

**Passive Ammonia-SCR Catalyst System for NO_x
Abatement from Lean-Burn Gasoline Engines:
NH₃ formation over TWC**

A Dissertation Presented for the
Doctor of Philosophy
Degree
The University of Tennessee, Knoxville

Vitaly Y. Prikhodko
August 2018

DEDICATION

I dedicate this work to my family who have supported me in pursuing my educational and career goals throughout the years, especially my wife, two children, and my parents.

ACKNOWLEDGMENTS

I would like to express my deep gratitude to Prof. Ke Nguyen, Dr. Stuart Daw and Dr. Jim Parks for their support, advise, guidance and time during my PhD studies. I would like to thank Prof. Jay Frankel and Prof. Joshua Fu for serving on my dissertation committee. Special thanks to Dr. Todd Topps and Josh Pihl for their friendship and sharing their expertise in the area of catalysis. I would also like to thank the entire Fuels, Engines and Emissions Research group at Oak Ridge National Laboratory (ORNL) for their assistance in my research; especially, Steve Whitted, Scott Curran, Zhiming Gao, Will Brookshear and Calvin Thomas. I would like to thank General Motors for technical guidance and Umicore for providing the catalyst samples used in this project.

I would like to express my appreciation to the U.S. Department of Energy for the financial support of this research and ORNL for supporting my graduate studies while being a full-time employee at ORNL.

ABSTRACT

This dissertation summarizes experimental and computational observations from investigations of a selective catalytic reduction (SCR) system for reducing nitrogen oxides (NO_x) in lean gasoline engine exhaust based on utilizing ammonia (NH_3) generated by a three-way catalyst (TWC) during brief periods of fuel-rich engine operation. NH_3 released from the TWC is stored and available to reduce NO_x on a downstream SCR catalyst during subsequent periods of lean engine operation. The experimental results include high-speed measurements of transient NH_3 formation on the TWC monolith catalysts, as the catalysts were exposed to lean gasoline engine exhaust from a commercial engine. In addition to the experimental investigations, dynamic computational simulations of NH_3 generation on the TWC catalyst were implemented to provide more detailed information about NH_3 generation on TWCs based on available reaction kinetic mechanisms. Based on the experimental and computational results, estimates of the potential fuel efficiency gains and emissions relevant to simulated drive cycles indicate that passive SCR can potentially achieve significant fuel efficiency benefits while still meeting regulated NO_x emissions limits for vehicles powered by lean gasoline engines. However, optimal performance of the system will most likely require development of emission control methods that include accurate models for SCR catalyst NH_3 storage and reaction under realistic drive-cycle transients.

TABLE OF CONTENTS

CHAPTER 1	INTRODUCTION AND BACKGROUND	1
1.1	GASOLINE ENGINES	3
1.2	EMISSIONS REGULATIONS	5
1.3	STOICHIOMETRIC GASOLINE EMISSIONS CONTROL	7
1.4	NO _x EMISSIONS CONTROL IN LEAN EXHAUST	7
1.4.1	<i>Lean NO_x trap</i>	8
1.4.2	<i>Urea selective catalytic reduction</i>	9
1.4.3	<i>Passive ammonia SCR</i>	10
1.5	RECENT STUDIES OF LEAN GDI VEHICLE	12
1.6	SCOPE OF THE PRESENT INVESTIGATION	15
CHAPTER 2	LITERATURE REVIEW.....	16
2.1	PATHWAYS OF NH ₃ FORMATION.....	17
2.2	IMPACT OF CATALYST FORMULATION ON NH ₃ FORMATION	18
CHAPTER 3	MATERIALS AND METHODS.....	21
3.1	LEAN GASOLINE ENGINE RESEARCH PLATFORM.....	21
3.1.1	<i>Engine Platform</i>	21
3.1.2	<i>Engine Controller</i>	26
3.1.3	<i>Gaseous emissions sampling</i>	28
3.2	CATALYSTS	29
3.3	EXPERIMENTAL CONDITIONS FOR THE ENGINE STUDY	30
3.4	COMPUTATIONAL STUDIES OF TWC NH ₃ PRODUCTION.....	32
3.4.1	<i>Gas phase mass balance</i>	34
3.4.2	<i>Solid phase mass balance</i>	36
3.4.3	<i>Gas and solid phase energy balances</i>	38
CHAPTER 4	RESULTS AND DISCUSSION.....	41
4.1	EXPERIMENTAL STUDY OF ENGINE FUELING IMPACT ON TWC NH ₃ GENERATION	41
4.2	COMPUTATIONAL STUDY OF TWC NH ₃ FORMATION MECHANISMS	47
4.3	EXPERIMENTAL STUDY OF A MODIFIED TWC FORMULATION ON NH ₃ GENERATION	60
4.4	IMPACT OF ADDITIONAL ENGINE ADJUSTMENTS TO INCREASE ENGINE-OUT NO _x	74
4.5	NH ₃ PRODUCTION DURING ENGINE ACCELERATION TRANSIENTS	84
CHAPTER 5	CONCLUSIONS AND RECOMMENDATIONS.....	89
	LIST OF REFERENCES	92
	APPENDIX	102
	VITA	122

LIST OF TABLES

Table 1.1 Tier 3 certification emissions standards for light-duty vehicles.	6
Table 3.1 BMW 2.0-liter lean gasoline direct injection engine specifications.....	23
Table 3.2 EEE-lube certification gasoline fuel properties.	23
Table 3.3 TWC properties.	30
Table 4.1 Pd-only TWC kinetic parameters and reaction rate expressions [95].	52
Table 4.2 Bench flow reactor TWC inlet conditions during rich/lean cycling experiments.....	53
Table 4.3 Average TWC inlet conditions during rich/lean cycling experiments performed on engine.	56
Table 4.4 Steady-state operating points for λ sweep experiments with TWC-NSC.....	62
Table 4.5 Steady-state operating points for λ sweep experiments with Pd-only TWC.	62
Table 4.6 Steady-state operating points for EGR, valve timing and spark timing sweep experiments with TWC-NSC.	75
Table 4.7 Steady-state operating points for valve timing and spark timing sweep experiments with TWC-NSC.....	80
Table 4.8 Average experimental conditions for load step and fixed load rich/lean cycling experiments with Pd-only TWC.	85

LIST OF FIGURES

Figure 1.1 Total U.S. petroleum consumption by economic sector [1].....	1
Figure 1.2 Total U.S. carbon emissions from fossil fuel consumption by economic sector [1].....	2
Figure 1.3 Emissions of gaseous criterial pollutants by economic sector in 2016 [1].	5
Figure 1.4 NO _x emissions of a European MY2008 BMW 1-series 120i lean gasoline vehicle equipped with a LNT over the US drive cycles [3, 59].....	11
Figure 1.5 Passive ammonia SCR approach to control NO _x emission from lean gasoline engines.	13
Figure 1.6 Fuel economy improvement of a European MY2008 BMW 1-series 120i lean gasoline vehicle operating in lean relative to stoichiometric only operation over US drive cycles [3, 59].....	14
Figure 3.1 BMW 120i lean gasoline vehicle on chassis dynamometer at ORNL.....	22
Figure 3.2 BMW N43B20 lean gasoline engine installed on the dynamometer test stand at ORNL.....	22
Figure 3.3 Cut-out of BMW N43B20 lean gasoline engine showing piezoelectric injector at the top center of the combustion chamber with spark plug in close proximity to the injector (http://www.bmwheaven.com).	24
Figure 3.4 Air-fuel equivalence ratio, λ , as a function of engine speed and load. Also shown three main combustion modes employed by the engine: lean stratified, lean homogeneous with additional stratification and homogeneous stoichiometric.	25
Figure 3.5 BMW engine injection and spark events for three main combustion modes: lean stratified, lean homogeneous and stoichiometric homogeneous.	27
Figure 3.6 TWC installed in the exhaust of the BMW lean gasoline engine at ORNL.	31
Figure 3.7 Schematic of the BMW lean gasoline engine and exhaust system at ORNL.	32

Figure 4.1 Steady-state variation of the experimental engine-out exhaust gas composition with λ . Engine operating conditions: 2000 rpm and 8 bar BMEP.	42
Figure 4.2 Steady-state variation of exhaust gas composition with λ at TWC outlet. Engine operating conditions: 2000 rpm and 8 bar BMEP; Pd-only Malibu-1 TWC; TWC at 731 °C inlet temperature and 64000 h ⁻¹ space velocity.	43
Figure 4.3 Steady-state concentrations of TWC inlet NO _x and outlet NH ₃ as a function of λ . Engine operating conditions: 2000 rpm and 8 bar BMEP; Pd-only Malibu-1 TWC; TWC at 731 °C inlet temperature and 64000 h ⁻¹ space velocity.	45
Figure 4.4 Steady-state TWC NO _x conversion and NH ₃ yield as a function of λ . Engine operating conditions: 2000 rpm and 8 bar BMEP; Pd-only Malibu-1 TWC; TWC at 731 °C inlet temperature and 64000 h ⁻¹ space velocity.	45
Figure 4.5 Fuel consumption penalty relative to stoichiometric operation as a function of λ . Engine operating conditions: 2000 rpm and 8 bar BMEP; Pd-only Malibu-1 TWC; TWC at 731 °C inlet temperature and 64000 h ⁻¹ space velocity.	47
Figure 4.6 Variation of experimental H _{2,eq} to NO _x ratio with λ at TWC inlet during steady state engine operation. Engine operating conditions: 2000 rpm and 8 bar BMEP.	50
Figure 4.7 Experimental (solid lines) and simulated (dashed lines) emissions at TWC inlet and outlet as a function of time during lean/rich cycling experiments with rich $\lambda=0.96$ on bench flow reactor.	55
Figure 4.8 Experimental (solid lines) and simulated (dashed lines) of NH ₃ yield at different λ s as a function of furnace temperature during rich phase of rich/lean cycling experiments on bench flow reactor.	57
Figure 4.9 Experimental (solid lines) and simulated (dashed lines) of C ₃ H ₈ conversion at different λ s as a function of furnace temperature during rich phase of rich/lean cycling experiments on bench flow reactor.	57
Figure 4.10 Experimental (solid lines) and simulated (dashed lines) of CO conversion at different λ s as a function of furnace temperature during rich phase of rich/lean cycling experiments on bench flow reactor.	58

Figure 4.11 Experimental (solid lines) and simulated (dashed lines) emissions at TWC inlet and outlet as a function of time during lean/rich cycling experiments with rich $\lambda=0.97$ on engine.....	59
Figure 4.12 Steady-state NH_3 yield at different λ values at 2000 rpm engine speed and 3, 5, and 8 bar BMEP engine loads; TWC-NSC.	63
Figure 4.13 Steady-state NH_3 yield at different λ values at 2000 rpm engine speed and 2, 4, and 8 bar BMEP engine loads; Pd-only TWC.....	63
Figure 4.14 λ and emissions at TWC inlet and outlet as a function of time during fixed load lean/rich cycling experiments at 2000 rpm 3 bar BMEP. Lean conditions: 2000 rpm 3 bar BMEP, $\lambda=1.7$, ave. $T_{\text{in}} = 393\text{ }^\circ\text{C}$, $\text{SV}=45000\text{ h}^{-1}$. Rich conditions: 2000 rpm 3 bar BMEP, $\lambda=0.96$, ave. $T_{\text{in}}=412\text{ }^\circ\text{C}$, $\text{SV}=29000\text{ h}^{-1}$. TWC-NSC.	66
Figure 4.15 λ and emissions at TWC inlet and outlet as a function of time during fixed load lean/rich cycling experiments at 2000 rpm 2 bar BMEP. Lean conditions: 2000 rpm 2 bar BMEP, $\lambda=2.0$, ave. $T_{\text{in}} = 459\text{ }^\circ\text{C}$, $\text{SV}=42000\text{ h}^{-1}$. Rich conditions: 2000 rpm 2 bar BMEP, $\lambda=0.96$, ave. $T_{\text{in}}=463\text{ }^\circ\text{C}$, $\text{SV}=28000\text{ h}^{-1}$. Pd-only TWC.....	67
Figure 4.16 NO_x and NH_3 emissions at TWC-NSC inlet and outlet as a function of time during fixed load lean/rich cycling experiments on (a) engine and (b) bench flow reactor.	68
Figure 4.17 λ trace during the transition from lean to rich during fixed load lean/rich cycling experiments at 2000 rpm 3 bar BMEP. Transitioning from lean $\lambda=1.7$ to rich $\lambda=0.96$	69
Figure 4.18 Engine out NO_x concentration entering (“rich NO_x in”) the TWC-NSC and corresponding existing NH_3 concentration (“rich NH_3 out”) during rich phase of fixed load lean/rich cycling experiments at 2000 rpm 3 bar BMEP.	71
Figure 4.19 Engine out NO_x concentration entering (“rich NO_x in”) the Pd-only TWC and corresponding existing NH_3 concentration (“rich NH_3 out”) during rich phase of fixed load lean/rich cycling experiments at 2000 rpm 2 bar BMEP.	71
Figure 4.20 Stored NO_x to NH_3 conversion during rich phase of fixed load lean/rich cycling experiments at 2000 rpm 3 bar BMEP over the TWC-NSC, lean average $T_{\text{in}} = 393\text{ }^\circ\text{C}$ and rich average $T_{\text{in}} = 412\text{ }^\circ\text{C}$	72

Figure 4.21 Engine out NO_x concentration entering (“rich NO_x in”) the TWC-NSC and corresponding existing NH_3 concentration (“rich NH_3 out”) during rich phase of fixed load lean/rich cycling experiments at 2000 rpm 5 bar BMEP, lean average $T_{\text{in}} = 494\text{ }^\circ\text{C}$ and rich average $T_{\text{in}} = 510\text{ }^\circ\text{C}$	73
Figure 4.22 Steady-state variation of the experimental engine out NO_x emissions with external EGR. Engine operating conditions: 2000 rpm and 5 bar BMEP, $\lambda=1$	77
Figure 4.23 Steady-state variation of the fuel consumption with external EGR. Engine operating conditions: 2000 rpm and 5 bar BMEP, $\lambda=1$	77
Figure 4.24 Steady-state variation of the experimental engine out NO_x emissions with internal EGR via variable valve timing. Engine operating conditions: 2000 rpm and 5 bar BMEP, $\lambda=1$	78
Figure 4.25 Steady-state variation of the fuel consumption with internal EGR via variable valve timing. Engine operating conditions: 2000 rpm and 5 bar BMEP, $\lambda=1$	78
Figure 4.26 Steady-state variation of the experimental engine out NO_x emissions with spark timing. Engine operating conditions: 2000 rpm and 5 bar BMEP, $\lambda=1$	79
Figure 4.27 Steady-state variation of the fuel consumption with spark timing. Engine operating conditions: 2000 rpm and 5 bar BMEP, $\lambda=1$	79
Figure 4.28 Steady-state concentrations of TWC inlet NO_x and outlet NH_3 as a function of λ for OEM valve timing (solid) and custom valve timing (open). Engine operating conditions: 2000 rpm and 5 bar BMEP; TWC-NSC; TWC at $514\text{ }^\circ\text{C}$ inlet temperature and 50000 h^{-1} space velocity.	81
Figure 4.29 Steady-state concentrations of TWC inlet NO_x and outlet NH_3 as a function of λ for OEM spark timing (solid) and custom spark timing (open). Engine operating conditions: 2000 rpm and 5 bar BMEP; TWC-NSC; TWC at $514\text{ }^\circ\text{C}$ inlet temperature and 50000 h^{-1} space velocity.	82
Figure 4.30 Steady-state NH_3 generation as a function of λ for OEM, custom spark and valve timings. Engine operating conditions: 2000 rpm and 5 bar BMEP; TWC-NSC; TWC at $514\text{ }^\circ\text{C}$ inlet temperature and 50000 h^{-1} space velocity.	82
Figure 4.31 Steady-state cumulative experimental engine out NO_x emissions resulting from adjusting valve and spark timing at 2000 rpm and 3, 5 and 8 bar BMEP.	83

Figure 4.32 NO _x and NH ₃ emissions at Pd-only TWC inlet and outlet as a function of time during (a) load step and (b) fixed load rich/lean cycling experiments with rich $\lambda=0.96$	86
Figure 4.33 Rich time duration as a function of rich λ during load step and fixed load rich/lean cycling experiments.....	86
Figure 4.34 Fuel consumption benefit as a function of rich λ during load step and fixed load rich/lean cycling experiments.....	88

CHAPTER 1

INTRODUCTION AND BACKGROUND

Transportation is the largest sector of petroleum consumption in the United States, accounting for 69.0% of total petroleum use and contributing to 34.7 % of total greenhouse gas emissions in the U.S as shown in Figure 1.1 and Figure 1.2, respectively. The light-duty vehicle fleet is the largest consumer of petroleum in the transportation sector, accounting for 63.1 % of the transportation petroleum use. This sector is largely dominated by gasoline vehicles, 99.5 % of light-duty vehicles are powered by gasoline engines [1]. Gasoline engines, therefore, represent the largest opportunity for reducing petroleum consumption and greenhouse gas emissions in the U.S.

Implementing fuel-efficient technologies for gasoline vehicles can significantly reduce U.S. petroleum consumption and greenhouse gas emissions. Fuel economy of a gasoline engine can be improved by as much as 10-20 % by operating the engine in lean combustion mode [2, 3]. Reduction of NO_x

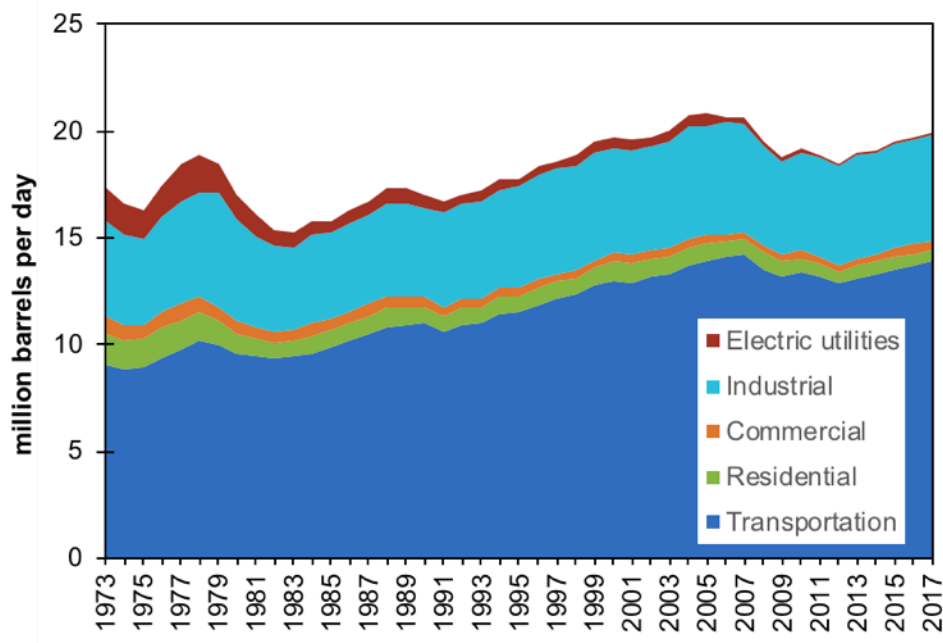


Figure 1.1 Total U.S. petroleum consumption by economic sector [1].

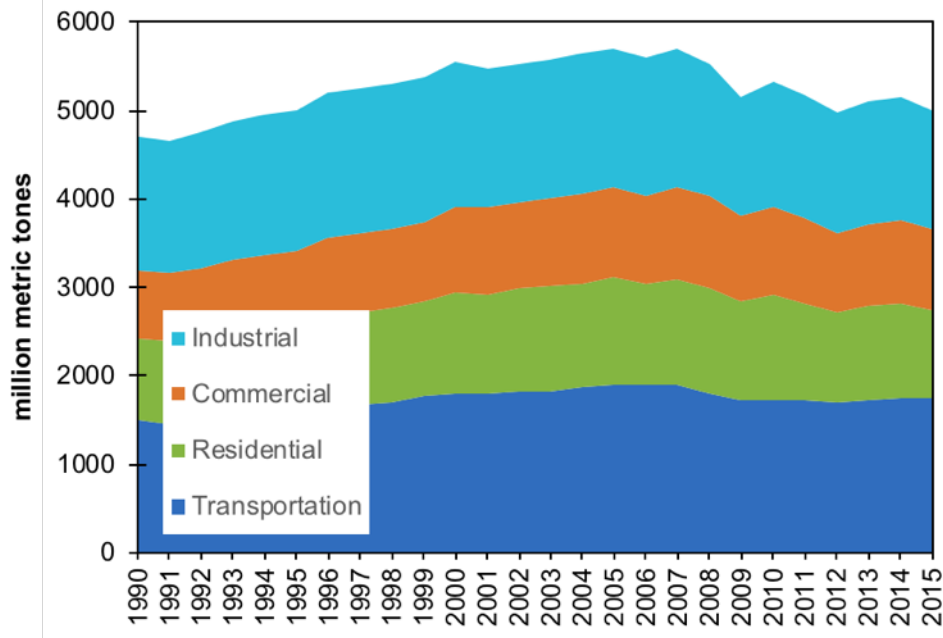


Figure 1.2 Total U.S. carbon emissions from fossil fuel consumption by economic sector [1].

emissions in fuel-lean (oxygen-rich) exhaust, however, is challenging with currently available technology. The most widely used post-engine emissions control device for gasoline vehicles is the three-way catalyst (TWC). While the TWC is highly effective for stoichiometric engine exhaust (that is, where there is just enough oxygen to completely consume the fuel), it is ineffective in reducing NO_x in the oxygen-rich exhaust of lean-burn gasoline engines. One of the newly proposed technical approaches for adapting TWCs to lean-burn engines is the so-called ‘passive’ SCR system. This consists of a close-coupled TWC combined with an under-floor SCR catalyst that utilizes ammonia (NH_3) generated by the TWC to reduce residual NO_x in the exhaust [4]. Ammonia is generated over the TWC during transient fuel-rich combustion events and subsequently stored on the SCR catalyst. When the engine returns to lean combustion, NO_x passes through the TWC and is reduced by the stored NH_3 on the SCR catalyst. This approach is particularly attractive for lean gasoline engine applications because it makes use of existing TWCs and can potentially control

lean NO_x at a lower cost compared to other available lean NO_x control technologies. The challenge is, however, to be able to control the transient fueling events needed to generate NH₃ in sufficient quantities to meet NO_x reduction requirements without consuming excessive amounts of fuel. Thus, it is necessary to evaluate the performance of both the engine and catalyst systems as a combined system rather than as individual components. Research reported here is aimed at investigating the key features of TWCs and their interaction with a lean gasoline engine to assist in making better assessments of the passive SCR technology as a potential fuel-efficient solution for controlling NO_x emissions from lean-burn gasoline engines. It is expected that the experimental and computational observations from this work will help resolve key technical questions involved in such assessments.

1.1 Gasoline engines

Gasoline spark-ignited internal combustion engines are generally classified both according to the relative amounts of air and fuel used for combustion (quantified by the air-to-fuel ratio or AFR), and how the air and fuel are introduced into the combustion chamber. In stoichiometric combustion, the amount of air introduced is exactly what is needed to completely consume the fuel and convert it to H₂O and CO₂ in the exhaust (for typical gasoline fuel, the stoichiometric AFR is about 14.7 g air/g fuel). For fuel-rich combustion (AFR<14.7), there is excess fuel relative to the air, and the exhaust contains unburned and partially burned hydrocarbons. In fuel-lean combustion (AFR>14.7), there is excess oxygen present and residual oxygen remains in the exhaust.

The air and fuel used for combustion can be mixed either inside or outside the combustion chamber. In external mixing, the fuel and the air are mixed outside the combustion chamber to create a relatively homogenous charge that enters the combustion chamber. One widely used approach for implementing this is port fuel injection (PFI). In PFI engines, fuel is injected at the intake port of

each cylinder, where it is vaporized by contacting with the hot intake valve and intake port walls. The fuel vapor then mixes with air before it enters each cylinder.

In direct injection (DI) engines, fuel is directly injected into the combustion chamber. Gasoline engines with internal air/fuel mixture formation are commonly referred to as gasoline direct injection (GDI) engines. The timing of the injection in the internal air/fuel mixture design determines the homogeneity of the mixture at the time the combustion is initiated. The closer the fuel introduction is to the start of the combustion, the more heterogeneous the mixture will be due to less time available for the fuel and the air to mix. In lean DI engines, a ring of ignitable mixture is created in the area of the spark plug, whereas the rest of the combustion chamber is filled with a very lean, non-ignitable mixture, thus creating charge stratification. Charge stratification can be desirable because it permits leaner engine operation (higher AFR) by allowing ignition and combustion to occur well below the lean flammability limit (that is, the maximum AFR at which ignition and combustion reliably occur with a homogeneous charge) [2, 5-9].

Lean DI combustion can lead to increased engine efficiency for three major reasons: 1) in DI, the fuel is vaporized by absorbing thermal energy from the air resulting in a lower mixture temperature, thus increasing the volumetric efficiency and power output [10-13], and allowing for higher compression ratios without producing knock [11, 14, 15]; 2) in lean combustion, the air flows unthrottled, thus minimizing the work done to pump the charge air into each cylinder and 3) the lower combustion temperature caused by air dilution reduces heat losses to the cylinder walls, leaving more energy in the expanding gases to do work [2]. Considering the above benefits, vehicles equipped with fuel-lean GDI engines are receiving increased scrutiny as a technology for increasing fuel economy [16-18].

1.2 Emissions regulations

Emissions regulations are a major constraint for all types of engines, because motor vehicles are currently one of the largest sources of air pollution. Four main regulated pollutants emitted by the vehicles are hydrocarbons (HC), carbon monoxide (CO), nitrogen oxides (NO_x) and particulate matter (PM). Transportation accounts for the majoring of CO and NO_x emissions as shown in Figure 1.3.

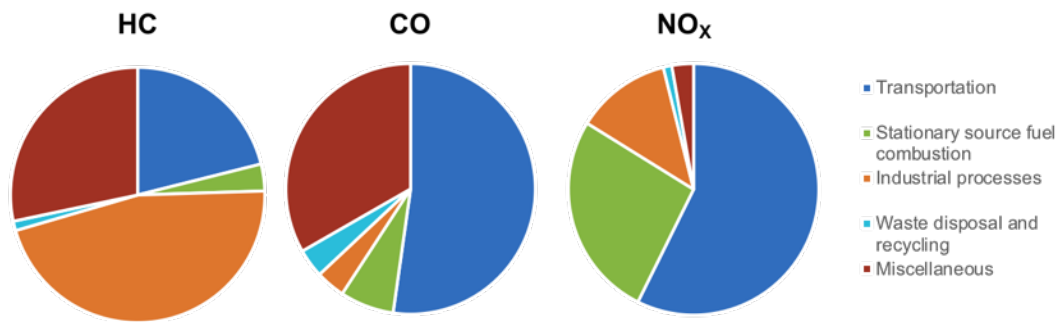


Figure 1.3 Emissions of gaseous critical pollutants by economic sector in 2016 [1].

Hydrocarbons (HCs) and carbon monoxide (CO) emissions are produced by incomplete combustion. HCs react with oxides of nitrogen to form ground level ozone (O₃), which is the primary component of smog, and they can also be inherently toxic. CO is a colorless and odorless poisonous gas that restricts the flow of oxygen to the body's organs. At high levels, CO can be fatal. Nitrogen oxides (primarily NO and NO₂ and referred to collectively as NO_x) are formed via oxidation of nitrogen under high pressure and temperature during combustion. NO_x emissions contribute to formation of ground level ozone, acid rain, and also cause various health problems. Particulate matter (PM) is a mixture of small particles and liquid droplets also formed during combustion. These are known to have adverse effects on human health and the environment. Small size particles

(less than 10 micrometers) are particularly dangerous to human health as they enter the lungs unrestricted causing serious health problems [19].

Recent increases in air pollution and a rising awareness of the harmful health and environmental effects have led to the establishment of the strict vehicle emissions standards by government agencies. In the USA, the Clean Air Act of 1970 set permissible limits for concentration levels of HC, CO and NO_x in vehicles exhaust. The recently approved U.S. Environmental Protection Agency (EPA) Tier 3 emission regulations were adopted in 2014 and phased in from 2017 to 2025. The new emissions standards require more than 80% reduction in NO_x and non-methane organic gases (NMOG), and 70% reduction in particulate matter compared to previous Tier 2 emission standards. Tier 3 emission standards for light-duty vehicles are shown in Table 1.1. The standards are separated into bins, and a manufacturer can certify a vehicle into one of seven standard bins as long as the manufacturer's fleet average is at bin 30 [20].

Table 1.1 Tier 3 certification emissions standards for light-duty vehicles.

Bin	NMOG+NO_x mg/mi	CO g/mi	PM mg/mi
Bin 160	160	4.2	3
Bin 125	125	2.1	3
Bin 70	70	1.7	3
Bin 50	50	1.7	3
Bin 30	30	1.0	3
Bin 20	20	1.0	3
Bin 0	0	0	0

The above emission standards are designed to be implemented within the same time frame as EPA and NHTSA (National Highway Traffic Safety Administration) standards to reduce greenhouse gas emissions (GHG) and

improve fuel economy. As the primary GHG, carbon dioxide (CO_2) is linked directly with fuel consumption. The 2025 Corporate Average Fuel Economy (CAFE) standard enacted by EPA and NHTSA will require an average industry fleet-wide level of 163 grams per mile of CO_2 emissions, which is equivalent to a mileage of 54.5 miles per gallon [16], which is more than 50% higher than the previous regulation. Even though CO_2 is not toxic and does not directly impair human health, small increases in its ambient concentration have effect on the environment by changing the average global temperature. Scientists predict that a rise of 2°C in average earth's temperature would cause severe changes in weather patterns resulting in disturbance of ecosystems and adverse side effects on human life [21].

Thus, passive SCR has the potential to be a major component of efforts to meet both the 2025 CAFE standards for fuel economy and the Tier 3 emission regulations.

1.3 Stoichiometric gasoline emissions control

In response to new emission standards in the 1980s, automakers equipped new gasoline cars with three-way catalysts (TWC), which simultaneously remove HCs, CO, and NO_x from stoichiometric exhaust. These catalysts currently consist of a ceramic monolith structure coated with precious metal catalysts, such as platinum, rhodium and/or palladium [22-24]. Since the 1980s, TWCs have been optimized for stoichiometric (nearly oxygen free) engine exhaust [25]. In reality, the fuel air mixture of stoichiometric engines is deliberately varied in time to produce brief periods of slightly lean and slightly rich exhaust. This dynamic variation allows TWCs to both oxidize HCs and CO and reduce NO_x .

1.4 NO_x emissions control in lean exhaust

A major technical challenge in commercializing lean burn GDI engines is demonstrating the control of nitrogen oxide emissions. As explained above,

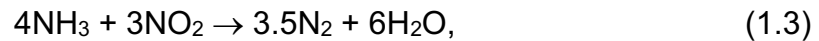
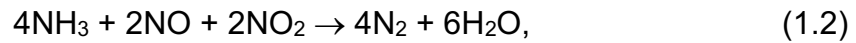
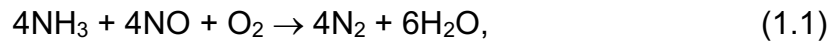
TWCs are not designed to reduce NO_x emissions when there are significant levels of oxygen present. To overcome this problem, two alternative catalytic technologies have been developed for NO_x removal: lean NO_x traps (LNTs) and ammonia selective catalytic reduction (SCR).

