EFFECT OF BIODIESEL COMPONENTS ON SELECTIVE REDUCTION OF NOx

A thesis submitted in fulfilment of the requirements for the degree of

MASTER OF SCIENCE

by

Kaveh Vossoughi

School of Mechanical Engineering

University of Birmingham

January 2015

I hereby declare that I am the sole author of this thesis.

I authorize the University of Birmingham to lend this thesis to other institutions or individuals for the purpose of scholarly research.

Kaveh Vossoughi

Signature

I further authorize the University of Birmingham to reproduce this thesis by photocopying or by other means, in total or in part, at the request of other institutions or individuals for the purpose of scholarly research.

Kaveh Vossoughi

Signature

This thesis is dedicated to my parents,

Eshrat** and **Jalil Vossoughi

for their continual support throughout the years.

Acknowledgements

This thesis would not have been possible without the help, support and contribution of a number of individuals throughout the course of my study, who I believe deserve special mention and acknowledgement. It is my pleasure to thank them.

I would like to express my sincerest gratitude to my supervisor, Dr Athanasios Tsolakis, for his patience, invaluable advice and guidance throughout the duration of this research. I also thank my co-supervisor, Dr. Karl Dearn, for his leadership and knowledge throughout this work.

I am very grateful to Dr. Jose Martin Herreros for his useful suggestions, advice and technical expertise. His contribution throughout all stages of my research was priceless.

Special thanks go to my fellow colleagues and friends Dr. Mohammad Hossein Naghashian, Isaline Lefort, Maria Bogarra Macias and Mohammed Fayad for their technical and moral support.

Kaveh Vossoughi

January 2015

Abstract

The reduction of nitrogen oxides (NO_X) from diesel engine exhausts gas through the addition of different methyl esters in hydrocarbon selective catalytic reduction (HC-SCR) over silver-alumina (Ag/Al_2O_3) environmental catalysts has been investigated. The selected methyl esters are those which are usually found in the majority of biodiesel composition from different feedstocks.

The effects of biodiesel components in removing NO_X have been found. However lighter methyl esters activate at higher temperatures compared to heavier, they reach to higher NO_X conversion and peak in around 40% of NO_x reduction. Those effects are a consequence of the formation of i) active hydrocarbon components and ii) nitrogen containing components such as NO_2 and NH_3, which in reaction with NO ideally will reduce NO_X components to produce N_2, H_20 and carbonaceous species.

Hydrogen (H_2) has been added in order to promote the conversion of NO_X and investigate the effects of methyl esters under the addition of hydrogen. It shows more effect on longer chain methyl esters similar to the activity on paraffinic hydrocarbon components. It is suggested that H_2 enhances the NO_X conversion by activation of oxygen into oxygenated reactive species, the formation of reactive species such as NH_3 and NO_2 as well as reduces coke formation and nitrates deposits on the catalyst active sites.

Table of Contents

Table of Figures

List of Tables

List of Abbreviations

Ag	Silver
Ag-Al_2O_3	Silver supported on alumina
$AgNO_3$	Silver nitrate
Al_2O_3	Alumina
BaO	Barium oxide
$BaCO_3$	Barium carbonate
$Ba(NO_3)_2$	Barium nitrate
C12:0	Methyl lauric
C14:0	Methyl myristic
C16:0	Methyl palmitic
C18:0	Methyl stearic
CI	Compression Ignition
CO	Carbon monoxide
CO_2	Carbon dioxide
$CO(NH_2)_2$	Urea
DOC	Diesel Oxidation Catalyst
DPF	Diesel Particulate Filter
EGR	Exhaust Gas Recirculation
F-T	Fischer-Tropsch
FTIR	Fourier Transform Infrared Spectroscopy
GTL	Gas-to-Liquid
H	Atomic Hydrogen
H_2	Hydrogen
H_2O	Water
HC	Hydrocarbon
HC:NO_x	Hydrocarbon to NO_x ratio
HC-SCR	Hydrocarbon Selective Catalytic Reduction
HNCO	Isocyanic Acid
IMEP	Indicated Mean Effective Pressure
LNT	Lean NO_x Trap
N_2	Nitrogen
N_2O	Nitrous oxide
NH_3	Ammonia
NH_3-SCR	Ammonia Selective Catalytic Reduction

NO	Nitric oxide or Nitrogen monoxide
NO_2	Nitrogen dioxide
NO_x	Nitrogen oxides
O	Atomic Oxygen
O_2	Oxygen
OH	Hydroxyl radicals
Pd	Palladium
PM	Particulate Matter
Pt	Platinum
Rh	Rhodium
RME	Rapeseed Methyl Ester
SCR	Selective Catalytic Reduction
SI	Spark Ignition
SO_2	Sulphur dioxide
THC	Total Hydrocarbon
TWC	Three Way Catalyst
ULSD	Ultra Low Sulphur Diesel

Chapter 1

INTRODUCTION

1 Introduction

1.1 Overview

Nowadays, after-treatment technologies are essential for the reduction of emissions from the engine exhaust gas to comply with the regulations imposed by the environmental governing bodies. Regulated emissions of carbon monoxide (CO) and unburnt hydrocarbons (HC) from the exhaust gas of diesel engines are lower than those from gasoline spark ignition (SI) engines. However, nitrogen oxides (NO_X) and particulate matter (PM) emissions are considerably higher due to diesel engines combustion conditions (lean-burn). NO_X is highly poisoning and plays a consequential role in the formation of acid rain and photochemical smog which causes health issues (McGeehan, et al., 2005). Even though the oxidation of CO and HC emissions is quite straightforward, the reduction of the NO_X emissions in the presence of excess oxygen is much harder, especially under low temperature exhaust gas conditions typical for diesel engines. As diesel engines operate in lean-burn conditions, three-way catalyst convertors are not able to function and reduce NO_X emission as in gasoline engines. In the excess of oxygen, reaction of CO directly with O_2 is dominant over the NO_X + CO reaction in the exhaust gas (Houel, et al., 2007a).

Up to now, several methods have been introduced and some are already in use in commercial scale to convert NO_X in diesel engine exhaust (Dong, et al., 2008). Urea-based selective catalytic reduction (Urea-SCR), lean NO_X traps (LNT) and hydrocarbon selective catalytic reduction (HC-SCR) are the most used approaches. Urea-SCR suffers from some disadvantages such as requirement for an extra on-board tank, corrosiveness, freezing in cold weather and decomposition of urea during over-injection or injection at low temperatures. High fuel penalty, durability and costly metal loading are concerns in the case of LNT (Johnson, et al., 2012). The drawbacks of these methods attract interest towards HC-SCR development.

This study is focused on silver-alumina catalyst HC-SCR which does not require a secondary fuel tank for the storage of the reducing agent and highly priced platinum group loadings (Parvulescu, et al., 1998). In addition, the implementation of the HC-SCR is the simplest among other technologies. A hydrocarbon component or a blend of different hydrocarbons is injected into the exhaust gas system, as a reducing agent, upstream the HC-SCR catalyst. NO_X emission react with fuel on the active sites of the catalyst and are reduced to N_2 downstream the HC-SCR catalyst (Komatsu, et al., 2006; Cant & Liu, 2000). The injected hydrocarbon also regenerates the catalyst, inhibiting deactivation from sulphur poisoning by high temperature treatment (Dong, et al., 2008). Silver aluminium oxide was used due to its high thermal stability and has been investigated showing high activity at NO_X reduction over wide temperature range (Houel, et al., 2007a).

1.2 Research aim and objectives

This dissertation focuses on the selective catalytic reduction of NO_X with hydrocarbon components as reducing agent over a silver based catalyst. The aim of this research work is to investigate the effect of the main individual methyl esters found in most biodiesel fuels as reducing agents of NOx emission in lean-burn exhaust gas for diesel engines utilising silver-alumina HC-SCR catalyst. In addition, the influence of hydrogen addition will be tested along with methyl esters.

The objectives of this study are as follows:

a) Investigation of the performance of biodiesel components (methyl esters) on the reduction of NO_X using HC-SCR at a specific temperature range. The influence of methyl esters chain length and physical properties on NOx reduction will be studied.

b) The impact of the addition of hydrogen as a promoter to the SCR NO_X into the exhaust system in the presence of different methyl esters.

1.3 Thesis outline

This research is based on selective catalytic reduction of NO_X emission from diesel engine exhaust gas over monolithic silver-alumina (Ag/Al_2O_3) catalyst. The thesis is divided into six chapters as follows:

Chapter 2: Literature review

An overview of the diesel engine operation and exhaust gas emissions are presented. This chapter also reviews current after-treatment technologies for the reduction of NO_X emission in diesel engines.

Chapter 3: Experimental setup

This chapter describes the details of the experimental equipment including engine, catalyst, fuels and instruments used for the exhaust gas emissions measurement.

Chapter 4: Effect of biodiesel components on NO_X conversion

Impact of methyl esters blends on the performance of the Ag/Al2O3 catalyst at low and high temperatures is investigated.

Chapter 5: Effect of hydrogen addition on NO_X conversion

In this chapter hydrogen is added to the exhaust gas steam to examine its promoting effect on the activity of methyl ester-SCR at low and high temperatures.

Chapter 6: Conclusions

A summary of the research work are presented. Future research recommendations are also outlined.

Chapter 2

LITERATURE REVIEW

2 Literature review

2.1 Diesel engine operation

Diesel engines operate by a process referred to as compression ignition (CI) which combust the air-fuel mixture by utilising the compression of an air charge. Over the past decade, interest in diesel engine has increased to a great extent (Baumgarten, 2006). They have substantial advantages over gasoline spark ignition engines including greater efficiency, higher engine durability and superior fuel economy and therefore produce lower rates of CO_2 (Heywood, 1988).

However, diesel engines are suffering from poor cold-weather start, higher weight to engine power ratio compare to SI engines, higher cost of production which includes utilising components with stronger materials due to the high compression ratio and higher maintenance cost. Diesel engine operation generally accompanies with high level of noise and vibration called diesel knock.

2.2 Nitrogen oxides (NO_X) emission

In the automotive after-treatment, NO_X is referred to as mixtures of NO_2 and NO. While NO_2 is a reddish brown colour gas with strong odour, NO is a colourless and odourless gas (Levendis, et al., 1994). NO accounts for most of (generally over 90%) the total NO_X emissions from the combustion of fossil fuels, with the rest being NO_2. Concentrations of NO_X in the exhaust gas from a typical diesel engine are between 100 and 1000 ppm (Burch, et al., 2002).

These emissions are considered as one of the most critical pollutants and contribute to the formation of smog or ground level ozone, human health and environmental hazard. The three primary mechanisms of the formation of NO_X in internal combustion engines consist of: i) the oxidation of nitrogen (N_2) found in combustion air at high temperatures and pressures occurring in the cylinder during combustion processes referring to as thermal NO_X mechanism; ii) the reaction of nitrogen contained in the fuel or additives to the fuel and oxygen; iii) the reaction of radicals derived from fuel and atmospheric nitrogen (Turns, 2000; Heywood, 1988).

