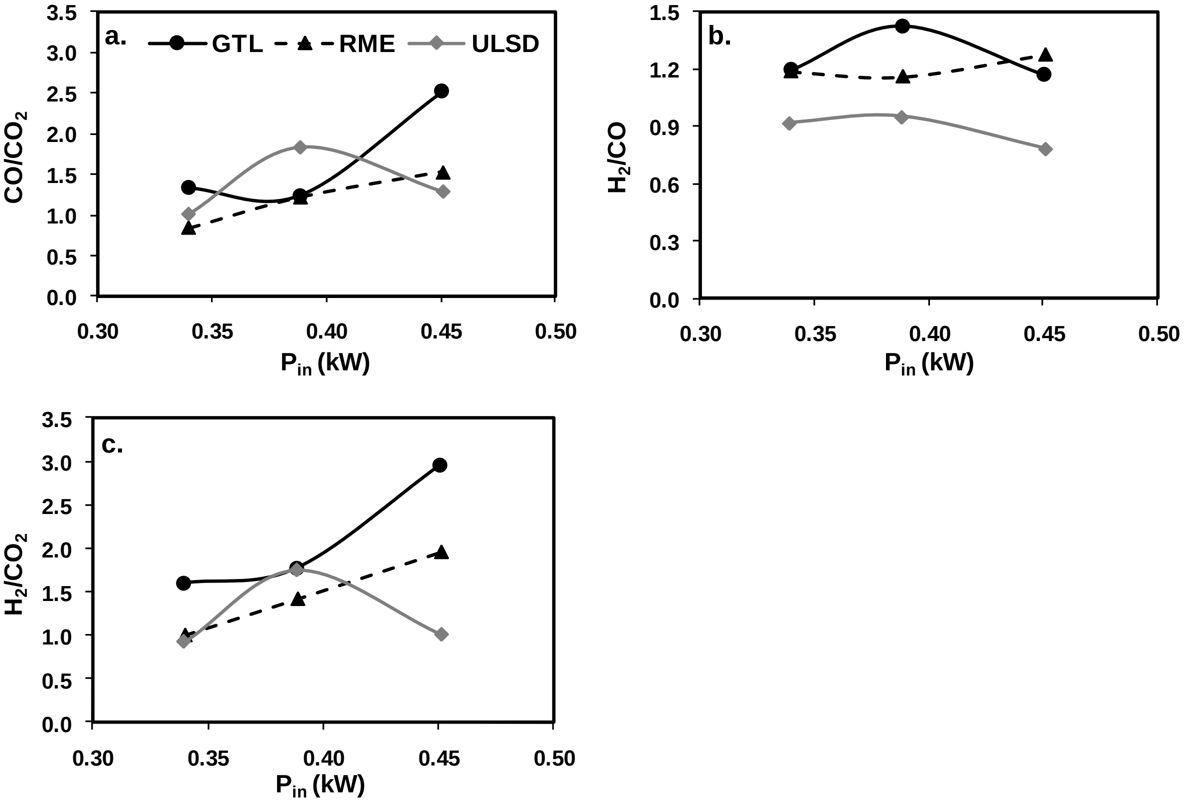


Figure 7.4: Effect of P_{in} (kW) on a) the CO/CO_2 ratio b) the H_2/CO ratio and c) the H_2/CO_2 ratio.

GTL fuel or the intermediate species formed during the fuel oxidation (e.g. homogenously at the catalyst inlet or heterogeneously in the catalyst) seem to be significantly more active in dry reforming compared to ULSD and RME, as can be seen from the significantly increased CO/CO_2 and reduced H_2/CO ratios (Figure 7.4). In the case of ULSD fuel reforming, as the input power increased (e.g. higher than 0.40 kW), diffusion limitations over the catalyst seem to affect the oxidation reactions resulting in lower reforming temperatures and conditions where the dry reforming reaction is kinetically limited.

7.3. Effect of Space Velocity for GTL

A way to increase the reformer peak temperature and input power is to increase the GHSV and optimize the fuel addition, for example, O/C ratio. Only the results for the GTL fuel are shown here to illustrate the trends that were common in the respective tests carried out for the study of the effect of SV. The GTL fuel reforming conditions and the mass flow rates into the reforming reactor are shown in Table 7.2.