1.4.1 Lean NO_x trap

In a lean NO_x trap (LNT), NO_x reduction is achieved by storing NO_x during normal lean exhaust conditions and then reducing the stored NO_x during periodic rich excursions of short duration [26-30]. A typical LNT catalyst consists of honeycomb-like ceramic monolith coated with three primary components: precious metals such as Pt, Pd and Rh, alkali or alkaline earth metals such as Ba and K, and a high surface area support material such as γ -Al₂O₃. During normal lean exhaust conditions, NO is oxidized to NO₂ over the precious metal sites and subsequently stored on alkali/alkaline earth metals in the form of nitrites and/or nitrates [31, 32]. The lean NO_x trap catalyst has a finite capacity to store NO_x, and once the storage sites approach saturation, NO_x starts to break through. Before the NO_x slip reaches unacceptable levels, the catalyst must be regenerated to recover some or all of the original storage capacity. The regeneration of the catalyst surface is accomplished by exposing LNT to a mixture of reduced species such as hydrocarbons, hydrogen (H₂) and carbon monoxide [29, 33]. These reductants can be obtained by injecting fuel into the exhaust upstream of the catalyst (referred to as in-pipe injection regeneration) or by altering the combustion process of the lean-burn engine so that periodic fuel-rich exhaust is produced (referred to as in-cylinder regeneration). During periodic rich excursions, NO_x is released from the storage sites and (ideally) reduced to N₂ over precious metals [34]. The reduction of NO_x is selective to N₂ under typical operating conditions [35]; however, at low temperatures and high reductant concentrations formation of NH₃ and N₂O can reach significant amounts [36-38].

1.4.2 Urea selective catalytic reduction

Ammonia SCR relies on selectivity of injected reductant to react with NO_x in oxygen-rich exhaust to form N₂ and H₂O [39-41]. Originally developed for stationary power plants, this catalyst technology has been successfully employed in mobile applications, in particular, to control NO_x emissions from diesel engines. In contrast to cyclic lean/rich operation of a LNT catalyst, SCR catalysts can function continuously at steady state by utilizing ammonia (NH₃) as the reductant. In diesel engine NO_x control, ammonia is typically supplied from the thermal decomposition of a urea solution, which hydrolyzes to NH₃ after it is injected into a hot exhaust. Selective reduction of NO_x by NH₃ in a SCR catalyst occurs according to the three main global reactions given as



and are known as the standard, fast and slow SCR reactions, respectively.

Similar to LNT catalysts, SCR catalysts are deposited on a honeycomb-like ceramic monolith substrate. The first generation automotive SCR catalysts were derived from titania supported vanadia catalyst (V₂O₅-WO₃/TiO₂) commonly used in stationary power plants. The vanadia-based SCR catalysts, however, are effective only in a narrow temperature region between 300 and 500 °C with a drastic decrease in activity and selectivity at temperatures above 500°C [42-45]. In addition, vanadia SCR catalysts have low thermal durability with toxic vanadia species beginning to volatilize at 650 °C [39]. Because of their low NO_x conversion performance at low temperatures and low thermal durability, vanadia-based SCR catalysts are unable to meet current stringent NO_x emissions regulations in the USA [46]. However, vanadia-based SCR catalysts may be

suitable in countries where the emission regulations are not as strict as in the USA and Europe [44].

Metal-exchanged zeolite SCR catalysts, on the other hand, have proved to be especially suited for automotive applications in established markets due to their lower temperature activity, higher thermal durability and higher ammonia storage capacity which are required for the transient conditions encountered in automotive applications [40, 47, 48]. Zeolites are microporous crystalline aluminosilicates that can be ion-exchanged with Cu or Fe, which are exceptionally active for the ammonia SCR of NO_x [39, 49-52]. Recent advances in Cu-zeolite SCR catalyst formulations have demonstrated high low-temperature NO_x reduction performance, greater resistance to hydrocarbon fouling and higher ammonia storage capacity than Fe-zeolite SCR catalysts [40, 53]. Coupled with good thermal stability, Cu-zeolite emerged as the best choice for NO_x abatement in light and heavy-duty automotive diesel applications in the U.S.

1.4.3 *Passive ammonia SCR*

The two lean NO_x control catalyst technologies employed in diesel vehicles in the U.S. add significant cost and complexity. Urea-SCR, for example, requires a secondary tank for urea storage and an urea injection system. Although the LNT utilizes fuel from the vehicle instead of a secondary tank, the catalyst contains high precious metal levels resulting in high catalyst cost. In addition, LNTs are susceptible to sulfur poisoning that requires periodic high temperature regeneration leading to thermal degradation and additional fuel penalty. Despite these difficulties, urea SCRs and LNTs have been commercialized in the U.S. to control NO_x from diesel vehicles. These technologies can potentially be adapted for NO_x control in lean gasoline applications [54-58].

Lean NO_x traps have been employed in Europe in vehicles with lean GDI engines to meet EURO V emission standards, and the resulting emissions and

fuel economy of one such vehicle have been recently characterized in the U.S. by Chambon et al. and Parks et al. for several U.S. drive cycles [3, 59]. The NO_x emission from these studies are displayed in Figure 1.4 for the US Federal Test Procedure-75 (FTP), US06 Supplemental Federal Test Procedure (US06) and Highway Fuel Economy Test (HFET) drive cycles. The current U.S. Tier 3 NO_x emission standard (0.03 g/mile NO_x + NMOG) is also shown in Figure 1.4 to illustrate how stringent this standard is. Although the vehicle used in these studies is not intended for the U.S. market, its relatively low NO_x performance illustrates the need for further advances in lean NO_x control technology to meet U.S. emission standards. Without such advances, the fuel economy of lean GDI engines won't be readily exploitable in the U.S.

Because of the high cost and complexity of utilizing LNT or urea-SCR technology for lean GDI engines, alternative lean NO_x control methods are being intensively studies. One promising alternative candidate, referred to as passive

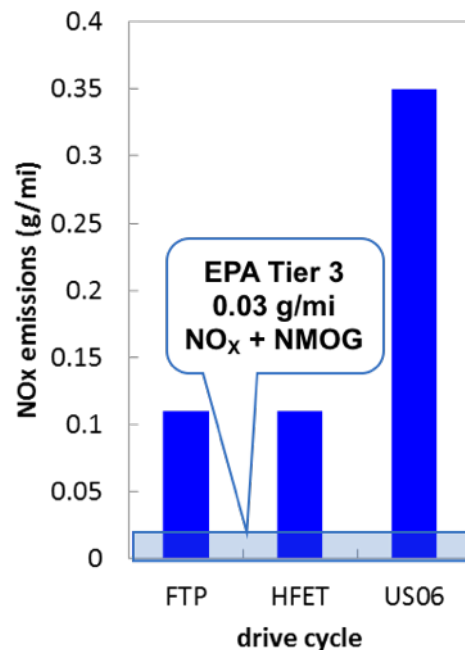


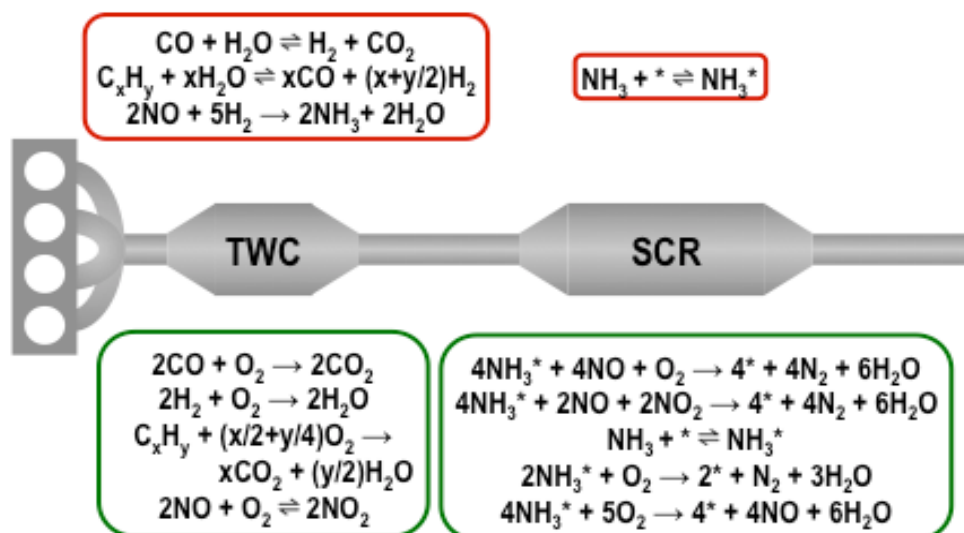
Figure 1.4 NO_x emissions of a European MY2008 BMW 1-series 120i lean gasoline vehicle equipped with a LNT over the US drive cycles [3, 59].

NH₃-SCR, has been introduced by General Motors and has shown considerable promise [4, 60, 61]. The passive SCR system, as illustrated in Figure 1.5, consists of a close-coupled TWC and an underfloor SCR catalyst. Ammonia is generated in the TWC during brief slightly fuel-rich engine transients and subsequently stored on the SCR catalyst. Once the engine returns to lean combustion, exhaust NO_x passes through the TWC and is reduced by the stored NH₃ on the SCR catalyst. The appeal of this approach is that it utilizes the TWC that is already onboard and eliminates or greatly reduces the need for urea dosing. Also, the SCR catalysts are much lower cost than the precious metal-based catalysts needed for LNTs. The passive NH₃ SCR system is a potential low cost and urea free approach for controlling nitrogen oxides emissions from lean burn gasoline engines. Thus, understanding the dynamics of NH₃ generation, storage and utilization in the passive SCR system, and the mechanisms associated with NO_x reduction during lean/rich cycling operation provide a potential path forward toward exploiting the fuel economy benefits of lean GDI engines.

1.5 Recent studies of lean GDI vehicle

The studies by Chambon et al. and Parks et al. of the emissions and fuel economy of a European Model Year (MY) 2008 BMW 1-series 120i (E87) passenger vehicle provided a suitable and relevant initial reference point for the present study. This vehicle is fitted with a 4-cylinder 2.0-liter lean GDI engine and was characterized in detail on a chassis dynamometer at Oak Ridge National Laboratory over several US drive cycles including FTP, HFET and US06 [3, 59]. For all the drive cycles, the fuel economy with lean operation was found to be better than for stoichiometric operation. Fuel economy improvements between 4 and 15%, depending on the drive cycle, were observed as illustrated in Figure 1.6. As expected the smallest fuel economy improvement is observed in the most aggressive drive cycle (US06), where the accessibility of lean

Periodic excursions to slightly rich AFR:
 NH_3 generated from NO over TWC, stored on SCR



Normal lean operation:
 NO_x reduced by NH_3 stored on SCR

Figure 1.5 Passive ammonia SCR approach to control NO_x emission from lean gasoline engines.

operation is limited due to more aggressive accelerations required by that drive cycle.

The vehicle's exhaust aftertreatment system, which is designed to meet EURO V emission standards, consisted of a TWC and a lean NO_x trap (LNT) and (as noted above) significantly exceeded U.S. Tier 3 emissions. High fuel savings potential of lean gasoline engines and the lack of cost-effective aftertreatment technologies that allow compliance with U.S. Tier 3 emission regulations is the main motivation of the present study. The work presented here is part of a broader effort by Oak Ridge National Laboratory to address the challenges of controlling NO_x from advanced, high-efficiency lean gasoline engines to enable their market introduction by conducting research on advanced catalysts and emission control systems.

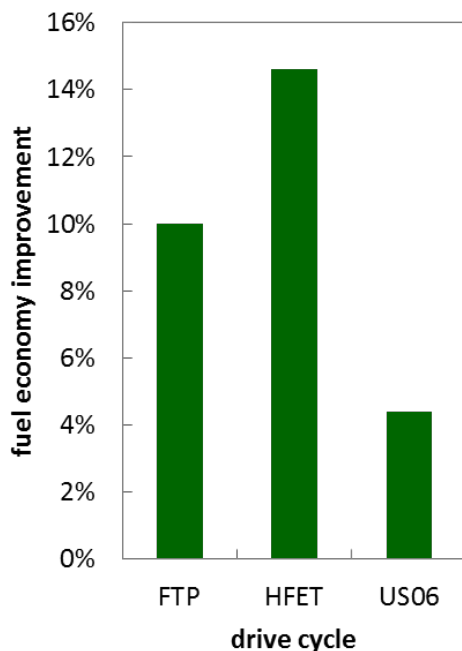


Figure 1.6 Fuel economy improvement of a European MY2008 BMW 1-series 120i lean gasoline vehicle operating in lean relative to stoichiometric only operation over US drive cycles [3, 59].

1.6 Scope of the present investigation

As explained above, demonstrating the potential benefits of passive NH_3 -SCR for lean GDI vehicles requires elucidating the collective performance of the engine, TWC, and SCR catalyst system under realistic operating conditions. Thus, the research plan included experiments and computational analyses designed to reveal the key performance characteristics of each of the individual system components in the context of the overall system performance. This included the dynamics of the engine operation and how it impacted the exhaust chemistry and the rates of NH_3 generation and NO_x conversion in the aftertreatment system. Particular emphasis was placed on understanding how the NH_3 yield from the TWC can be maximized and optimally used for NO_x SCR and how this can potentially affect fuel economy. Steady-state and transient experiments with the lean BMW GDI engine were performed on an engine research platform installed at the Fuels Engines and Emissions Research Center (FEERC) at Oak Ridge National Laboratory (ORNL). A series of model TWCs with different formulations were coupled to the engine in order to observe the effects of the major TWC's components. Experimental measurements included NH_3 generation in the TWCs for a range of fueling conditions, and these were compared with computational predictions based on recently derived reaction mechanisms.

The effects of engine operating parameters such as the air-fuel equivalence ratio, spark timing and exhaust gas recirculation on NO_x emissions, NH_3 formation and fuel consumption were experimentally determined to reveal how these might be manipulated to control the system performance. The results established a basis for estimating the potential drive cycle fuel efficiency gains possible. Combined with other available data, the ORNL engine experiments suggest some specific pathways forward for optimizing fuel efficient lean GDI vehicles that might be compliant with Tier 3 NO_x emission standards.

CHAPTER 2

LITERATURE REVIEW

The concept of passive ammonia SCR was introduced by General Motors in 2010 [4] and has shown considerable promise as an alternative candidate for NO_x control from lean gasoline engines. The passive SCR system, as illustrated in Figure 1.5, consists of a close-coupled TWC and an underfloor SCR catalyst. As explained by Li et al., the basic concept behind passive SCR is to exploit the potential for generating NH₃ in a post-engine TWC such that the NH₃ can be used in a downstream SCR catalyst to reduce NO_x released by the engine. A key challenge is to develop suitable methods for understanding and exploiting the NH₃ generation process and how that process can be maximized by engine fueling shifts such that the consumption of excess fuel is minimized while still meeting NO_x reduction targets.

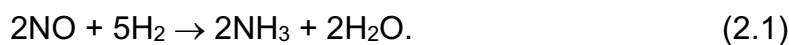
In their original study, Li et al. [4] demonstrated a passive SCR system for a 2.2-liter lean burn gasoline engine coupled to a transient dynamometer that was able to achieve >85 % NO_x conversion over the New European Driving Cycle (NEDC). This system included a close-coupled TWC that generated sufficient NH₃ to achieve this level of NO_x control at an air-to-fuel ratio of 14.2 with a fuel penalty of less than 1%. The NO_x reduction performance of this passive SCR system was shown to depend highly on the NH₃ storage capacity of the SCR catalyst. Since Cu-zeolite SCR catalysts typically have higher NH₃ storage capacity than Fe-zeolite, the former exhibited better NO_x conversion performance in Li et al.'s passive SCR system. The operating window of SCR in their system was shown to be limited to 400 °C due to much lower NH₃ storage capacity at higher temperatures.

In-situ NH₃ generation is a critical component of passive SCR, and as such there have been more studies in recent years focusing on how NH₃ generation can be promoted under some circumstances over precious metal catalysts. Even though NO_x reduction to NH₃ is known to occur in TWCs under reducing conditions [62-67], commercial TWCs have not been designed to optimize this

function. In fact, NH₃ formation over current TWCs has often been considered undesirable because of the toxicity and impact of NH₃ on the formation of particulate matter [63]. Thus, much of the previous research on TWC functionality has focused on suppressing NH₃ formation. The following sections review highlights from recent studies pertinent to promoting NH₃ generation over precious metal catalysts.

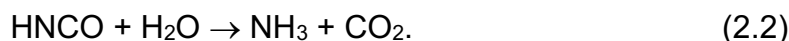
2.1 Pathways of NH₃ formation

In the presence of NO and H₂, one direct pathway for NH₃ formation is through the reaction between NO and H₂ [68-70], as



According to the stoichiometry in Equation 2.1, a H₂ to NO_x ratio of 2.5 must be fulfilled in order to completely convert the incoming NO_x to NH₃. At lower [H₂]/[NO_x] ratios, when there is a deficiency in H₂, NO_x can be converted to other products including N₂O and N₂ [68, 71].

When CO is present in the exhaust, NH₃ can also be formed from the intermediate species isocyanic acid (HNCO), which hydrolyzes to NH₃ and CO₂ [68, 72-76], depicted as



Oh et al. [68] investigated mechanisms of NH₃ formation from NO + H₂ mixtures over a commercial three-way catalyst containing only Pd (Pd supported on Al₂O₃). Little NH₃ formation was observed at [H₂]/[NO_x] < 1. As the ratio increased, the amount of NH₃ formed gradually increased reaching 100 % NH₃ selectivity at H₂ to NO_x ratio of 2.5. Including the CO in the feed significantly increased the amount of NH₃ formation for [H₂]/[NO_x] < 2.5. The increase in NH₃ formation in the presence of CO was attributed to the isocyanate hydrolysis route of NH₃ formation. Oh et al. concluded that the isocyanate route contributed significantly to NH₃ formation at lower [H₂]/[NO_x] ratio, when there was a

stoichiometric deficiency in H_2 relative to NO_x . At higher ratios, when H_2 was present in an excess, NO reduction became selective to NH_3 according to the reaction in Equation 2.1.

In the presence of multiple reductants (CO and HC) and oxidants (O_2), H_2 and NO_x are also consumed or produced by other competing reactions in the catalyst. For optimal NH_3 production, NO_x needs to react preferentially with H_2 and not CO or HC, while H_2 needs to react preferentially with NO_x and not O_2 . The competing reactions are discussed in more detail in Section 4.2. The relative rates of formation of NH_3 vs. other co-products in the presence of multiple reductants and oxidants reflects the catalyst selectivity, which highly depends on catalyst formulation. The impact of catalyst formulation on NH_3 formation is discussed in the next section.

2.2 Impact of catalyst formulation on NH_3 formation

The majority of TWCs consist of a honeycomb-like ceramic monolith structure coated with precious metal catalysts, such as platinum, rhodium and/or palladium dispersed over a high surface area support material such as $\gamma-Al_2O_3$. Besides the precious metals, TWCs often contain other components, which function as catalyst promoters or stabilizers. Cerium, for example, is often included in TWC and it serves multiple functions. It enhances precious metal dispersion and activity, stabilizes the washcoat layer, improves thermal stability, promotes water-gas-shift and steam reforming reactions, functions as an oxygen storage component (OSC) and is the basis for on-board diagnostics [77-80].

The type of metal employed, and the support material used in the TWC formulation have significant effects on the NH_3 formation. Kobylinski et al. [81] studied reduction of NO by CO and H_2 using Ru, Rh, Pd, Pt supported on Al_2O_3 . The study revealed that the activity of these metals for NO reduction was in the following order $Ru > Rh > Pd > Pt$. Under rich conditions, Pt and Pd exhibited higher selectivity to NH_3 than Rh and Ru. Even though Ru had the highest

activity for NO_x reduction, it forms RuO_2 and RuO_4 which can result in complete loss of Ru from the catalyst support.

Adams et al. [82] studied the formation of NH_3 over silica, alumina and titania supported Pt and Pd catalysts in the gas mixtures with direct source of H_2 ($\text{NO} + \text{H}_2$) and also H_2 supplied in the form of water via water-gas-shift (WGS) reaction ($\text{NO} + \text{H}_2\text{O} + \text{CO}$). At temperatures below 300 °C, Pt showed higher NH_3 generation activity when H_2 was directly available, while Pd performed better with WGS-assisted reaction. This was attributed to low WGS activity of Pt at low temperatures due to Pt susceptibility to CO poisoning at low temperatures. At temperatures above 300 °C, Pt was more active in both reactions.

In addressing the role of the support material in promoting NH_3 generation, Adams et al. [82] investigated alumina and silica support materials. These materials have high surface area and are commonly utilized in automotive applications. Titania was also investigated as a potential support material to promote the formation of cyanate species when CO and NO present in the feed (the isocyanate route of NH_3 formation). With the direct supply of H_2 , titania-supported catalysts showed low (< 50 %) NO to NH_3 selectivity, while almost full conversion was achieved over alumina and silica-supported catalysts. Low activity over titania was attributed to significant loss of surface area after the samples were calcinated, which implied low thermal stability of titania-supported catalysts. Silica-supported catalysts exhibited low NH_3 activity under WGS-assisted reactions compared to alumina. Adams et al. identified the alumina-supported Pd catalyst as a promising formulation for passive SCR applications because of its high NH_3 generation potential over broad range of temperatures and exhaust conditions.

As mentioned earlier, one common feature of commercial TWCs is the inclusion of an oxygen storage component (OSC) in the washcoat, which assists three-way functionality under near stoichiometric conditions and also enhances water-gas-shift and steam-reforming reactions and is the basis for on-board diagnostics. For these reasons, inclusion of an OSC in the TWC is mostly likely

be needed for passive SCR applications. Adams et al. [72] investigated the formation of NH_3 over alumina-supported Pd catalysts modified with various amounts of cerium (0-38 wt. %). When H_2 was directly available in the feed stream, $\text{Pd}/\text{Al}_2\text{O}_3$ and $\text{Pd}/\text{Ce}/\text{Al}_2\text{O}_3$ exhibited similar performance in converting NO_x to NH_3 over a wide temperature range. However, when H_2 was supplied in the form of water via water-gas-shift (WGS) reaction ($\text{NO} + \text{H}_2\text{O} + \text{CO}$), catalysts that contained cerium exhibited higher NH_3 yield. This was attributed to the enhanced water-gas-shift properties of ceria that resulted in higher H_2 availability for NH_3 formation compared to $\text{Pd}/\text{Al}_2\text{O}_3$ catalysts. Increasing ceria content resulted in increased improvement in WGS-assisted NH_3 formation.

Since passive SCR relies on periodic switching between lean and rich operation, the presence of high oxygen storage capacity can potentially delay NH_3 formation on the transition from lean to rich, which would require longer rich time to generate desired levels of NH_3 and lead to higher fuel penalty. This in part can be mitigated by a 2-step purge proposed by Theis et al. [83], where, upon switching to rich, a relatively rich purge is employed initially to remove the oxygen stored on a TWC followed by a less rich conditions to continue generating NH_3 . The 2-step purge was shown to decrease the delay in NH_3 production while minimizing the CO slip and fuel consumption.

Other studies have revealed similar results that Pd-based catalysts exhibit higher selectivity of NO_x conversion to NH_3 than other precious metal-based catalysts, and offer a great potential for being utilized in the passive SCR application [60, 68, 72, 82-84]. Most of the experimental studies found in the literature related to the subject of this dissertation were performed under simulated exhaust conditions. The experimental and computational engine conditions utilized in the present work are intended to further advance the understanding of how the NH_3 yield from the TWC can be maximized and optimally used for NO_x SCR under realistic exhaust conditions, and how this can potentially affect fuel consumption. The experimental engine work is based on the results contained in the publications by Prikhodko et al. [85-88].

CHAPTER 3

MATERIALS AND METHODS

This chapter describes the experimental and computations methods used in the present investigation. Section 3.1 describes the lean gasoline engine setup located at ORNL, and Section 3.2 contains details about the TWC catalysts evaluated. Section 3.3 contains a brief description of the experimental conditions, and the chapter concludes in Section 3.4 with a description of the computational model that was implemented in MATLAB to simulate the TWC performance.

3.1 Lean gasoline engine research platform

3.1.1 Engine Platform

The work presented here was conducted on a BMW N43B20 lean gasoline engine installed in a test cell at Oak Ridge National Laboratory's National Transportation Research Center. The engine was removed from a European Model Year (MY) 2008 BMW 1-series 120i (E87) vehicle and installed on a dynamometer test stand. This engine represents the state-of-the-art in lean gasoline engine technology, and it was commercially available in Europe through MY2011. Figure 3.1 and Figure 3.2 are photographs of the vehicle and engine, respectively, as they were installed on dynamometers at ORNL.

For the experiments summarized here, the 4-cylinder, 2.0-liter naturally aspirated gasoline engine was coupled to a motoring direct current dynamometer that controlled engine speed and load. Table 3.1 summarizes the engine specifications.

The engine was fueled with a EEE-lube certification gasoline fuel containing low sulfur levels. The fuel was acquired from Haltermann Solutions. Fuel properties are listed in Table 3.2.

The engine uses a spray guided direct injection fueling system, in which the piezoelectric injector is located at the top center of the combustion chamber



Figure 3.1 BMW 120i lean gasoline vehicle on chassis dynamometer at ORNL.

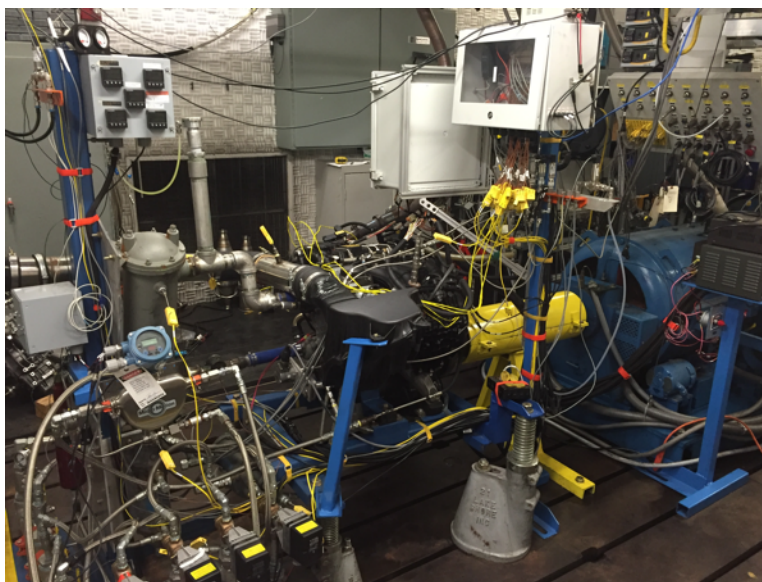


Figure 3.2 BMW N43B20 lean gasoline engine installed on the dynamometer test stand at ORNL.

Table 3.1 BMW 2.0-liter lean gasoline direct injection engine specifications.

Specification	Value
Engine Model Number	N43B20
Displaced volume	1995 cm ³
Number of cylinders	4
Stroke	90 mm
Bore	84 mm
Compression ratio	12.0:1
Rated Power	125 kW at 6700 rpm
Rated Torque	210 Nm at 4250 rpm

Table 3.2 EEE-lube certification gasoline fuel properties.

Fuel Property	Value
Lower Heating Value, kJ/kg	42715
Density, kg/liter	0.742
C, weight fraction	0.8598
H, weight fraction	0.1314
Oxygen, weight %	<0.01
Sulfur, mg/kg	4
Aromatics, volume %	27.4
Olefins, volume %	0.9
Saturates, volume %	71.8
Research Octane Number (RON)	96.4
Motor Octane Number (MON)	88.4

in close proximity to the spark plug. This geometry allows ignition of the fuel near the injection point, resulting in shorter mixture formation time, an extended lean operating range and significant fuel efficiency gains compared to other lean gasoline combustion system designs [2, 9]. An engine cut-out depicting this geometry is shown in Figure 3.3.

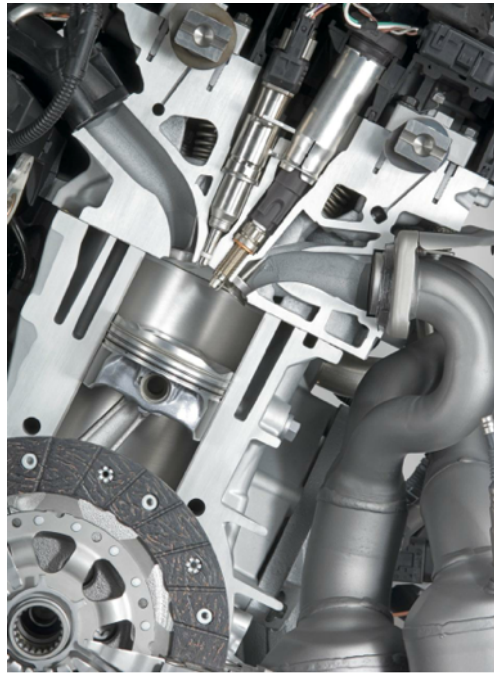


Figure 3.3 Cut-out of BMW N43B20 lean gasoline engine showing piezoelectric injector at the top center of the combustion chamber with spark plug in close proximity to the injector (<http://www.bmwheaven.com>).

The overall air-fuel equivalence ratio, or λ (ratio of actual AFR to stoichiometric AFR), during lean operation ranges between 1.3 and 2.2. The engine, however, only operates lean over a portion of the engine's speed and load range, up to 4500 rpm and 75% load as shown in Figure 3.4. One of the primary factors limiting lean operation at higher engine speed and loads is formation of a stable and ignitable mixture near the spark plug. At higher engine speeds, the time available for the mixture formation decreases, which in turn limits lean operation. At higher loads, the injected amount of fuel increases in

order to meet the required power demand and at some point, the amount of fuel is too large for efficient combustion to take place. Outside the lean operating range, at higher engine speeds (>4500 rpm) and loads ($>75\%$), the engine operates in the stoichiometric combustion mode. The engine can also operate in the stoichiometric mode over its entire operating range.

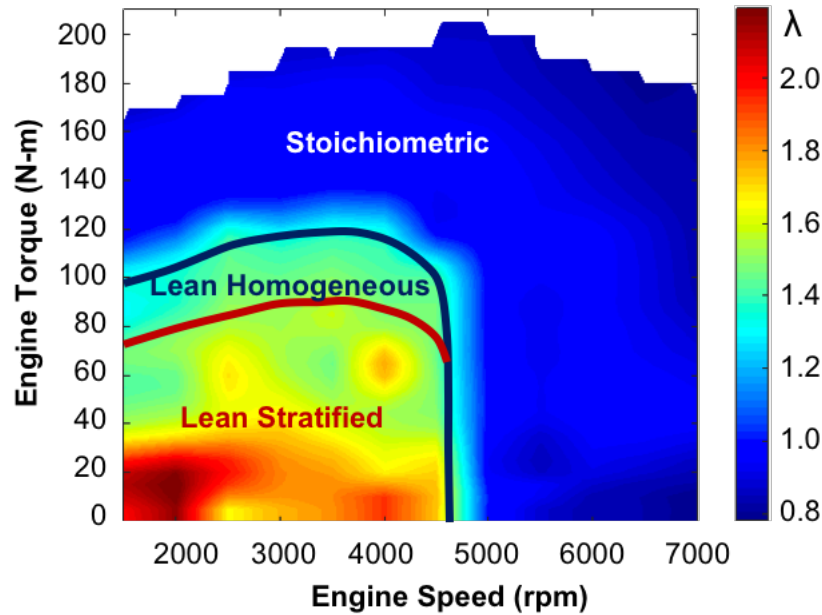


Figure 3.4 Air-fuel equivalence ratio, λ , as a function of engine speed and load. Also shown three main combustion modes employed by the engine: lean stratified, lean homogeneous with additional stratification and homogeneous stoichiometric.