The formation of NO from molecular N_2 (thermal mechanism) in which the atomic oxygen, N_2 and hydroxyl radicals are in equilibrium can be explained by the extended Zeldovich mechanism as follows:

$$O + N_2 \leftrightarrow NO + N$$

$$N + O_2 \leftrightarrow NO + O$$

$$N + OH \leftrightarrow NO + H$$

The reaction mechanism which explains the production of NO_2 has been proposed as follows:

$$NO + HO_2 \leftrightarrow NO_2 + OH$$

However, the decomposition of NO_2 and formation of NO can proceed at high temperatures. NO_2 reacts with active O and H radicals through the reactions illustrated below:

$$NO_2 + O \leftrightarrow NO + O_2$$

$$NO_2 + H \leftrightarrow NO + OH$$

2.3 NO_X emission control technologies

Despite employing recent combustion technologies and cleaner fuels, the exhaust gas from diesel engines still require other approaches such as soot trap, EGR and exhaust gas after-treatment to reduce pollutant emissions to meet strict emission regulations (Abu-Jrai, et al., 2006; Kitano, et al., 2005).

NO_X removal technology by utilising a three-way catalyst (TWC) for exhaust gas from gasoline engines has already been developed. The TWC converts harmful NO_X to N_2

on supported precious metals including platinum, rhodium and palladium via CO, unburnt HCs and H_2. In the same time the remaining CO and HCs are oxidised to carbon dioxide (CO_2) and water (H_2O). However, the TWC cannot perform properly for diesel engines because oxidation of unburnt HCs is dominant with excess of oxygen over the reduction of NO_X to N_2. In addition, the concentrations of H_2 and CO from diesel engine operation in contrast with SI engines are low. Therefore, new after-treatment technologies are desired in order to convert NO_X emission (York, et al., 2010).

After-treatment technologies including lean NO_X trap (LNT), urea selective catalytic reduction (Urea-SCR) and hydrocarbon-SCR (HC-SCR) have been established in order to reduce significantly NO_X emission to meet new legislations.

2.4 Lean NO_X trap (LNT)

Lean NO_X trap (LNT) which is also referred to as NO_X adsorber catalyst (NAC) is an alternative after-treatment approach introduced to operate 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 (Mital, et al., 2003).

The concept involves NO_X adsorption on the catalyst under lean exhaust conditions which is then NO_X reduced and released during rich modes of the engine for a short period. The process consists of three primary components (Epling, et al., 2004):

- An oxidising catalyst e.g. Pt
- A NO_2 adsorbent (storage medium) e.g. $BaCO_3$
- A reducing catalyst e.g. Rh

These key mechanisms are summarised by the following stages (Majewski and Khair, 2006; Majewski, et al., 2007; Brogan, et al., 1998)

a) Oxidation of NO to nitrogen dioxide: NO, the primary component of NO_X, on the active catalyst sites react with oxygen to form NO_2 through the reaction

$$2NO + O_2 \rightarrow 2NO_2$$

b) NO_2 storage: The formed NO_2 is then adsorbed by the storage medium, in this case barium carbonate ($BaCO_3$), to produce barium nitrate $(BaNO_3)_2$ which is a stable NO_X containing compound

$$BaCO_3 + NO_2 + \frac{1}{2}O_2 \rightarrow Ba(NO_3)_2 + CO_2$$

c) Nitrates release from the adsorbent: Once the adsorber catalyst saturation developed, in order to start the regeneration process the exhaust gas temperature is required to be elevated by switching to rich condition. Under this condition reducing species including HCs, H_2 and CO replace the O_2. During this step the stored nitrate species become unstable thermodynamically and they are desorbed forming NO_2 and NO (Brogan, et al., 1998)

$$Ba(NO_3)_2 \rightarrow BaO + 2NO + 1\frac{1}{2}O_2$$

$$Ba(NO_3)_2 \rightarrow BaO + 2NO_2 + \frac{1}{2}O_2$$

d) Reduction of NO to nitrogen: At the final step, in the presence of HCs, H_2 and CO the released NO_X is reduced over the catalyst through a conventional TWC. The reaction pathways are

$$NO_2 + \ CO \rightarrow NO + CO_2$$

$$NO + CO/HC \longrightarrow \frac{1}{2}N_2 + CO_2/H_2O$$

2.5 Ammonia and Urea selective catalytic reduction (NH_3-SCR and Urea-SCR)

Ammonia/Urea-SCR is utilising pure ammonia (NH_3) or urea $(NH_2)_2CO$ as reducing agents to reduce NO_X emission, typically injected into the exhaust gas upstream a catalyst. Since ammonia is toxic, hazardous and has a high vapour pressure, it makes challenges to store and use safely. Therefore, ammonia is normally replaced by non-toxic urea. Urea is a solid, odourless and colourless organic compound which is highly soluble in water (Twigg, 2007).

The following steps illustrate the urea-SCR process for NO_X emission reduction (Koebel, et al.,2000):

a) Liquid urea is heated in the hot exhaust gas to evaporate and then, decomposed to NH_3 and isocyanic acid (thermal decomposition):

$$(NH_2)_2CO\ (l) \rightarrow NH_3 + HNCO$$

b) Isocyanic acid reacts with the water vapour in the exhaust forming ammonia and CO_2 (exothermic hydrolysis reaction):

$$HNCO + H_2O \rightarrow NH_3 + CO_2$$

c) Ammonia selectively reduces NO_X to produce N_2 and H_2O. Since NO is the main component of NO_X the primary reaction in ammonia-SCR is (Koebel, et al.,2000; Majewski and Khair, 2006; Chatterjee, et al., 2008):

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

There is much slower reaction of NO with NH_3 which does not require O_2:

$$4NH_3 + 6NO \rightarrow 5N_2 + 6H_2O$$

In addition, there is also a faster reaction mechanism which involves NO and NO_2 reacting with NH_3:

$$4NH_3 + 2NO + 2NO_2 \rightarrow 4N_2 + 6H_2O$$

Another reaction mechanism in NH_3-SCR is the reduction of NO_2 without NO:

$$8NH_3 + 6NO_2 \rightarrow 7N_2 + 12H_2O$$

At high temperatures, NO_X conversion activity reduces due to undesired reactions which decrease the concentration of NH_3 forming other emissions. For instance, the production of nitrous oxide (N_2O) which is one of greenhouse gases as shown below:

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

Effective catalysts for the reduction of NO_X using NH_3-SCR process include Vanadium oxide based, Cu-Zeolite and Fe-Zeolite catalysts (Twigg, 2007). These catalysts are now in production given above 80% for the reduction of NO_X emissions from diesel exhaust gas. The performance difference of these catalysts in NO_X reduction lies in resistance to evaluated temperatures and their ammonia storage capabilities (Chi, 2009).

2.6 Hydrocarbon selective catalytic reduction (HC-SCR)

An alternative technology to control NO_X emission in diesel engine exhaust gas is HC-SCR. In this process, the catalysts selectively reduce NO_X to N_2 under lean exhaust conditions using hydrocarbons. A variety of HC reductants can be employed in HC-SCR depend upon the catalyst. This enables HC-SCR to be effective over a wide range of temperatures. The key step for gaining high reduction activity of SCR at low temperatures is the oxidative activation of HCs. HC-SCR has remarkable advantage of using unburnt hydrocarbons exist in the exhaust gas as the reductant.

Silver-loaded alumina (Ag/Al_2O_3) with a 2 wt.% silver loading is one the most promising catalysts for selective catalytic reduction of NO_X by different HCs (Shimizu and Satsuma, 2007; Shimizu, et al., 2007). It has been identified from past studies that Ag/Al_2O_3 has several advantages over other HC-SCR catalysts (e.g. Pt supported on alumina and Cu-Zeolite). These include relatively high thermal durability, low activity for the oxidation of SO_2 and high selectivity to nitrogen (compared to Pt/Al_2O_3 catalysts which produce large quantities of N_2O) (Shibata, et al., 2002; Schmieg, et al., 2008; Kim, et al., 2005).However, Ag/Al_2O_3 suffers from deactivation at low temperatures (<300 °C) typical of diesel exhaust gas.

2.7 Fuel options for selective catalyst reduction of NO_X

From past studies it has been identified that hydrocarbon type injected to exhaust gas influences the Ag/Al_2O_3 performance towards conversion of NO_X (Iliopoulou, et al., 2004; Thomas, et al., 2005). Various hydrocarbons have been investigated as reductants on the Ag/Al_2O_3 catalyst showing high NO_X conversion at high temperatures catalyst but, at low temperatures the SCR catalyst has been deactivated mostly due to coking (hydrocarbons consist of aromatics specially) and the soot on its surface (Houel, et al., 2007a). High chain length, unsaturated paraffin HC for instance improves the activity of the catalyst and allows reduction of NO_X at low temperature. But at high temperatures as chain length and saturation level increase, deposition of coke on the catalyst surface suppress the reduction of NO_X. Aromatic content hydrocarbons also have been proven that increase production of coke on the catalyst limiting the activity the HC-SCR (Angelidis, et al., 2002; Iliopoulou, et al., 2004).

Gas-to-liquid (GTL) fuel produced through the Fischer-Tropsch (F-T) process has been previously studied showing higher performance on NO_X reduction compare to conventional diesel, as it does not comprise unsaturated hydrocarbons and aromatic (Houel, et al. 2007a). Light alcohols except methanol (C1) have been found as good reductants for the HC-SCR. Ethanol has the highest reduction rate of NO_X and as the hydrocarbon chain length of alcohol increases, the conversion performance of the component declines (Thomas, et al., 2005).

There is limited research on the performance of biodiesel components (methyl esters) over the Ag/Al_2O_3 catalyst.

2.8 Biodiesel

Biodiesel consists of different mono-alkyl esters with different saturation degrees and chain lengths of fatty acids. Biodiesel composition varies depending upon which source (such as animal fats, used vegetable oil, rapeseed oil, etc.) it is obtained from. The concentrations of methyl esters in three different biodiesel fuels are represented in Table 1. These fuels compare to ULSD fuels have higher distillation temperatures and higher molecular weight (Monyem and Gerpen, 2001). Over the years, the interest in using biodiesel has significantly increased in regard to reducing emissions by replacing fossil fuels with renewable and more sustainable energy sources. Biodiesel fuels are normally produced with high percentages of purity (>98%) from base catalysed ransesterification (Zhou and Boocock, 2006; Schuchardt, et al., 1998). The most common form of biodiesel in Europe is RME.

The challenge therefore is to increase substantially the production of biofuels by using innovative feedstock, processes and technologies, which are both competitive and sustainable.