Since contact time decreases with increasing SV; a careful balance has to be struck whereby the reformer is producing the optimum syngas composition for the specific task it is required for. From Figure 7.5, it was observed that the H_2 production was low at the SV of 25k h^{-1}, but significantly improved with the increase in reactor input power, peaking at ~ 15 % for the input power of 0.34 kW. However, at the SV of 35k h^{-1}, the H_2 yield was further improved to a maximum of ~ 19 % due to the increase in the reaction temperature, which enhances the reaction rate of the steam and dry reforming reactions. A further increase of the SV to 45k h^{-1}, led to a substantial decrease in H_2 production with a corresponding peak of ~ 15 % H_2 being measured in the reforming product gas.

Table 7.2: GTL fuel PO_x reforming conditions.

SV (h^{-1})	Air Flow (L h^{-1})	P_{in} (kW)	GTL Flow (mL h^{-1})	GTL Flow (g h^{-1})
25k	3	0.26	26.8	21.03
		0.29	30.6	24.01
		0.34	35.5	27.85
35k	4	0.34	35.5	27.85
		0.39	40.6	31.85
		0.45	47.1	36.95
45k	5	0.32	44.1	34.60
		0.49	50.8	39.86
		0.56	59.0	46.29

Analysis of the results leads to the conclusion that SV plays an important role in the reaction kinetics that lead to the production of hydrogen in a fuel reformer. From the results, the trend is such that, in terms of H_2 yield 25k h^{-1} < 35k h^{-1} > 45k h^{-1}. It is thereby speculated that the SV of 35k h^{-1} was near optimum for maximized H_2 production. Optimization of the reforming process is therefore paramount to the syngas composition and process efficiency. This is because at the lower SV there is a longer contact time between the HC fuel-rich input gas feed and the reforming catalyst active surface, which may lead to the unfavorable complete oxidation reaction. Whereas on the other hand, if the SV were too high, there may not be enough time for the required reactions to take place efficiently resulting in poor H_2 yields.

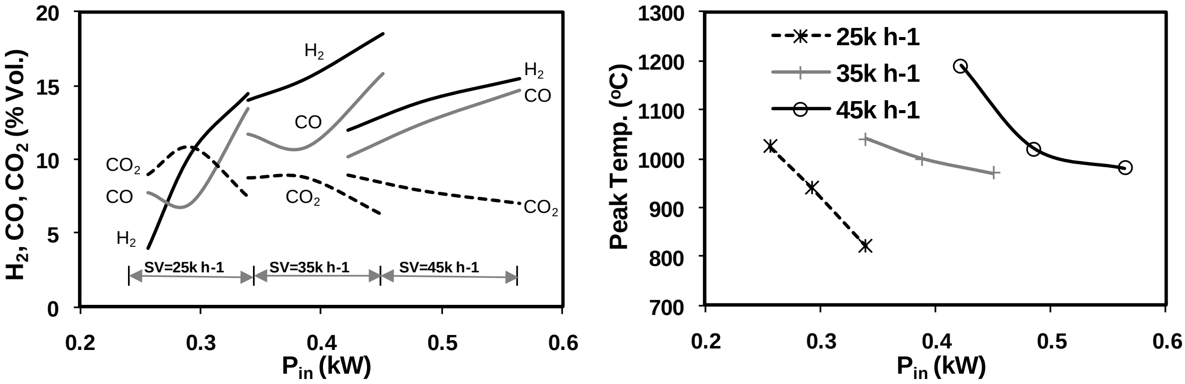


Figure 7.5: Effect of GHSV on a) GTL reformate gas concentrations (H_2, CO and CO_2) and b) peak reactor temperature.

The CO_2, CO and peak reactor temperatures (Figure 7.5) follow similar trends to those observed by varying the power input. The CO_2 concentration decreases as the input power is increased due to the prominence of the dry reforming reaction, whereas CO increases due to the lack of the water gas shift reaction (reaction 2.28) over the catalyst length. Furthermore, because increased fuel amount addition into the reactor is an endothermic process, there is a corresponding decrease in peak reactor temperature at each given test condition. Typical ratio relations i.e. CO/CO_2 and H_2/CO_2 for varying space velocity for GTL reforming are shown in Figure 7.6.