The engine can operate in three different combustion modes: lean stratified, lean homogeneous with additional stratification (referred to as lean homogeneous for simplicity) and stoichiometric homogeneous. The engine also uses multiple fuel enrichment strategies to control temperature at high loads, NO_x emissions and cold start [3, 89]. The three main combustion modes are described below.

In lean stratified combustion, the fuel is injected late in the compression stroke close to top dead center (TDC), as shown in Figure 3.5, creating an

ignitable mixture at the spark plug, while the rest of the combustion chamber contains a very fuel-lean, non-ignitable mixture. Each injection is followed by multiple spark events. The overall stoichiometric air-to-fuel ratio, λ , in the lean stratified mode ranges from 1.6 to 2.2.

At higher loads (55-75%) more fuel is delivered to meet the torque requirement, and the engine switches to lean homogeneous combustion, in which a portion of the fuel is injected during the intake stroke to create a globally well-mixed lean homogeneous fuel-air mixture. Additional fuel is injected late in the compression stroke to create a stratified fuel-air mixture in the spark plug region; and this second fuel injection is immediately followed by multiple spark events. The overall λ ratio in the lean homogeneous mode ranges from 1.4 to 1.6.

At higher speeds and loads, the engine operates with stoichiometric combustion ($\lambda=1$). A portion of the fuel is injected during the intake stroke and a second smaller injection occurs early in the compression stroke creating a well-mixed homogeneous mixture. A single spark event occurs close to TDC.

For some experiments in this study, it was necessary to operate the engine fuel-rich ($\lambda<1$), and this was achieved by manual fuel injection adjustments to achieve the desired λ .

3.1.2 Engine Controller

To achieve the required combustion control, the factory engine control unit was replaced with a custom full-pass control system developed by National Instruments - Powertrain Controls Group. The controller algorithms were implemented using LabVIEW to mimic the OEM combustion strategies and also enable full control of all engine parameters including fuel injection quantity and timing, and spark timing.

Control of the air-fuel equivalence ratio was based on feedback from universal exhaust gas oxygen (UEGO) sensors mounted on a custom-built exhaust manifold at each of the cylinder exhaust runners. This control strategy

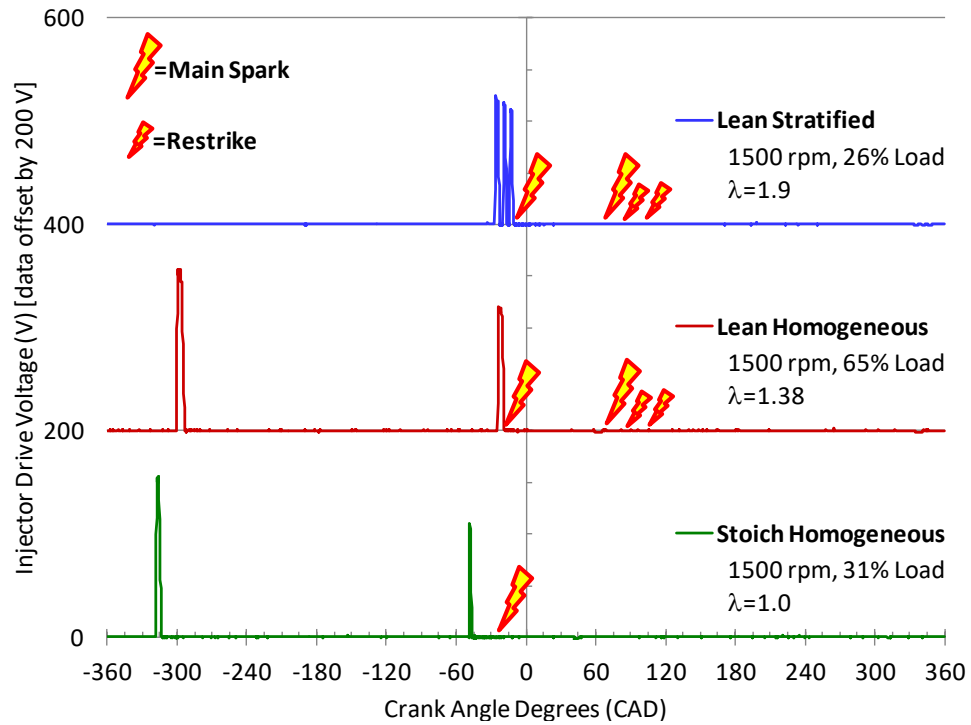


Figure 3.5 BMW engine injection and spark events for three main combustion modes: lean stratified, lean homogeneous and stoichiometric homogeneous.

made it possible to overcome combustion instability issues associated with variable injector calibrations.

3.1.3 Gaseous emissions sampling

To characterize catalyst performance, raw exhaust gas was sampled at catalyst entrance and exit locations and routed through heated stainless-steel lines to gas analyzers. According to standard practice, gas samples were passed through a heated filter to remove particulates to protect the gas analyzers.

Multiple species concentrations were determined by an MKS MultiGas Model 2030 continuous gas analyzer. The MultiGas is a Fourier-Transform Infrared gas analyzer with a heated 5.11 m multi-pass gas cell capable of measuring multiple gases including NH_3 , CO, CO_2 , NO and NO_2 . The spectrometer collects infrared spectra and compares them to reference spectra in order to determine the concentration of target species. The reference spectra and methods for analysis are built into the software provided by MKS.

Total hydrocarbon emissions were measured with a California Analytical Instruments (CAI) heated flame ionization detector (HFID). The detector relies on measuring the flow of ions between two electrodes when HCs, exposed to the hydrogen flame, undergo ionization. The voltage supplied to the electrodes is proportion to the number of carbon atoms in the HCs. The hydrogen flame is continuously maintained from a supply of 40% hydrogen in helium and air.

H_2 and O_2 measurements were made with a magnetic sector mass spectrometer with a capillary sampling system (SpaciMS). SpaciMS is a mass-spectrometry-based technique that allows intra-catalyst sampling measurements by inserting a capillary probe inside the catalyst channel. This technique was originally developed by researchers at ORNL and Cummins, Inc. [90]. For the purpose of this study, the sampling with this instrument was performed at catalyst inlet or outlet locations.

3.2 Catalysts

In this work, two TWCs with different washcoat formulations were experimentally characterized on the lean gasoline engine in order to identify the roles played by major catalyst components on NH_3 generation functionality. The TWCs were selected based on an earlier screening of model TWC formulations on a bench flow reactor at ORNL [91]. The flow reactor screening revealed that a commercial Pd-only TWC achieved the highest NH_3 selectivity and the best estimated fuel consumption. The flow reactor studies also suggested that addition of a NO_x storage component (NSC) to TWCs might have the potential to improve fuel consumption by extending lean operation and thereby preserving NH_3 inventory.

The Pd-only TWC used in the engine studies was the front portion of a commercial dual zone catalyst formulation from a 2009 PZEV (Partial Zero-Emissions Vehicle) Chevrolet Malibu. The Chevrolet Malibu TWC is a single 1.3-liter monolith with a dual zone catalyst formulation. The front 0.6-liter portion of the catalyst contains 4.4 g of Pd and no dedicated oxygen storage component (OSC), while the rear portion has a lower total precious metal loading (1.0 g, with 4:1 of Pd:Rh ratio) plus an OSC. For the present study, the front portions of three Chevrolet Malibu TWCs were cut out, mounted in series in a stainless steel can and installed in the engine exhaust in a close-coupled configuration. The combined volume of the Pd-only Malibu TWC was 1.3 liters. The catalyst was degreened on the engine for twenty hours at temperatures ranging between 650 and 750 °C prior to evaluation.

The TWC with NSC (referred to as TWC-NSC in this manuscript) is a prototype TWC provided to ORNL by Umicore. The catalyst formulation contains Pt, Pd, Rh and oxygen and NO_x storage materials. A 1.3-liter catalyst monolith was installed in the engine exhaust in a close-coupled configuration. Prior to evaluation, it was degreened in the engine exhaust for approximately 20 hours with a maximum inlet temperature of 850 °C. Catalysts properties are

summarized in Table 3.3. The engine experimental setup with a TWC in the exhaust is shown in Figure 3.6 and the corresponding schematic in Figure 3.7.

Table 3.3 TWC properties.

	Pt/Pd/Rh loading (g/liter)	Contains OSC (Yes/No)	Contains NSC (Yes/No)
Pd-only TWC	0.00/7.33/0.00	No	No
TWC-NSC	2.47/4.17/0.05	Yes	Yes

Omega type-K ungrounded thermocouples were used to measure the TWC inlet and exit gas temperatures as well as the temperature at the middle of the TWC. For measuring the inlet and exit gas temperatures, thermocouples of 1.6 mm in diameter were inserted through a Swagelok adapter welded onto the catalyst can and positioned in the radial center of the catalyst can approximately 10 mm from the face of the catalyst as shown in Figure 3.7. For the mid-bed temperature, a thermocouple, smaller in diameter (0.5 mm), was inserted through a 6.4 mm stainless-steel guide tube located in the back of the catalyst can and positioned in the radial center of the TWC. The pressure at the inlet and exit of the TWC was measured with Omega PX series pressure transducers.

3.3 Experimental conditions for the engine study

Both steady-state and transient experiments were performed on the lean gasoline engine. The steady-state experiments evaluated the influence of engine control parameters on the formation of NH_3 over the TWC during slightly rich operation. Air-fuel equivalence ratio, spark timing and exhaust gas recirculation rate were varied over a number of engine speed and load points to produce a range of exhaust gas compositions, temperatures and catalyst space velocities. As explained in Chapter CHAPTER 4, these experiments were implemented to assess the

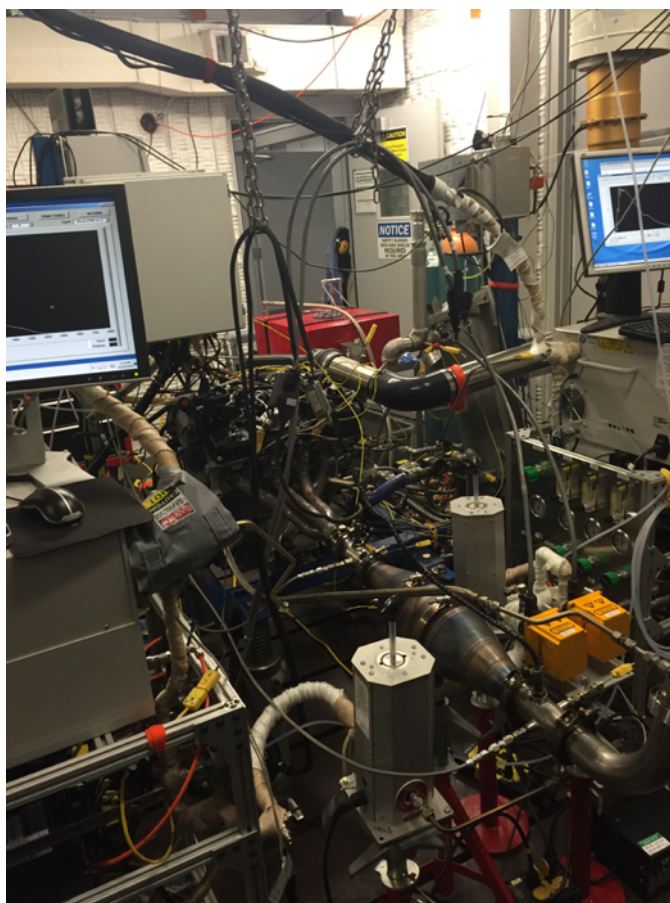


Figure 3.6 TWC installed in the exhaust of the BMW lean gasoline engine at ORNL.

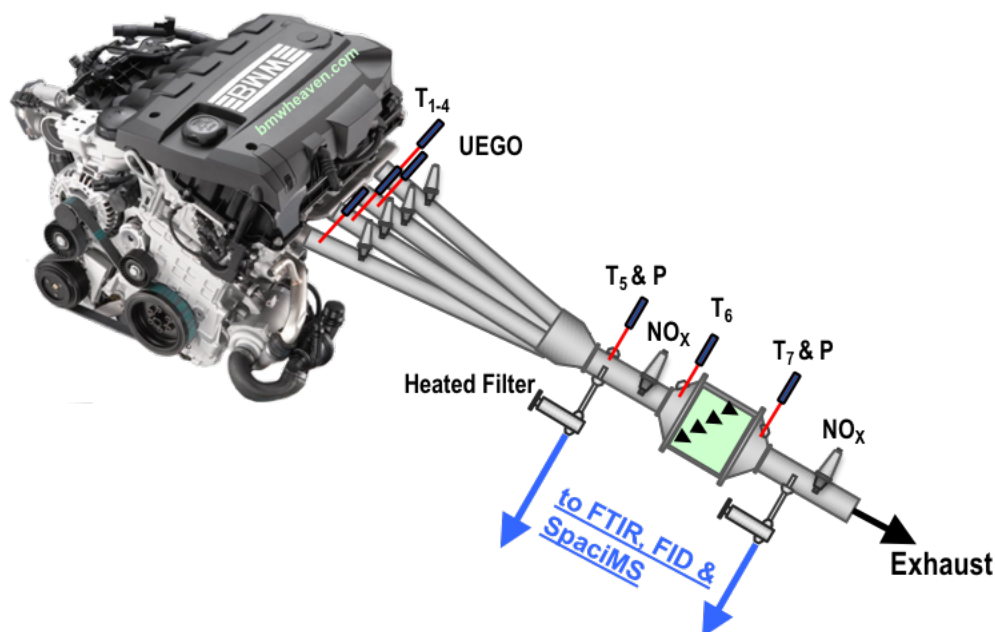


Figure 3.7 Schematic of the BMW lean gasoline engine and exhaust system at ORNL.

trade-off between NH_3 generation and fuel penalty as a result of increased fuel consumption from running rich.

To assess NO_x reduction, NH_3 formation, reductant utilization and fuel efficiency improvements under realistic operating conditions, a series of rich/lean cycling experiments were performed where the engine alternated between rich and lean operation. These experiments were designed to be representative of the conditions a passive SCR system would encounter under realistic driving conditions. These experiments are described in greater detail in Chapter CHAPTER 4.

3.4 Computational studies of TWC NH_3 production

An existing computational kinetics model of TWC function was adapted to help interpret the observed NH_3 generation trends in the experimental investigations. The original TWC model had been implemented in MATLAB by Stuart Daw for internal research studies at ORNL [92] and was specifically

adapted to be consistent with the experimental requirements of both the ORNL bench flow reactor and the experimental engine setup. A copy of the detailed MATLAB code is included in the Appendix. Key assumptions made by the model are:

- The collective behavior of all the TWC monolith channels can be approximated by the performance of a single 'average' channel.
- Each average channel is approximated as a series of constant volume continuous-stirred tank reactor (CSTR) stages arranged in the axial flow direction and in which differential mass balances are applied to account for transient flow and reaction effects on species concentrations [93].
- The operating pressure of all the TWC stages is set at atmospheric pressure.
- The inlet boundary conditions at the first stage of each channel at each point in time are equal to the transient composition, flow, and temperature of the experimentally measured TWC inlet conditions.
- The initial conditions for each TWC stage are based on the starting experimentally measured inlet conditions.
- The transient inlet conditions to each CSTR stage after the TWC inlet are equal to the exit conditions of the preceding stage.
- The number of stages is increased until no significant change in the transient axial concentration profiles is observed to reach an approximation of the plug flow limit.
- The catalyst reaction temperature in each stage at each point in time is approximated by interpolating the experimentally measured thermocouple temperatures for the appropriate axial location.
- In the gas phase in each stage, the time dependent gas composition, velocity, temperature, and pressure at any point in time are uniform (i.e., there are no cross-flow gradients).

- At the channel wall in each stage, the catalyst state, species concentrations, and temperature at each point in time are uniform (i.e., there are no spatial gradients within the washcoat).
- All reactions occur in the catalytic washcoat at the channel wall.
- Mass transfer between the gas and wall washcoat are approximated by laminar boundary-layer correlations for circular tubes combined with pseudo-steady-state approximation [94] to relate the gas and washcoat species concentrations within each stage.
- Heat and mass transfer between stages occur in the gas phase only (i.e., there is no significant axial heat or mass transport through the washcoat).
- For the differential mass balances in each stage, a semi-implicit time integration can be used with a time step size based on the smallest characteristic flow and reaction rate time scales.
- The reaction rate in each stage is determined from the global reaction mechanism and kinetic parameter values proposed by Gong [69, 95].

3.4.1 Gas phase mass balance

Utilizing the series CSTR approximation reduces the system of partial differential mass balances for each stage in the average channel to a series of ordinary differential equations (ODEs), one for each tracked species i in a mixture containing n components ($i = 1, 2, 3 \dots n$) that is present in each stage

$$[F C_{i,f}] - [F C_i] - [k_{i,m} (C_i - C_{i,s}) V] = \left[\frac{dN_i}{dt} \right] \quad (3.1)$$

where

F (m^3 / s) is the volumetric time varying flow rate through the reactor,

$C_{i,f}$ ($\text{moles} / \text{m}^3$) = concentration of species i at the reactor inlet at time t ,

C_i (moles / m^3) = concentration of species i in the bulk gas and at each stage outlet at time t ,

$C_{i,s}$ (moles / m^3) = concentration of species i at the washcoat surface in each stage at time t ,

$k_{i,m}$ (1 / s) = volumetric mass-transfer coefficient of species i across the boundary layer in each stage,

V (m^3) = the volume of each stage,

N_i (moles) = the number of moles of species i in each stage at time t ,

t (s) = time ($t \geq 0$).

For purposes of time integration, the initial condition in each stage is set to $C_i = C_{i,0}$ at $t = 0$, which is the experimentally measured inlet concentration of each species at the beginning.

For each constant volume stage, Equation 3.1 can be rewritten as

$$\frac{1}{\tau} [C_{i,f} - C_i] - [k_{i,m} (C_i - C_{i,s})] = \left[\frac{dC_i}{dt} \right] \quad (3.2)$$

where τ (s) = V / F is the average gas residence time in each stage. The first term in Equation 3.2 represents the time rate of change of species i across the reactor volume. The second term represents the time rate of transport of species i to the catalyst surface (at the stage wall), which depends on the mass transfer coefficient $k_{i,m}$, which varies for each species, and the concentration gradient between the gas phase concentration C_i and the concentration of species i at the surface of the washcoat $C_{i,s}$.

The volumetric mass-transfer coefficient, $k_{i,m}$, can be determined from dimensionless Sherwood number (Sh) correlations such as that from [94, 96, 97]

$$Sh_i = Sh_0 \left\{ 1 + 0.095 Re Sc_i \frac{Dh}{L} \right\}^{0.45} \quad (3.3)$$

where

$Sh_0 = 3.66$ is the initial reference Sherwood number for gas-wall mass transfer at the channel entrance,

Re = the Reynolds number,

Sc_i = the Schmidt number of species i ,

Dh (m) = characteristic hydraulic diameter of the channel,

L (m) = respective axial distance from the channel entrance.

The time varying solution for species concentrations at the exit of each stage that results from integration of the species mass-balances provides the inlet conditions for each succeeding stage.

3.4.2 Solid phase mass balance

Since the reaction kinetics for catalysts are typically based on surface concentrations, one is still faced with accounting for concentration gradients between the bulk gas and washcoat surface in TWC simulations. As summarized above, the gas-solid interface at the wall is treated as a discontinuity and separate species balances are written for gas and solid phases. The species concentrations in each phase are related through boundary-layer mass transfer coefficients and the pseudo-steady state approximation, which is based on the assumption of very rapid development of the boundary layer concentration gradients which is consistent with the recognition that the mass of the boundary layer near the wall is very small in comparison to the bulk fluid and solid surface concentrations. Thus the species concentration gradients in the boundary layer should rapidly reach a near steady-state condition very quickly relative to changes in the bulk gas and solid surface. This makes it possible to relate the bulk and surface concentrations using the so-called pseudo-steady-state approximation, in which the rates of transport for each species between the bulk gas and washcoat are equated with the net surface reaction rate [94].

The key relationship for boundary layer mass transfer for each reacting species i in a mixture containing n components ($i = 1, 2, 3 \dots n$)

$$\left[\begin{array}{c} \text{moles transported} \\ \text{to catalyst surface} \end{array} \right] = \left[\begin{array}{c} \text{moles reacted} \\ \text{at catalyst surface} \end{array} \right] \quad (3.4)$$

which for reactor volume can be expressed as

$$k_{i,m} (C_i - C_{i,s}) V = V \sum_k R_{i,s}^k \quad (3.5)$$

where $R_{i,s}^k$ (moles / m³ s) is the surface reaction rate of species i (depleting or generation) in the k -step chemical reaction, expressed in terms of the reactor volume. The reactor volume, V , cancels from both sides to give

$$k_{i,m} (C_i - C_{i,s}) = \sum_k R_{i,s}^k. \quad (3.6)$$

The surface reaction rate for species i in the k -step chemical reaction is typically to be determined by the Arrhenius rate law

$$R_{i,s}^k = A_i^k e^{\left(\frac{-Ea_i^k}{R_g T_s}\right)} C_{j,s}^m C_{i,s}^n \quad (3.7)$$

where

A_i^k (moles^{1-m-n} / m^{3(1-m-n)} s) = the Arrhenius kinetic pre-exponential factor in the k -step chemical reaction involving species i ,

Ea_i^k (kJ / mole) = the Arrhenius activation energy in the k -step chemical reaction involving species i ,

R_g (kJ / mole K) = the ideal gas constant,

T_s (K) = the washcoat temperature,

$C_{j,s}$ (moles / m^3) is the instantaneous washcoat concentrations of species j that react with species i in each reaction,

$C_{i,s}$ (moles / m^3) = instantaneous concentrations of species i at the washcoat surface,

m = the reaction order for species j ,

n = the reaction order for species i .

By combining Equations 3.6 and 3.7, the concentration of i at the surface $C_{i,s}$ can be related to the bulk gas concentration C_i , given the reaction kinetic parameters, the solid temperature T_s , and the concentrations of other species on the surface $C_{j,s}$

$$k_{i,m} (C_i - C_{i,s}) = \sum_k A_i^k e^{\left(\frac{-Ea_i^k}{R_g T_s}\right)} C_{j,s} C_{i,s}. \quad (3.8)$$

By using semi-implicit numerical methods for integrating the above differential mass balances with simultaneous updates of all the species concentrations at each time step, ORNL researchers have found that the above relationships can be used to produce suitable approximations of the transient species profiles in TWC monolith reactors [92].

3.4.3 Gas and solid phase energy balances

In general, the TWC computational model utilized in the present study can also account for time-varying temperature changes due to chemical reactions and heat transfer by also integrating the differential energy balances for each CSTR stage in conjunction with integrating the differential mass balances. For the gas phase in each stage, this results in

$$\rho_g c_{pg} \frac{dT_g}{dt} = h_g a_s (T_s - T_g) + \frac{\rho_g c_{pg} (T_{g,i} - T_g)}{\tau_g} \quad (3.9)$$

where

ρ_g (kg / m^3) = the mass density of the bulk gas calculated using the ideal-gas law,

c_{pg} ($J / kg K$) = the specific heat of the bulk gas (assumed constant),

T_s (K) = the washcoat surface temperature at time t ,

T_g (K) = the bulk gas temperature at time t ,

T_{gi} (K) = the exhaust temperature at the stage inlet at time t and

h_g ($W / m^2 K$) = the heat transfer coefficient between the bulk gas and washcoat.

The initial condition is $T_g = T_{g,0}$ at $t = 0$ and based on the starting experimentally measured temperature.

Likewise, for the solid (washcoat) phase, the differential heat balance in each stage results in

$$\rho_s c_{ps} \frac{dT_s}{dt} = h_g a_s (T_g - T_s) - h_a a_w (T_s - T_o) - \sum_k R_k \Delta H_k \quad (3.10)$$

where

ρ_s (kg / m^3) = the mass density of the washcoat and wall, assumed constant,

c_{ps} ($J / kg K$) = the specific heat of the washcoat and wall, function of T_s ,

T_s (K) = the washcoat surface temperature at time t ,

T_g (K) = the bulk gas temperature at time t ,

T_o (K) = the ambient temperature, assumed to be constant,

h_g ($W / m^2 K$) = the heat transfer coefficient between the bulk gas and washcoat,

h_a ($W / m^2 K$) = the heat transfer coefficient between the ambient environment and wall/washcoat,

R_k and ΔH_k = the specific rate and enthalpy (heat release) of the k reaction.

The non-idealities of the experimental engine setup made determination of the appropriate external boundary conditions for the differential energy balances

uncertain, however, due to the complexity of the TWC wall construction and the effective heat transfer coefficient between the TWC wall and external environment. The variation in the effective surface reaction enthalpies with composition also presented additional computational complexities, so it was decided, for this study, that direct utilization of the measured experimental temperatures in the simulations (as explained in the discussion of results below) would avoid the potential errors introduced by integrating the differential heat and mass balances simultaneously with uncertain values for the external heat transfer and surface reaction heat parameters.

CHAPTER 4

RESULTS AND DISCUSSION

Successful implementation of passive SCR NO_x reduction depends on efficient and selective NH₃ generation on the TWC catalyst and utilization over the SCR catalyst. Since at least a brief period of fuel-rich engine operation is necessary for NH₃ generation, some combination of engine management and emissions system control is needed to optimize fuel consumption. The experiments described here were designed to reveal the major engine and catalyst-based factors affecting NH₃ production. Section 4.1 deals with the role of engine fueling (quantified in terms of λ) in controlling selectivity for NH₃ production by the TWC; Section 4.2 summarizes insights into the NH₃ formation mechanism on TWCs using a computational model; Section 4.3 discusses additional experimental observations regarding the effects of TWC formulation on NH₃ production; Section 4.4 summarizes experimental observations about the effects of spark timing, exhaust gas recirculation, and valve timing on engine-out NO_x emissions, and TWC NH₃ production; Section 4.5 considers the potential importance of acceleration events in minimizing fuel consumption. Finally, all the above points are considered to analyze the expected fuel economy benefits of passive SCR NO_x control in transient drive cycles. The analysis also reveals key remaining technical challenges to be addressed for optimizing exhaust system design and control.

4.1 Experimental study of engine fueling impact on TWC NH₃ generation

Engine fueling state is typically classified into one of three modes based on the air-fuel equivalence ratio (i.e., the ratio of the actual air/fuel ratio to the stoichiometric ratio of the air required to completely consume the fuel): stoichiometric ($\lambda = 1$), rich ($\lambda < 1$) and lean ($\lambda > 1$). An example of the observed trends in steady-state engine-out gas species with λ for the experimental engine is shown in Figure 4.1. The standard deviation (measurement of error) in

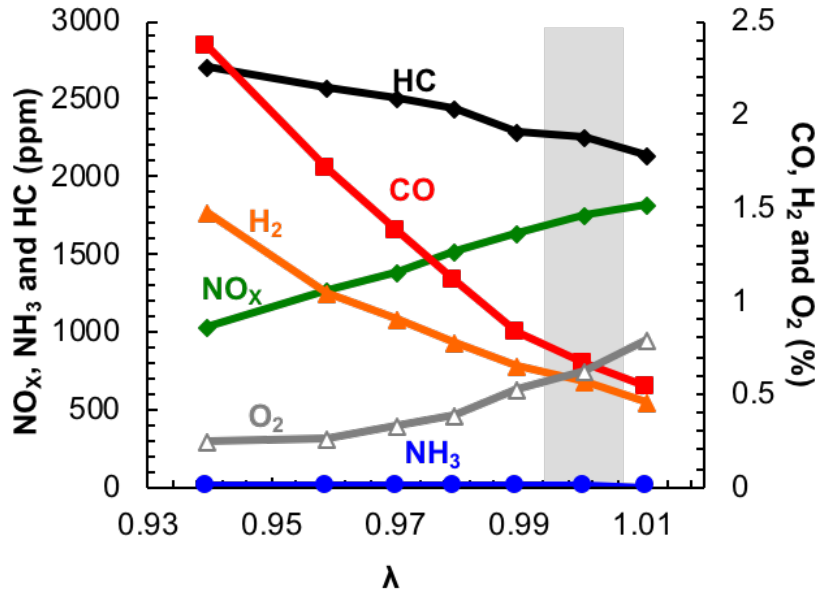


Figure 4.1 Steady-state variation of the experimental engine-out exhaust gas composition with λ . Engine operating conditions: 2000 rpm and 8 bar BMEP.

measured emissions during steady-state engine operation is less than 2% and omitted on all of the steady-state plots for clarity. The depicted trends are consistent with those typically observed for SI gasoline engines [9, 10, 80]. For $\lambda < 1$, the mixture of fuel and air in the combustion chamber contains excess fuel, and there is insufficient oxygen to burn all the fuel, resulting in unburned hydrocarbons and partial oxidation products (CO and H₂) in the exhaust. As depicted in Figure 4.1, as the amount of excess fuel increases, the CO and H₂ emissions increase sharply with decreasing λ . The HC emissions are less sensitive with λ because they are primarily formed in the crevices of the combustion chamber and the oil film layer [98, 99], where the flame cannot propagate. On the other hand, CO and H₂ emissions form at the flame front where there is incomplete oxidation of HCs, and their concentrations rise rapidly as the mixture becomes richer. NO_x forms in the hot burned zone, after the flame front, and its formation strongly depends on temperature and oxygen

concentration. As the mixture is enriched, the temperature and the oxygen concentration fall, and NO_x emissions decrease.

As exhaust passes through a TWC, the gas composition changes substantially. Figure 4.2 shows example of experimental emission concentrations measured in the exhaust at the outlet of the Pd-only TWC (Malibu-1) as a function of λ . These species concentration trends are typical for precious metal containing TWCs [9, 10, 79, 80]. As shown in Figure 4.2, at stoichiometric exhaust conditions ($\lambda = 1$), the TWC is very effective in converting the three regulated pollutants (NO_x , CO and HC) to CO_2 , H_2O and N_2 . At these conditions, there are enough reductants to reduce NO_x and enough oxygen to oxidize CO and HC. The range of λ near stoichiometric, where high conversion efficiencies of these three pollutants are achieved, is narrow, and with a slight

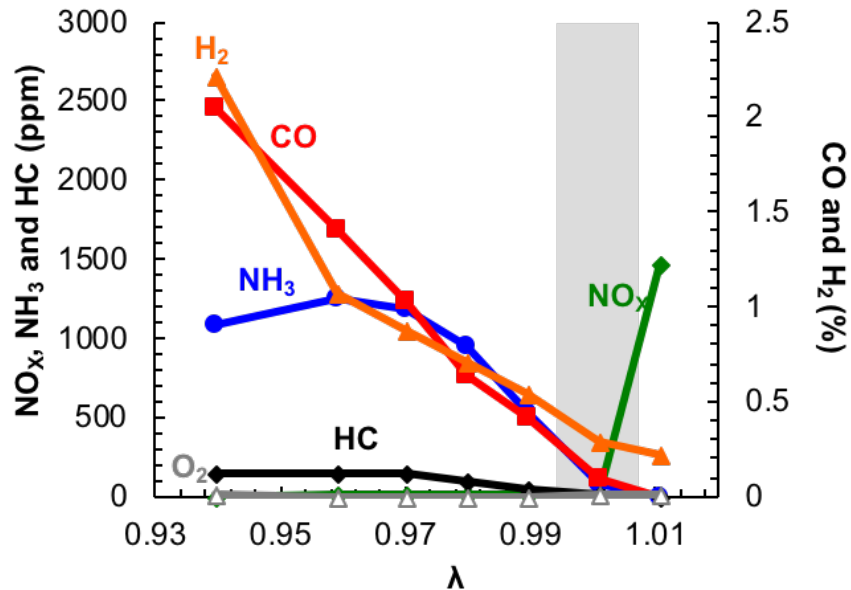
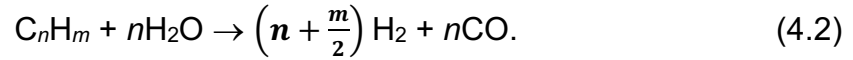


Figure 4.2 Steady-state variation of exhaust gas composition with λ at TWC outlet. Engine operating conditions: 2000 rpm and 8 bar BMEP; Pd-only Malibu-1 TWC; TWC at 731 °C inlet temperature and 64000 h^{-1} space velocity.

deviation from the stoichiometric exhaust conditions, the catalyst can no longer effectively convert all three species.