Table 1: Concentrations of different components in selected biodiesel fuels.

Basic esters (% w/w$_{bio}$)	**Animal fat** (Lapuerta, et al., 2009)	**RME (rapeseed methyl ester)** (Pinzi, et al., 2013)	**Waste cooking oil** (Lapuerta, et al., 2008)
Caprylic (C8:0)	0.11	0.00	0.00
Capric(C10:0)	0.00	0.00	0.00
Lauric(C12:0)	0.00	1.96	0.00
Myristic (C14:0)	2.52	1.75	0.14
Palmitic (C16:0)	28.36	4.07	10.54
Palmitoleic (C16:1)	0.00	5.24	0.64
Margaric (C17:0)	0.00	0.00	0.00
Margaroleic (C17:1)	0.00	0.00	0.13
Stearic (C18:0)	15.74	1.13	4.02
Oleic (C18:1)	42.20	77.62	54.74
Linoleic (C18:2)	9.43	8.23	28.03
Linolenic (C18:3)	0.60	0.00	0.29
Arachidic (C20:0)	0.16	0.00	0.37
Gadoleic (C20:1)	0.86	0.00	0.44
Behenic (C22:0)	0.01	0.00	0.66

Combustion of biodiesel has advantages such as lower concentrations of unburned hydrocarbons, carbon oxide (CO) and particulate matter (PM) compared to conventional diesels e.g. ULSD (Chuepeng, et al., 2007; Graboski and McCormick, 1998). These benefits are mostly related to oxygenated components in the biodiesel chemical composition; however these species cause larger production of NO_X emission in the exhaust gas from the combustion process (Szybist, et al., 2005; Tsolakis, et al., 2007). Some methods have been introduced to decrease the level of NO_X emission such as using exhaust gas recirculation (EGR) and blends of biodiesel with conventional diesel fuel (Theinnoi, et al. 2009).

2.9 Hydrogen impact on the performance of the Ag/Al_2O_3 catalyst on NO_X reduction

It has been identified from previous studies that presence of hydrogen can improve the NO_X conversion remarkably (Siteshebo, et al., 2009). H_2 is acting as a promoter when appropriate amount of hydrocarbon is injected to the exhaust system. It has the highest influence on the performance of long chained hydrocarbons especially at low temperatures (Richter, et al. 2004).

However in a real engine access to hydrogen is limited, there are few methods of achieving hydrogen like fuel reforming. Hydrogen improves the oxidation of nitric oxide (NO) to nitrogen dioxide (NO_2) and the production of reactive species over the HC-SCR at lower temperature enabling a larger NO_X reduction to be achieved (Sazama, et al. 2005). H_2 also induces removal of carbon species on the catalyst surface significantly (Houel, et al. 2007b). Therefore, based on its promoter mechanisms, similar effects are expected to be observed on the hydrocarbon components in this research.

2.10 Summary

Even though there have been substantial improvements - as explained in this chapter - for the reduction of NO_X emission from diesel exhaust gas, more advanced after-treatment systems will essential to be developed to meet the future emission targets. There are currently two main alternative catalyst methods for the reduction of NO_X: selective catalyst reduction and NO_X storage catalyst. SCR of NO_X includes HC-SCR and ammonia-SCR. Of these alternatives, hydrocarbon-SCR has practical advantages in terms of engine operation, implementation, cost and durability.

A number of catalysts have been tested in the HC-SCR. Alumina-supported silver catalysts, which have been reported to have moderate tolerance to SO_2 and water, are popular candidate for practical use. Several reports have revealed the potential of Ag/Al_2O_3 in practical applications, however there are still many obstacles that need to be solved before such systems are made commercially available. For instance, coking of the catalyst and poor low temperature activity are two of the major problems currently faced with silver catalysts. One solution to overcome this problem is using hydrogen with SCR of NO_X as a promoter for reductant in order to shift the operating temperature to a lower region. The HC-SCR performance of supported silver catalysts is known to be very sensitive to the type of hydrocarbons. As it has been proven that some oxygenated hydrocarbons such as alcohols are effective reductant for SCR of NO_X, therefore biodiesel or its components seems to be appropriate candidates to be used in HC-SCR for the reduction of NO_X.

Chapter 3

EXPERIMENTAL SETUP

3 Experimental Setup

3.1 Fuels

Biodiesel components methyl lauric (C12:0), methyl myristic (C14:0), methyl palmitic (C16:0) and methyl stearic (C18:0) were used as hydrocarbon reductants in order to convert NO_X emission to N_2. The properties of these methyl esters are illustrated in Table 2. As in room temperature methyl palmitic and methyl stearic are solid (i.e. with melting points that are higher than 30 °C), they are not appropriate to be tested in the system. Therefore, the solid methyl esters (C16:0 and C18:0) were mixed with ULSD, RME and GTL (Gas-to-Liquid) separately with different volumes. These fuels have advantage of being used for combustion in the same time; therefore one tank is required only. In addition, since biodiesels contain high percentages of methyl esters, the results will be less influenced by non-methyl ester components activity.

The study was carried out using 15, 30, 50 and 75% of methyl palmitic and methyl stearic by volume into ULSD, RME and GTL. The blended hydrocarbons were upheld at 20 °C and the stability was checked after 48 hours. The results showed that a blend fraction of 40% was enough to avoid phase separation of HCs blend. In the case of 50% or higher (by volume) methyl palmitate (C16:0) and methyl stearate (C18:0), solid phase separation was seen. 40% of methyl esters and 60% of ULSD were selected as reactants in HC-SCR for NO_X conversion.

Table 2. Properties of the components tested as reductants on HC-SCR

Properties	ULSD	C12:0	C14:0	C16:0	C18:0
Purity (% v/v)	100	≥98	≥98	≥97	≥96
Chemical formula	$C_{14}H_{26.09}$	$C_{13}H_{26}O_2$	$C_{15}H_{30}O_2$	$C17H_{34}O_2$	$C_{19}H_{38}O_2$
Density at 40°C (kg/m3)	812.1	871	868	850.5	849.6
Aromatic (wt%)	43.3	0	0	0	0
Viscosity at 40°C (cSt)	2.47	2.23	2.96	4.38	5.58
Boiling point (°C)	263	262	295	338	352
Molecular weight (kg/kmol)	211.7	214.3	242.4	270.5	298.5
Lubricity at 60°C (µm)	312	330	299	148	243

3.2 Engine setup and experimental facilities

All experiments in this study were carried out on a single-cylinder, direct injection experimental diesel engine. The exhaust gas flow produced from this engine was used for NO_X conversion. A schematic of the experimental setup and HC-SCR arrangements used in this study is demonstrated in Figure 1. Ultra-low sulphur diesel (ULSD) was used for the operation of engine supplied by Shell Global Solutions, UK. The engine was running with load set at 1.5 bar indicated mean effective pressure (imep) and fixed speed of 1500 rpm for all experiments. The engine was set to these conditions so that the results will be comparable with previous studies (Herreros, et al., 2014; Arve, et al., 2007). Table 3 shows details of the main engine specifications. At various points thermocouples were placed in the system and continuously measured real time temperatures using PicoLog software at all time.

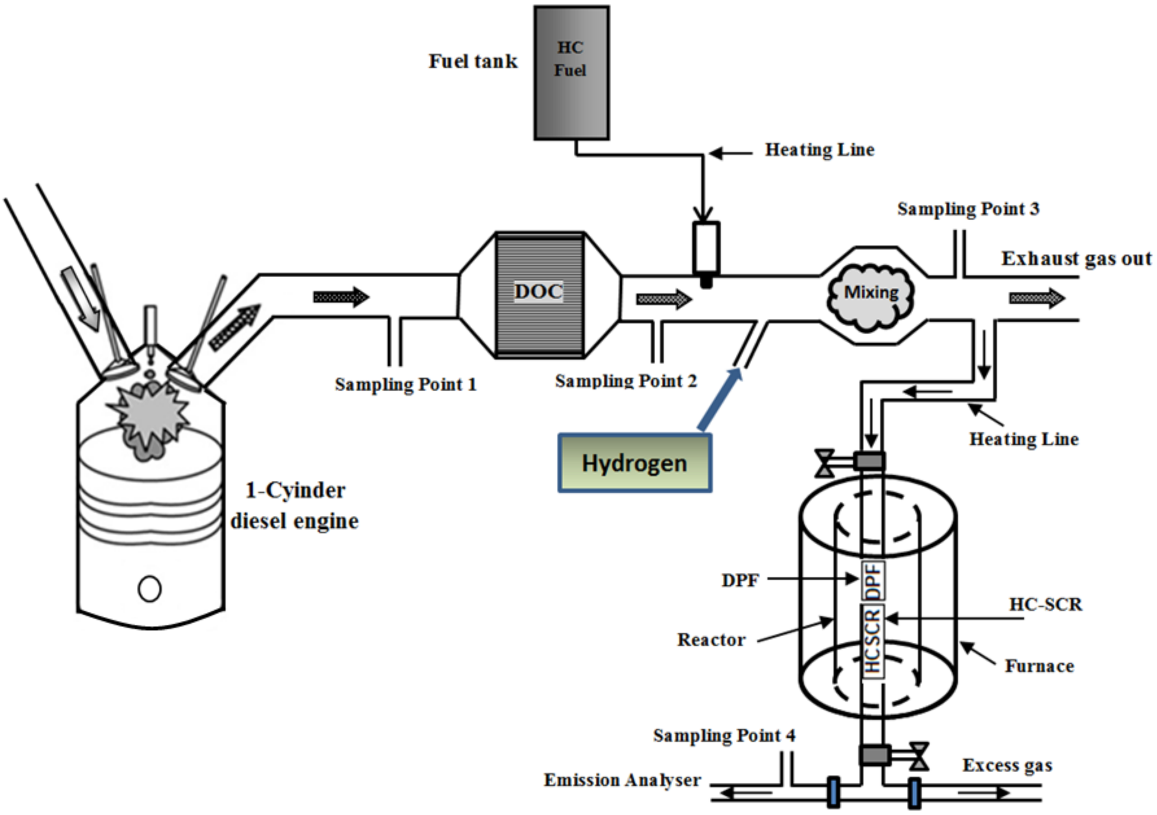


Figure 1: The simplified schematic of experimental facilities

Table 3: Test engine specifications

Engine Specification	Data
Number of cylinders	1
Bore/Stroke	98.4mm/101.6mm
Connecting Rod Length	165mm
Displacement Volume	733cm3
Compression Ratio	15.6:1
Rated Power	8.36Kw@2500rpm
Peak Torque	39.2Nm@1500rpm
Injection System	Three holes pump-line-nozzle
Injection Timing	22°bTDC
Engine Piston	Bowl-in-piston

3.3 Catalysts used

The HC-SCR catalyst was a Ag/Al_2O_3 (2% wt.) catalyst which was prepared by impregnating ϒ-alumina (surface area ~150 m^2/g) with aqueous $AgNO_3$ before drying and calcining in air for 2 hours at 500 °C to achieve a silver loading of 2% wt. This was made to an aqueous suspension, which was then uniformly coated onto ceramic monolith substrates (diameter 115mm, length 75mm) with high cell density (600psi) provided by Johnson Matthey.