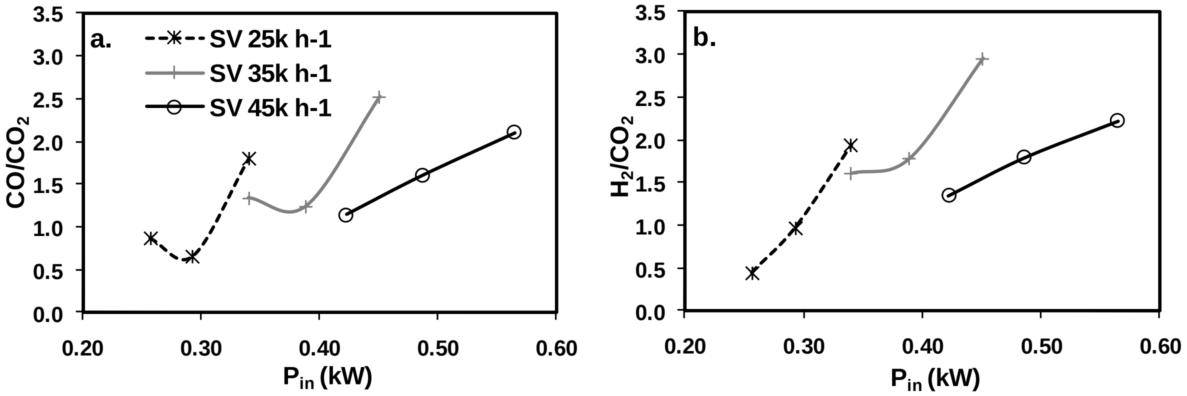


Figure 7.6: Effect of Space velocity (i.e. Input Power) for GTL fuel on **a)** the CO/CO_2 ratio and **b)** the H_2/CO_2 ratio.

From the ratio analysis of the GTL fuel reforming at different SV (Figure 7.6); it can be observed that SV generally increases the SRR and DRR activity over the reforming catalyst, as signified by the increasing CO/CO_2 and H_2/CO_2 ratios. This trend usually leads to better H_2 production, therefore resulting in higher reforming efficiency.

7.4. HC Speciation

Hydrocarbon selective catalytic reduction (HC-SCR) is a simple after-treatment technique developed for diesel engines. Among many catalysts explored for lean HC-SCR of NO_x, $Ag-Al_2O_3$ catalysts show the best activity for NO_x reduction under high temperature lean-burn exhaust gas conditions. But for them to be considered commercially, their low temperature (< 350 °C) activity needs improvement. $Ag-Al_2O_3$ catalysts utilize various HC-type fuels as reductants to selectively reduce NO_x in lean exhausts, but the type and quantity of the reductant has to be critically controlled (Shimizu et al., 2001). Hydrogen addition into the exhaust gas upstream the catalysts in the presence of unburned or injected HCs improves the low temperature NO_x conversion dramatically and also prevents catalyst coking; as a result this has stimulated interest in HC-SCR as a method of NO_x removal from lean burn engine exhausts (Houel et al., 2007a; Theinnoi et al., 2007; Satokawa et al., 2007). Further discussion is offered in Chapter 2.

Satokawa (2000) and Satokawa et al. (2003) reported that the addition of small amounts of H_2 gas into the exhaust gas stream of lean exhaust systems in the presence of short chain HCs had a tendency to improve the NO_x activity of lean NO_x catalysts. From our studies, HC species (C_1-C_6) were measured, as they fall into this low chain category. From Figure 7.7, it can be observed that the most prominent HC species was ethylene (C_2H_4) for all reformates from the respective fuels. Ethylene is a reactive HC species that could aid after-treatment lean NO_x catalysis; however regulation of the quantity would be important. Elghawi et al. (2008) also found a similar trend in their studies on PO_x of diesel, RME and GTL, in that; ethylene was always the most prominent HC constituent after the reforming process.

Overall, the ULSD and RME fuels produced the most HCs when they were reformed over the catalyst, with GTL producing the least. It has been reported that the amounts of HC as well as the speciation have an important role to play in enhancing the NO_x activity of lean NO_x catalysts, especially in diesel engine exhaust. Houel et al. (2005 and 2007a) during their studies on Ag-Al_2O_3 catalysts found that in the presence of H_2, the HC:NO_x ratio of the exhaust gas played an important role in the NO_x reduction reactions, with low ratios not allowing for the efficient reduction of NO_x, whereas high ratios led to the deactivation of the catalysts through the formation of carbon species over the surface, giving rise to low NO_x reduction activity. Eränen et al. (2000) had earlier also reported similar findings, stating that the HC:NO_x ratio had significant influence in the amount of NO_x reduced over the Ag-Al_2O_3 SCR catalyst, in their engine bench tests; with increased NO_x conversion being observed at higher exhaust gas temperatures (> 350 °C) with higher HC:NO_x ratios.