In the fuel-lean exhaust ($\lambda > 1$), the TWC is still able to remove CO and HC emissions, but the excess oxygen prevents NO_x reduction. In the fuel-rich exhaust ($\lambda < 1$), all the oxygen present gets consumed by oxidation reactions. As the mixture gets richer, there is insufficient oxygen present in the exhaust for complete oxidation of CO and HC, and their concentrations increase. In a TWC, CO and HC can also be consumed through water gas shift (WGS) and steam reformation reactions to produce H₂



Under rich conditions, the NO_x reduction activity is high. The TWC converts the incoming NO_x to a mixture of N₂ and NH₃, with selectivity to NH₃ strongly depending on λ . To further illustrate this point, the concentration of NO_x and NH₃ at the TWC inlet and outlet locations, respectively, are plotted in Figure 4.3 along with the NO_x conversion efficiency and the NH₃ yield in Figure 4.4. Quantitative measures of NO_x conversion and the NH₃ yield are defined by

$$\text{NO}_x \text{ conversion} = \frac{\text{Inlet NO}_x - \text{Outlet NO}_x}{\text{Inlet NO}_x} * 100\%, \quad (4.3)$$

$$\text{NH}_3 \text{ yeild} = \frac{\text{Outlet NH}_3}{\text{Inlet NO}_x + \text{Inlet NH}_3 + 2 * \text{Inlet N}_2\text{O}} * 100\%. \quad (4.4)$$

As the engine fueling mixture gets richer, NH₃ generation sharply increases as λ decreases until it reaches a maximum at $\lambda = 0.96$, and then slowly

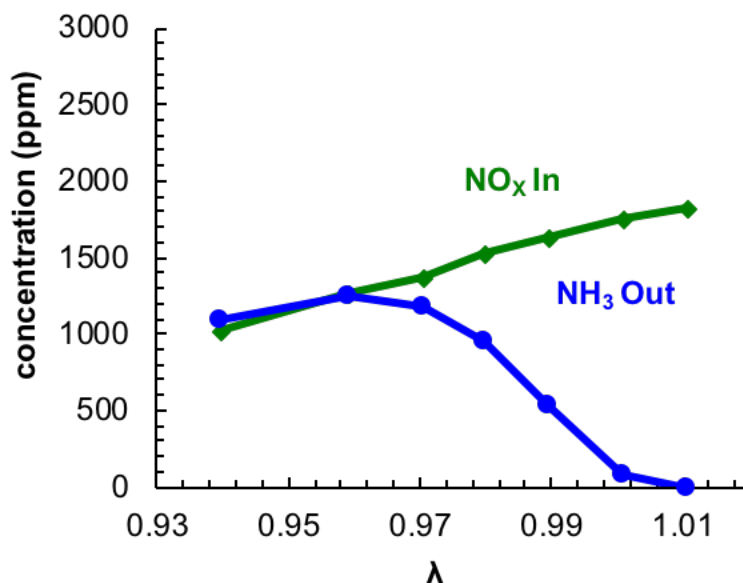


Figure 4.3 Steady-state concentrations of TWC inlet NO_x and outlet NH_3 as a function of λ . Engine operating conditions: 2000 rpm and 8 bar BMEP; Pd-only Malibu-1 TWC; TWC at 731 °C inlet temperature and 64000 h^{-1} space velocity.

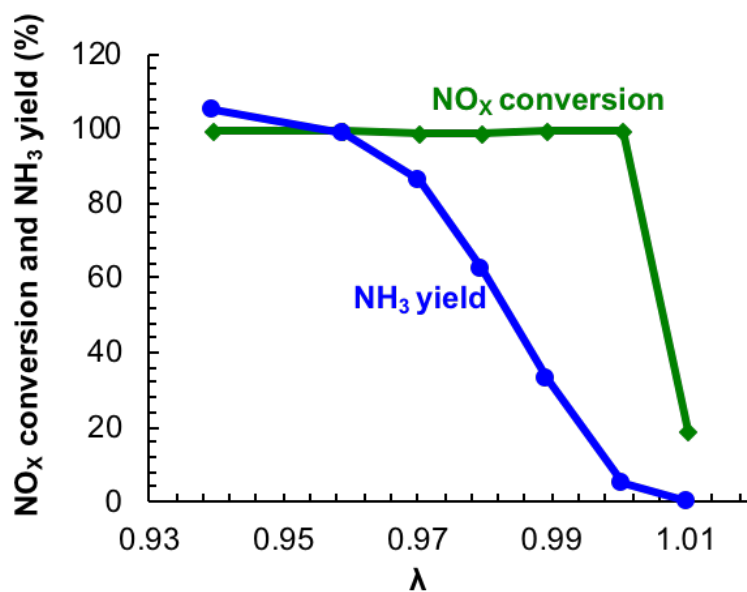


Figure 4.4 Steady-state TWC NO_x conversion and NH_3 yield as a function of λ . Engine operating conditions: 2000 rpm and 8 bar BMEP; Pd-only Malibu-1 TWC; TWC at 731 °C inlet temperature and 64000 h^{-1} space velocity.

decreases with lower λ values as the feed gas NO_x level decreases. The TWC inlet NO_x and outlet NH_3 concentrations are identical for $\lambda < 0.96$, indicating that all of the NO_x is converted to NH_3 , which can also be seen from the equal NO_x conversion and NH_3 yield. These results indicate that in this λ region NH_3 formation is limited by the NO_x availability at the catalyst inlet. For $\lambda > 0.96$, on the other hand, the NH_3 generation is limited by the reductant availability, as illustrated by the decreasing concentration of HC, CO and H_2 in Figure 4.1, and as λ increases the reduction of NO_x becomes selective to N_2 .

The results shown in Figures 4.1-4.4 reveal the critical importance of λ in determining steady-state engine-out and TWC-out gas compositions. Thus, in the context of a passive SCR emission control system, occasional engine fueling excursions to rich λ will be necessary to generate significant levels of NH_3 . Two important but competing processes need to be considered in this process: richer mixtures generate reductants that in turn control NH_3 selectivity, but richer mixtures also decrease engine-out NO_x , thus, limiting the amount of NO_x available for NH_3 generation in the TWC. In addition, rich operation consumes excess fuel and this penalty must be considered when selecting the appropriate engine operating strategies. The expected fuel penalty relative to the stoichiometric engine operation for running the engine rich is illustrated in Figure 4.5. The fuel penalty at the point of maximum NH_3 production ($\lambda = 0.96$) is 3.0 % and decreases with leaner λ .

The steady-state λ sweep results presented above demonstrate that NH_3 generation is limited by the air-fuel equivalence ratio and the amount of inlet NO_x . Thus, λ and engine-out NO_x emissions are primary engine parameters affecting NH_3 generation, which in turn must be accounted for in utilizing passive SCR. The efficiency of NH_3 generation in a passive SCR approach would, therefore, benefit from high engine out NO_x during rich operation and high NH_3 selectivity, which suggests that it is important to keep λ as close to stoichiometric as possible. These issues are discussed further below.

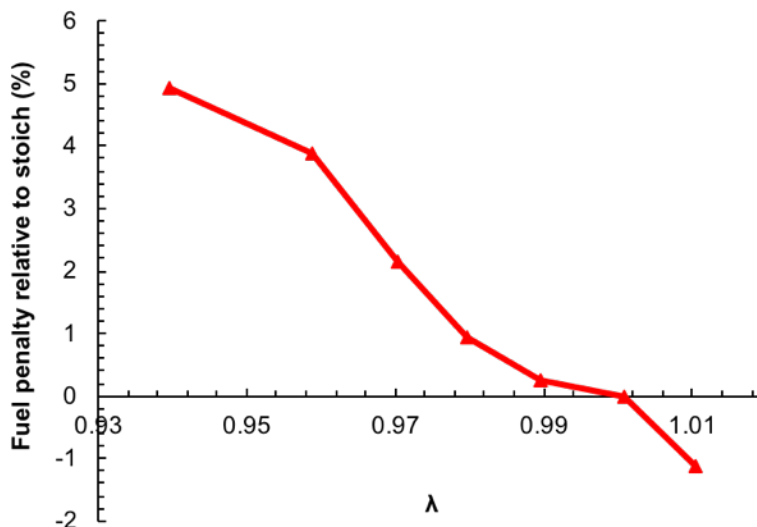
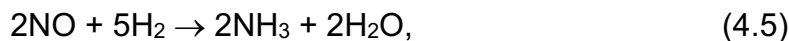


Figure 4.5 Fuel consumption penalty relative to stoichiometric operation as a function of λ . Engine operating conditions: 2000 rpm and 8 bar BMEP; Pd-only Malibu-1 TWC; TWC at 731 °C inlet temperature and 64000 h⁻¹ space velocity.

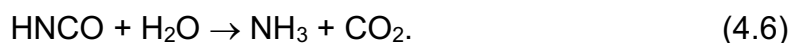
4.2 Computational study of TWC NH₃ formation mechanisms

One direct pathway for NH₃ formation is through the reaction between NO and H₂



H₂ is always present to some degree in SI engine exhaust as a result of incomplete combustion, and, as was shown in Figure 4.1, the H₂ concentration in exhaust is very sensitive to λ .

NH₃ can also be formed from the intermediate species isocyanic acid (HNCO), which hydrolyzes to NH₃ and CO₂ [68, 72-76]

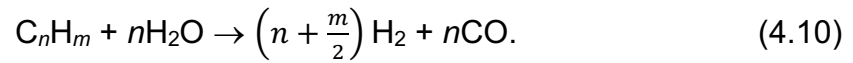


Although the isocyanate mechanism has been observed for some precious metal catalysts in the presence of CO and H₂O, it was assumed in this study that direct reaction with H₂ is the dominant route of NH₃ formation relevant to the engine exhaust conditions studied here. This is consistent with other recent studies of TWC kinetics reported in the literature [68-70].

According to the stoichiometry in Equation 4.5, a H₂ to NO_x ratio of 2.5 is required to completely convert all of the incoming NO_x to NH₃. When there is a deficiency in H₂ (H₂/NO_x < 2.5), NO_x can be converted to other products, including N₂O and N₂ [68, 71]



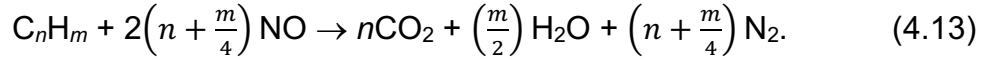
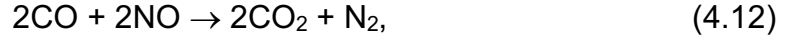
In the presence of multiple reductants and oxidants, H₂ and NO_x are also consumed or produced by other competing reactions in the catalyst. H₂ can be formed over TWC through the water gas shift and steam reforming reactions



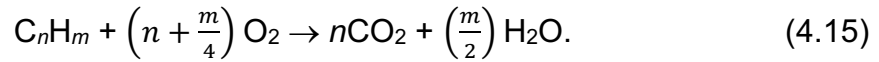
O₂, which can still be present in exhaust after rich combustion, can remove H₂ via oxidation reaction



CO and HC compete with H₂ for NO_x reduction



And they can also be consumed by oxidation



The relative rates of formation of NH_3 (Equation 4.5) vs. other co-products in the presence of multiple reductants (CO and HC) and oxidants (O_2) reflects the catalyst selectivity. For optimal NH_3 production, NO_x needs to react preferentially with H_2 and not CO or HC, while H_2 needs to react preferentially with NO_x and not O_2 .

In order to quantify NH_3 generating potential in the presence of multiple reductants and oxidizers, it is sometimes useful to consider an “equivalent H_2 ” level, which is the sum of the reductants (H_2 , CO and HC) minus the oxidizers (O_2) [100]

$$\text{H}_{2,\text{eq}} = \text{H}_2 + \text{CO} + 2.9 \text{ HC} - 2\text{O}_2. \quad (4.16)$$

The stoichiometric coefficients in Equation 4.16 are based on the oxidation reactions in Equations 4.11, 4.14 and 4.15, where the C_nH_m was assumed to be $\text{CH}_{1.8}$ based on the C to H ratio of the gasoline fuel. Using this metric to quantify NH_3 generating potential, the $\text{H}_{2,\text{eq}}$ to NO_x ratio at the TWC inlet corresponding to the λ sweep experiments presented in Section 4.1 is shown in Figure 4.6. For all

of the rich conditions, the $H_{2,eq}$ to NO_x ratios are significantly greater than 2.5. Thus, at the catalyst inlet, there should be enough reductants to convert all of the NO_x to NH_3 , and higher engine out reductant concentrations at richer λ result in higher NH_3 yields (see Figure 4.4). In the present experiments however, much higher $H_{2,eq}$ to NO_x ratios ($\gg 2.5$) were needed to achieve high NH_3 yields. To better resolve the complex kinetic interactions controlling NH_3 formation and reductant consumption processes in a TWC, the computational model with simplified global kinetics summarized in Section 3.4 was adapted to predict trends that could be compared with the experimental observations.

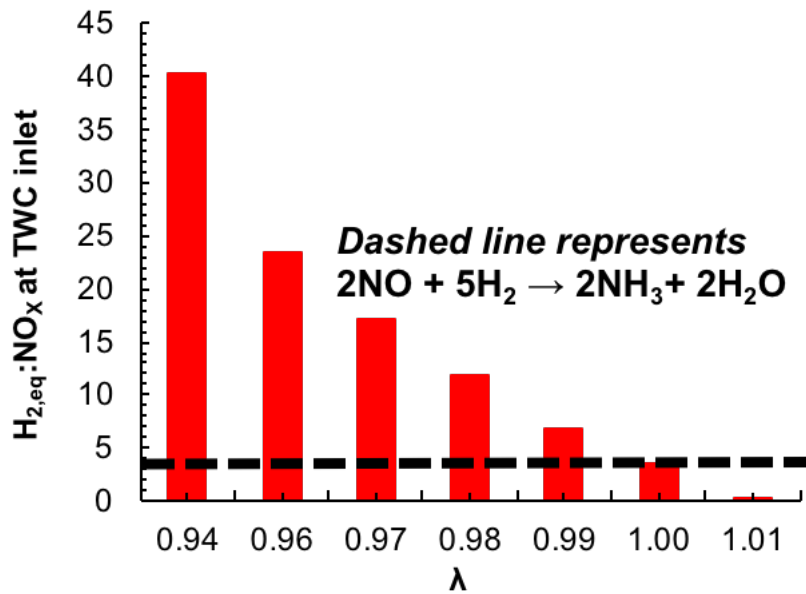
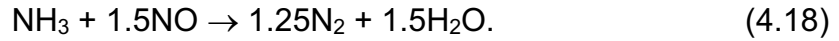
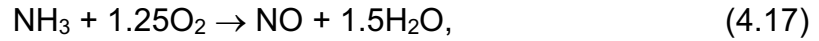


Figure 4.6 Variation of experimental $H_{2,eq}$ to NO_x ratio with λ at TWC inlet during steady state engine operation. Engine operating conditions: 2000 rpm and 8 bar BMEP.

Briefly, the computational TWC model was implemented in MATLAB with recent values for the kinetic rate constants available in the literature. In addition to a small number of key reactions and species, the MATLAB version included differential heat and mass balances for all species and the effects of catalyst size, geometry, location and precious metal content. While a number of kinetic

study results are available in the literature for NH₃ formation over precious metal catalysts, some of these were specific to lean NO_x trap catalysts [36, 101], which have important formulational differences with TWCs. Perhaps more relevant are the studies with TWCs, including [68-70, 95, 102]. The study by Gong [95], in particular, was found to be based on similar experimental conditions and the same Pd-only TWC as the one utilized in this dissertation. Therefore, the TWC kinetics from Gong were used to define kinetic rate parameters for computational simulations here.

In addition to the reactions already listed above, the computational model also included reactions for NH₃ oxidation by NO and O₂



In total, the computational model included 12 reactions and 9 species: H₂, CO, C₃H₆, C₃H₈, O₂, NO, NH₃, H₂O and CO₂. Since the engine exhaust contains many different hydrocarbons, the HC kinetics was approximated by dividing the HCs into two groups: one with high rate of catalytic activity and the other with a low rate. According to the scheme of Gong [95], the highly reactive HCs are identified with propene (C₃H₆), while the less reactive are identified with propane (C₃H₈). The Pd-only TWC studied here did not have a dedicated oxygen storage component such as Ce₂O₃ and, therefore, the oxidation-reduction mechanism for an oxygen storage component Ce₂O₃ was not included. In summary, the kinetic parameters recommended by Gong [95] that were used for computational simulations in the present study are listed in Table 4.1. It should be noted that these expressions represent global reaction rates based on Langmuir-Hinshelwood principles [95], where inhibition effects by accumulated surface species are accounted for by the denominator terms.

Table 4.1 Pd-only TWC kinetic parameters and reaction rate expressions [95].

No	Reaction	Rate Expression	A (mole/ mole-site·s)	E (J/mole)
1	$\text{CO} + 0.5\text{O}_2 \rightarrow \text{CO}_2$	$[\text{CO}]^*[\text{O}_2]/G_1$	$3.54 \cdot 10^{12}$	110450
2	$\text{C}_3\text{H}_6 + 4.5\text{O}_2 \rightarrow 3\text{CO}_2 + 3\text{H}_2\text{O}$	$[\text{C}_3\text{H}_6]^*[\text{O}_2]/G_1$	$5.92 \cdot 10^{13}$	120530
3	$\text{C}_3\text{H}_8 + 5\text{O}_2 \rightarrow \text{CO}_2 + 4\text{H}_2\text{O}$	$[\text{C}_3\text{H}_8]^*[\text{O}_2]/G_1$	$9.40 \cdot 10^{14}$	165160
4	$\text{H}_2 + 0.5\text{O}_2 \rightarrow \text{H}_2\text{O}$	$[\text{H}_2]^*[\text{O}_2]/G_1$	$1.67 \cdot 10^{12}$	111450
5	$\text{CO} + \text{NO} \rightarrow \text{CO}_2 + 0.5\text{N}_2$	$[\text{CO}]^*[\text{NO}]/G_1$	$2.15 \cdot 10^9$	52374
6	$\text{C}_3\text{H}_6 + 9\text{NO} \rightarrow 3\text{CO}_2 + 3\text{H}_2\text{O} + 4.5\text{N}_2$	$[\text{C}_3\text{H}_6]^*[\text{NO}]/G_1$	$8.24 \cdot 10^9$	80063
7	$\text{H}_2 + \text{NO} \rightarrow \text{H}_2\text{O} + 0.5\text{N}_2$	$[\text{H}_2]^*[\text{NO}]/G_1$	$4.64 \cdot 10^8$	69237
8	$\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$	$([\text{CO}]^*[\text{H}_2\text{O}] - [\text{H}_2]^*[\text{CO}_2])/G_2/G_1$	$1.80 \cdot 10^5$	56720
9	$\text{C}_3\text{H}_6 + 3\text{H}_2\text{O} \rightarrow 3\text{CO} + 6\text{H}_2$	$[\text{C}_3\text{H}_6]^*[\text{H}_2\text{O}]/G_1$	$6.43 \cdot 10^6$	53620
10	$\text{NH}_3 + 1.25\text{O}_2 \rightarrow \text{NO} + 1.5\text{H}_2\text{O}$	$[\text{NH}_3]^*[\text{O}_2]/G_1$	$3.00 \cdot 10^{13}$	139300
11	$\text{NO} + 2.5\text{H}_2 \rightarrow \text{NH}_3 + \text{H}_2\text{O}$	$[\text{NO}]^*[\text{H}_2]/G_1$	$7.39 \cdot 10^9$	44720
12	$\text{NH}_3 + 1.5\text{NO} \rightarrow 1.25\text{N}_2 + 1.5\text{H}_2\text{O}$	$[\text{NH}_3]^*[\text{NO}]/G_1$	$1.50 \cdot 10^{10}$	121400

The inhibition terms in the rate expressions listed in Table 4.1 are

$$G_1 = \left(1 + 4.314 e^{\frac{485}{T_s}} [\text{CO}] + 1.289 e^{-\frac{166}{T_s}} [\text{C}_3\text{H}_6]\right)^2 \left(1 + 2.147 * 10^{-4} e^{\frac{10163}{T_s}} [\text{CO}]^2 [\text{C}_3\text{H}_6]^2\right) \left(1 + 8.699 * 10^5 e^{-\frac{3685}{T_s}} [\text{NO}]\right), \quad (4.19)$$

$$G_2 = e^{\left(\frac{-41034 + 44.19T_s - 5.553 * 10^{-3}T_s^2}{8.314T_s}\right)}. \quad (4.20)$$

The basic functionality of the MATLAB model was validated with experimental measurements for a core sample of the same TWC catalyst on an

automated bench-scale flow reactor [91] at Oak Ridge National Laboratory. The controlled experiments performed on the bench flow reactor were designed to mimic conditions observed on the engine. Transient cycling experiments were performed. In these experiments, the exhaust alternated between rich ($\lambda=0.95$ - 0.99) and lean ($\lambda=2.00$) operating conditions and were designed to be representative of the conditions a passive SCR system would encounter under realistic driving conditions. The rich/lean cycling bench reactor experimental conditions are summarized in Table 4.2. The experiments were performed with the furnace temperature set at 300, 400, 500 or 600 °C. The results of the cycling experiments performed on the engine will be covered in more detail in later sections.

Table 4.2 Bench flow reactor TWC inlet conditions during rich/lean cycling experiments.

	Lean	Rich				
λ	2.0	0.95	0.96	0.97	0.98	0.99
O ₂ (%)	10	0.96	1.02	1.07	1.13	1.17
CO (%)	0.2	2.0	1.8	1.6	1.4	1.2
H ₂ (%)	0	1.0	0.9	0.8	0.7	0.6
NO (ppm)	360	600	600	600	600	600
C ₃ H ₈ (ppm C ₁)	1900	3000	3000	3000	3000	3000
H ₂ O (%)	6.6	11	11	11	11	11
CO ₂ (%)	6.6	11	11	11	11	11
TWC SV (hr ⁻¹)	45000	27000	27000	27000	27000	27000

The experimental time-resolved feed data collected at the TWC inlet were used as the inlet conditions for the model. Predicted exhaust species obtained with the model were compared with the effluent experimental measurements downstream of the TWC. In order to focus on dynamics of chemical reactions occurring within the catalyst and isolate the effects of solving the energy equations for axial and temporal temperature variation, the experimental

temporal temperature measured at the catalyst inlet, middle and outlet locations were used instead.

The measured and simulated emissions of NO, NH₃, C₃H₈ and CO at the TWC inlet and outlet during the rich/lean cycling experiments on the bench flow reactor with rich $\lambda = 0.96$ are shown in Figure 4.7. Model simulations using the kinetic rate parameters from Gong [95] exhibited good performance in predicting the emission trends observed experimentally. During the lean phase of the cycle, the TWC is effective in oxidizing CO and C₃H₈ but unable to reduce NO_x in the presence of excess oxygen, and the model captures these trends accurately. As the gas mixture changes to rich, the experimental effluent NO_x concentration rapidly decreases to zero. After a short delay, NH₃ increases instantaneously to steady-state levels. The measured delay in NH₃ production coincide with high initial CO and C₃H₈ conversion. Subsequently, the measured CO emissions began to slip, while the catalyst still exhibited high C₃H₈ activity. As the catalyst transitions between lean and rich conditions, it undergoes oxidation and reduction processes, which contributes to the observed delay in NH₃ production and high initial CO conversion. The model does not include a mechanism for simulating this process, and, therefore, predicted a step change in effluent NO, NH₃, CO and C₃H₈ concentrations. However, including an oxygen storage mechanism in the model can improve the accuracy of predicting the rich/lean transients. The simulated rich C₃H₈ consumption is significantly under-predicted with the current kinetics. The current reaction mechanism does not include the steam reforming reaction of C₃H₈ (Equation 4.10), which can be an important reaction for C₃H₈ consumption in the oxygen deficient environment. The kinetic model includes the reaction for steam reforming of C₃H₆ only, and it is expected that the accuracy of C₃H₈ consumption would improve with inclusion of the C₃H₈ steam reforming reaction.

To summarize the observed influence of λ and temperature on NH₃ production, and C₃H₈ and CO consumptions during the rich phase of the cycle, NH₃ yields, and CO and C₃H₈ conversions are plotted for experimental and

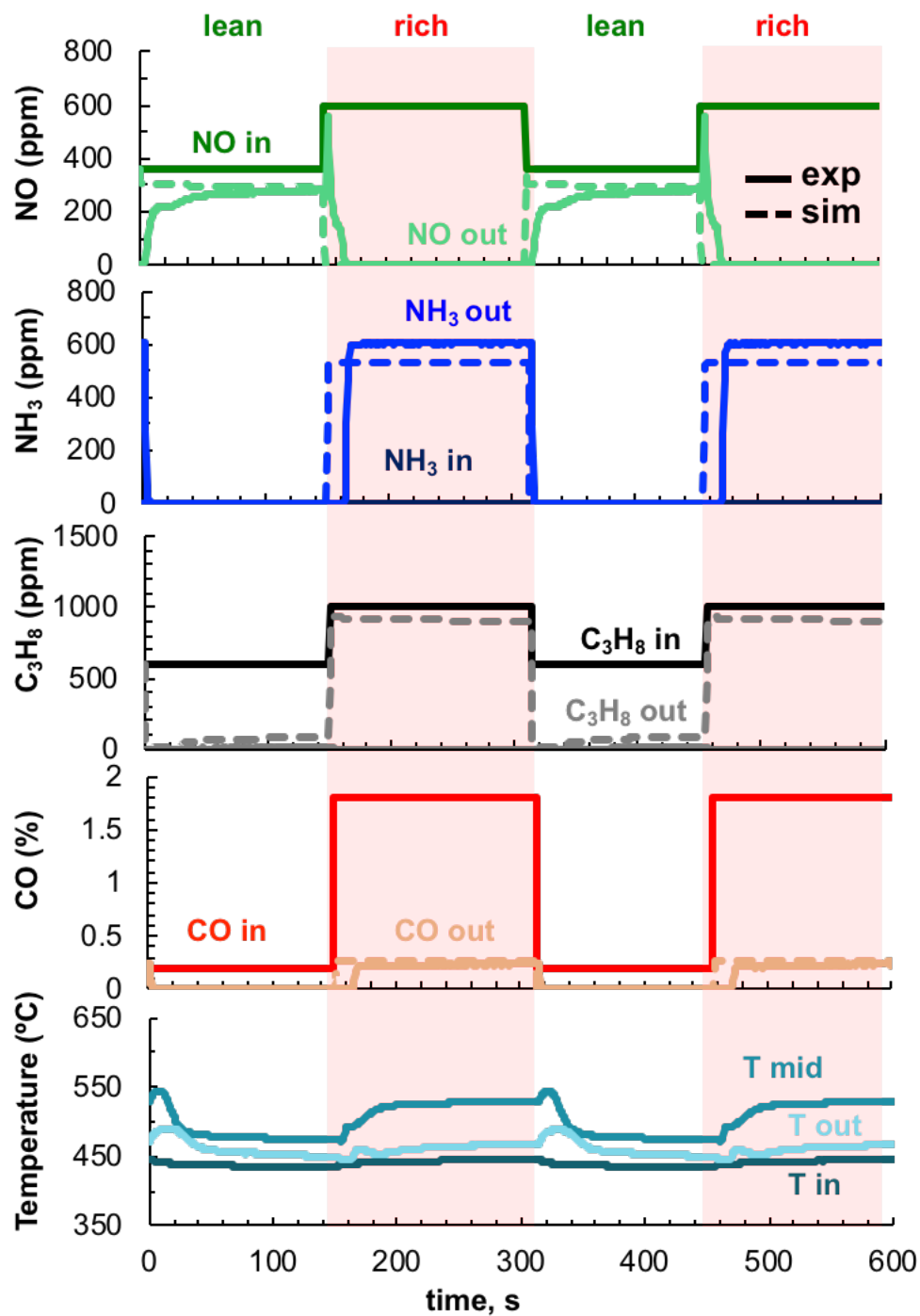


Figure 4.7 Experimental (solid lines) and simulated (dashed lines) emissions at TWC inlet and outlet as a function of time during lean/rich cycling experiments with rich $\lambda=0.96$ on bench flow reactor.

simulated results in Figure 4.8, 4.9 and 4.10, respectively. In general, the model captures the experimental trends observed from λ and temperatures dependencies, however, the reaction constants for water gas shift, steam reforming and NO reduction reactions most likely need to be adjusted to improve the accuracy of the model.

The model was also validated against rich/lean cycling experiments performed on the engine. The engine operating conditions for these experiments are summarized in Table 4.3.

Table 4.3 Average TWC inlet conditions during rich/lean cycling experiments performed on engine.

	Lean	Rich
Engine Speed, rpm	2000	2000
Engine Load BMEP, bar	2	2
λ	2.10	0.96-0.99
inlet T, °C	443	468
SV, h⁻¹	45000	28000

The measured and simulated emissions of NO, NH₃, HC and CO at the TWC inlet and outlet during rich/lean cycling experiments performed on the engine with rich $\lambda = 0.97$ are compared in Figure 4.11. Model simulations predicted the emission trends observed experimentally on the engine even more accurately than for the bench flow reactor. The delay in NH₃ production described above was not observed during engine evaluations. This, in part, is conjectured to be due to the response of the engine during the lean-to-rich transition. During the transition, the engine controller temporarily overshoots the target λ to a much richer one. This overshoot produces a large flux of reductants that quickly reduces the catalyst and minimizes the delay in onset of NH₃

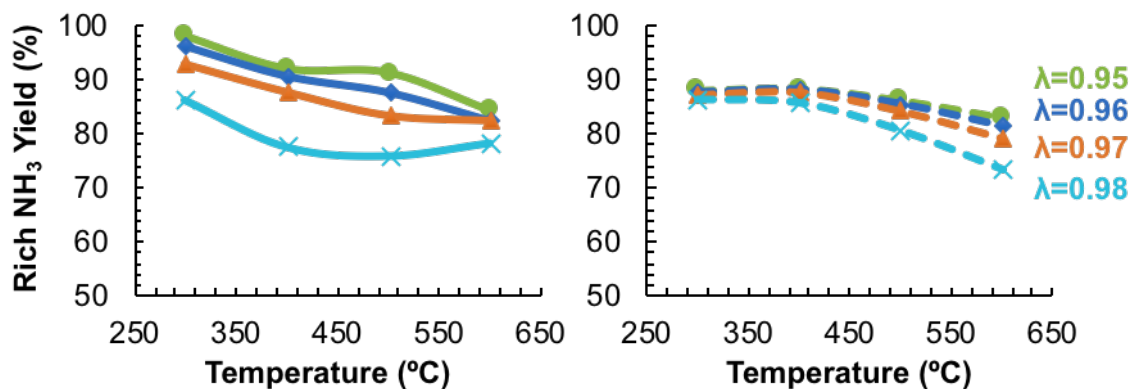


Figure 4.8 Experimental (solid lines) and simulated (dashed lines) of NH₃ yield at different λ s as a function of furnace temperature during rich phase of rich/lean cycling experiments on bench flow reactor.