In order to remove unburnt hydrocarbon contents of the exhaust gas stream produced from combustion process which can affect the results, a platinum based diesel oxidation catalyst (DOC) coated onto a cordierite honeycomb monolith substrate was placed in the exhaust system. This enables measuring NO_X reduction from only HC injected into the exhaust system downstream the DOC. Upstream the SCR a SiC-diesel particulate filter (DPF) was placed to eliminate carbonaceous species reducing their impact on poisoning of the HC-SCR catalyst by blocking the active sites. The HC-SCR catalyst was placed 3cm downstream of the DPF in a reactor rig.

3.4 Experimental procedure

The base NO_X concentration of the engine exhaust gas was measured from sampling point 1 for each test using a MultiGas 2030 Fourier Transform Infrared Spectroscopy (FTIR). Then, in order to calculate NO_X reduction within a temperature range of 200 °C to 450 °C, the NO_X concentration was recorded from sampling point 2 (downstream of HC-SCR catalyst) every 10 °C.

The concentrations of other engine exhaust gas emissions NO, NO_2, N_2O, CO, CO_2, NH_3 and total hydrocarbons were monitored at both sampling points during experiments using the FTIR. The injected reactants were 40% of volume of methyl lauric (C12:0), methyl myristic (C14:0), methyl palmitic (C16:0) and methyl stearic (C18:0) each blended with 60% of ULSD. In Table 2 the hydrocarbons components properties are listed. As it can be seen from Table 2 methyl esters lubricity are well below the allowance 460 µm. This means that these blends could be used as fuel for the combustion in the engine, therefore there is no requirement for a second fuel tank.

The experiments were carried out as follows:

a) Impact of different methyl esters blended with ULSD on conversion of NO_X in HC-SCR catalyst. The methyl esters blends were injected individually using an electronic syringe pump into the exhaust downstream of the DOC. The syringe system regulates the fuel flow rate injected to a thermal atomiser vaporising hydrocarbon components to be mixed later with the exhaust gas flow. From previous studies (Arve, et al., 2009) HC: NO_X for reactant blends was chosen to be injected at a constant ratio of 3:1. Then, the NO_X reduction was monitored every 10 °C within a temperature ramp of 200 to 450 °C which is the typical diesel engine operating temperature range.

b) The methyl esters blends were injected with the same ratio of 3:1, in addition with 8000 ppm of hydrogen into the exhaust gas stream. NO_X conversion was monitored every 10 °C in a continuous temperature ramp from 200 to 450 °C.

Chapter 4

EFFECT OF BIODIESEL COMPONENTS IN NO$_X$ CONVERSION

4 Effect of biodiesel components in NO_X conversion

The effects of the different bio-compounds on NO_X reduction to N_2 on 2% wt. Ag/alumina were studied at the temperature range of 150- 450 °C. The following equation was used to calculate NO_X conversion:

$$NO_X\, conversion\ (\%) = \frac{[NO_X\,]_{inlet} - [NO_X\,]_{outlet}}{[NO_X\,]_{inlet}} \times 100$$

Figure 2 represents NO_X emission conversion when methyl lauric (C12:0), methyl myristic (C14:0), methyl palmitic (C16:0) and methyl stearic (C18:0) blended with 60% volume of ULSD used as NO_X emissions reducing agent. At low temperatures, below 300 °C, none of the components shows any activity of NOx conversion except methyl laurate where some activity was detected from 280 °C. For longer chain length methyl esters the light-off temperatures (the temperature at which reductant starts reducing NO_X emission – 10% NO_X reduction in this study) are higher. These activities are similar to the results discerned from alkanes and alcohols which longer chain length hydrocarbons have higher NOx reduction activities at low temperatures. C12:0 reaches the peak activity at considerably high temperature 440 °C, but C14:0 and C16:0 the peak activities are at lower temperature (400 °C) occur. C18:0 results show two peaks, one at 380 °C and lower one at 440 °C.

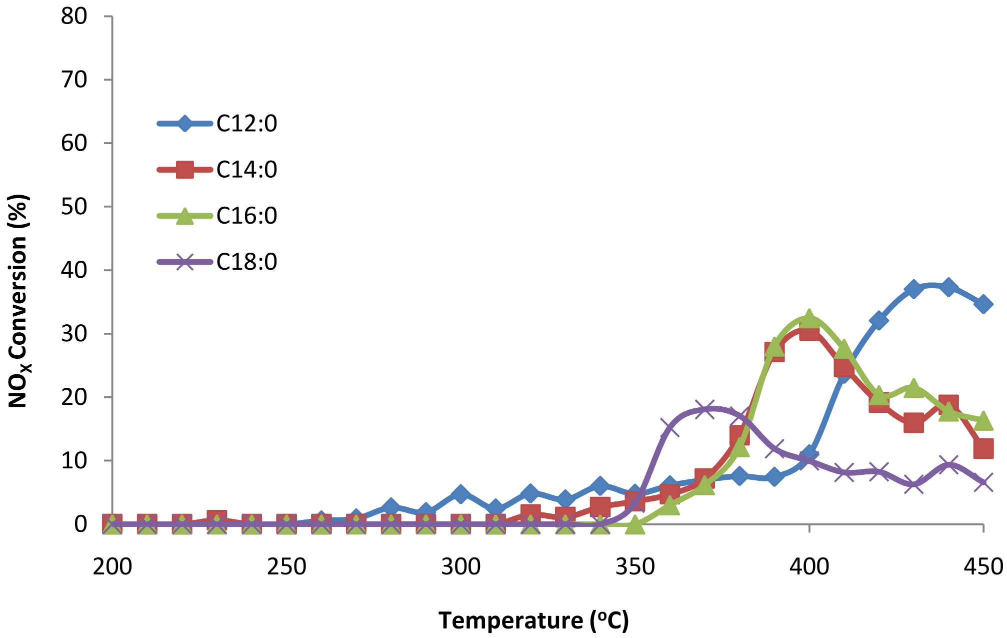


Figure 2: NOx conversion rate of 40% biodiesel components with 60% ULSD over Ag/Al_2O_3 catalyst[1]

These low NOx conversions at low and medium temperatures and decreasing in light-off temperatures as methyl esters chain length increases is explained as follows:

---

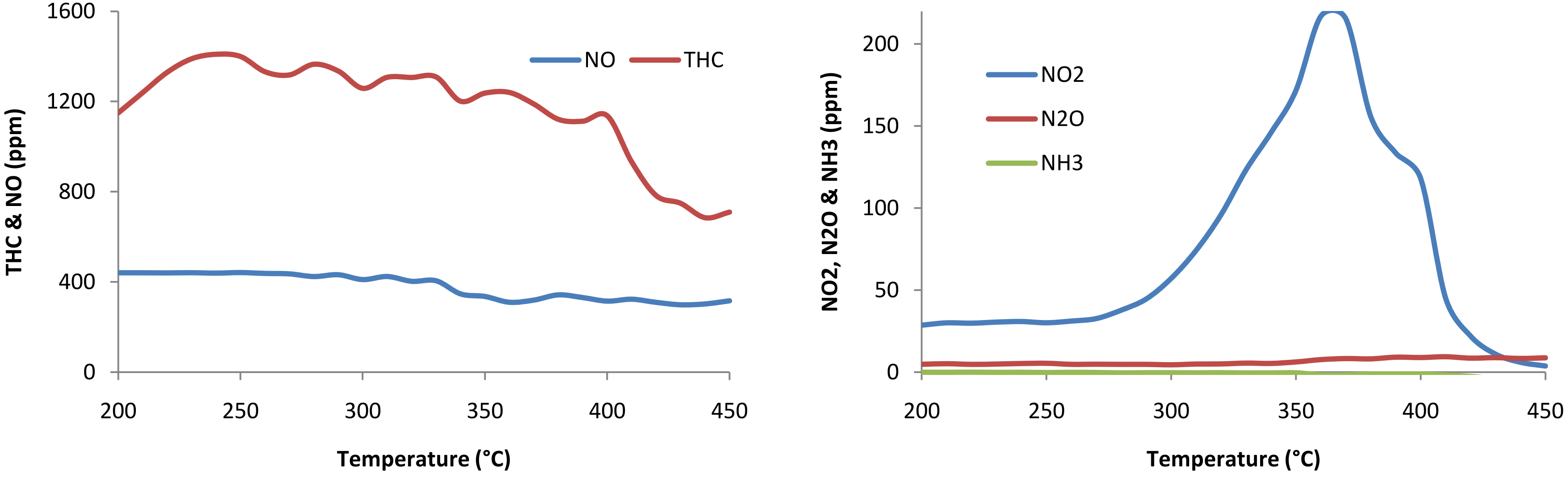
[1] The vertical axis is expanded up to 80% in order to help the visual comparison with

4.1 Low-medium temperature

Catalyst poisoning: Figures 3 and 4 show exhaust gas components downstream the catalyst. As it can be seen, at low temperatures, significant amount of hydrocarbon lost without any NOx conversion in result. Since oxidation of hydrocarbons happens at higher temperature therefore they must be condensed or deposited on catalyst surface and cause catalyst poisoning and hinders further reactions. This also correlates with high concentration of Aromatics (43.3 wt%) and unsaturated hydrocarbons incorporate in ULSD contents in blends with methyl esters. Aromatics obstruct the catalyst activity by the deposition of coke on the catalyst surface. As chain length increases the coke deposition rate also increases inhibiting catalyst activity (Houel, et al., 2007a; Arve, et al., 2009).

Low reactivity: At low temperatures methyl esters remain stable and resist breaking down in order to produce active hydrocarbons required for reactions with NO_X and ammonia. In addition, the decomposition of hydrocarbons is the first step in the formation of intermediate species like nitrate compounds and acetates which are key intermediate components for catalyst surface reactions yielding production of N_2, water and carbon oxides (Johnson, et al., 2012; Herreros, et al., 2014).