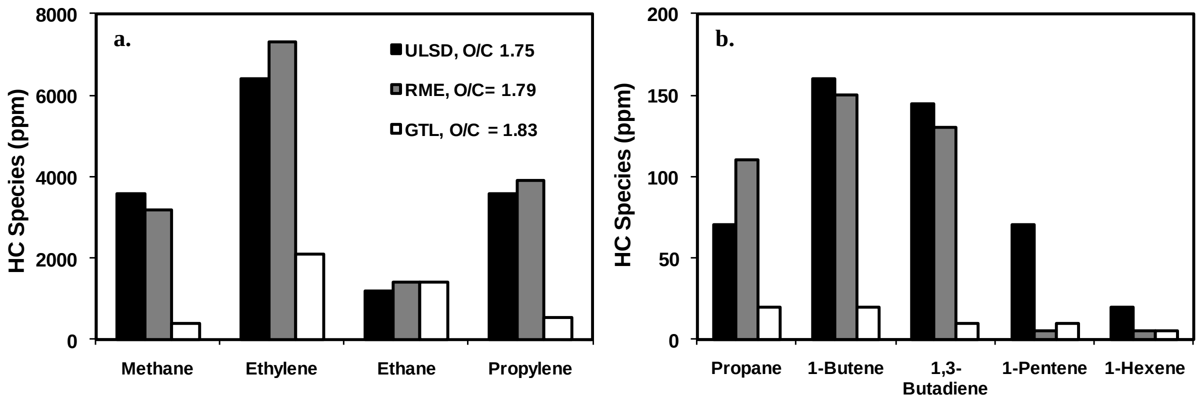


Figure 7.7: Species formation under the same input power for the three respective fuels at approximately constant GHSV.

Since most lean NO_x catalysts are susceptible to coking in the presence of increased (excess) amounts of HCs (Houel et al., 2005), optimized amounts need to be able to be produced on demand for different operating conditions of a typical diesel engine. In this study, GTL had the least amounts of these short chain HCs; therefore it will be the most favourable of all the fuels to use for reforming purposes in conjunction with a HC-SCR system. Typically, at low exhaust gas temperatures (typical of light duty vehicles) it is preferable to have longer chain HCs as reductants due to their lower oxidation temperatures when compared to short chain HCs. At high temperatures, the short chain HCs produced from the reforming process of the respective fuels (Figure 7.7) would probably have a more pronounced influence on the HC-SCR of NO_x in the presence of H_2 over Ag-Al_2O_3 catalysts. Improved overall NO_x activity may be observed without the need for an external exhaust HC dosing system (dependent on operating mode, Chapter 4) as well as without the need for an onboard H_2 storage tank on-board the vehicle.

7.5. Coupling Fuel Reforming with HC-SCR Technology

For HC-SCR system applications, hydrogen could be stored on-board the vehicle and used when required, however, this has safety and practicality implications. Perhaps a more favourable option would be the production of hydrogen on-board in a diesel mini fuel reformer (Han et al., 2007; Tsolakis et al., 2004; Slinn et al., 2008; Alvarez-Galvan et al., 2008) and using it on-demand. Presented herein is a comparison of the effect of the reformate produced in partial oxidation (PO_x) and exhaust gas reforming on the Ag-Al_2O_3 HC-SCR catalyst activity on reducing NO_x emissions. A single engine condition was utilized, namely, an engine load of ~ 35 % at an engine speed of 1200 rpm with approximately 30 % EGR. In both cases the NO_x concentration at the HC-SCR catalyst inlet (155 ppm) was not affected by the reformate addition into the bulk engine exhaust gas; however the total HCs were increased by around 300 - 400 ppm. The H_2 measured at the SCR catalyst inlet in this section is not from a bottled source but rather, is from the reforming process itself i.e. partial oxidation or exhaust gas fuel reforming.

In the case of PO_x reforming, 8 l/min of air was introduced into the reformer (operating at an inlet temperature of 200 ºC) with 78.6 ml/hr ULSD fuel giving reforming conditions of O/C = 1.76, $O_2/C = 0.88$, $H_2O/C = 0$, SV ~ 20k h^{-1}. The H_2 concentration measured at the inlet of the SCR catalyst, after the reformate was diluted with the engine exhaust gas, was approximately 3200 ppm. The overall NO_x conversion achieved was ~ 58 % while the fuel penalty was in the region of 10 % (Figure 7.8).