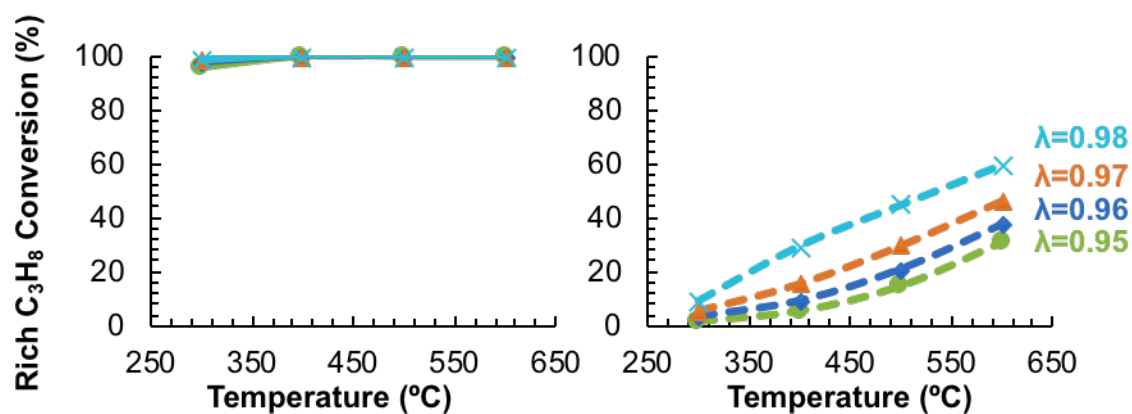


Figure 4.9 Experimental (solid lines) and simulated (dashed lines) of C₃H₈ conversion at different λ s as a function of furnace temperature during rich phase of rich/lean cycling experiments on bench flow reactor.

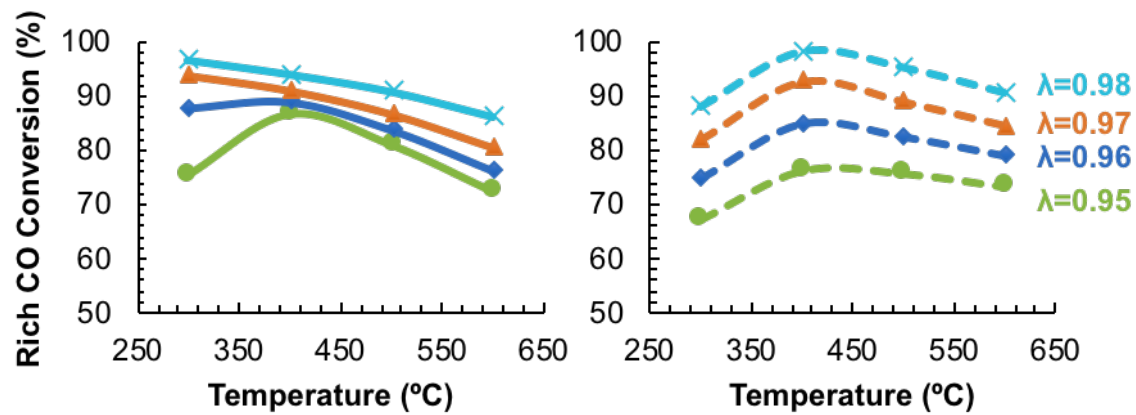


Figure 4.10 Experimental (solid lines) and simulated (dashed lines) of CO conversion at different λ s as a function of furnace temperature during rich phase of rich/lean cycling experiments on bench flow reactor.

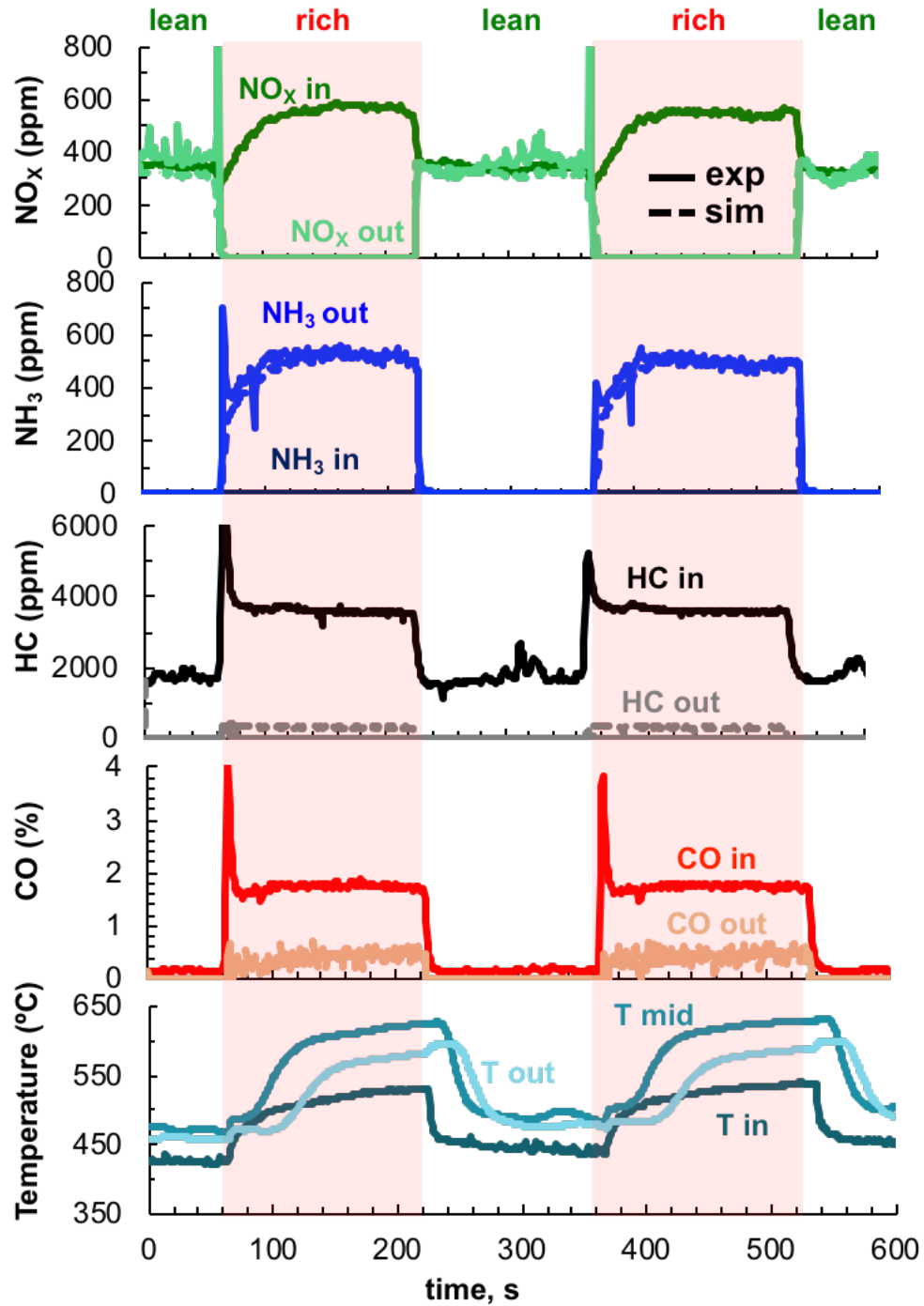


Figure 4.11 Experimental (solid lines) and simulated (dashed lines) emissions at TWC inlet and outlet as a function of time during lean/rich cycling experiments with rich $\lambda=0.97$ on engine.

production. NH_3 increases instantaneously as soon as the engine switches to rich operation.

The MATLAB model appears to track NO_x and NH_3 effluent concentrations accurately as well as CO consumption. In addition, the model seems to predict the consumption of total HC more accurately for the engine than the bench reactor. This may be because the HCs coming out from the engine are split into highly reactive C_3H_6 and less reactive C_3H_8 for simulation. The split was adjusted in the simulations described here until good agreement with experimental data was obtained. Another potential improvement might be made by adding other HC reactions such as steam reforming of C_3H_8 to the kinetics.

Overall, the relative success of the MATLAB TWC model evaluated in this study for simulating the bench reactor and engine experiments implies that the global reaction kinetics proposed by Gong [95] are a reasonable approximation of the competing processes involved in generating and consuming NH_3 in TWCs. Thus, models based on these kinetics would appear to be useful tools for guiding the optimization of passive SCR operating strategies and evaluating improved catalyst formulations. One key area where improvements are needed, however, would be in the reaction kinetics for HC species.

4.3 Experimental study of a modified TWC formulation on NH_3 generation

As discussed in Section 4.1, the fuel efficiency benefits of NH_3 passive SCR NO_x control are maximized by achieving high NH_3 selectivity at λ values as close to stoichiometric as possible. Even though NO_x reduction to NH_3 is known to occur in TWCs under reducing conditions [62-67], commercial TWCs have not been designed to optimize this function. In fact, NH_3 formation over current TWCs has often been considered undesirable because of the toxicity and impact of NH_3 on the formation of particulate matter [63]. Thus, much of the previous research on TWC functionality has focused on suppressing NH_3 formation. This has recently begun to change, however, resulting in more studies of how NH_3

generation can be promoted under some circumstances over precious metal catalysts [68, 71, 72, 82, 84, 91, 103, 104]. Some of these studies have revealed that Pd-based catalysts exhibit higher selectivity of NO_x conversion to NH_3 than Pt or Rh-based catalysts, while Rh catalysts exhibit the least selectivity toward NH_3 [68, 81, 82, 105-107].

One common feature of commercial TWCs is the inclusion of an oxygen storage component (OSC) in the washcoat, which assist three-way functionality under near stoichiometric conditions. The oxygen storage component (OSC) also enhances water-gas-shift and steam-reforming reactions and is the basis for on-board diagnostics [78-80]. Since passive SCR relies on periodic switching between lean and rich operation, the presence of oxygen storage can potentially delay NH_3 formation on the transition from lean to rich [83, 103], which would require longer rich time to generate desired levels of NH_3 and lead to higher fuel penalty. On the other hand, it has been proposed that including a NO_x storage component (NSC) in the washcoat can extend lean operation by storing NO_x on the TWC [84, 103] and, thereby, preserving NH_3 inventory on the downstream SCR catalyst and reducing the fuel penalty of the passive SCR system. The potential impact of OSC and NSC components in TWCs motivated the inclusion of experimental measurements in this study comparing a Pd-only TWC with a TWC having both OSC and NSC functionalities (referred to as TWC-NSC). The primary motivation for this part of the present study was not to identify an optimal TWC formulation for passive SCR system, but rather to identify the major roles played by OSC and NSC components on NH_3 generation functionality.

The steady-state λ sweep results described above in Section 4.1 demonstrate that NH_3 selectivity is driven by the air-fuel equivalence ratio. These results were for the Pd-only TWC with the engine operating at 2000 rpm 8 bar BMEP. To assess the effects of the TWC-NSC on NH_3 selectivity under steady-state reducing conditions, the λ sweep experiments were performed over a number of engine speed and load conditions providing a wide range of exhaust temperatures and space velocities, and results for the two TWC formulations are

compared. The engine operating points with corresponding catalyst inlet temperatures and space velocities are shown in Table 4.4 and Table 4.5 for TWC-NSC and Pd-only TWC, respectively.

Table 4.4 Steady-state operating points for λ sweep experiments with TWC-NSC.

Speed (rpm)	BMEP (bar)	TWC inlet T (°C)	TWC SV (h ⁻¹)
2000	3	436	39000
2000	5	514	50000
2000	8	625	71000

Table 4.5 Steady-state operating points for λ sweep experiments with Pd-only TWC.

Speed (rpm)	BMEP (bar)	TWC inlet T (°C)	TWC SV (h ⁻¹)
2000	2	524	27000
2000	4	582	38000
2000	8	712	64000

To summarize the observed influence of λ on the NH₃ production during steady-state rich operation, the measured net NH₃ yield at different λ values is plotted in Figure 4.12 and Figure 4.13 for TWC-NSC and Pd-only TWC, respectively, for each of the operating points evaluated, where the NH₃ yield is defined by Equation 4.4. For each TWC formulation NH₃ yield increased as the exhaust mixture became richer for all of the engine operating points, reaching greater than 90% yield at $\lambda = 0.96$. These results imply that these TWCs are able to produce high NH₃ yields at slightly rich conditions over a wide range of

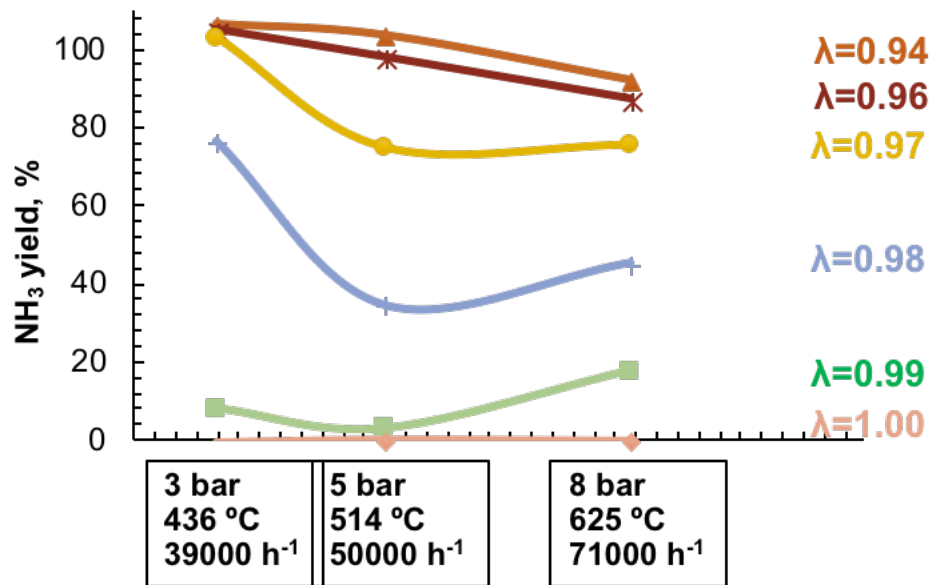


Figure 4.12 Steady-state NH_3 yield at different λ values at 2000 rpm engine speed and 3, 5, and 8 bar BMEP engine loads; TWC-NSC.

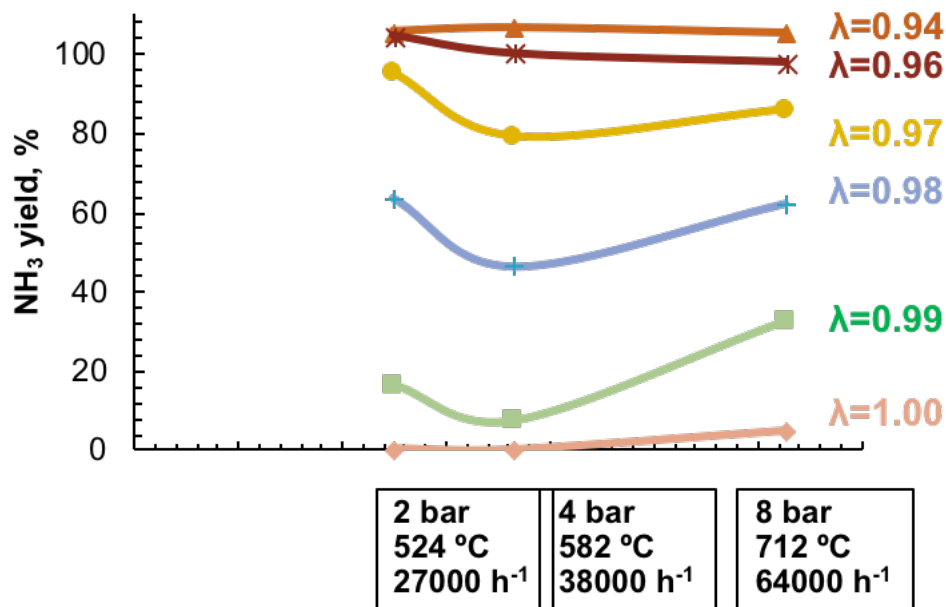


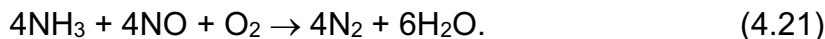
Figure 4.13 Steady-state NH_3 yield at different λ values at 2000 rpm engine speed and 2, 4, and 8 bar BMEP engine loads; Pd-only TWC.

range with $\lambda \leq 0.96$. A decreasing trend in the NH_3 yield was observed at higher engine loads and is speculated to be due to increasing exhaust temperatures. This trend is consistent with results from flow reactor studies showing decrease in NH_3 yield at higher temperatures [82, 84, 91]. It is conjectured that the much steeper decrease in NH_3 yield for the TWC-NSC is most likely due to presence of multiple active material in the washcoat that are less selective to NH_3 . For example, Pt and Rh present in the TWC-NSC are less active in NH_3 production than Pd and most likely contribute to the observed decrease in NH_3 yield.

The steady-state NH_3 measurements summarized here imply that NH_3 can be generated under reducing conditions for a wide range of engine exhaust conditions, with NH_3 selectivity and yield affected by the air-fuel equivalence ratio and catalyst formulation. However, for steady-state operation, the TWC remains in a reduced state, which does not necessarily reflect the transients in passive SCR strategies, where the TWC undergoes repeated oxidation and reduction. The redox state is known to change NH_3 formation behavior [83, 103], particularly for a TWC that contains oxygen and NO_x storage materials as in the case of TWC-NSC.

To assess the effects of utilizing a TWC catalyst with oxygen and NO_x storage components under realistic operating conditions, a series of rich/lean cycling experiments were also performed. These experiments were designed to be representative of the conditions a passive SCR system would encounter under real world driving conditions. For the experiments presented in this section, the engine speed and load were fixed for both lean and rich portions of the cycle. These experiments are referred to as fixed load cycling and are designed to represent “cruise” driving conditions. A feedback control strategy based on cumulative NH_3 produced by the TWC during rich operation and NO_x emissions during lean operation was implemented with the engine controller. In this manner, control set points for cumulative NH_3 production and $\text{NH}_3 : \text{NO}_x$ ratio allowed control of the lean/rich cycle timing. A $\text{NH}_3 : \text{NO}_x$ ratio of one (1) was

used for these cycling experiments, reflecting the theoretical stoichiometry for NO reduction by the standard SCR reaction given as



The rich cycle timing was such that the NH_3 produced during rich operation would use approximately 25 % of the NH_3 storage capacity of an SCR catalyst (0.027 mol per liter of catalyst) and was selected based on prior flow reactor measurements. The NH_3 capacity utilization was intentionally kept low to prevent NH_3 slip during the lean phase, which was observed in flow reactor experiments with higher NH_3 loadings.

The measured emissions of NO_x , NH_3 , N_2O , CO and HC at the TWC inlet and outlet during the fixed load experiments with rich $\lambda = 0.96$ are shown in Figure 4.14 and Figure 4.15 for TWC-NSC and Pd-only TWC, respectively. The average inlet temperature of the TWC-NSC in the lean phase was 393 °C. At this temperature, the NO_x storage properties of the TWC appeared to affect the delay in the NO_x breakthrough, which started early in the lean phase and steadily increased until it reached the feed gas NO_x level after approximately 2 minutes. As the cumulative NO_x reached the set threshold, the engine switched to rich operation, causing the effluent NO_x concentration to drop to zero for the duration of the rich phase. After a short delay, a sharp transient increase in NH_3 production during the early onset of rich engine operation was observed, which quickly decreased to the expected steady-state levels of NO_x that would be expected if all of the feed gas NO_x were converted to NH_3 . This sharp NH_3 production was not observed on a Pd-only TWC as shown in Figure 4.15. It also appeared that the stored NO_x in the TWC-NSC was converted to NH_3 upon switching to rich conditions.

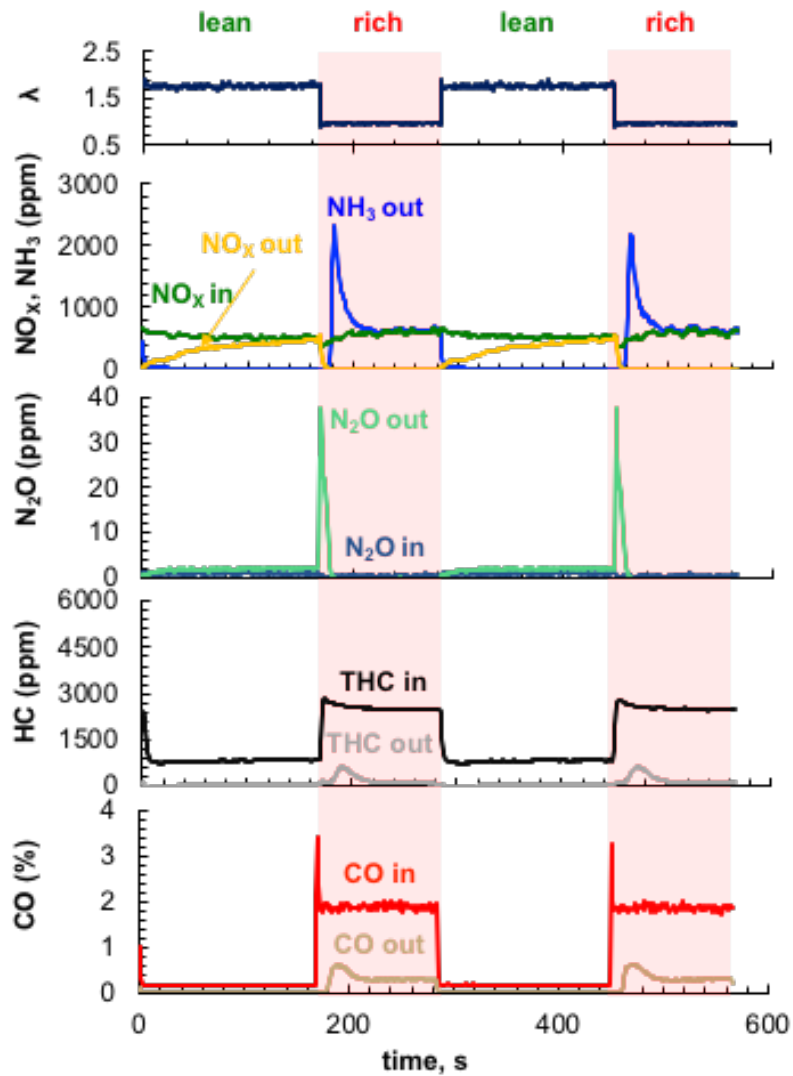


Figure 4.14 λ and emissions at TWC inlet and outlet as a function of time during fixed load lean/rich cycling experiments at 2000 rpm 3 bar BMEP. Lean conditions: 2000 rpm 3 bar BMEP, $\lambda=1.7$, ave. $T_{\text{in}} = 393\text{ }^{\circ}\text{C}$, $\text{SV}=45000\text{ h}^{-1}$. Rich conditions: 2000 rpm 3 bar BMEP, $\lambda=0.96$, ave. $T_{\text{in}}=412\text{ }^{\circ}\text{C}$, $\text{SV}=29000\text{ h}^{-1}$. TWC-NSC.

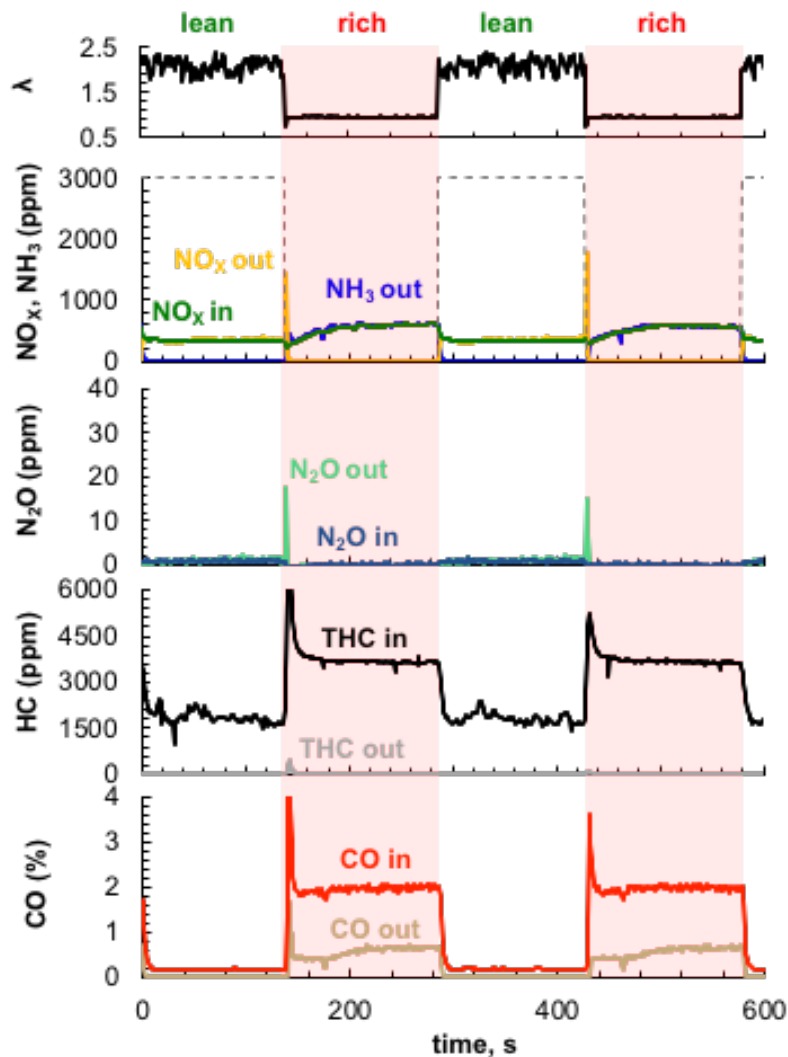


Figure 4.15 λ and emissions at TWC inlet and outlet as a function of time during fixed load lean/rich cycling experiments at 2000 rpm 2 bar BMEP. Lean conditions: 2000 rpm 2 bar BMEP, $\lambda=2.0$, ave. $T_{\text{in}} = 459^\circ\text{C}$, $\text{SV}=42000\text{ h}^{-1}$. Rich conditions: 2000 rpm 2 bar BMEP, $\lambda=0.96$, ave. $T_{\text{in}}=463^\circ\text{C}$, $\text{SV}=28000\text{ h}^{-1}$. Pd-only TWC.

The large NH_3 production for the TWC-NSC in the experiments described above was much higher compared to results from bench flow reactor studies of the same catalyst [91] as depicted in Figure 4.16.

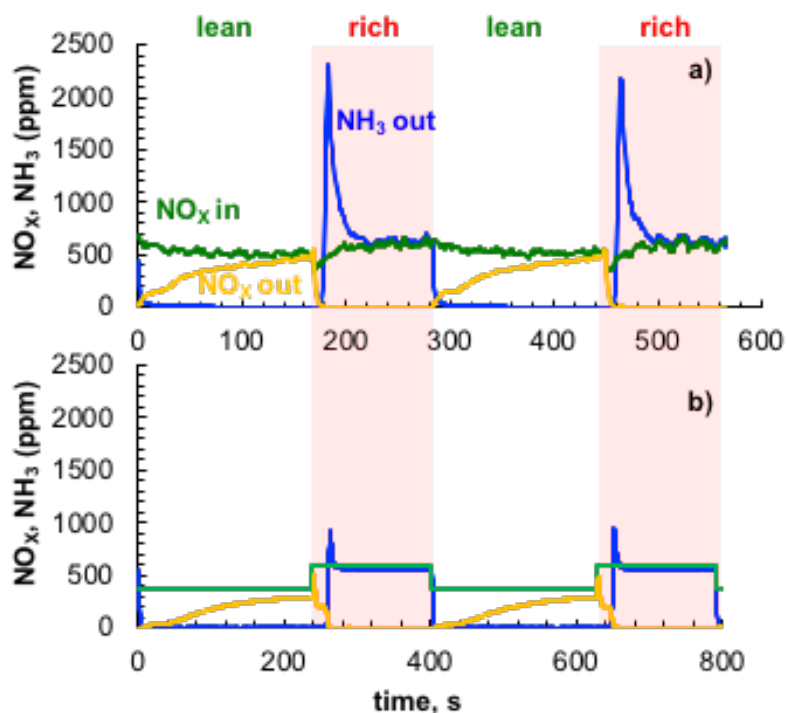


Figure 4.16 NO_x and NH_3 emissions at TWC-NSC inlet and outlet as a function of time during fixed load lean/rich cycling experiments on (a) engine and (b) bench flow reactor.

It is conjectured that the sharp increase in NH_3 production is at least partly due to the response of the engine during the 1 second transient that occurs when the fueling switches from lean to rich. During this 1 second transient, the engine controller temporarily overshoots the target $\lambda = 0.96$ to much richer $\lambda \sim 0.90$ as depicted in Figure 4.17. This overshoot produces a large flux of reductants, as indicated by the spikes in engine out CO and HC emissions in Figure 4.14. The increased availability of reductants would be expected to drive the reduction of the stored NO_x to NH_3 . Such rapid NH_3 production might be beneficial during transient driving conditions with limited time at high load operation. This

transient, often referred to as a “tip-in”, could be a primary contributor to the size of the peak of NH_3 production during rich operation. The tip-in event is similar to a 2-step purge proposed by Theis et al. [83], where, upon switching to rich, a relatively rich λ is employed initially to remove the oxygen stored on a TWC followed by a less rich λ to continue generating NH_3 . The 2-step purge was shown to decrease the delay in NH_3 production while minimizing the CO slip and fuel consumption.

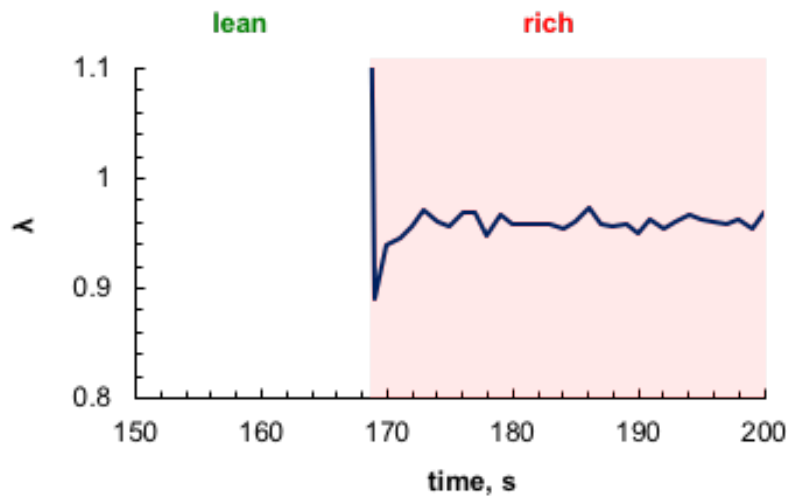


Figure 4.17 λ trace during the transition from lean to rich during fixed load lean/rich cycling experiments at 2000 rpm 3 bar BMEP. Transitioning from lean $\lambda=1.7$ to rich $\lambda=0.96$.