Methyl lauric (C12:0)



Methyl myristic (C14:0)

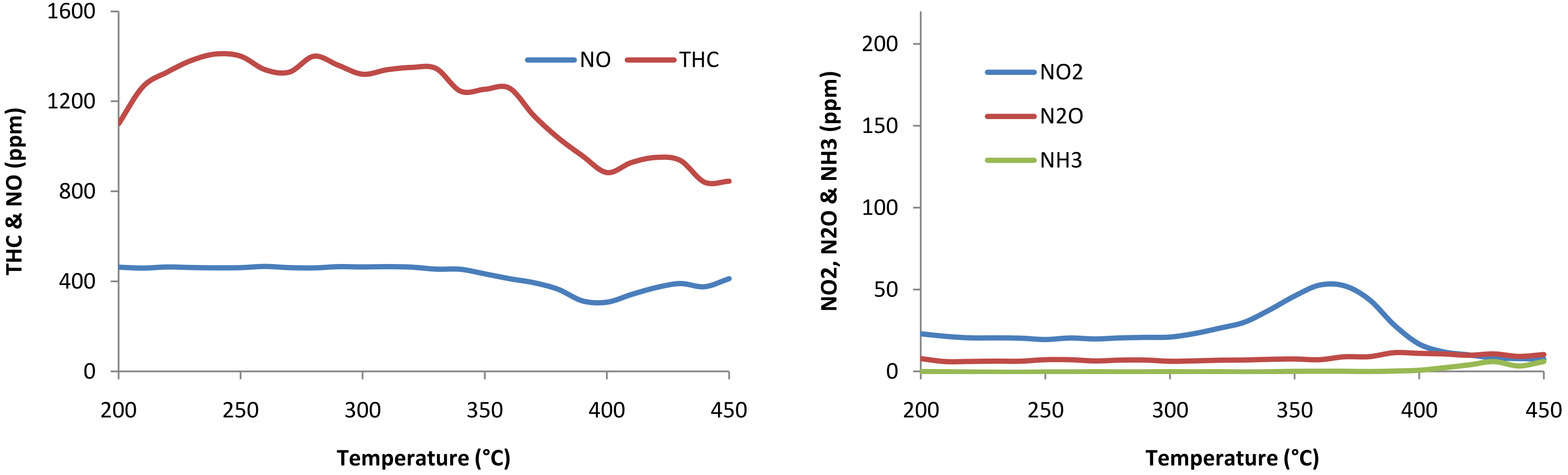
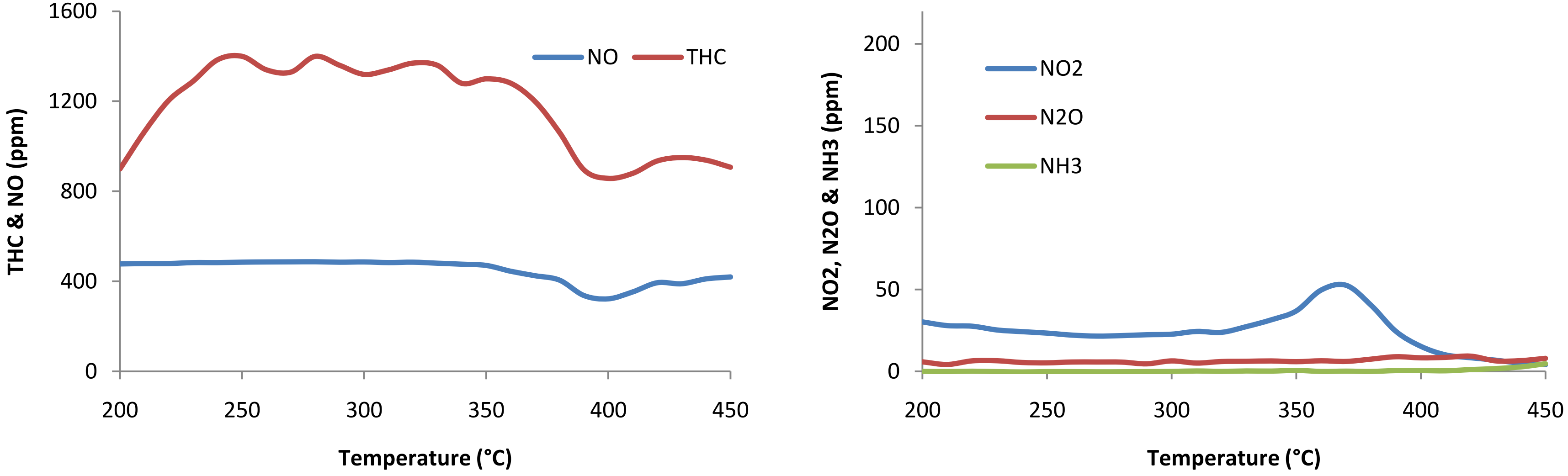


Figure 3: Effect of C12:0 and C14:0 on THC, NO, NO2, N2O and NH3 concentration downstream the HC-SCR catalyst.

Methyl palmitic (C16:0)



Methyl stearic (C18:0)

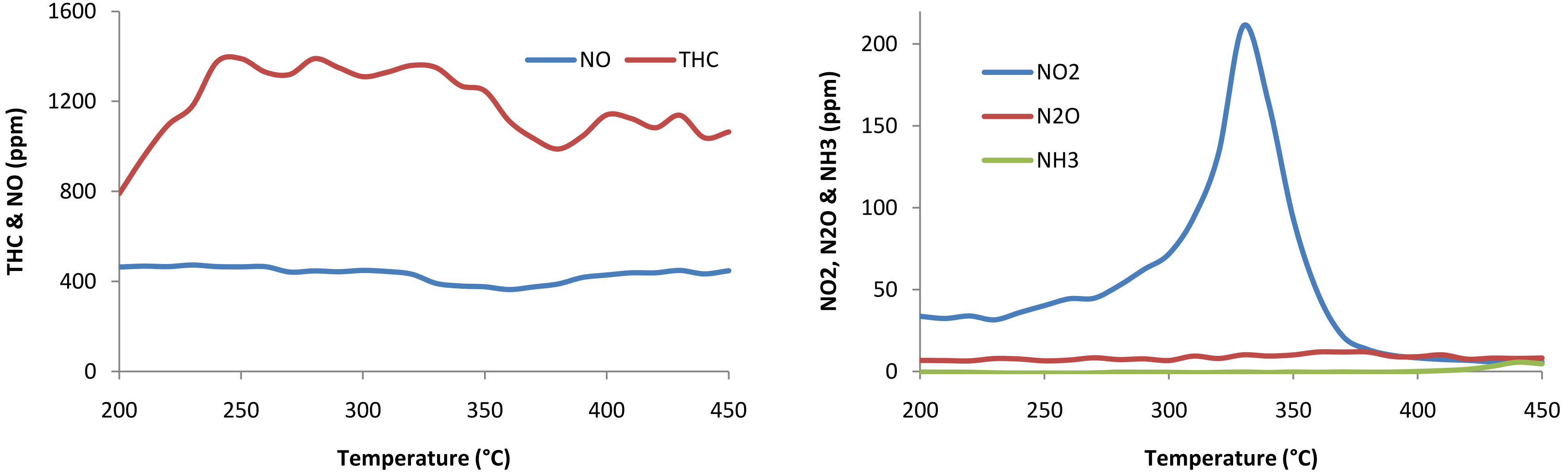


Figure 4: Effect of C16:0 and C18:0 on THC, NO, NO2, N2O and NH3 concentration downstream the HC-SCR catalyst

High boiling points: Properties of selected methyl esters are detailed in Table 2. Boiling points of these components are in a high range of 262 °C to 352 °C contribute to partially condensation after injection either in the exhaust pipe downstream catalyst or deposition on the catalyst surface. Consequently, these lead to deactivation of the catalyst and also reduce gas phase reactions which have been mentioned as a considerable portion of the HC-SCR activities in reducing NO_X emissions. Low concentration of THC (Total hydrocarbons) detected at low temperatures downstream catalyst without significant effect on NO_X reduction also prove this fact (Figure 3 and 4).

NO_2 and NH_3 production: Ammonia with NO and NO_2 contribute to a series of fast reactions on HC-SCR which lead to NO_X conversion:

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

As it can be seen from figure 3 and 4, concentrations of NH_3 at low temperatures in the exhaust gas for all reductants are almost zero. Due to inadequate production of NH_3 attributed to the low reactivity of methyl esters, these effective reactions are negligible. Even though NO_2 is a part of NO_X emissions aimed to be reduced in the SCR catalyst, it is useful because it reacts with NO and NH_3 and hydrocarbon reductants in series of reactions lead to conversion of NO_X to N_2. At low temperatures less quantity of NO oxidises and produces NO_2.

Polarity and water solubility: Previous studies proposed that polar oxygenates components possess advantage to compete with water for adsorption on the catalyst surface (Burch, et al., 2002; Thomas, et al., 2005). In contrast to alcohols which are highly polar and water soluble methyl esters suffer from lack of these properties.

Mobility /molecular weight: Biodiesel components have relatively high molecular mass with long chain length. In addition, viscosity of methyl palmitic (C16:0) and methyl stearic (C18:0) are high. These are disadvantage factors that result in lower mobility. Then, the ability of methyl esters molecules to access active sites of catalyst reduces and this is the least for longest chain component, methyl stearic.

4.2 High temperature

At temperatures above 350 °C the catalyst is active in reducing NO_X emissions. As expected lower chain length methyl esters activation and performance window are toward higher temperature in comparison to heavier methyl esters. As can be observed from figure 2, for all reactants a fall-down in activity is perceptible at higher temperatures. This is due to domination of direct hydrocarbons oxidation over selectivity to NO_X reduction at higher temperatures. This signifies less active hydrocarbons species available to react and convert NO_X to N_2. The NH_3 excess spillage also shows that there are not enough hydrocarbons to react with. More HC: NO_X ratio is required to keep NO_X conversion at high levels (He, et al., 2002).

Fuel penalty: For a given engine condition, fuel penalty can be determined as the rate of the hydrocarbon reductants consumption (by energy or mass) divided by the fuel required for the engine combustion (see appendix). As it can be seen from table 4, fuel penalty for lighter methyl esters is slightly lower than higher chain length components. Since these calculations include 60% ULSD content in the blends, fuel penalty for pure methyl esters would be less than represented numbers.

Table 4: Fuel penalty by energy for constant HC:NO$_X$ ratio of 3.

Reductant	Fuel penalty (% energy)
Methyl lauric (C12:0)	6.25
Methyl myristic (C14:0)	6.31
Methyl palmitic (C16:0)	6.35
Methyl stearic (C18:0)	6.40

Chapter 5

EFFECT OF HYDROGEN ADDITION ON NO$_X$ CONVERSION

5 Effect of hydrogen addition on NO_X conversion

Addition of hydrogen into Ag/Al_2O_3 catalyst with a hydrocarbon reductant promotes performance of conversion of NO_X over the catalyst. Hydrogen improves de-NOX activity of all methyl esters blends in total temperature range as it can be seen from Figure 5. In the case of Methyl laurate (C12:0) and methyl palmitic (C16:0) the peak activities move towards lower temperatures similar to the impact of hydrogen on other hydrocarbons proposed in past studies. Although overall NO_X reduction activities of methyl myristic (C14:0) and methyl stearic (C18:0) enhanced, the peak activities shift forward. These are unexpected results. The influence of hydrogen at low/medium temperatures and high temperatures individually is explained as follows:

5.1 Low-medium temperature

Silver oxide (Ag_2O) clusters: It is suggested that high activity of the SCR reaction in the presence of hydrogen is related to high concentrations of Ag clusters which observed from UV-Vis spectroscopy (Breen & Burch, 2006).