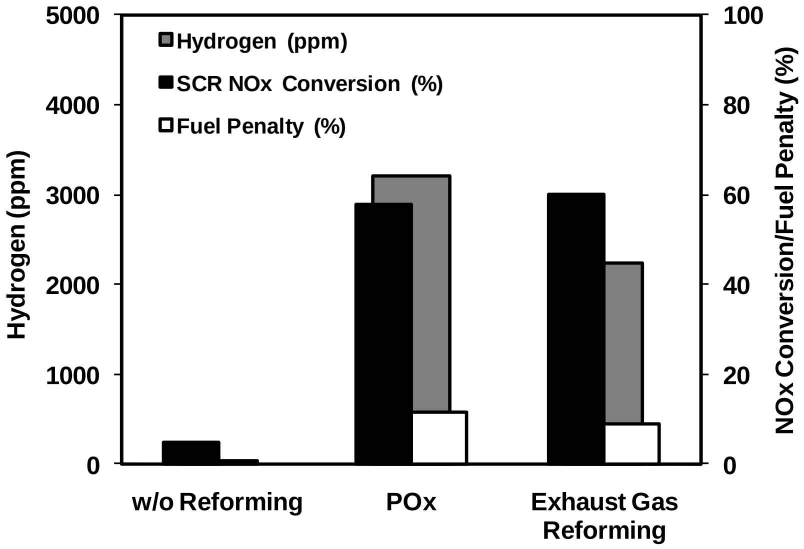


Figure 7.8: A comparison between the PO_x and Exhaust gas fuel reforming for use in a HC-SCR Ag-Al_2O_3 catalyst system.

For the exhaust gas fuel reforming, 10 l/min of the diesel engine exhaust gas (i.e. source of O_2, H_2O, CO_2 and heat) was catalytically reacted with 60 ml/hr of ULSD fuel, giving reforming conditions of O/C = 1.87, O_2/C = 0.94, H_2O/C = 0.36, SV ~ 25k h^{-1}. The H_2 concentration measured at the inlet of the SCR catalyst from the exhaust gas fuel reforming was lower than that from the PO_x reforming, peaking at approximately 2240 ppm. However, the fuel penalty was approximately 6 %, which was lower than that for the PO_x reforming process. Despite the lower concentration of H_2 at the SCR catalyst inlet, NO_x reduction from exhaust gas fuel reforming was measured at a stable 60 % (Figure 7.8).

The fuel penalties are very high even given the fact that a diesel engine is more efficient than the conventional gasoline engine, 10 % is too much of a margin to lose in respect of how much more the former costs to manufacture. In this respect, the fuel penalty needs to be as low as possible, ideally below 1 %. With this in mind, research is on-going into how best to minimise the fuel penalty of the reformer and maintain the same output gas compositions.

From the results, it can be observed that the H_2 produced from the two reforming processes is sufficient to improve the NO_x activity over the Ag-Al_2O_3 SCR catalyst (Figure 7.8). On the other hand, the fuel penalty was quite high but can be improved by a) optimizing the fuel reformer design and configuring it to convert the HC into H_2 and promote the WGS reaction, something proposed and discussed by Abu-Jrai et al. (2008); b) designing an Ag-Al_2O_3 based SCR catalyst that is active in NO_x reduction with CO or incorporating an additional SCR catalyst as explored by Abu-Jrai et al. (2007) using Pt-based catalysts; c) optimizing the reactants ratios whilst simultaneously reducing the reformer size (i.e. reformer monolith size). Optimization of the exhaust gas fuel reforming process using a prototype mini fuel reformer integrated within the engine exhaust system is currently under investigation in order to further improve (apart from the H_2 production) fuel economy. The on-board reformer system has since been trialled and the latest fuel penalty is in the range of 2 to 3 %, which is still high but approaching acceptable limits.

7.6. Summary

In the work presented in this chapter, hydrogen production from the partial oxidation of diesel-type fuels followed the trend GTL > RME > ULSD. Also observed in the reformate were varying amounts of short chain HCs, which were measured and quantified. It was found that the short chain HC production followed the trend RME > ULSD > GTL, with ethylene being the most prominent species. Therefore, given the higher amounts of hydrogen produced, with smaller quantities of short chain HCs, GTL would be more favourable for lean NO_x after-treatment units, as only small amounts of HCs in the presence of H_2 are required. Excess amounts observed in the case of RME and ULSD would possibly lead to lean NO_x catalyst deactivation through coke deposition onto the surface. It has therefore been proven that hydrogen can be produced through the partial oxidation of diesel-type fuel to controllable extents by varying SV and/or fuel flow rate (which both vary input power) over the reforming catalyst.