In the present experiments, the measured delay in NH_3 production in the TWC-NSC coincided with high initial CO and HC conversion. Subsequently, it appeared that when oxygen and NO_x were depleted from the catalyst surface and reducing conditions established, the CO and HC emissions began to slip. At richer λ , the delay was minimized, and the onset of NH_3 production and CO and HC slip began immediately on the transition from lean to rich. In the absence of the tip-in, the delay in NH_3 production was significant as depicted in Figure 4.16 for the flow reactor, where a delay of 20 seconds was observed under similar

exhaust conditions. The prolonged delay in NH_3 formation might be expected to have negative effects on the fuel efficiency of a passive SCR system. This further emphasizes the importance of the tip-in in the case of a TWC with oxygen or NO_x storage components, where extra reductants are needed to remove the stored oxygen or NO_x and reduce the delay in NH_3 production. However, in the case of the Pd-only TWC, an excessively rich λ is unnecessary and probably should be avoided in order to minimize the CO and HC slip and fuel consumption.

It was observed that the delay in NH_3 production in the TWC-NSC also coincided with N_2O formation. A 40 ppm N_2O spike was observed simultaneously with the switch from lean to rich and was followed by the onset of NH_3 production. This reveals the complexity of the NO_x reduction mechanism on the catalyst surface when the TWC transitions through oxidation/reduction conditions [36, 37]. Once the reducing conditions are established, N_2O emissions were not observed for the duration of the rich phase; small traces of N_2O (~2ppm) are detected during the lean portion of the cycle. The peak and width of the N_2O spike decreased at higher temperatures (as in the case of 2000 rpm 5 bar BMEP cycling) and richer λ , respectively. N_2O formation is an important issue due to its high global warming potential (298 times that of CO_2) [108]. Even low levels of N_2O can have a high impact on greenhouse gas emissions, and if not carefully controlled, N_2O can reduce the overall benefit of passive SCR.

To summarize the influence of rich λ on the NH_3 production during the fixed load lean/rich cycling experiments, engine out NO_x concentrations entering the TWC and corresponding exiting NH_3 concentrations during the rich phase are plotted in Figure 4.18 and Figure 4.19 for TWC-NSC and Pd-only TWC, respectively. As shown in Figure 4.18, the NH_3 concentration exiting the TWC-NSC significantly exceeded the inlet NO_x concentration under rich conditions. At 2000 rpm 3 bar BMEP fixed load cycling, the average inlet catalyst temperature in lean phase was 393 °C. At this temperature, it appeared that some of the NO_x

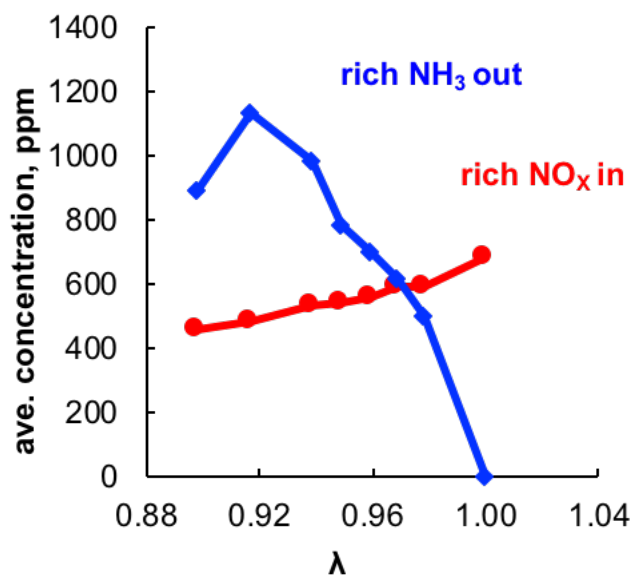


Figure 4.18 Engine out NO_x concentration entering (“rich NO_x in”) the TWC-NSC and corresponding existing NH_3 concentration (“rich NH_3 out”) during rich phase of fixed load lean/rich cycling experiments at 2000 rpm 3 bar BMEP.

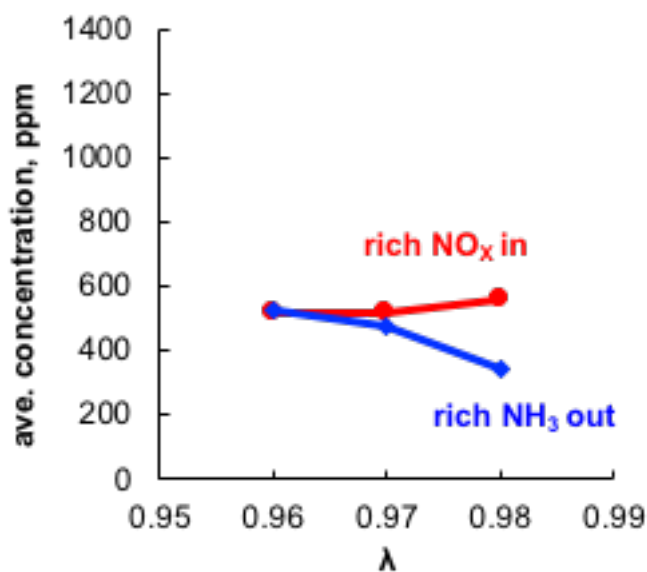


Figure 4.19 Engine out NO_x concentration entering (“rich NO_x in”) the Pd-only TWC and corresponding existing NH_3 concentration (“rich NH_3 out”) during rich phase of fixed load lean/rich cycling experiments at 2000 rpm 2 bar BMEP.

was stored, and upon switching to rich conditions, some of the stored NO_x was converted to NH_3 . The conversion of the stored NO_x to NH_3 increased with richer λ as shown in Figure 4.20, reaching 100 % stored NO_x to NH_3 conversion at $\lambda = 0.92$. In the Pd-only TWC, NH_3 production in the rich phase was limited by the NO_x available at the catalyst inlet and the NH_3 production profile would be expected to behave similar to the one observed under steady-state λ sweeps.

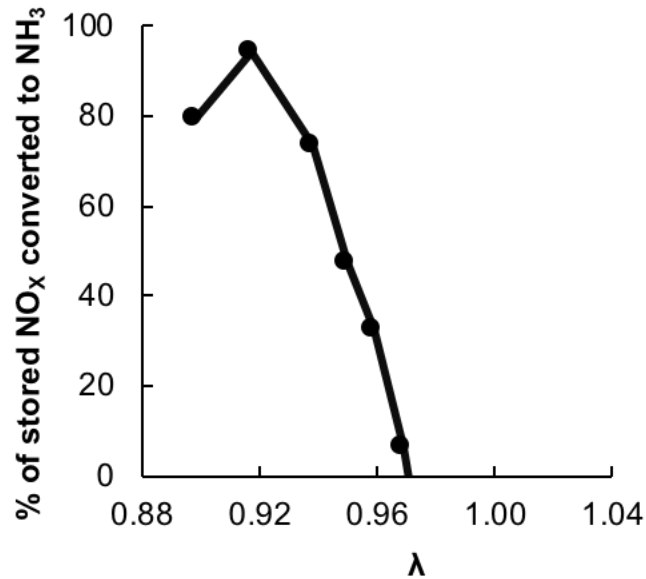


Figure 4.20 Stored NO_x to NH_3 conversion during rich phase of fixed load lean/rich cycling experiments at 2000 rpm 3 bar BMEP over the TWC-NSC, lean average $T_{\text{in}} = 393^\circ\text{C}$ and rich average $T_{\text{in}} = 412^\circ\text{C}$.

The above results indicate that NSC offers two benefits for passive SCR. First, by storing NO_x during the lean phase, it enables longer lean operation for a fixed inventory of NH_3 , and second, by converting some of the stored NO_x to NH_3 , shorter rich times are needed to produce a fixed dose of NH_3 . Since the fuel penalty associated with passive SCR NO_x control depends on the fraction of time that the engine is running rich rather than lean, both longer lean times and shorter rich times will decrease the passive SCR fuel penalty.

However, these benefits can only be realized when NO_x is stored on the catalyst. The amount of NO_x the TWC-NSC can store decreases at higher temperatures, so the benefit can primarily be realized at low to moderate temperatures (300-500 °C) with little to no benefit at higher temperatures [91]. At higher operating temperatures, where the catalyst shows limited NO_x storage activity, there is no NH_3 production spike at the rich onset, and NH_3 generation is limited to feed gas NO_x concentrations as shown in Figure 4.21. The average inlet catalyst temperature in lean phase was 494 °C for this case, and there was limited NO_x storage at this temperature.

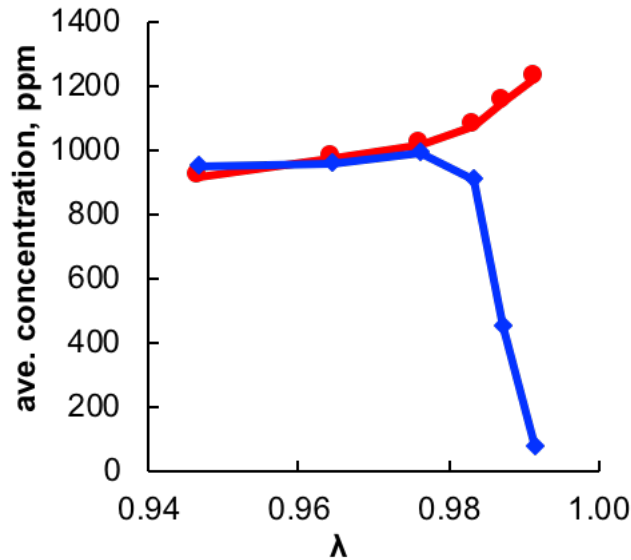


Figure 4.21 Engine out NO_x concentration entering (“rich NO_x in”) the TWC-NSC and corresponding existing NH_3 concentration (“rich NH_3 out”) during rich phase of fixed load lean/rich cycling experiments at 2000 rpm 5 bar BMEP, lean average $T_{\text{in}} = 494$ °C and rich average $T_{\text{in}} = 510$ °C.

The results from the above experiments imply that a TWC with NSC can enable longer lean times and increased NH_3 production with benefits strongly depending on the engine-out temperature and rich λ level. The temperature dictates how much NO_x is stored and rich λ (tip-in in particular) dictates how much and how rapidly stored NO_x is converted to NH_3 .

4.4 Impact of additional engine adjustments to increase engine-out NO_x

For passive SCR NO_x control, increased engine-out NO_x emissions can be beneficial during rich operation because the increased NO_x can be converted to NH₃, which increases SCR potential and reduces rich operating time. This can be accomplished by manipulating specific engine parameters during rich excursions, including exhaust gas recirculation (EGR), valve timing, and spark timing. Of course, these engine changes must be balanced against the associated fuel consumption penalties. In this section, the experimental trends observed for changes in both engine out NO_x emissions and fuel consumption in response to adjustments to EGR, valve timing and spark timing are summarized. The associated implications for passive SCR NO_x control are also discussed.

The effect of steady-state λ on engine out NO_x emissions was discussed in Section 4.1. As was shown in Figure 4.1, as the experimental fueling mixture was enriched, NO_x emissions decreased. NO_x formation strongly depends on temperature and oxygen concentrations. In the rich mixtures, excess fuel prevents full release of the thermal energy of the fuel, thereby reducing the peak cylinder temperature and decreasing NO_x emissions. λ also impacts TWC NH₃ selectivity, so it has an even larger effect on passive SCR performance. As explained below however, even though EGR, valve timing and spark timing have less impact on NH₃ selectivity, their manipulation can be used to boost engine-out NO_x and improve passive SCR performance.

Similar to the steady-state λ sweep experiments described in Section 4.1, experimental sweeps in EGR, valve timing and spark timing were made to quantify how these operating parameters impacted exhaust composition and fuel consumption under steady-state operation. The experimental parameter levels are summarized in Table 4.6. The valve timing is controlled with exhaust camshaft measured in crank angle degrees (CAD).

Table 4.6 Steady-state operating points for EGR, valve timing and spark timing sweep experiments with TWC-NSC.

Speed (rpm)	BMEP (bar)	EGR Rate (%)	Valve Timing (CAD)	Spark Timing (DBTDC)	TWC inlet T (°C)	TWC SV (h ⁻¹)
2000	3	0 - 7	22 - 43	26 - 44	436	39000
2000	5	0 - 5	25 - 43	24 - 42	514	50000
2000	8	-	30 - 43	18 - 28	625	71000

Exhaust gas recirculation is known to significantly affect SI engine-out emissions [9, 10, 109-112]. The recirculated gases increase the inert gas concentration and heat capacity in the cylinder charge mixture, reducing the flame temperature and decreasing NO_x formation. However, increasing EGR can also reduce combustion rate, leading to potential combustion instabilities and increased pumping work, thereby increasing fuel consumption.

EGR can be implemented in two ways: externally (via EGR valve) and internally (via intake and exhaust valve overlap). External EGR employs an electrically activated control valve and a pressure differential between the intake and exhaust ports to draw a portion of the exhaust into the intake, where it mixes with fresh air before entering the combustion chamber. In the present experiments, external EGR was limited to 6 - 7 % by a significant deterioration in combustion at higher levels. But this limit can vary among engines depending on the combustion chamber design, speed and load, and the air-fuel equivalence ratio. EGR control by intake and exhaust valve overlap allows residual gases from each combustion event to remain in the cylinder during successive events, thereby diluting the injected charge. The engine used in this study utilizes both external and internal EGR for emissions control, the effects of both techniques were studied and discussed below.

The observed effect of external EGR on engine-out NO_x at 2000 rpm 5 bar BMEP stoichiometric engine operation ($\lambda = 1$) is illustrated in Figure 4.22.

The OEM EGR level at this operation point is 0 %. As depicted, significant reductions in NO_x were achieved by increasing EGR. However, increasing EGR also increased fuel consumption as shown in Figure 4.23. These experimental trends imply that targeting low EGR levels during rich transients can both increase engine out NO_x and reduce fuel consumption.

Internal EGR is controlled by adjusting the time when intake and exhaust valves are both opened (referred to as valve overlap). Large valve overlap increases the trapped residual gases, resulting in reduced flame temperature and decreased NO_x . The engine used in this study is equipped with a variable valve timing (VVT) mechanism, which allows adjustment of the internal EGR level. The observed effect of VVT on NO_x emissions at 2000 rpm 5 bar BMEP stoichiometric engine operation ($\lambda = 1$) is illustrated in Figure 4.24. The results in this figure are plotted against the exhaust camshaft phase. The OEM camshaft phase at this operating point is at 43 crank angle degrees (CAD). As depicted in the figure, a significant increase in NO_x concentration was achieved by advancing the exhaust camshaft. Advancing the exhaust camshaft also resulted in improved fuel consumption as shown in Figure 4.25. Reduced valve overlap thus tended to increase engine-out NO_x and improve fuel consumption during steady-state rich fueling.

Since SI engine combustion is initiated by the spark, spark timing can clearly affect the resulting emissions and efficiency [10, 109, 113]. Advancing the timing (igniting earlier in the compression stroke) increases peak cylinder pressure, resulting in higher temperature and NO_x emissions. Figure 4.26 illustrates the observed trends in steady-state NO_x emissions as a function of spark timing in the present experiments. In this case, the engine was operating at a 2000 rpm and 5 bar BMEP. The OEM spark timing at this operating point is 28 crank angle degrees before top dead center (DBTDC). As shown in the figure, NO_x emissions steadily increased with advancing spark timing. But as

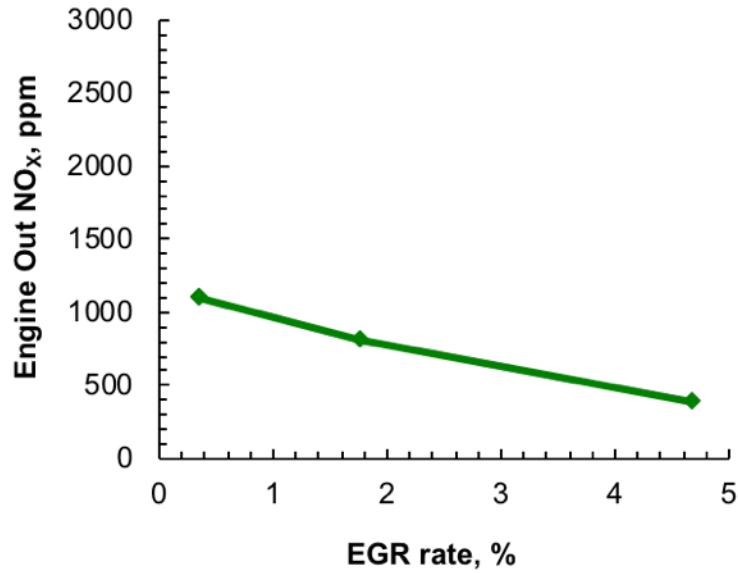


Figure 4.22 Steady-state variation of the experimental engine out NO_x emissions with external EGR. Engine operating conditions: 2000 rpm and 5 bar BMEP, $\lambda=1$.

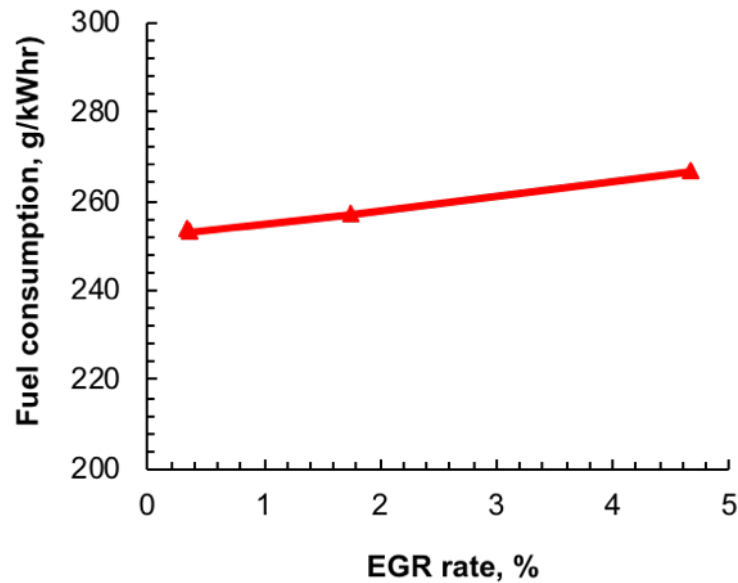


Figure 4.23 Steady-state variation of the fuel consumption with external EGR. Engine operating conditions: 2000 rpm and 5 bar BMEP, $\lambda=1$.

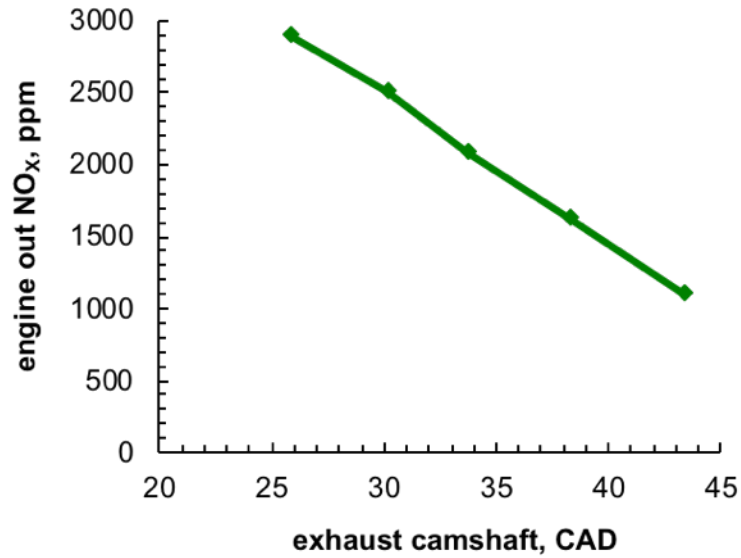


Figure 4.24 Steady-state variation of the experimental engine out NO_x emissions with internal EGR via variable valve timing. Engine operating conditions: 2000 rpm and 5 bar BMEP, $\lambda=1$.

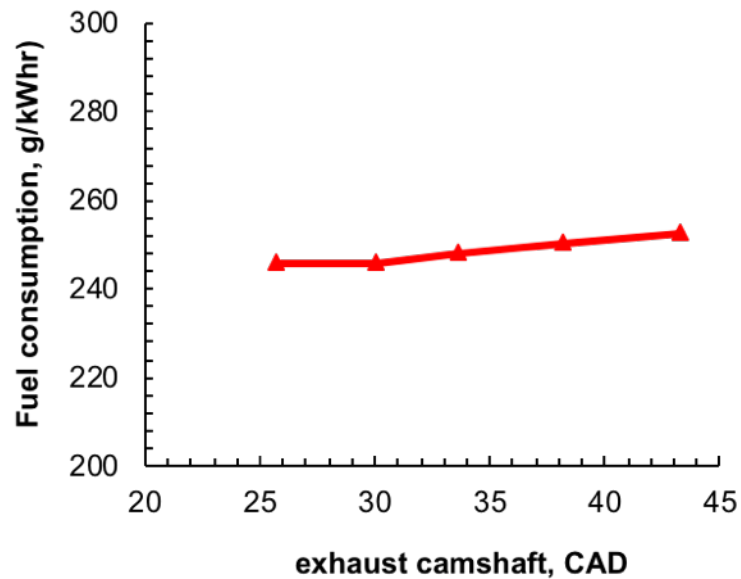


Figure 4.25 Steady-state variation of the fuel consumption with internal EGR via variable valve timing. Engine operating conditions: 2000 rpm and 5 bar BMEP, $\lambda=1$.

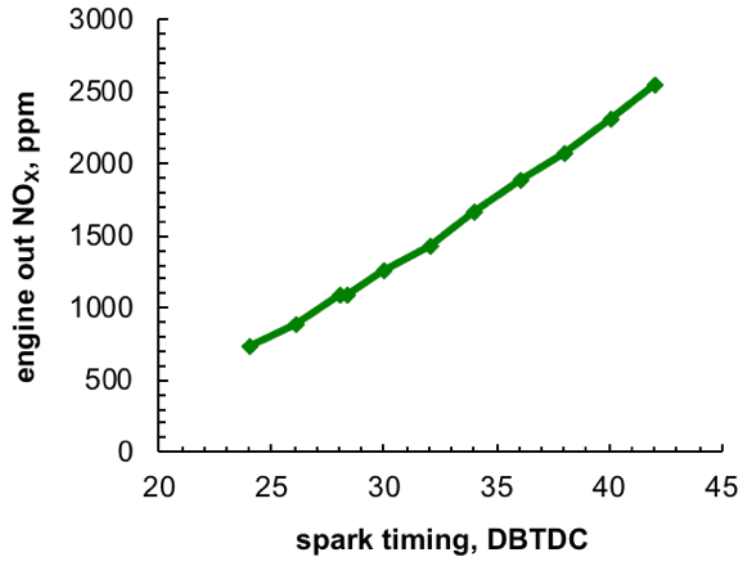


Figure 4.26 Steady-state variation of the experimental engine out NO_x emissions with spark timing. Engine operating conditions: 2000 rpm and 5 bar BMEP, $\lambda=1$.

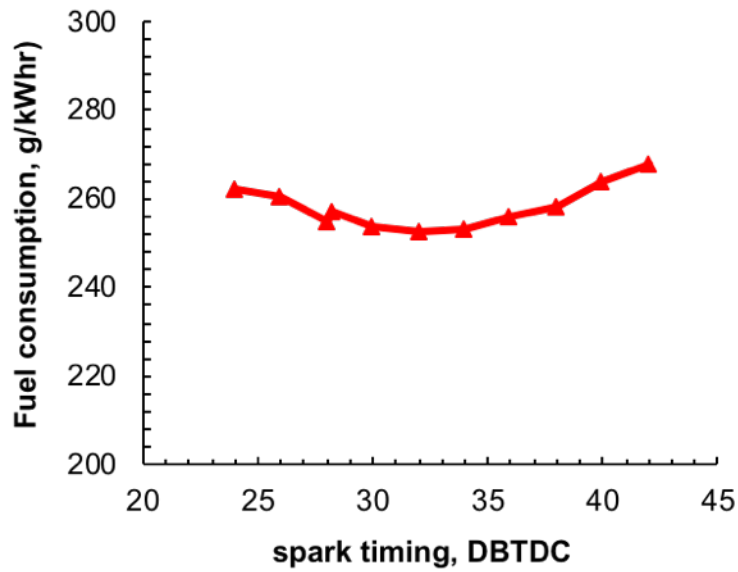


Figure 4.27 Steady-state variation of the fuel consumption with spark timing. Engine operating conditions: 2000 rpm and 5 bar BMEP, $\lambda=1$.

expected, fuel consumption is minimized at a spark timing where the maximum break torque (MBT) occurs. Further advances in timing past MBT can lead to inefficient combustion and knock. Thus, MBT spark timing can potentially be used to guide control strategies for increasing engine-out NO_x emissions while minimizing fuel consumption.

The steady-state EGR, valve timing and spark timing sweep measurements described above were made at $\lambda = 1$ fueling conditions. To study the effects of increased NO_x emission resulting from adjustments of these parameters on NH₃ production, λ sweep experiments discussed in Section 4.1 were repeated for selected valve timing and spark timing values listed in Table 4.7. The external EGR levels were held fixed at the OEM settings in these experiments (producing the maximum engine out NO_x available with external EGR), therefore the objective here was to reveal the additional NO_x increases possible from adjusting valve overlap and spark timing.

Table 4.7 Steady-state operating points for valve timing and spark timing sweep experiments with TWC-NSC.

Speed (rpm)	BMEP (bar)	Valve Timing (exhaust camshaft, CAD)		Spark Timing (DBTDC)	
		OEM	Custom	OEM	Custom
2000	3	42	34	32	40
2000	5	43	34	28	38
2000	8	43	34	19	24

The effect of adjusting the intake and exhaust valves overlap by advancing the exhaust camshaft from 43 to 34 crank angle degrees on the engine out NO_x emissions and NH₃ production as a function of λ is shown in Figure 4.28. As depicted in the figure, advancing exhaust camshaft phasing

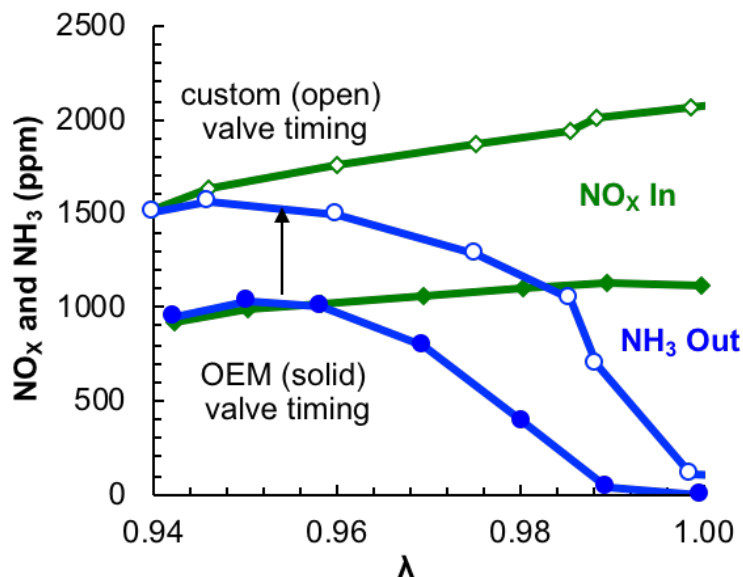


Figure 4.28 Steady-state concentrations of TWC inlet NO_x and outlet NH₃ as a function of λ for OEM valve timing (solid) and custom valve timing (open). Engine operating conditions: 2000 rpm and 5 bar BMEP; TWC-NSC; TWC at 514 °C inlet temperature and 50000 h⁻¹ space velocity.

resulted in 70 - 80 % increase in engine out NO_x emissions, with most of the NO_x converted to NH₃ by the TWC. Similar trends were observed with advancing the spark timing to MBT timing. Advancing the spark from 28 to 38 crank angle degrees before top dead center resulted in 70 - 80 % increase in engine out NO_x emissions, with most of the NO_x converted to NH₃ as shown in Figure 4.29.

To summarize the observed influence of adjusting the valve and spark timing on NH₃ production during steady-state rich operation, the measured NH₃ at different λ values is plotted in Figure 4.30 for 2000 rpm 5 bar BMEP operating point. The measured NH₃ is expressed in grams of NH₃ generated per kilogram of fuel burned and indicative on the efficiency of NH₃ generation. The NH₃ production increases as the exhaust mixture became richer for all of the operating conditions with significant increase in NH₃ production as a result of adjusting spark and valve timing. These results indicate that while λ controls NH₃ selectivity, valve timing and spark timing can enable higher NH₃ production,

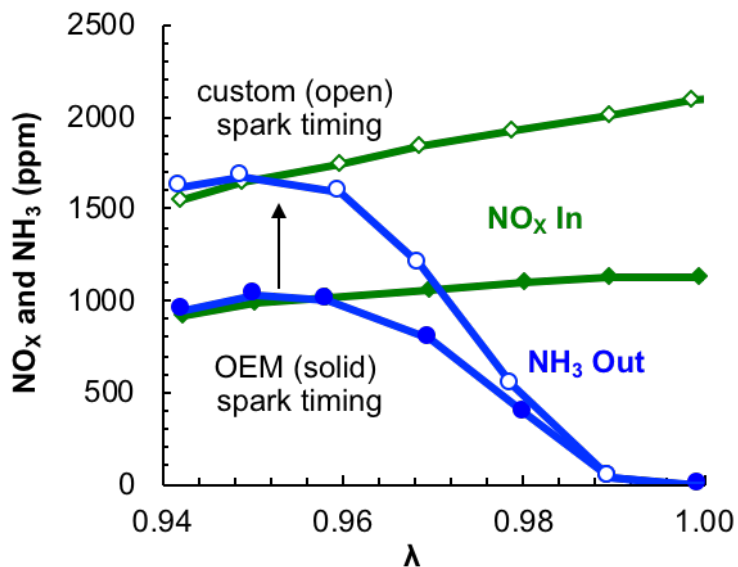


Figure 4.29 Steady-state concentrations of TWC inlet NO_x and outlet NH_3 as a function of λ for OEM spark timing (solid) and custom spark timing (open). Engine operating conditions: 2000 rpm and 5 bar BMEP; TWC-NSC; TWC at 514 °C inlet temperature and 50000 h^{-1} space velocity.

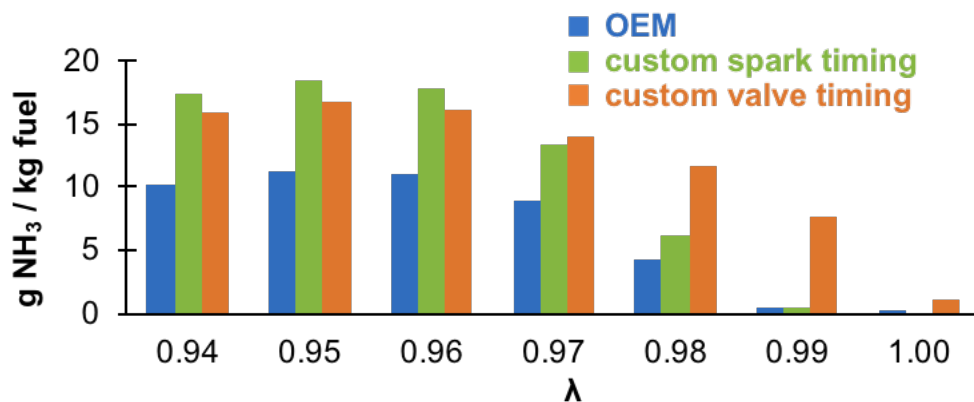


Figure 4.30 Steady-state NH_3 generation as a function of λ for OEM, custom spark and valve timings. Engine operating conditions: 2000 rpm and 5 bar BMEP; TWC-NSC; TWC at 514 °C inlet temperature and 50000 h^{-1} space velocity.

thereby reducing the amount of required rich operating time in a passive SCR system.