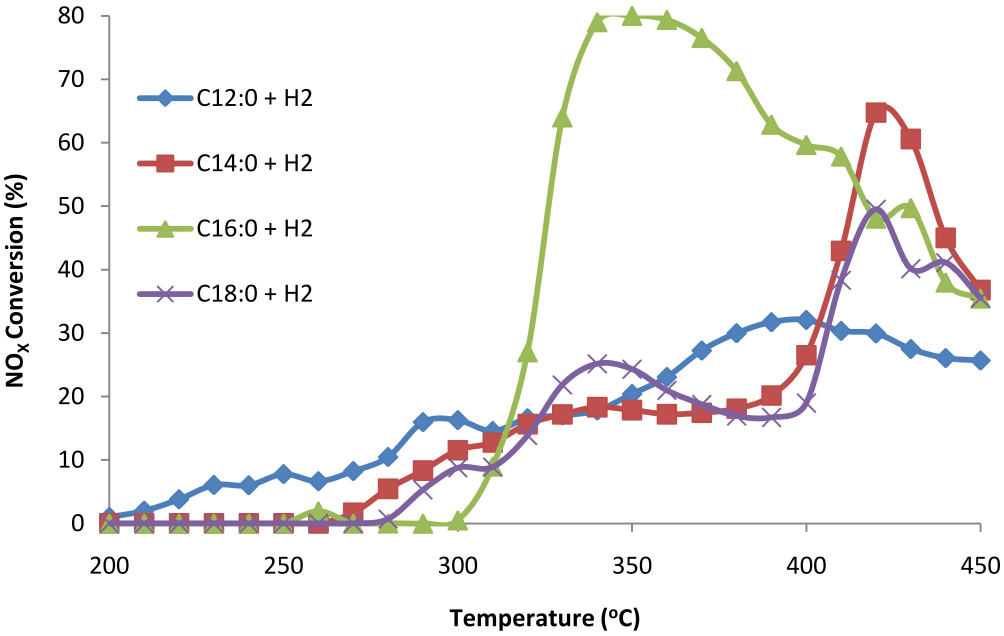


Figure 5: NO_X conversion rate of 40% biodiesel components with 60% ULSD over Ag/Al_2O_3 catalyst with addition of 8000ppm of hydrogen

NO_2 production: Hydrogen also facilitates production of NO_2 by NO oxidation, enables the formation of N_2 from the following reaction (Breen & Burch, 2006):

$$\{HCs\} + NO_2 \rightarrow N_2 + CO_2 + H_2$$

$$\{HCs\} + NO_2 + NO \rightarrow N_2 + CO_2 + H_2$$

$$8NH_3 + 6NO_2 \rightarrow 7N_2 + \ 12H_2O$$

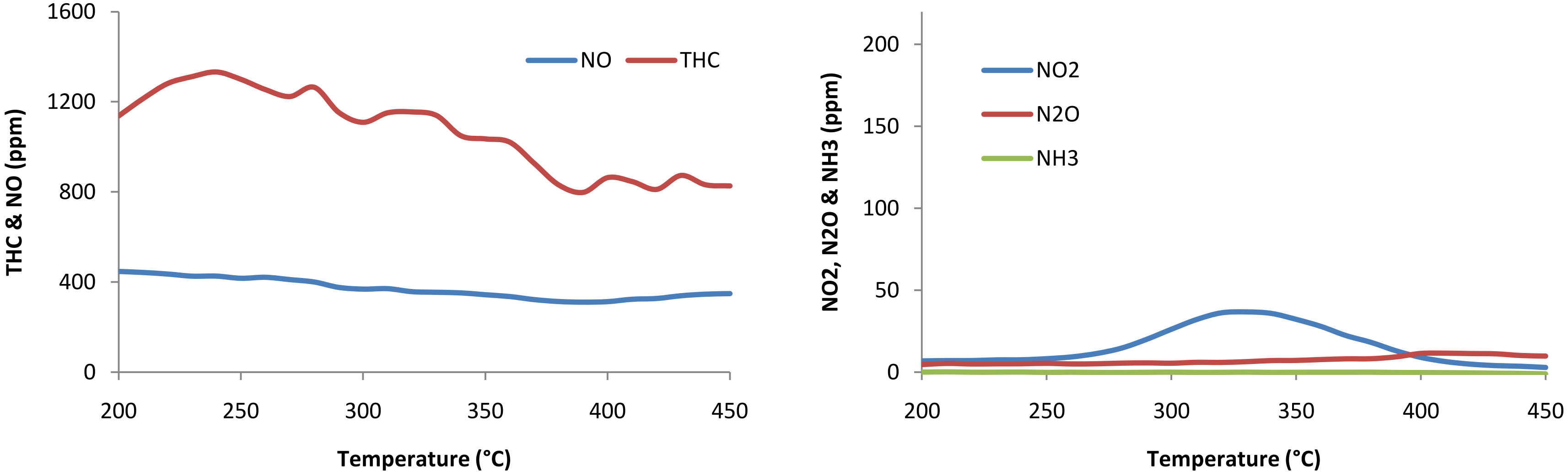
Figure 5 demonstrated that for all methyl esters the NO_2 peak productions with addition of hydrogen are at lower temperatures compared to NO_2 productions without hydrogen.

Partial oxidation of HCs: The formation of surface acetate and active hydrocarbons components from partial oxidation of hydrocarbons is the main step in SCR reaction and its rate directly influence the rate of NO_X conversion. H_2 has a significant impact on the oxidation reaction and accelerates the proposed rate. Figures 6 and 7 show higher conversion of total HCs for all methyl ester blends in the presence of H_2. Hydrogen also assists the production rate of large variety of key intermediate compounds by oxidation of the surface species (Richter, et al., 2004; Shimizu, et al., 2007).

Acetate production/nitrates removal: Exhaust gas flow form nitrates on the Ag/Al_2O_3 catalyst surface and decreases NO_X reduction by blocking active catalyst sites. By utilising transient in situ IR measurements Shibata et al. found addition of hydrogen to exhaust flow remarkably enhances the formation of surface acetate and simultaneously removes surface nitrates.

Gas phase reaction: Eranan, et al. (2003) reported that gas phase reaction alongside with surface reactions has an important role in HC-SCR over Ag/Al_2O_3. They suggested that hydrogen activates NO_X species involved in the gas phase reactions.

Methyl lauric (C12:0) & Hydrogen



Methyl myristic (C14:0) & Hydrogen

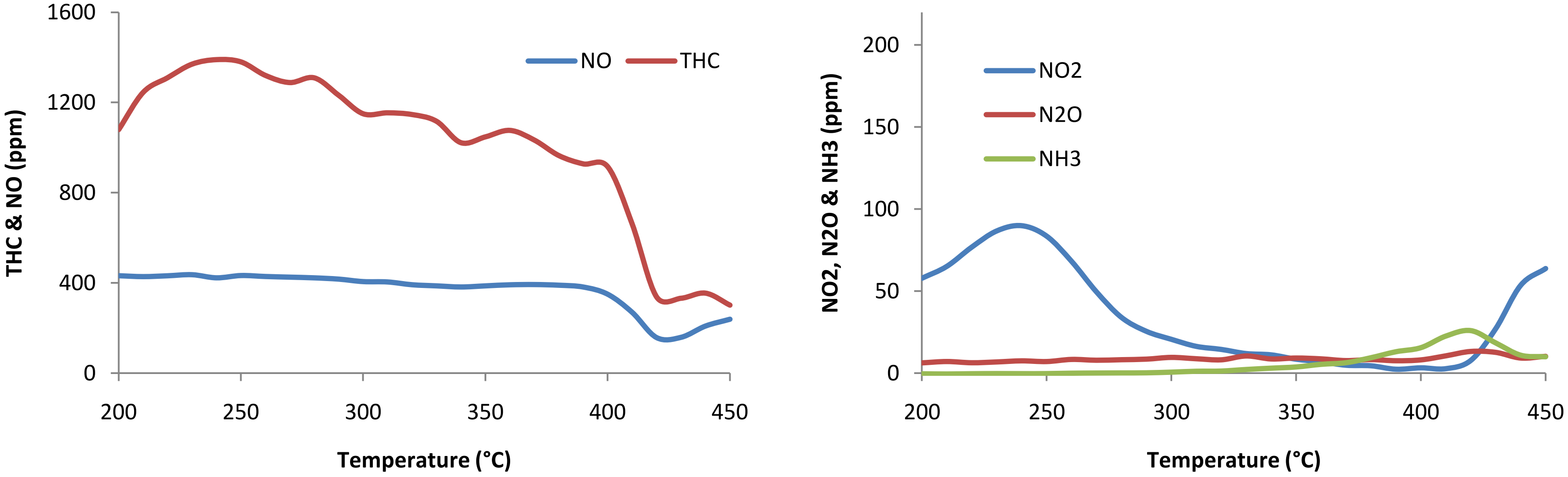
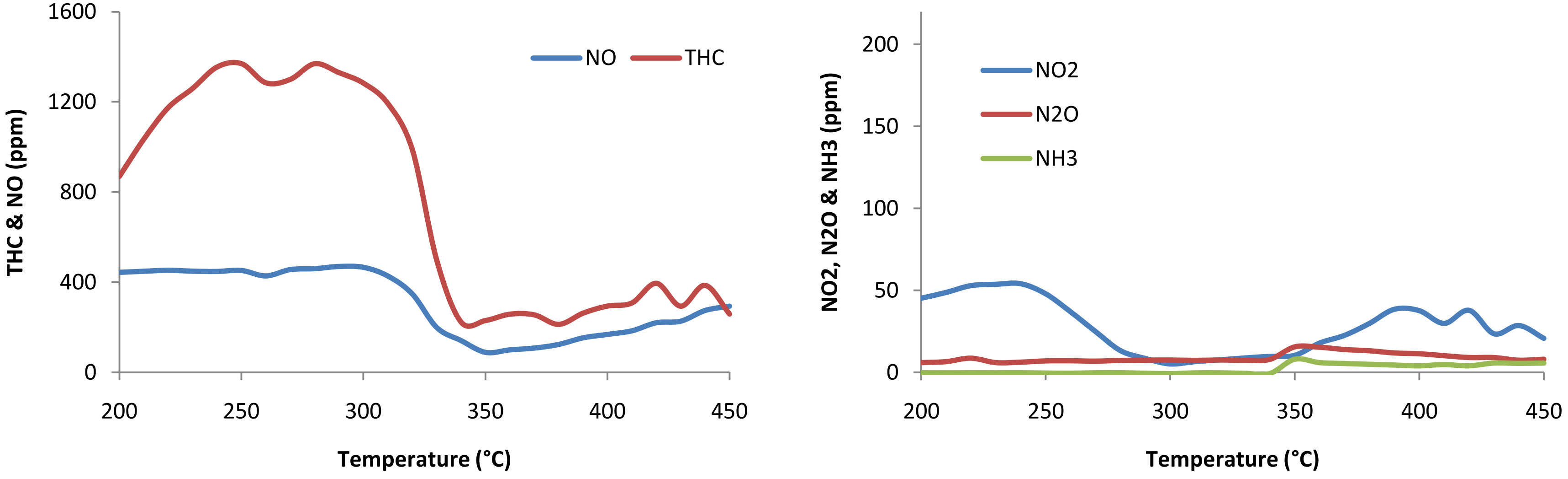


Figure 6: Effect of C12:0 and C14:0 with hydrogen addition on THC, NO, NO2, N2O and NH3 concentration downstream the HC-SCR catalyst.