Additionally, in terms of after-treatment, it has also been shown that the partial oxidation and the exhaust gas fuel reforming of ULSD can produce the H_2 amounts required for the HC-SCR of NO_x over Ag-Al_2O_3 catalysts. Furthermore, an external exhaust dosing system may not be required at particular conditions as there are inherent HCs in the reformate, which could help further improve the Ag-Al_2O_3 activity in the presence of increased H_2 production. Besides, exhaust gas fuel reforming when compared to PO_x, leads to better fuel economy and similar NO_x conversion results over an Ag-Al_2O_3 catalyst (for the H_2 amount produced).

CHAPTER 8

CONCLUSIONS

8.1. Concluding Remarks

Findings from the experimental investigation into the reduction of NO_x emissions from diesel engine exhaust have been presented and discussed in this research thesis. A silver-alumina ($Ag-Al_2O_3$) HC-SCR of NO_x system, which mimics an actual full system prototype configuration, has been tested on a single cylinder Lister Petter TR1 diesel engine. Various fuels were used to conduct the experiments, namely, ultra low sulphur diesel (ULSD), rapeseed methyl ester (RME) and low temperature Fischer-Tropsch synthetic gas-to-liquid diesel (GTL). Several techniques including the use of diesel oxidation catalysts, hydrogen addition, fuel injection and fuel reforming were explored in detail and their effects on the NO_x efficiency of $Ag-Al_2O_3$ catalysts assessed. Discussed in this Chapter, are the general conclusions drawn from the investigative experimental studies that form this research thesis.

8.1.1. Promoting HC-SCR of NO_x in diesel engine exhaust by hydrogen

A silver-alumina ($Ag-Al_2O_3$) hydrocarbon selective catalytic reduction (HC-SCR) monolith catalyst was prepared and tested for NO_x emissions control. The work was based on ongoing laboratory experiments, catalyst research and process development. During the low temperature '*passive*' (i.e. no externally added hydrocarbons into exhaust) operation of the HC-SCR reactor system, the addition of hydrogen significantly improved the NO_x reduction activity over the Ag-based SCR catalysts using the whole engine exhaust gas from a single cylinder diesel engine.

Furthermore, a comparison test of the $Ag-Al_2O_3$ catalysts in the form of pelletized powder and a wash-coated monolith, under '*active*' (i.e. hydrocarbon injection into exhaust) HC-SCR operation; it was found that powdered $Ag-Al_2O_3$ catalysts gave significantly better initial NO_x reduction activity. However, the catalyst activity deteriorated rapidly with time due to poisoning species adsorption (e.g. HCs, nitrates, particulate matter (PM), etc). On the other hand, for $Ag-Al_2O_3$ coated monolithic catalysts, NO_x reduction activity was lower but remained constant for the duration of the test period due to physical and chemical differences.

Overall, the HC-SCR of NO_x with $Ag-Al_2O_3$ catalysts has been confirmed to be viable with the use of catalyst coated monoliths in the presence of H_2 although better durability and efficiency is still required. As a result, there is a necessity for the optimisation of monolith coating technologies and development of more active catalysts for wider operating temperature ranges and greater durability.

8.1.2. Improving the low temperature NO_x reduction activity of an $Ag-Al_2O_3$ catalyst

An improvement in passive HC-SCR operation over $Ag-Al_2O_3$ catalysts was proven possible with the implementation of a prototype oxidation catalyst (PC) upstream the SCR catalysts. The PC was used to cleanse the diesel exhaust gas by reducing potential catalyst poisoning species and by possibly generating more reactive species which would aid the SCR catalyst NO_x reduction activity. The influence of the PC on the SCR catalyst NO_x activity was primarily dependent on the engine exhaust gas temperature and space velocity (SV).

Nevertheless, the PC was found to have significant influence on the overall reduction of HCs, CO and PM across all engine operating conditions. During HC-SCR at low temperatures, with H_2 addition, there were sufficient HC species available for the reduction of NO_x, over the $Ag-Al_2O_3$ catalyst. However, there was a decrease in NO_x reduction at higher engine exhaust gas temperatures, attributed to the reduced HC concentrations relative to the NO_x produced by the engine and also the HC oxidation reaction being more predominant than the HC - NO_x reduction reaction. At these particular conditions the active injection of HC-species would be necessary for improved NO_x reduction activity over the Ag-based SCR catalysts studied.