As previously discussed, NH_3 generation over a TWC is limited by the air-fuel equivalence ratio and the amount of inlet NO_x . The above results indicate that valve timing and spark timing are important parameters in determining engine out NO_x levels, while lambda is critical in determining the selectivity of NO_x to NH_3 reduction. These parameters can be optimized for a passive SCR application to deliver desired NO_x levels, while also potentially reducing the fuel consumption. Significant increase in the NO_x emissions have been demonstrated by varying these parameters independently. The combined benefit from varying these parameters can be utilized further for additive benefit and shown in Figure 4.31. It is important to note that the engine out NO_x emissions significantly increase as the engine load rises as shown in the figure, which further increases the NH_3 generation potential. This issue is discussed in the next section.

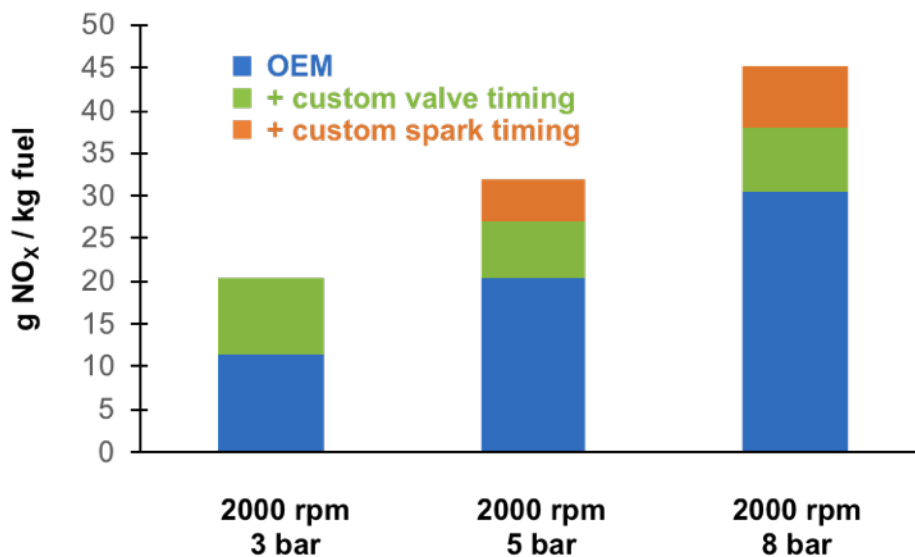


Figure 4.31 Steady-state cumulative experimental engine out NO_x emissions resulting from adjusting valve and spark timing at 2000 rpm and 3, 5 and 8 bar BMEP.

4.5 NH₃ production during engine acceleration transients

As discussed in the previous section, engine out NO_x emissions significantly increase as the engine load rises. The higher combustion temperatures that accompany increased engine load promote formation of NO_x. Higher engine loads characteristically occur during periods of vehicle acceleration, and, therefore, acceleration periods can be utilized to further increase the NH₃ generation potential for passive SCR. Furthermore, acceleration events are also associated with stoichiometric or slightly rich fueling. This creates additional opportunities for fuel efficient NH₃ generation as discussed in Section 4.1. This section summarizes the observed effects of transient acceleration events on NH₃ generation and fuel consumption for the experimental engine. To assess the effects of acceleration on NH₃ production and fuel consumption in the experimental engine, a series of rich/lean cycling experiments were performed. These experiments were designed to be representative of the conditions a passive SCR would encounter under real world driving conditions. The experiments were carried out at a fixed engine speed of 2000 rpm for both lean and rich portion of the cycle. However, the engine load was alternated between 8 bar BMEP during rich phase and 2 bar BMEP during lean phase of the cycle. These experiments are referred to as load step cycling and were designed to represent acceleration driving events, as compared to the fixed load cycling experiments described in Section 4.3. In the latter, engine load was fixed at 2 bar BMEP for both lean and rich portions of the cycle to represent “cruise” driving conditions. A Pd-only TWC was utilized in all of the cycling experiments presented in this section. The lean/rich cycling experimental details are summarized in Table 4.8.

A feedback control strategy based on cumulative NH₃ produced by the TWC during rich operation and NO_x emissions during lean operation was implemented on the engine to control lean/rich cycle timing. The mode switch was triggered when the TWC outlet NO_x or NH₃ (NO_x : NH₃ = 1) reached 0.027 mol per liter of catalyst. This amount represents approximately 25% of the NH₃

storage capacity of a small pore Cu-zeolite SCR catalyst at 300 °C based on prior flow reactor measurements, which showed that at higher NH₃ loadings (> 50 %), NH₃ slip can occur due to NH₃ release during the switch from rich to lean conditions.

Table 4.8 Average experimental conditions for load step and fixed load rich/lean cycling experiments with Pd-only TWC.

	Load Step		Fixed Load	
	Lean	Rich	Lean	Rich
Speed, rpm	2000	2000	2000	2000
BMEP, bar	2	8	2	2
λ	2.10	0.96-0.99	2.10	0.96-0.98
inlet T, °C	467	544	443	468
SV, h⁻¹	43000	61000	45000	28000

The measured emissions of NO_x and NH₃ at the TWC inlet and outlet during the load step and fixed load experiments with rich $\lambda = 0.96$ are shown in Figure 4.32 (a) and (b), respectively. As expected, the observed emission trends are similar for both cycling experiments. During the lean phase of the cycle NO_x passes through the TWC mostly unreacted. As the engine transitions to rich operation, the effluent NO_x drops, and NH₃ increases instantaneously to the feed gas NO_x levels indicating complete reduction of NO_x to NH₃. The important difference between the two cycling experiments is the much higher engine out NO_x levels during the rich phase of load step cycling. The higher NO_x concentrations and higher exhaust flow rates that accompany high engine load increase the NO_x flux that gets converted to NH₃ by the TWC, and for a fixed lean NO_x inventory, which was set to match rich NH₃ based on the engine control algorithm, results in a much shorter rich time duration required to produce the same amount of NH₃ as depicted in Figure 4.33.

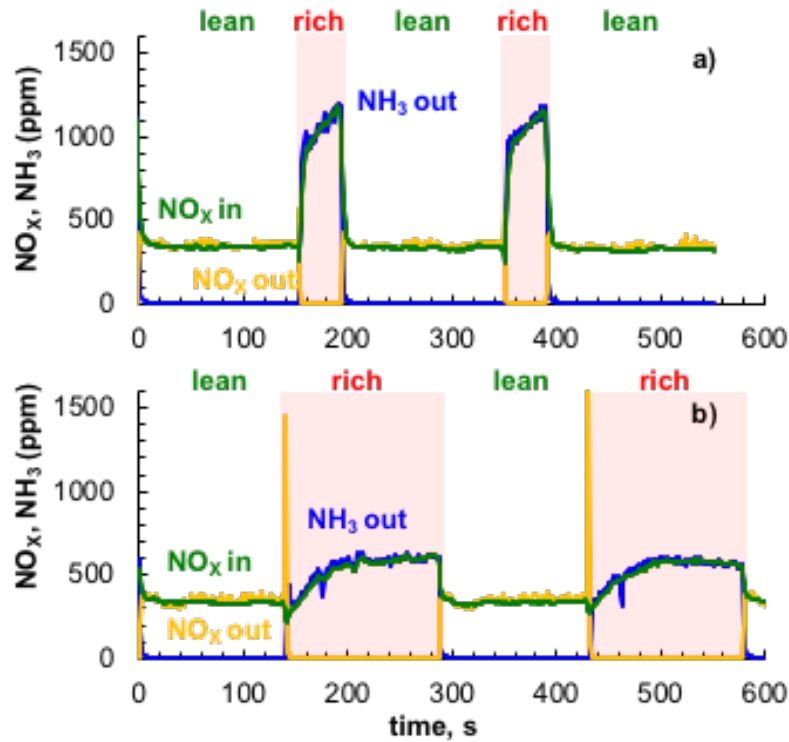


Figure 4.32 NO_x and NH_3 emissions at Pd-only TWC inlet and outlet as a function of time during (a) load step and (b) fixed load rich/lean cycling experiments with rich $\lambda=0.96$.

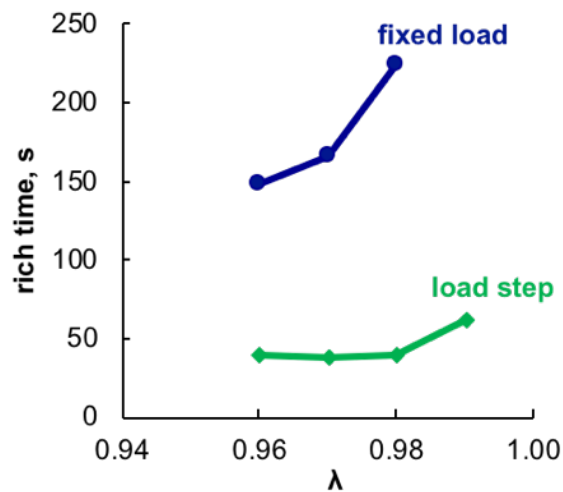


Figure 4.33 Rich time duration as a function of rich λ during load step and fixed load rich/lean cycling experiments.

As discussed in Section 4.1, as the engine fueling mixture gets richer, NH_3 selectivity increases and more NO_x is converted to NH_3 , which results in shorter rich times. As shown in Figure 4.33 rich time duration decreases until it reaches a minimum at $\lambda = 0.97$ and 0.96 for load step and fixed load cycling, respectively, which correspond to λ s of maximum NH_3 production. As λ is further enriched, NH_3 production falls into the λ region where its production becomes limited by engine out NO_x , and as the feed gas NO_x levels decrease, less NH_3 is made and a slight increase in rich time duration is observed.

Comparisons of the fuel consumption for lean/rich load step and fixed load cycling vs. the stoichiometric-only cycling provide estimates of the potential fuel consumption benefits resulting from engine accelerations. To maintain a consistent power basis, the measured fuel consumptions were normalized to brake specific fuel consumption (BSFC) as displayed in Figure 4.34. The maximum fuel consumption improvement was 11.8 % at rich $\lambda = 0.97$ and 6.4 % at rich $\lambda = 0.96$ for load step and fixed load cycling, respectively. The maximum fuel benefit from running lean under these conditions is 13.9 %, which translates to 2.1 and 7.5 % fuel consumption penalty for load step and fixed load, respectively.

The lower fuel penalty in the load step cycling experiments is due to much higher engine out NO_x emissions during rich fueling, resulting in much shorter rich time to achieve the desired level of NH_3 generation. This emphasizes the importance of acceleration events during transient drive cycles, which create opportunities for higher engine out NO_x , higher TWC NH_3 production, and a net reduction in fuel consumption for passive SCR. Also, in fixed load cycling where the default engine operation is lean, switching to rich operation to generate NH_3 not only incurs a fuel penalty but also loses the efficiency benefit of lean operation. In load step cycling, on the other hand, the engine has to run stoichiometric or slightly rich already, and therefore presents an explicit opportunity for minimizing fuel consumption. Acceleration events, therefore, offer natural opportunities for enhancing passive SCR performance.

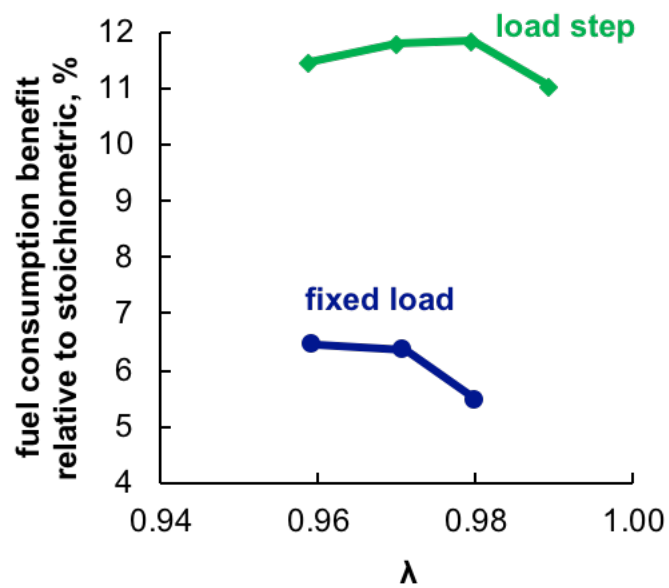


Figure 4.34 Fuel consumption benefit as a function of rich λ during load step and fixed load rich/lean cycling experiments.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

Passive selective catalytic reduction (SCR) of gasoline engine-out NO_x with NH_3 generated in a three-way catalyst (TWC) upstream of the SCR catalyst appears to be a feasible strategy for meeting NO_x emission limits with minimal fuel penalties. However, this dissertation work has revealed the following points regarding the performance of the key components of passive SCR systems:

- There need to be sufficient opportunities for exploiting transient fuel-rich periods of engine operation to generate NH_3 in the TWC.
- Air-fuel equivalence ratio (λ) and engine-out NO_x emissions both have a strong effect on NH_3 generation in TWCs.
- Fuel-rich transients for generating NH_3 should be as close to stoichiometric as possible. For the engine and TWCs studied here, λ between 0.96 and 0.97 exhibited the optimal NH_3 production.
- The Pd-only TWC studied here exhibited high selectivity for NH_3 formation over a wide range of operating conditions and appears to be a promising formulation for utilization in passive SCR.
- TWCs need an oxygen storage component (OSC) to properly function, but high levels of OSC can potentially delay NH_3 formation and reduce fuel economy.
- Recently proposed global reaction mechanisms that include a direct pathway for NH_3 formation from NO and H_2 appear to replicate the essential transient response characteristics of the TWCs studied here.
- Manipulation of exhaust gas recirculation (EGR), valve timing, and spark timing can increase engine-out NO_x during fuel-rich transients, enabling higher TWC NH_3 production and reducing the extent of fuel-rich operation.

- Lowering engine-out NO_x during lean operation is beneficial as it preserves SCR catalyst NH₃ inventory and reduces the need for NH₃ generation.
- Including a NO_x storage component in the TWC washcoat can reduce the need for fuel-rich transients and preserve NH₃ inventory on the SCR catalyst, as long as the TWC temperature is <500 °C.
- Front-end biasing of fuel-rich periods (rich λ tip-in) is beneficial for maximizing NH₃ generation in TWCs with oxygen and NO_x storage.
- Acceleration events create an important opportunity for higher NO_x reduction performance and fuel efficiency gains.

The two TWC formulations studied here exhibited high activity for NH₃ formation and HC conversion, but their CO emissions were high and need to be further investigated. Since this study did not include the effects of catalyst aging and catalyst poisons (such as sulfur) on NH₃ generation, additional studies of these factors are also needed.

Another area not addressed by the present study is the storage and utilization of NH₃ by SCR catalysts under transient engine operation, where significant variation in SCR temperatures are expected. With NH₃ storage capacity highly dependent on exhaust temperature, proper system architecture and/or active thermal management is likely be required for effective NH₃ utilization over SCR catalyst, and thus should be the focus of future work.

Control of the overall passive SCR process is more challenging than current urea SCR processes because it depends explicitly on fuel-rich engine operation, which must be implemented in the context of transient load and speed demands. As such, the amount of time available for rich operation can depend on driver requested power demand; in addition, control algorithms must adjust to provide as much lean operation as possible for greatest fuel efficiency. Ultimately, development of commercially feasible passive SCR systems will require consideration of the collective interaction of all of the major system

components addressed above, including the engine, the TWC, and the SCR catalyst. Thus, passive SCR is most likely to be successful when combined with advanced adaptive and/or model-based control algorithms that can track global performance while manipulating engine parameters (such as λ , exhaust gas recirculation (EGR), spark timing and valve timing) in response to drive cycle demands and fuel properties, and also account for TWC and SCR catalyst aging and formulation variation effects.

LIST OF REFERENCES

- [1] S. C. Davis, S. E. Williams, and R. G. Boundy, "Transportation & Energy Data Book: Edition 36.1," 2018.
- [2] C. Schwarz, E. Schünemann, B. Durst, J. Fischer, and A. Witt, "Potentials of the Spray-Guided BMW DI Combustion System," in *SAE Technical Paper 2006-01-1265*, 2006, no. 724.
- [3] P. Chambon, S. Huff, K. Norman, K. D. D. Edwards, J. Thomas, and V. Y. Prikhodko, "European Lean Gasoline Direct Injection Vehicle Benchmark," in *SAE Technical Paper 2011-01-1218*, 2011.
- [4] W. Li, K. L. Perry, K. Narayanaswamy, C. H. Kim, and P. Najt, "Passive Ammonia SCR System for Lean-burn SIDI Engines," *SAE Int. J. Fuels Lubr.*, vol. 3, no. 1, pp. 2010-01-0366, Apr. 2010.
- [5] United States Environmental Protection Agency, "A Study of Stratified Charge for Light Duty Power Plants : Volume 3. Executive Summary," 1975.
- [6] S. Kono, "Development of the Stratified Charge and Stable Combustion Method in DI Gasoline Engines," in *SAE Technical Paper 950688*, 1995.
- [7] L. Schmidt, J. Seabrook, J. Stokes, M. F. Ahmad Zuhdi, S. Begg, M. Heikal, and J. King, "Multiple Injection Strategies for Improved Combustion Stability under Stratified Part Load Conditions in a Spray Guided Gasoline Direct Injection (SGDI) Engine," in *SAE Technical Paper 2011-01-1228*, 2011.
- [8] R. Ortmann, S. Arndt, J. Raimann, R. Grzeszik, and G. Würfel, "Methods and Analysis of Fuel Injection, Mixture Preparation and Charge Stratification in Different Direct Injected SI Engines," in *SAE Technical Paper 2001-01-0970*, 2001, vol. 2001, no. 724.
- [9] Bosch GmbH, *Automotive Handbook*, 9th Editio. Robert Bosch GmbH, 2014.
- [10] J. Heywood, *Internal Combustion Engine Fundamentals*. McGraw-Hill, Inc, 1988.
- [11] W. Anderson, J. Yang, D. D. Brehob, J. K. Vallance, and R. M. Whiteaker, "Understanding the Thermodynamics of Direct Injection Spark Ignition (DISI) Combustion Systems: An Analytical and Experimental Investigation," in *SAE Technical Paper 962018*, 1996.
- [12] L. P. Wyszynski, C. R. Stone, and G. T. Kalghatgi, "The Volumetric Efficiency of Direct and Port Injection Gasoline Engines with Different Fuels," in *SAE Technical Paper 2002-01-0839*, 2002, vol. 2002, no. 724.
- [13] G. Saliba, R. Saleh, Y. Zhao, A. A. Presto, A. T. Lambe, B. Frodin, S. Sardar, H. Maldonado, C. Maddox, A. A. May, G. T. Drozd, A. H. Goldstein, L. M. Russell, F. Hagen, and A. L. Robinson, "Comparison of Gasoline Direct-Injection (GDI) and Port Fuel Injection (PFI) Vehicle Emissions: Emission Certification Standards, Cold-Start, Secondary Organic Aerosol Formation Potential, and Potential Climate Impacts," *Environ. Sci. Technol.*, vol. 51, no. 11, pp. 6542–6552, Jun. 2017.
- [14] H. Eichseder, E. Baumann, P. Müller, and S. Rubbert, "Gasoline Direct Injection - A Promising Engine Concept for Future Demands," in *SAE*

- Technical Paper 2000-01-0248*, 2000, vol. 2000, no. 724.
- [15] M. Pontoppidan, C. Pancotti, P. Francia, G. Montanari, and F. Damasceno, "DGI - Direct Gasoline Injection Status of Development for Spark-Ignited Engines," in *SAE Technical Paper 2002-01-3519*, 2002.
 - [16] National Highway Traffic Safety Administration, "Corporate Average Fuel Economy for MY 2017-MY 2025 Passenger Cars and Light Trucks," 2012.
 - [17] National Academy of Sciences, "Cost, Effectiveness, and Deployment of Fuel Economy Technologies for Light-Duty Vehicles," National Academies Press, Washington, D.C., Sep. 2015.
 - [18] US DRIVE ACEC Tech Team, "Advanced Combustion and Emission Control Roadmap," 2018.
 - [19] United States Environmental Protection Agency, "Criteria Air Pollutants." [Online]. Available: <https://www.epa.gov/criteria-air-pollutants>. [Accessed: 05-Dec-2018].
 - [20] United States Environmental Protection Agency, "Regulations for Emissions from Vehicles and Engines." [Online]. Available: <https://www.epa.gov/regulations-emissions-vehicles-and-engines>. [Accessed: 05-Dec-2018].
 - [21] United States Environmental Protection Agency, "Carbon Pollution from Transportation." [Online]. Available: <https://www.epa.gov/air-pollution-transportation/carbon-pollution-transportation>. [Accessed: 05-Dec-2018].
 - [22] J. J. Mooney, C. E. Thompson, and J. C. Dettling, "Three-Way Conversion Catalysts Part of the New Emission Control System," in *SAE Technical Paper 770365*, 1977.
 - [23] B. J. Cooper, B. Harrison, E. Shutt, and I. Lichtenstein, "The Role of Rhodium in Rh/Pt Catalysts for CO/HC/NO_x and SO₄ = Emission Control-The Influence of Oxygen on Catalyst Performance," in *SAE Technical Paper 770367*, 1977.
 - [24] J. S. Hepburn, K. S. Patel, M. G. Meneghel, and H. S. Gandhi, "Development of Pd-only Three Way Catalyst Technology," in *SAE Technical Paper 941058*, 1994.
 - [25] Y. Kaneko, H. Kobayashi, R. Komagome, O. Hirako, and O. Nakayama, "Effect of Air-Fuel Ratio Modulation on Conversion Efficiency of Three-Way Catalysts," in *SAE Technical Paper 780607*, 1978.
 - [26] N. Miyoshi, S. Matsumoto, K. Katoh, T. Tanaka, J. Harada, N. Takahashi, K. Yokota, M. Sugiura, and K. Kasahara, "Development of New Concept Three-Way Catalyst for Automotive Lean-Burn Engines," in *SAE Technical Paper 950809*, 1995.
 - [27] W. S. Epling, L. E. Campbell, A. Yezerets, N. W. Currier, and J. E. Parks, "Overview of the Fundamental Reactions and Degradation Mechanisms of NO_x Storage/Reduction Catalysts," *Catal. Rev.*, vol. 46, no. 2, pp. 163–245, Dec. 2004.
 - [28] Y. Su and M. D. Amiridis, "In situ FTIR studies of the mechanism of NO_x storage and reduction on Pt/Ba/Al₂O₃ catalysts," *Catal. Today*, vol. 96, no. 1–2, pp. 31–41, Oct. 2004.

- [29] R. L. Muncrief, K. S. Kabin, and M. P. Harold, "NO_x storage and reduction with propylene on Pt/BaO/alumina," *AIChE J.*, vol. 50, no. 10, pp. 2526–2540, Oct. 2004.
- [30] S. Roy and A. Baiker, "NO_x Storage–Reduction Catalysis: From Mechanism and Materials Properties to Storage–Reduction Performance," *Chem. Rev.*, vol. 109, no. 9, pp. 4054–4091, Sep. 2009.
- [31] F. Prinetto, G. Ghiotti, I. Nova, L. Lietti, E. Tronconi, and P. Forzatti, "FT-IR and TPD Investigation of the NO_x Storage Properties of BaO/Al₂O₃ and Pt–BaO/Al₂O₃ Catalysts," *J. Phys. Chem. B*, vol. 105, no. 51, pp. 12732–12745, Dec. 2001.
- [32] P. Broqvist, H. Grönbeck, E. Fridell, and I. Panas, "Characterization of NO_x Species Adsorbed on BaO: Experiment and Theory," *J. Phys. Chem. B*, vol. 108, no. 11, pp. 3523–3530, Mar. 2004.
- [33] R. L. Muncrief, P. Khanna, K. S. Kabin, and M. P. Harold, "Mechanistic and kinetic studies of NO_x storage and reduction on Pt/BaO/Al₂O₃," *Catal. Today*, vol. 98, no. 3, pp. 393–402, Dec. 2004.
- [34] J. R. Theis, J. A. Ura, J. J. Li, G. G. Surnilla, J. M. Roth, and C. T. Goralski, "NO_x Release Characteristics of Lean NO_x Traps During Rich Purges," in *SAE Technical Paper 2003-01-1159*, 2003.
- [35] I. Nova, L. Castoldi, L. Lietti, E. Tronconi, and P. Forzatti, "On the dynamic behavior of 'NO_x-storage/reduction' Pt–Ba/Al₂O₃ catalyst," *Catal. Today*, vol. 75, no. 1–4, pp. 431–437, Jul. 2002.
- [36] J.-S. Choi, W. P. Partridge, J. a. Pihl, M.-Y. Kim, P. Kočí, and C. S. Daw, "Spatiotemporal distribution of NO_x storage and impact on NH₃ and N₂O selectivities during lean/rich cycling of a Ba-based lean NO_x trap catalyst," *Catal. Today*, vol. 184, no. 1, pp. 20–26, Apr. 2012.
- [37] Š. Bártová, P. Kočí, D. Mráček, M. Marek, J. a. Pihl, J.-S. Choi, T. J. Toops, and W. P. Partridge, "New insights on N₂O formation pathways during lean/rich cycling of a commercial lean NO_x trap catalyst," *Catal. Today*, vol. 231, no. 3, pp. 145–154, Aug. 2014.
- [38] W. P. Partridge and J.-S. Choi, "NH₃ formation and utilization in regeneration of Pt/Ba/Al₂O₃ NO_x storage-reduction catalyst with H₂," *Appl. Catal. B Environ.*, vol. 91, no. 1–2, pp. 144–151, Sep. 2009.
- [39] S. Brandenberger, O. Kröcher, A. Tissler, and R. Althoff, "The State of the Art in Selective Catalytic Reduction of NO_x by Ammonia Using Metal-Exchanged Zeolite Catalysts," *Catal. Rev.*, vol. 50, no. 4, pp. 492–531, Dec. 2008.
- [40] M. Colombo, I. Nova, and E. Tronconi, "A comparative study of the NH₃-SCR reactions over a Cu-zeolite and a Fe-zeolite catalyst," *Catal. Today*, vol. 151, no. 3–4, pp. 223–230, Jun. 2010.
- [41] M. Colombo, I. Nova, and E. Tronconi, "Detailed kinetic modeling of the NH₃–NO/NO₂ SCR reactions over a commercial Cu-zeolite catalyst for Diesel exhausts after treatment," *Catal. Today*, vol. 197, no. 1, pp. 243–255, Dec. 2012.
- [42] D. Chatterjee, T. Burkhardt, M. Weibel, I. Nova, A. Grossale, and E.

- Tronconi, "Numerical Simulation of Zeolite- and V-Based SCR Catalytic Converters," *SAE Tech. Pap. 2007-01-1136*, vol. 2007, no. 724, 2007.
- [43] E. Tronconi, I. Nova, C. Ciardelli, D. Chatterjee, and M. Weibel, "Redox features in the catalytic mechanism of the 'standard' and 'fast' NH_3 -SCR of NO_x over a V-based catalyst investigated by dynamic methods," *J. Catal.*, vol. 245, no. 1, pp. 1–10, Jan. 2007.
- [44] J. W. Girard, C. Montreuil, J. Kim, G. Cavataio, and C. Lambert, "Technical Advantages of Vanadium SCR Systems for Diesel NO_x Control in Emerging Markets," *SAE Int. J. Fuels Lubr.*, vol. 1, no. 1, pp. 2008-01-1029, Apr. 2008.
- [45] T. Maunula, A. Viitanen, T. Kinnunen, and K. Kanninen, "Design of Durable Vanadium - SCR Catalyst Systems for Heavy - Duty Diesel Applications," in *SAE Technical Paper 2013-26-0049*, 2013, vol. 5, no. 2.
- [46] G. Cavataio, J. Girard, J. E. Patterson, C. Montreuil, Y. Cheng, and C. K. Lambert, "Laboratory Testing of Urea-SCR Formulations to Meet Tier 2 Bin 5 Emissions," in *SAE Technical Paper 2007-01-1575*, 2007, vol. 2007, no. 724, pp. 776–790.
- [47] A. Grossale, I. Nova, and E. Tronconi, "Study of a Fe-zeolite-based system as NH_3 -SCR catalyst for diesel exhaust aftertreatment," *Catal. Today*, vol. 136, no. 1–2, pp. 18–27, Jul. 2008.
- [48] J. Li, H. Chang, L. Ma, J. Hao, and R. T. Yang, "Low-temperature selective catalytic reduction of NO_x with NH_3 over metal oxide and zeolite catalysts—A review," *Catal. Today*, vol. 175, no. 1, pp. 147–156, Oct. 2011.
- [49] R. Q. Long and R. T. Yang, "Catalytic Performance of Fe-ZSM-5 Catalysts for Selective Catalytic Reduction of Nitric Oxide by Ammonia," *J. Catal.*, vol. 188, no. 2, pp. 332–339, Dec. 1999.
- [50] R. Q. Long and R. T. Yang, "Reaction Mechanism of Selective Catalytic Reduction of NO with NH_3 over Fe-ZSM-5 Catalyst," *J. Catal.*, vol. 207, no. 2, pp. 224–231, Apr. 2002.
- [51] C. Lambert, R. Hammerle, R. McGill, M. Khair, and C. Sharp, "Technical Advantages of Urea SCR for Light-Duty and Heavy-Duty Diesel Vehicle Applications," in *SAE Technical Paper 2004-01-1292*, 2004, no. 724.
- [52] J. M. Fedeyko, H.-Y. Chen, T. H. Ballinger, E. C. Weigert, H.-L. Chang, J. P. Cox, and P. J. Andersen, "Development of Thermally Durable Cu/SCR Catalysts," in *SAE Technical Paper 2009-01-0899*, 2009, pp. 367–373.
- [53] V. Y. Prikhodko, J. A. Pihl, S. A. Lewis, and J. E. Parks, "Hydrocarbon Fouling of SCR During PCCI Combustion," *SAE Int. J. Engines*, vol. 5, no. 3, 2012.
- [54] M. Takeuchi and S. Matsumoto, " NO_x Storage-Reduction Catalysts for Gasoline Engines," *Top. Catal.*, vol. 28, no. 1–4, pp. 151–156, Apr. 2004.
- [55] P. Nag, B. B. Ghosh, R. K. Das, and M. DuttaGupta, " NO_x Reduction in SI Engine Exhaust Using Selective Catalytic Reduction Technique," in *SAE Technical Paper 980935*, 1998, vol. 1353, no. 724, pp. 153–156.
- [56] J. R. Theis, "Selective Catalytic Reduction for Treating the NO_x Emissions

- from Lean-Burn Gasoline Engines: Durability Assessment,” *SAE Int. J. Fuels Lubr.*, vol. 1, no. 1, pp. 2008-01-0811, Apr. 2008.
- [57] J. R. Theis, “Selective Catalytic Reduction for Treating the NO_x Emissions from Lean-Burn Gasoline Engines: Performance Assessment,” *SAE Int. J. Fuels Lubr.*, vol. 1, no. 1, pp. 2008-01-0810, Apr. 2008.
- [58] M. Hori, A. Okumura, H. Goto, M. Horiuchi, M. Jenkins, and K. Tashiro, “Development of New Selective NO_x Reduction Catalyst for Gasoline Leanburn Engines,” in *SAE Technical Paper 972850*, 1997.
- [59] J. E. Parks, V. Y. Prikhodko, W. Partridge, J. Choi, K. Norman, S. Huff, and P. Chambon, “Lean Gasoline Engine Reductant Chemistry During Lean NO_x Trap Regeneration,” *SAE Int. J. Fuels Lubr.*, vol. 3, no. 2, pp. 956–962, Oct. 2010.
- [60] C. H. Kim, K. Perry, M. Viola, W. Li, and K. Narayanaswamy, “Three-Way Catalyst Design for Urealess Passive Ammonia SCR: Lean-Burn SIDI Aftertreatment System,” in *SAE Technical Paper 2011-01-0306*, 2011.
- [61] K. Narayanaswamy, P. M. Najt, W. Li, K. L. Perry, and C. H. Kim, “Modelling of passive ammonia selective catalytic reduction system for lean-burn spark ignition direct injection engines,” *Proc. Inst. Mech. Eng. Part D J. Automob. Eng.*, vol. 225, no. 10, pp. 1365–1376, Jul. 2011.
- [62] T. Huai, T. D. Durbin, J. W. Miller, J. T. Pisano, C. G. Sauer, S. H. Rhee, and J. M. Norbeck, “Investigation of NH₃ Emissions from New Technology Vehicles as a Function of Vehicle Operating Conditions,” *Environ. Sci. Technol.*, vol. 37, no. 21, pp. 4841–4847, 2003.
- [63] N. V. Heeb, A. M. Forss, S. Brühlmann, R. Lüscher, C. J. Saxer, and P. Hug, “Three-way catalyst-induced formation of ammonia-velocity- and acceleration-dependent emission factors,” *Atmos. Environ.*, vol. 40, no. 31, pp. 5986–5997, 2006.
- [64] R. Suarez-Bertoa, A. A. Zardini, and C. Astorga, “Ammonia exhaust emissions from spark ignition vehicles over the New European Driving Cycle,” *Atmos. Environ.*, vol. 97, pp. 43–53, 2014.
- [65] R. Suarez-Bertoa, P. Mendoza-Villafuerte, F. Riccobono, M. Vojtisek, M. Pechout, A. Perujo, and C. Astorga, “On-road measurement of NH₃ emissions from gasoline and diesel passenger cars during real world driving conditions,” *Atmos. Environ.*, vol. 166, pp. 488–497, Oct. 2017.
- [66] N. V. Heeb, C. J. Saxer, A.-M. Forss, and S. Brühlmann, “Correlation of hydrogen, ammonia and nitrogen monoxide (nitric oxide) emissions of gasoline-fueled Euro-3 passenger cars at transient driving,” *Atmos. Environ.*, vol. 40, no. 20, pp. 3750–3763, Jun. 2006.
- [67] N. V. Heeb, C. J. Saxer, A.-M. Forss, and S. Brühlmann, “Trends of NO-, NO₂-, and NH₃-emissions from gasoline-fueled Euro-3- to Euro-4-passenger cars,” *Atmos. Environ.*, vol. 42, no. 10, pp. 2543–2554, Mar. 2008.
- [68] S. H. Oh and T. Triplett, “Reaction pathways and mechanism for ammonia formation and removal over palladium-based three-way catalysts: Multiple roles of CO,” *Catal. Today*, vol. 231, pp. 22–32, Aug. 2014.