Methyl palmitic (C16:0) & Hydrogen



Methyl stearic (C18:0) & Hydrogen

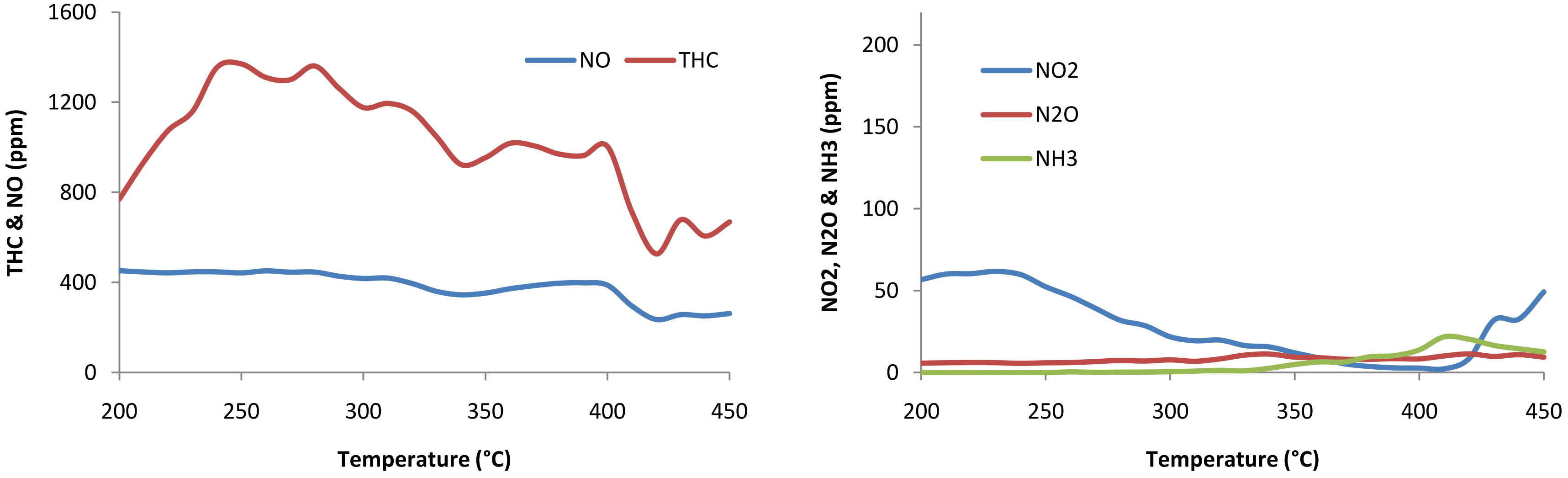


Figure 7: Effect of C16:0 and C18:0 with hydrogen addition on THC, NO, NO2, N2O and NH3 concentration downstream the HC-SCR catalyst.

5.2 High temperature

At temperatures higher than 400°C for C12:0, C14:0 and C18:0 methyl esters-SCR in the presence of H_2, NO_X production rate declines. This fall-off occurs at 350°C for C16:0. Hydrogen becomes more effective towards complete oxidation of hydrocarbons to CO_X and water instead of promoting hydrocarbons by partial oxidation to active species (He, et al., 2008). Direct oxidation of H_2 and production of water also becomes dominant in high temperatures. Therefore HC-SCR reactions suffer from low concentrations of active reductants to convert NO_X.

At low temperatures concentrations of N_2O and NH_3 in the presence of hydrogen are negligible. But at high temperatures (>350°C) compared to when H_2 not injected to exhaust flow, N_2O and NH_3 increase, as it can be seen from Figures 6 and 7. N_2O has much higher greenhouse impact compared to the other nitrogen oxides. Even though the amount does not exceed 16ppm for all reactants, still it is a disadvantage for H_2-SCR at high temperature exhaust flow. H_2 increases the production of NH_3 and in addition, the domination of hydrocarbon oxidation to SCR reactions at high temperatures result in NH_3 spillage.

Chapter 6

CONCLUSIONS

6 Conclusions

6.1 Concluding remarks

With more strict emission legislation being imposed by the environmental governing bodies as concerns the emissions from vehicles; diesel after-treatment is now an essential element in the emissions reduction. Hydrocarbon selective catalytic reduction (HC-SCR) over silver supported on alumina (Ag-Al_2O_3) catalysts is one of the most promising after-treatment technologies for NO_x emissions reduction, which employs hydrocarbons as the reductants for NO_X in lean-burn gas streams. Simplicity to implement and cost effectiveness are advantages of HC-SCR over other technologies. Successful reducing agents include heavier paraffins and certain light alcohols have been reported.

Results from the experimental investigation of the reduction of NO_X emission from diesel engine exhaust gas have been discussed and presented in this thesis. The blends of biodiesel components (methyl esters) with ultra-low sulphur diesel ULSD were used to carry out the experiments. Promoting effect of hydrogen on HC-SCR is also investigated.

6.1.1 Selective catalytic reduction of NO_X by biodiesel components with different chain length blended with ULSD

A silver supported (Ag/Al_2O_3) hydrocarbon selective catalytic reduction catalyst was prepared and examined for the reduction of NO_x emission. Four selected biodiesel components blends with different chain length were injected into the exhaust gas of diesel engine upstream of the HC-SCR.

It was found that high chain length methyl ester activity window is towards lower temperatures while the lighter methyl ester (methyl laurate) peak activity has been identified at high temperature 440 °C. The highest performance also was seen from the methyl laurate (C12:0) which was 40%. methyl stearic (C14:0) and methyl myristic (C16:0) had similar NO_X reduction activity which peak at 400 °C around 35%.

6.1.2 Promoting effect of hydrogen addition on HC-SCR

Selective catalytic reduction of NO_X by hydrocarbons (HC-SCR) in the presence of excess oxygen seems to be a practical method to reduce NO_X emission from lean burn diesel exhaust.

Hydrogen significantly improved all reductants activities on NO_X emission conversion. H_2 widens the active operating temperature window over the catalyst by remarkably improving the low temperature catalyst activity.

6.2 Future work

- The concentration of hydrocarbon injected into to the exhaust gas stream influences the activity of Ag/Al_2O_3 catalyst for the reduction of NO_X. Higher amount of hydrocarbon generally required at higher temperature to compensate the HCs oxidised while at lower temperature the HC concentration should be less to prevent the catalyst deactivation resulting from carbon species deposition. Research on different $HC:NO_X$ ratio to find out the optimal ratio of hydrocarbons to be injected in HC-SCR.

- Further research into the $H_2:NO_X$ ratio injected into the exhaust gas on the selective reduction of methyl esters. This will avoid unnecessary consumption of hydrogen. Finally, the optimum combination of $HC:NO_X$ and $H_2:NO_X$ ratios, simultaneously.

- Choose one or two methyl ester and investigate the NO_X reduction activity of their blends with other oxygenated hydrocarbons such as light alcohols (e.g. ethanol and butanol) or HCs with high activity of NOX emission conversion at low temperature such as long chain paraffins (e.g. n-decane and n-dodecane). Blending heavy methyl esters tested in this research with alcohols which have high NO_X reduction at low temperature could improve the activity of silver-alumina (Ag/Al2O3) over total range of temperatures typical for the diesel engine exhaust gas.

References

Abu-Jrai, A., Tsolakis, A., Theinnoi, K., Cracknell, R., Megaritis, A., Wyszynski, M. L. & Golunski, S. E. 2006, Effect of Gas-to-Liquid Diesel Fuels on Combustion Characteristics, Engine Emissions, and Exhaust Gas Fuel Reforming. Comparative Study, *Energy & Fuels,* 20: 2377-2384.

Angelidis, T.N., Christoforou, S., Bongiovanni, A. & Kruse, N., 2002, On the promotion by SO_2 of the SCR process over Ag/Al_2O_3: influence of SO_2 concentration with C_3H_6 versus C_3H_8 as reductant, *Applied Catalysis B* 39 (3): 197–204.

Arve, K., Eränen, K., Snåre, M., Klingstedt, F. & Murzin, D.Y., 2007, Selective catalyst reduction of NOX over Ag/Al2O3 using various biodiesels as reducing agents, *Topics in Catalysis Vols* 42-43.

Arve, K., Carucci, J.R.H., Eränen, K., Aho, A. & Murzin, D.Y., 2009, Kinetic behaviour of HC-SCR over Ag/alumina catalyst using a model paraffinic second generation biodiesel compound, *Applied Catalysis B* 90 (3): 603–612.

Baumgarten, C. 2006, Mixture formation in internal combustion engines, Springer.

Breen, J.P. & Burch, R. 2006, A review of the effect of the addition of hydrogen in the selective catalytic reduction of NOx with hydrocarbons on silver catalysts, *Topics in Catalysis* 39: 53-58.

Brogan, M. S., Clark, A. D. & Brisley, R. J. 1998, Recent Progress in NO_X Trap Technology, *SAE Technical Paper* 980933.

Burch, R., Breen, J.P. & Meunier, F.C. 2002, A review of the selective reduction of NO_X with hydrocarbons under lean-burn conditions with non-zeolitic oxide and platinum group metal catalysts, *Applied Catalysis B: Environmental* 39: 283-303.

Cant, N.W. & Liu, I.O.Y., 2000, The mechanism of the selective reduction of nitrogen oxides by hydrocarbons on zeolite catalysts, *Catalysis Today* 63 (2–4): 133–146.

Chatterjee, S., Walker, A.P. & Blakeman, P.G. 2008, Emission control options to achieve Euro IV and Euro V on heavy duty diesel engines, *SAE Paper* No. 2008-28-0021.