8.1.3. Temperature dependence of Ag-Al_2O_3 catalysts during HC-SCR of NO_x

The temperature dependence of Ag-Al_2O_3 monolith catalysts for HC-SCR during experimental fast steady-state test ramps, under passive conditions, was studied on a single cylinder diesel engine through the use of three different diesel fuels, namely, ULSD, RME and GTL. It was found that, on average, the H_2-assisted NO_x reduction activity followed the trend GTL > ULSD > RME, for all the conditions tested. At lower exhaust temperatures, attributed to lower engine load operating conditions, the NO_x conversion was enhanced compared to that at higher temperatures, for all fuels. At high engine loads, the oxidation of HCs due to the corresponding higher exhaust gas temperatures, coupled with the increased engine NO_x output, led to lower HC:NO_x ratios and possibly hindered the selectivity for NO_x reduction.

As a result of the reduced HC:NO_x ratios at higher temperatures, active injection of HCs would be necessary to maximize the NO_x conversion at these particular conditions. Furthermore, it is proposed that with additional H_2 in the exhaust system, further improvements in NO_x reduction at high engine speed-load conditions could be achieved (with selective HC injection), for all the respective fuels. From the transient-like operation of the Ag-Al_2O_3 catalysts, it has been shown that the NO_x activity was improved due to higher average temperatures, alluding to the fact that maybe the Ag-Al_2O_3 catalyst will be better suited for heavy duty applications.

8.1.4. Partial oxidation and exhaust gas fuel reforming

The partial oxidation of ULSD, RME and GTL (almost 100 % paraffinic), was investigated for the purpose of hydrogen and intermediate hydrocarbon species production over a prototype reforming catalyst, for the potential use in HC-SCR of NO_x emissions from diesel engine exhaust gas. The presence of small amounts of hydrogen can substantially improve the effectiveness of hydrocarbons in the selective reduction of NO_x over lean NO_x catalysts, particularly at low temperatures (150 - 350 ^oC).

During this study, H_2 production followed the trend GTL > RME > ULSD, respectively. In conjunction with the H_2 production, the short chain HC species (C_1 - C_6) produced by the PO_x reforming of the respective fuels were measured. The results show that USLD produced more short chain HCs collectively than the other respective fuels, with GTL producing the least. The fact that a hydrogen-rich gas was produced with inherent short-chain HCs; there can as a result be an influential positive effect on HC-SCR activity for NO_x when the reformates of the fuels are used as reductants in real diesel engine exhaust, more so for GTL.

Furthermore, it has been shown that sufficient H_2 for HC-SCR catalysis can be produced from the PO_x of HC fuels and in this particular study, from ULSD, RME and GTL fuels. Furthermore, the exhaust gas fuel reforming process has been proven to be just as effective at yielding adequate H_2 amounts for the HC-SCR reaction, as the PO_x process.

8.2. Future Work and Recommendations

- Research into the incorporation of other after-treatment technologies e.g. particulate matter (PM) filtration devices and diesel oxidation catalysts to the HC-SCR system investigated in this research thesis. This would be a necessary next step towards a roadworthy prototype Ag-Al_2O_3 HC-SCR system, were it proven to be successful. Adaptive response systems will be required for the injection of required HC amounts (either for regeneration or SCR purposes), especially during the transition from low to high temperature exhaust regions, for greater catalyst durability and maintained NO_x efficiencies.
- Fuel reforming could be used as the source for the required H_2 and HC-species, in the case of low temperature Ag-Al_2O_3 HC-SCR of NO_x catalysis. Laboratory scale experimental rigs will still have to be used for the investigation into the possible minimisation of the reforming catalyst and hence the reactor; but still maintaining high H_2 yield from the process. Methods of controlling the reactant species in the reformate for improved HC-SCR of NO_x need to be devised as the catalyst has been proven to be very sensitive to the amount and species of reductant.
- Reformer catalyst light-off temperature optimization for lesser delay in start-up of syngas (reformate) production is essential, especially for an on-board application. Currently, a system has been devised that incorporates a reforming catalyst whose primary heat source for light-off is the engine exhaust gas temperature. Work is ongoing for the smooth operation of the system for consistent syngas production. Once fully operational, the system will be able to

feed required H_2-rich gas to various components for specific purposes e.g. for combustion, after-treatment, regeneration etc.

- Advantages for the use of Ag-Al_2O_3 HC-SCR system include primarily its simplicity and relative lower expense when compared to other lean NO_x technologies. However, its efficiency is not as good as the other technologies currently in production or being fine tuned among research groups for light duty applications e.g. Urea-SCR and NO_x-adsorber catalysis. Although these systems are more expensive, newer catalyst technologies are always emerging and the cost will drop accordingly as better and more innovative techniques are found. With this in mind, better performing and more durable Ag-Al_2O_3 HC-SCR catalysts in terms of NO_x activity need to be produced and proven, to the scale of the systems that are in production at present, before they can be accepted as a viable option for NO_x emissions reduction in light duty applications.