Chi, J. N. 2009, Control challenges for optimal NO_X conversion efficiency from SCR after-treatment systems, *SAE Paper* No. 2009-01-0905

Chuepeng, S., Tsolakis, A., Theinnoi, K., Xu, H.M., Wyszynski, M.L. & Qiao J. 2007, A study quantitive impact on emissions of high proportion RME-based biodiesel blends, *SAE International Paper* No. 2007-01-0072.

Dong, H., Shuai, S., Li, R., Wang, J., Shi, X. & He, H. 2008, Study of NO_X selective catalytic reduction by ethanol over Ag/Al_2O_3 catalyst on a HD diesel engine, *Chemical Engineering Journal* 135 (3): 195–201.

Epling, W. S., Campbell, L. E., Yezerets, A., Currier, N. W. & Parks, J. E. 2004, Overview of the Fundamental Reactions and Degradation Mechanisms of NO_X Storage/Reduction Catalysts, *Catalysis Reviews,* 46: 163-245.

Eranen, K., Lindfors, L.E., Klingstedt, F. & Murzin D.Y. 2003, Continuous reduction of NO with octane over a silver/alumina catalyst in oxygen-rich exhaust gases: combined heterogeneous and surface-mediated homogeneous reactions, *Journal of Catalysis* 219 (1): 25-40.

Graboski, M.S. & McCormick. R.L. 1998, Combustion of fat and vegetable oil derived fuels in diesel engines, *Progress in Energy and Combustion Science* 24: 125-165.

He, H., Xiuli, Z., Qiang, W., Changbin, Z. & Yul, Y. 2008, Review of Ag/Al2O3-reductant system in the selective catalytic reduction of NO_X, *Catalysis Surveys from Asia* 12 (1): 38–55.

Herreros, J.M., George, P., Umar, M. & Tsolakis, A. 2014, Enhancing selective reduction of NOx with alternative reactants/promoters, *Chemical Engineering* 252: 47-54.

Heywood, J.B. 1988, *Internal Combustion Engine Fundamentals*, McGraw-Hill, ISBN 0-07-100499-8.

Houel, V., Millington, P., Rajaram, R. & Tsolakis, A. 2007a, Fuel effects on the activity of silver hydrocarbon-SCR catalysts, *Applied Catalysis B: Environmental* 73: 203-207.

Houel, V., Millington, P., Rajaram, R. & Tsolakis, A. 2007b, Promoting functions of H_2 in diesel-SCR over silver catalysts, *Applied Catalysis B: Environmental* 77: 29-34.

Iliopoulou, E.F., Evdou, A.P., Lemonidou, A.A. & Vasalos, I.A. 2004, Ag/alumina catalysts for the selective catalytic reduction of NO_X using various reductants, *Applied Catalysis A* General 274: 179–189.

Johnson, W.L., Fisher, G.B. & Toops, T.J., 2012, Mechanistic investigation of ethanol SCR of NO_X over Ag/Al_2O_3, *Catalysis Today* 184 (1): 166–177.

Spivey, J.J., Kim, M.H. & Nam, I.-S. 2005, New opportunity for HC-SCR technology to control NOx emission from advanced internal combustion engines, *Catalysis: Volume 18,* The Royal Society of Chemistry.

Kitano, K., Sakata, I. & Clark, R. 2005, Effects of GTL Fuel Properties on DI Diesel Combustion, *SAE Technical Paper* No. 2005-01-3763.

Koebel, M., Elsener, M. & Kleemann, M. 2000, Urea-SCR: a promising technique to reduce NO_X emissions from automotive diesel engines, *Catalysis Today* 59: 335-345.

Komatsu, T., Tomokuni, K. & Yamada, I. 2006, Outstanding low temperature HC-SCR of NO_X over platinum-group catalysts supported on mesoporous materials expecting diesel-auto emission regulation, *Catalysis Today* 116 (2): 244–249.

Lapuerta, M., Herreros, J.M., Lyons, L.L., Garcia-Contreras, R. & Briceno, Y. 2008, Effect of the alcohol type used in the production of waste cooking oil biodiesel on diesel performance and emissions, *Fuel* 87: 3161-3169.

Lapuerta, M., Rodriguez-Fernandez, J., Oliva, F. & Canoria, L. 2009, Biodiesel from low-grade animal fats: diesel engine performance and emissions, *Energy & Fuel* 23: 121-129.

Levendis, Y., Pavlatos, I. & Abrams, R. 1994, Control of Diesel Soot, Hydrocarbon and NO_X Emissions with a Particulate Trap and EGR, *SAE Technical Paper* 940460.

Majewski, W.A. & Khair, M. K. 2006, *Diesel emissions and their control*, SAE International, ISBN: 978-0-7680-0674-2.

Majewski, W.A. Revised 2007, *Diesel Oxidation Catalyst,* [Online]. DieselNet, Available at: <https://www.dieselnet.com/tech/cat_nox-trap.php#int> [Accessed 16 August 2014].

Mcgeehan, J. A., Yeh, S., Couch, M., Hinz, A., Otterholm, B., Walker, A. P. & Blakeman, P. G. 2005, On the road to 2010 emissions: Field test results and analysis with DPF-SCR system and ultra low sulfur diesel fuel, *SAE International Paper* 2005-01-3716.

Monyem, A. & Van Gerpen, J.H. 2001, The effect of biodiesel oxidation on engine performance and emissions, *Biomass and Bioenergy* 20: 317-325.

Parvulescu, V., Grange, P. & Delmon, B., 1998, Catalytic removal of NO, *Catalysis Today* 46 (4): 233–316.

Pinzi, S., Rounce, P., Herreros, J.M., Tsolakis, A. & Dorado, M.P. 2013, The effect of biodiesel fatty acid composition on combustion and diesel engine exhaust emissions, *Fuel* 104: 170-182.

Richter, M., Bentrup, U., Eckelt, R., Schneider, M., Pohl, M. M. & Fricke, R. 2004, The effect of hydrogen on the selective catalytic reduction of NO in excess oxygen over Ag/Al_2O_3, *Applied Catalysis B: Environmental*, 51: 261-274.

Sazama, P., Čapek, L., Drobná, H., Sobalík, Z., Dědeček, J., Arve, K. & Wichterlová, B. 2005, Enhancement of decane-SCR-NOx over Ag/alumina by hydrogen. Reaction kinetics and in situ FTIR and UV-vis study, *Journal of Catalysis*, 232, 302-317.

Schmieg, S. J., Blint, R. J. & Deng, L. 2008, Control Strategy for the Removal of NOx from Diesel Engine Exhaust using Hydrocarbon Selective Catalytic Reduction. *SAE Int. J. Fuels Lubr.* 1(1):1540-1552.

Schuchardt, U., Sercheli, R. & Vagas, R.M. 1998, Transesterification of vegetable oils: A review. *Journal of the Brazilian Chemical Society* 9, No. 1: 199-210.

Shibata, J., Shimizu, K., Satsuma, A. & Hattori, T. 2002, Infl

uence of hydrocarbon structure on selective catalytic reduction of NO by hydrocarbons over Cu-Al_2O_3, *Applied Catalysis B: Environmental,* 37: 197-204.

Shimizu, K., Tsuzuki, M. & Satsuma A. 2007a, Effects of Hydrogen and Oxygenated Hydrocarbons on the Activity and SO_2-tolerance of Ag/Al_2O_3 for Selective Reduction of NO. *Applied of Catalysis B: Environmental,* 71: 80–84.

Shimizu, K., & Satsuma, A. 2007b, Reaction Mechanism of H_2-Promoted Selective Catalytic Reduction of NO with NH_3 over Ag/Al_2O_3, *Journal of Physical Chemistry C,* 111: 2259-2264.

Shimizu, K., Tsuzuki, M., Kato, K., Yokota, S., Okumura, K. & Satsuma, A. 2007c, Reductive activation of O_2 with H_2-reduced silver clusters as a key step in the H_2-promoted selective catalytic reduction of NO with C_3H_8 over Ag/Al_2O_3, *The Journal of Physical Chemistry C* 111, 950-959.

Sitshebo, S., Tsolakis, A. & Theinnoi, K. 2009, Promoting hydrocarbon-SCR of NOx in diesel engine exhaust by hydrogen and fuel reforming, *International Journal of Hydrogen Energy* 34 (18) 7842–7850.

Szybist, J.P., Kirby, S.R. & Boehman, A.L. 2005, NO*x* emissions of alternative diesel fuels: A comparative analysis of biodiesel and FT diesel, *Energy & Fuels* 19: 1484-1492.

Theinnoi, K., York, A.P.E., Tsolakis, A., Chuepeng, S., Cracknell, R.F. & Clark, R.H. 2009, Engine performance and emissions from the combustion of lowtemperature Fischer-Tropsch synthetic diesel fuel and biodiesel (RME) blends, *International Journal of Vehicle Design* 50: 196-212.

Thomas, J.F., Lewis, S.A., Bunting, B.G., Storey, J.M., Graves R.L. & Park P.W. 2005, Hydrocarbon selective catalytic reduction using a silver-alumina catalyst with light alcohols and other reductants, *SAE Paper No.* 2005-01-1082.

Tsolakis, A., Megritis, A., Wyszynski, M.L. & Theinnoi, K. 2007, Engine performance and emissions of a diesel engine operating on diesel-RME (rapeseed methyl ester) blends with EGR (exhaust gas recirculation), *Energy* 32: 2072-2080.

Turns, S.R. 2000, An *Introduction to Combustion: Concepts and Applications*, McGraw-Hill Education.

Twigg, M.V. 2007, Progress and future challenges in controlling automotive exhaust gas emissions. *Applied Catalysis B: Environmental* 70: 2-15.

York, A.P.E., Tsolakis, A., Buschow, K. H. J., Robert, W. C., Merton, C. F., Bernard, I., Edward, J. K., Subhash, M. & Patrick, V. 2010, Cleaner Vehicle Emissions, *Encyclopedia of Materials: Science and Technology.* Oxford: Elsevier.

Zhou, W. & Boocock, D.G.B. 2006, Phase behavior of the base-catalyzed transesterification of soybean oil, *Journal of the American Oil Chemists' Society* 83 No. 12: 1041-1045.

Appendix: Fuel penalty calculation

$$Fuel\ Energy\ Input_{engine} = Mass\ flowrate\ of\ fuel\ engine \times Lower\ Heating\ Value$$

$$\begin{aligned} &Reductant\ Energy\ Input_{HC-SCR} \\ &\qquad = Mass\ flowrate\ of\ reductant \times Lower\ Heating\ Value \end{aligned}$$

$$Fuel\ Penalty = \frac{Reductant\ Energy\ Input_{HC-SCR}}{Fuel\ Energy\ Input_{engine}} \times 100$$