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APPENDICES

APPENDIX A: Measuring Equipment Technical Data

Table A.1: Technical data for the Horiba Mexa 7100 AnalyzerTable

Species	**Range**	**Resolution**	**Noise**[*] (peak to peak width in 5 min)
CO	Min. range 0 – 100 ppm Max. range 0 – 12 % vol	1 ppm 0.01 %	± 1 % FS
CO_2	Min. range 0 – 5000 ppm Max. range 0 – 20 % vol	1 ppm 0.01 %	± 1 % FS
THC	Min. range 0 – 10 ppm C_1 Max. range 0 – 50000 ppm C_1	1 ppm	± 1 % FS
O_2	Min. range 0 – 5 % vol Max. range 0 – 25 % vol	0.01 %	± 1 % FS for zero ± 1.5 % FS in measurement
NO/NO_x	Min. range 0 – 10 ppm Max. range 0 – 10000 ppm	1 ppm	< 20 ppm: ± 1.5 % FS > 20 ppm: ± 1 % FS

Table A.1.1: Other technical data for the Horiba Mexa 7100 Analyzer

Specification	**Value**[*]
Zero/Span Drift	Zero: ± 1 % FS per 8 hrs Span: ± 1 % FS per 8 hrs (ambient temp. fluctuation within ± 5 °C)
Linearity	± 1 % FS or 2 % ind. val. (whichever is smaller)
Repeatability	± 0.5 FS

[*] FS = Full Scale Measurement

Table A.2: Technical data for the AVL DiGas 440 analyzer

Species	Range	Resolution	Accuracy
CO	0 – 10 % vol	0.01 % vol	< 0.6 % vol: ± 0.03 % vol ≥ 0.6 % vol: ± 5 % ind val.
CO_2	0 – 20 % vol	0.1 % vol	< 10 % vol: ± 0.5 % vol ≥ 10 % vol: ±5 % ind. val.
THC	0 – 20000 ppm vol	≤ 2000 ppm: 1 ppm vol > 2000 ppm: 10 ppm vol	< 200 ppm vol: ±10 ppm vol ≥ 200 ppm vol: ± 5 % ind. val.
O_2	0 – 22 % vol	0.01 % vol	< 2 % vol: ± 0.1 % vol ≥ 2 % vol: ± 5 % ind. val.
NO	0 – 5000 ppm vol	1 ppm vol	< 500 ppm vol: ± 50 ppm vol ≥ 500 ppm vol: ± 10 % ind. val.

Table A.3: Technical data for the SMPS

Specification	Value
Particle Type	Solids and non-volatile liquids
Particle size range	10 – 1000 nm
Maximum input concentration	10^8 particles/cm^3 at 10 nm
Voltage	10 – 10000 VDC
Sheath air flow rate	2 – 15 L/min
Aerosol air flow	0.2 – 2 L/min

APPENDIX B: Publications and Awards to Date

B.1. Publications

Sitshebo S., Tsolakis A., Theinnoi K., (2009) **Promoting Hydrocarbon-SCR of NO_x in diesel engine exhaust by hydrogen and fuel reforming.** International Journal of Hydrogen Energy 34: 7842-7850

Sitshebo S., Tsolakis A., Theinnoi K., Rodríguez-Fernández J. (2009) **Improving the low temperature NO_x reduction activity over a $Ag\text{-}Al_2O_3$ catalyst.** Chemical Engineering Journal 158: 402-410

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Theinnoi K., Sitshebo S., Houel V. and Rajaram R.R., Tsolakis A. (2008) **Hydrogen promotion of low-temperature passive hydrocarbon-SCR over a silver catalyst.** Energy & Fuels 22: 4109–4114

Elghawi U., Theinnoi K., Sitshebo S., Tsolakis A., Wyszynski M.L., Xu H.M., Cracknell R.F., Clark R.H. and Mayouf A. (2008) **GC-MS determination of low hydrocarbon species (C_1–C_6) from a diesel partial oxidation reformer.** International Journal of Hydrogen Energy 33: 7074-7083

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Theinnoi K., Houel V., Rajaram R.R., Tsolakis A., Sitshebo S., Golunski, S.E. and Cracknell R.F. (2009) **Fuels combustion effects on a passive mode silver/alumina HC-SCR catalyst activity in reducing NO_x.** Chemical Engineering Journal 158: 468-473

B.2. Awards

- **Austin Rover Prize:** awarded by the University of Birmingham for the best paper in Automotive Engineering (2009)