- [69] J. Gong and C. Rutland, "Three Way Catalyst Modeling with Ammonia and Nitrous Oxide Kinetics for a Lean Burn Spark Ignition Direct Injection (SID) Gasoline Engine," in *SAE Technical Paper 2013-01-1572*, 2013.
- [70] K. Ramanathan, C. S. Sharma, and C. H. Kim, "Global Kinetics for Ammonia Formation and Oxidation Reactions in a Commercial Three-Way Catalyst," *Ind. Eng. Chem. Res.*, vol. 51, no. 3, pp. 1198–1208, Jan. 2012.
- [71] E. C. Adams, M. Skoglundh, P. Gabrielsson, and P.-A. Carlsson, "Passive SCR: The Effect of H₂ to NO Ratio on the Formation of NH₃ Over Alumina Supported Platinum and Palladium Catalysts," *Top. Catal.*, vol. 59, no. 10–12, pp. 970–975, Jul. 2016.
- [72] E. C. Adams, M. Skoglundh, T. Elmqvist, and P.-A. Carlsson, "Water–gas-shift assisted ammonia formation over Pd/Ce/alumina," *Catal. Today*, no. April, pp. 0–1, May 2017.
- [73] M. L. Unland, "Isocyanate intermediates in the reaction nitrogen monoxide + carbon monoxide over a platinum/aluminum oxide catalyst," *J. Phys. Chem.*, vol. 77, no. 16, pp. 1952–1956, Aug. 1973.
- [74] M. L. Unland, "Isocyanate Intermediates in Ammonia Formation over Noble Metal Catalysts for Automobile Exhaust Reactions," *Science (80-.)*, vol. 179, no. 4073, pp. 567–569, Aug. 1973.
- [75] R. J. H. Voorhoeve, C. K. N. Patel, L. E. Trimble, and R. J. Kerl, "Hydrogen Cyanide Production During Reduction of Nitric Oxide over Platinum Catalysts," *Science (80-.)*, vol. 190, no. 4210, pp. 149–151, Oct. 1975.
- [76] R. J. H. Voorhoeve, C. K. N. Patel, L. E. Trimble, and R. J. Kerl, "Hydrogen Cyanide Production During Reduction of Nitric Oxide over Platinum Catalysts: Transient Effects," *Science (80-.)*, vol. 200, no. 4343, pp. 761–763, May 1978.
- [77] J. Kašpar, P. Fornasiero, and M. Graziani, "Use of CeO₂-based oxides in the three-way catalysis," *Catal. Today*, vol. 50, no. 2, pp. 285–298, Apr. 1999.
- [78] S. H. Oh, "Effects of cerium addition on the CO-NO reaction kinetics over alumina-supported rhodium catalysts," *J. Catal.*, vol. 124, no. 2, pp. 477–487, Aug. 1990.
- [79] J. T. Kummer, "Catalysts for automobile emission control," *Prog. Energy Combust. Sci.*, vol. 6, no. 2, pp. 177–199, Jan. 1980.
- [80] G. C. Koltsakis and A. M. Stamatelos, "Catalytic automotive exhaust aftertreatment," *Prog. Energy Combust. Sci.*, vol. 23, no. 1, pp. 1–39, 1997.
- [81] T. Kobylinski and B. Taylor, "The Catalytic Chemistry of Nitric Oxide: II. Reduction of nitric oxide over noble metal catalysts," *J. Catal.*, vol. 33, pp. 376–384, 1974.
- [82] E. C. Adams, M. Skoglundh, M. Folic, E. C. Bendixen, P. Gabrielsson, and P.-A. Carlsson, "Ammonia formation over supported platinum and palladium catalysts," *Appl. Catal. B Environ.*, vol. 165, pp. 10–19, Apr. 2015.
- [83] J. R. Theis, J. Kim, and G. Cavataio, "Passive TWC+SCR Systems for Satisfying Tier 2, Bin 2 Emission Standards on Lean-Burn Gasoline

- Engines,” *SAE Int. J. Fuels Lubr.*, vol. 8, no. 2, pp. 2015-01-1004, Apr. 2015.
- [84] C. D. DiGiulio, J. A. Pihl, J. E. Parks, M. D. Amiridis, and T. J. Toops, “Passive-ammonia selective catalytic reduction (SCR): Understanding NH₃ formation over close-coupled three way catalysts (TWC),” *Catal. Today*, vol. 231, no. X, pp. 33–45, Aug. 2014.
 - [85] V. Y. Prikhodko, J. E. Parks, J. A. Pihl, and T. J. Toops, “Passive SCR for lean gasoline NO_x control: Engine-based strategies to minimize fuel penalty associated with catalytic NH₃ generation,” *Catal. Today*, vol. 267, pp. 202–209, Jun. 2016.
 - [86] V. Y. Prikhodko, J. E. Parks, J. A. Pihl, and T. J. Toops, “Ammonia Generation over TWC for Passive SCR NO_x Control for Lean Gasoline Engines,” *SAE Int. J. Engines*, vol. 7, no. 3, pp. 2014-01-1505, Apr. 2014.
 - [87] V. Prikhodko, J. Pihl, T. Toops, and J. Parks, “Effects of NO_x Storage Component on Ammonia Formation in TWC for Passive SCR NO_x Control in Lean Gasoline Engines,” in *SAE Technical Paper 2018-01-0946*, 2018, no. X, pp. 1–9.
 - [88] V. Y. Prikhodko, J. E. Parks, J. A. Pihl, and T. J. Toops, “Ammonia Generation and Utilization in a Passive SCR (TWC+SCR) System on Lean Gasoline Engine,” *SAE Int. J. Engines*, vol. 9, no. 2, pp. 2016-01–0934, Apr. 2016.
 - [89] J. A. Pihl, J. A. Lewis, T. J. Toops, and J. E. Parks, “Lean NO_x Trap Chemistry Under Lean-Gasoline Exhaust Conditions: Impact of High NO_x Concentrations and High Temperature,” *Top. Catal.*, vol. 56, no. 1–8, pp. 89–93, May 2013.
 - [90] W. P. Partridge, J. M. E. Storey, S. A. Lewis, R. W. Smithwick, G. L. Devault, M. J. Cunningham, N. W. Currier, and T. M. Yonushonis, “Time-Resolved Measurements of Emission Transients By Mass Spectrometry,” in *SAE Technical Paper 2000-01-2952*, 2000, vol. 2000-01-29, no. 724.
 - [91] J. A. Pihl, V. Y. Prikhodko, T. J. Toops, and J. E. Parks, “TWC formulation effects on NH₃ generation for passive SCR applications in lean gasoline engine exhaust Acknowledgments,” in *24th North American Meeting of the Catalysis Society*, 2015.
 - [92] S. Daw, “Personal Communication.” 2016.
 - [93] O. Levenspiel, *Chemical Reaction Engineering*, 2nd Editio. Wiley, 1972.
 - [94] R. E. Hayes and S. T. Kolaczowski, *Introduction to Catalytic Combustion*, 1 edition. CRC Press, 1998.
 - [95] J. Gong, “Passive Ammonia SCR and Filtration Modeling for Fuel-neutral Engine,” University of Wisconsin - Madison, 2014.
 - [96] Z. Gao, V. K. Chakravarthy, and C. S. Daw, “Comparisons of the simulated emissions and fuel efficiencies of diesel and gasoline hybrid electric vehicles,” *Proc. Inst. Mech. Eng. Part D J. Automob. Eng.*, vol. 225, no. 7, pp. 944–959, Jul. 2011.
 - [97] F. P. Incropera and D. P. DeWitt, *Fundamentals of Heat and Mass Transfer*, 5 edition. Wiley, 2001.

- [98] G. D'Errico, G. Ferrari, A. Onorati, and T. Cerri, "Modeling the Pollutant Emissions from a S.I. Engine," in *SAE Technical Paper 2002-01-0006*, 2002, no. 2002-01-0006.
- [99] L. Li, G. Li, and D. Qiu, "A Study of Crevice HC Mechanism Based on the Transient HC Test Data and the Double Zone Combustion Model," in *SAE Technical Paper 2008-01-1652*, 2008, no. 724.
- [100] V. Y. Prikhodko, J. E. Parks, J. A. Pihl, and T. J. Toops, "Passive SCR for lean gasoline NOX control: Engine-based strategies to minimize fuel penalty associated with catalytic NH₃ generation," *Catal. Today*, vol. 267, pp. 202–209, Jun. 2016.
- [101] A. LINDHOLM, N. CURRIER, J. LI, A. YEZERETS, and L. OLSSON, "Detailed kinetic modeling of NO_x storage and reduction with hydrogen as the reducing agent and in the presence of CO₂ and H₂O over a Pt/Ba/Al catalyst," *J. Catal.*, vol. 258, no. 1, pp. 273–288, Aug. 2008.
- [102] K. Ramanathan and C. S. Sharma, "Kinetic Parameters Estimation for Three Way Catalyst Modeling," *Ind. Eng. Chem. Res.*, vol. 50, no. 17, pp. 9960–9979, Sep. 2011.
- [103] E. C. Adams, M. Skoglundh, P. Gabrielsson, M. Laurell, and P.-A. Carlsson, "Ammonia formation over Pd/Al₂O₃ modified with cerium and barium," *Catal. Today*, vol. 267, no. x, pp. 210–216, Jun. 2016.
- [104] E. C. Adams, M. Skoglundh, and P.-A. Carlsson, "Ammonia formation from nitric oxide over Pd-based catalysts in multicomponent feed gas compositions," *Catal. Commun.*, vol. 95, pp. 26–30, May 2017.
- [105] G. Pirug and H. P. Bonzel, "A low-pressure study of the reduction of NO by H₂ on polycrystalline platinum," *J. Catal.*, vol. 50, no. 1, pp. 64–76, Oct. 1977.
- [106] M. Shelef and H. S. Gandhi, "Ammonia Formation in Catalytic Reduction of Nitric Oxide by Molecular Hydrogen," *Ind. Eng. Chem. Prod. Res. Dev.*, vol. 11, no. 4, pp. 393–396, 1972.
- [107] J. C. Schlatter and K. C. Taylor, "Platinum and palladium addition to supported rhodium catalysts for automotive emission control," *J. Catal.*, vol. 49, no. 1, pp. 42–50, Jul. 1977.
- [108] L. a. Graham, S. L. Belisle, and P. Rieger, "Nitrous oxide emissions from light duty vehicles," *Atmos. Environ.*, vol. 43, no. 12, pp. 2031–2044, Apr. 2009.
- [109] L. J. Muzio and G. C. Quartucy, "Implementing NO_x control: Research to application," *Prog. Energy Combust. Sci.*, vol. 23, no. 3, pp. 233–266, 1997.
- [110] M. A. Freeman and R. C. Nicholson, "Valve Timing for Control of Oxides of Nitrogen (NO_x)," in *SAE Technical Paper 720121*, 1972.
- [111] A. M. Pourkhesalian, A. H. Shamekhi, and F. Salimi, "NO_x Control Using Variable Exhaust Valve Timing and Duration," in *SAE Technical Paper 2010-01-1204*, 2010.
- [112] S. V Bohac and D. N. Assanis, "Effect of Exhaust Valve Timing on Gasoline Engine Performance and Hydrocarbon Emissions," in *SAE*

Technical Paper 2004-01-3058, 2004.

- [113] J. Gong and C. Rutland, "A Quasi-Dimensional NO_x Emission Model for Spark Ignition Direct Injection (SIDI) Gasoline Engines," in *SAE Technical Paper 2013-01-1311*, 2013, vol. 2013-01-13.

APPENDIX

This appendix contains the detailed Matlab code of the TWC model used in this study. The Matlab code includes the main script for TWC simulation along with the required subroutines.

```
%Main script for TWC simulations. Key assumptions are as follows:
% - Each monolith channel is divided into a series of CSTR reactors (stages).
% - The temperature and composition of gas entering the 1st stage are specified
%   as functions of time as discrete values vs. time.
% - Transient mass and heat balances in each stage are integrated with
%   Euler integration using time step sizes controlled by rate-limiting transport
%   time scales.
% - A pseudo-steady-state approximation is used to relate the bulk and surface
%   gas species concentrations and account for the effects of boundary layer
%   mass transport.
% - Integrations are done over a series of time intervals set by the
%   intervals between the specified inlet gas temperature and composition
%   values. The interval integrations are repeated for each stage to cover
%   the entire simulation time.
% - The rates of multiple reactions are used to determine the
%   generation and sink terms for mass and energy in each stage over time.
% - Reaction rates are determined based on Arrhenius kinetics and the
%   temperatures and species concentrations at the wall surface.
% - Reaction rates are adjusted to account for boundary layer mass
%   transfer and used to estimate surface gas concentrations.
% - Mass and heat transfer between the bulk gas and wall surface are
%   estimated from boundary layer correlations and the geometry and flow
%   conditions.
% - The rate-limiting time scale used for integration is based on the
%   minimum of the boundary layer mass transfer time and the gas residence
%   time in each stage.
%
%Required subroutines include:
% - cat_mon_malibu1() to generate key catalyst and monolith parameters
% - rxnparams_vyp() to generate the reaction kinetic parameters
% - mhtp() to generate the boundary layer transport parameters
% - Rkin() to estimate reaction rates
%
%Originally created by C.S. Daw, 11/16/2016
%
%Modified by V.Y. Prikhodko (VYP) 3/3/2017 to account for species generation
term, global %kinetics from Jian Gong [95] and catalyst reaction temperature in
```

each stage is %determined by interpolating the experimentally measured temperatures.

```
clear; %Clear initial workspace
```

```
%Define key global constants
```

```
global Rgas Rgas2
```

```
Rgas=8.314; %1st version of ideal gas constant (J/mole K)
```

```
Rgas2=8.21e-5; %2nd version of ideal gas constant (m^3 atm/mole K)
```

```
%-----
```

```
%%
```

```
%-----
```

```
%Problem set up section. This is where the monolith parameters, initial  
%conditions, inlet gas conditions vs. time, reaction kinetics, and  
%axial discretization are defined.
```

```
%Call function cat_mon to set catalyst and monolith parameters
```

```
cat_mon_malibu1(); %Generates key catalyst and monolith parameters (VYP)
```

```
global rhos Cp_o Cp_1 Cp_2; %Monolith density and heat capacity terms
```

```
global Cpg; %Exhaust gas heat capacity (J/kg K)
```

```
global cat_length; %Monolith length (m)
```

```
global cat_dia; %Monolith diameter (m)
```

```
global eps; %Monolith void fraction (-)
```

```
global Ga; %Monolith channel surface area/volume (m^2/m^3 or 1/m)
```

```
global Ga_ext; %External heat transfer area (m^2/m^3 or 1/m)
```

```
global ht_amb; %External heat transfer coefficient (W/m^2 K)
```

```
global T_amb; %External ambient temperature (K)
```

```
global O2_capacity; %Catalyst O2 capacity (moles O2/m^3)
```

```
%Global variables generated by function cat_mon_malibu1:
```

```
% Catcase= Name of the current case
```

```
% eps= hole (void) fraction in monolith (-)
```

```
% channel_density= channel density (1/cm^2)
```

```
% Ga= channel wall surface area per unit volume (1/m)
```

```
% Dh= channel hydraulic diameter (m)
```

```
% cat_length= monolith length (m)
```

```
% cat_dia= monolith diameter (m)
```

```
% cat_volume= monolith volume (m^3)
```

```
% Ga_ext= external monolith surface area per unit volume (1/m)
```

```
% eps_wash= void fraction in the washcoat (-)
```

```
% Sh_o= Reference Sherwood number for gas-wall mass transfer (-)
```

```
% cNu_o= Reference Nusselt number for gas-wall heat transfer (-)
```

```
% rhos= monolith solid density (kg/m^3)
```

```
% rlams= monolith solid thermal conductivity (W/m K)
```

```
% Cp_o= reference value for solid heat capacity (J/kg K)
```

```
% Cp_1= 1st auxiliary coefficient for solid heat capacity (J/kg K^2)
```

```

% Cp_2= 2nd auxiliary coefficient for solid heat capacity (J*K/kg)
% cat_loading= active sites mol-site/m3 of catalyst
% O2_capacity= oxygen storage capacity of monolith (moles O2/m^3)
% Cpg= reference gas heat capacity (J/kg K)
% rlam_o= factor for gas thermal conductivity (W/m K)*1/(K^rlam_exp)
% rlam_exp= exponent for gas thermal conductivity (-)
% Pr= gas Prandtl number (-)
% T_amb= ambient temperature (K)
% ht_amb= external monolith heat transfer coefficient (W/m^2 K)
% dx= length of each stage (m)

%Convert O2 storage capacity to a Ce2O3 molar basis
ms=2*O2_capacity; %Total possible Ce2O3 conc. (moles/m^3 monolith)

%Get rxn. parameters to be made global and set with rxnparams function
global ngs nss rxst A Ea Hr MWg
[ngs,nss,namgs,namss,rxst,A,Ea,Hr,rxo,MWg] = rxnparams_vyp(); %(VYP)
%Outputs generated here:
%ngst= No. of tracked gas species
%nsst= No. of tracked solid species
%namgs= Character array with gas species names
%namss= Character array with solid species names
%rxst= Rxn. stoichiometric coefficients-Index1=Rxn. no.,Index2=Species no.
%A= Reaction pre-exp.factor (moles/mole-site s)- Index=reaction number
%Ea=Activation energy vector (J/mole)- Index=reaction number
%Hr=Heat of reaction (J/mole of unit reactant consumed)
%rxo= reaction order array (-) - Index1=Rxn. no., Index2=Species no.
%Kp=inhibition const. array (-)- Index1=K no., Index2=col 1=P1, col2=P2
%MWg=molecular wt. of each gas species (g/mole)

%%
%*****IMPORT EXP DATA (VYP)*****
%Insert subroutine here that manipulates experimental data to match model
%setup.

% Since the exhaust contains many different hydrocarbons, the HC kinetics is
%approximated by dividing HC into two groups: highly reactive C3H6 and less
%reactive C3H8. Split HC accordingly.

%Get and set initial conditions inside monolith, experimental values at time=0s
[Tg0,Pg,Ts0,yH2,yCO,yC3H6,yC3H8,yO2,yNO,yNH3,yH2O,yCO2,yN2,xs0] =
import_exp_data;
% Tg0=experimental temperature array (K) of inlet, mid and outlet temperatures
% P=Inlet gas pressure (atm), can be assumed constant
% Ts0= Initial solid wall temperature (K), assumed to be the same as Tg0

```

```

% yH2,yCO,yC3H6,yC3H8,yO2,yNO,yH2O,yCO2,yN2= gas species mole
fractions (-)
% xs= Fraction of O2 storage capacity still available

yg0=[yH2,yCO,yC3H6,yC3H8,yO2,yNO,yNH3,yH2O,yCO2,yN2]';%Init. gas
comp. vector
Tg=Tg0; %Set gas temperature at time 0 at inlet, mid and outlet
Ts=Ts0; %Set surface temperature at time 0
yg=yg0; %Set gas composition at time 0
xs=xs0; %Set surface compsiton at time 0

%Get inlet gas conditions vs. time
[dti,Tgin,Vgf,yH2in,yCOin,yC3H6in,yC3H8in,yO2in,yNOin,yNH3in,yH2Oin,yCO2i
n, yN2in]= import_exp_data;

ygin=[yH2in;yCOin;yC3H6in;yC3H8in;yO2in;yNOin;yNH3in;yH2Oin;yCO2in;yN2i
n];
%dti= time interval between measurements (s)
%Tgin= experimental temperature array (K) of inlet, mid and outlet temperatures
%Vgf= Inlet gas volumetric flow at each time step(m^3/s)
%yH2in,yCOin,yC3H6in,yC3H8in,yO2in,yNOin,yH2Oin,yCO2in,yN2in= Species
%inlet mole fractions at each time(-)

%Set number of inlet time intervals to process
nit=length(Tgin); %No. of inlet measurements (1+no. of time intervals)

%Create simulation time vector. Values are incremented by the measurement
%time interval.
simtime=0:dti:(nit-1)*dti; %Simulation times (s)

%Define axial discretization
nstages=5; %Number of effective cstr stages, needs to be odd number for
%temperature interpolation to work
dx=cat_length/nstages; %Length of each cstr stage

%%
%Interpolate temperature to number of stages (VYP)

if rem(nstages,2) %if nstages is odd, then continue
    nstages_x=[1;(1+nstages)/2;nstages]; %stages corresponding to where T was
measured (in,mid,out).
    nstages_xq=[1:1:nstages]'; %all stages that T needs to be interpolated to
    Tgin_q=interp1(nstages_x,Tgin,nstages_xq); %interpolated T at each stage
    Tg0_q=interp1(nstages_x,Tg0,nstages_xq);

```

```

    Tg_q=interp1(nstages_x,Tg,nstages_xq); %Set gas temperature at time 0 at
inlet, mid and outlet
    Ts_q=Tg_q;
end

```

```

%End problem set up section

```

```

%-----

```

```

%%

```

```

%-----

```

```

%Timescale assessment section

```

```

%Determine gas residence times for all time intervals
velocity=Vgf./(eps*pi*cat_dia^2/4); %Gas channel velocity vs. time (m/s)
taugin=dx./velocity; %Gas res. times in each stage (s)
%Gas res. times in each stage (s)
tcon=min(taugin); %Min. gas residence time over entire simulation (s)

```

```

%Calc. minimum m.t. time scale for H2 transport at max expected T
Tmax=1000; %Max expected T (K)
vmax=max(velocity); %Max expected gas velocity (m/s)
zmin=.1*cat_length; %Min cat axial location (m)
[Rem,cNum,htcm,Scm,Shm,ktcm] = mhtp(Tmax,zmin,vmax,2);
tmt=1/ktcm;%Min. m.t. time scale for H2 rxns. (s)
%Note: This is the smallest possible time scale for H2 reactions to occur

```

```

%Set integration time step based on transport time scales
tmin=min(tcon,tmt); %Minimum dynamic time scale (s)
sf=10; %Speed up factor applied to min time scale (-)
tmin=tmin*sf; %Adjusted min time scale (s)
tratio=ceil(dti/tmin);%Integer ratio of input time step/integ. time scale
dt=dti/tratio; %Integration time step

```

```

%End timescale assessment section.

```

```

%-----

```

```

%%

```

```

%-----

```

```

%Integration section. This is where the ODEs for each axial segment are
%integrated vs. time. Each integration is carried out over the input gas
%time intervals (usually based on the frequency at which engine-out
%measurements are made). For each measurement interval, the heat and
%species rate ODEs are integrated stepwise using the minimum time step
%size required by H2 diffusion in the boundary layer (which is the fastest
%process that can occur). Over each measurement interval, it is assumed
%that the inlet conditions to the 1st stage can be interpolated onto the

```

```

%integration time steps, so that the integration results reflect transient
%responses to linear changes in the inputs between measurement intervals.
%The integration process is repeated for each succeeding stage using
%interpolated values of the final states of the preceding stage at the
%end of each measurement time interval as the input to the next stage.

%Initialize generation/sink rate vectors for each species
Rgeng=zeros(ngs,1);%Init. gas species gen. rates w/o m.t. (moles/m^3 s)
Rgengm=Rgeng; %Init. Rgeng with m.t. corr.(moles/m^3 s)
Rgens=zeros(nss-1,1);%Init. net gen. rate for solid species 1 (moles/m^3 s)

%Initialize vectors for inlet gas T and comp. in each interval
Tgij=zeros(1,tratio);%Inlet gas temperatures for each interval
ygij=zeros(ngs,tratio); %Inlet gas compositions for each interval

%Initialize arrays used to save the integration results for each stage vs. time.
Tgsave=Tg0_q.*ones(1,nit);%Exit gas T (K)
Tssave=Tg0_q.*ones(1,nit);%Exit wall T (K)
ygsave=ones(ngs,nit); %Exit gas comp.
ygsave(:,1)=yg0; % (VYP)
xssave=ones(nss,nit); %Exit surface comp.
xssave(:,1)=xs0;

%Begin stepwise integrations for each axial stage for the simulation
%period. Integrations occur over discrete time intervals defined by the
%measurement time intervals for the incoming exhaust gas. This process
%is repeated for all the incoming time intervals for each stage
%sequentially to generate a temporal profile for the exit gas temperature
%and composition.

%Start incrementing over cstr stages
for kij=1:nstages %Begin stage increment loop (index kij)

z=(kij-1)*dx+dx/2; %Axial position of current stage (kij)

for i=1:nit-1 %(VYP) was (nit-1) %Begin loop over inlet time intervals (i) for stage
%kij

%Set initial temp. and conc. increments to use for inlet T and conc.
%during each integration step for stage kij.
%dTgi=diff(Tgin)./tratio; %Inlet T increments in each integ. step
dTgi=diff(Tgin_q(kij,:))./tratio;
dygi=((diff(ygin'))')./tratio;%Inlet conc. increments for each integ. step

%Specify kij stage gas inlets for time interval i

```

```

%Tgi=Tgin(1,i); %Inlet gas temperature at start of ith interval
Tgi=Tgin_q(kij,i);
ygi=ygin(:,i); %Inlet gas comp. at start of ith interval

for m=1:tratio; %Inlet gas T & C for stage kij during interval i
    Tgij(1,m)=Tgi+(m-1)*dTgi(1,i);%Inlet gas T
    ygij(:,m)=ygi(:,1)+(m-1).*dygi(:,i);%Inlet gas comp.
end

taug=taugin(1,i); %Residence time in stage kij for ith time interval

for j=1:tratio %Begin integ. loop for ith inlet time interval in stage kij

%Calc. what surface rxn. rates would be at current bulk gas concentrations
%and surface temperature (VYP)
yH2=yg(1,1);yCO=yg(2,1);yC3H6=yg(3,1);yC3H8=yg(4,1);yO2=yg(5,1);
yNO=yg(6,1);yNH3=yg(7,1);yH2O=yg(8,1);yCO2=yg(9,1);yN2=yg(10,1);

[Rrate] =
Rkin_vyp(A,Ea,Tgij(1,j),yCO,yO2,yCO2,yC3H6,yC3H8,yH2,yNO,yNH3,yH2O,xs);
%Assume Ts=Tg
%Rrate(i,1)= Reaction rate for rxn. i (moles target species/m^3 s)
%No global variables used.

%Calc. what net generation/sink rates would be for each gas species
%without mass-transfer resistance. Note: Species with net consumption
%at the surface have negative rates. Species with net generation have
%positive rates.
for k=1:ngs %Increment over gas species
    Rgeng(k,1)=sum(Rrate.*rxst(:,k));%Gen. rate for species k (mole/m^3 s)
end %End gas species increment

%Calc. what net generation/sink rates would be for each solid species
%without mass-transfer resistance.
for m=1:nss %Increment over solid species
    Rgens(m,1)=sum(Rrate.*rxst(:,ngs+m));%Gen. rate for spec. m(mole/m^3 s)
end

%Estimate current values of mass and heat transfer parameters in gas
%boundary layer.
[Re,cNu,htc,Sc,Sh,ktc] = mhttp(Tgij(1,j),z,velocity(1,i),MWg);
%Global variables used: Ga Dh Sh_o cNu_o rlam_o rlam_exp Pr
% Ga= channel wall surface area per unit volume (1/m)
% Dh= channel hydraulic diameter (m)
% Sh_o= Reference Sherwood number for gas-wall mass transfer (-)

```

```

% cNu_o= Reference Nusselt number for gas-wall heat transfer (-)
% rlam_o= factor for gas thermal conductivity (W/m K)*1/(K^rlam_exp)
% rlam_exp= exponent for gas thermal conductivity (-)
% Pr= gas Prandtl number (-)
%Explicit inputs:
% Tg=Gas temperature (K)
% z=axial position relative to entrance (m)
% velocity= gas velocity in monolith channels (m/s)
% MWg= vector of gas molecular weights (g/mole)

%Calc. limiting (max) mass-transfer rates for each gas species
cgt=Pg/Rgas2/Tgij(1,j); %Total gas mole concentration (mole/m^3)
RmL=cgt.*ktc.*yg; %Limiting mass-transfer rates (mole/m^3 s) [maximum
possible rate of species transport to the surface, that is when concentration of
species at the surface is 0]

%Calc. species consumption rates when both surface reaction and mass
%transfer are taken into account. Note: Only species undergoing
%consumption at the surface are limited by boundary layer mass transfer.
Ra1=(Rgeng(:,1)<0).*Rgeng.*RmL./(RmL-Rgeng); % (moles/m^3 s)

%Est. washcoat surface gas concentrations. This applies to species
%undergoing both depletion and generation at the surface. Because the
%combined flow of reactant and product gases can create net convection
%toward or away from the surface (the so-called Stefan flow) a correction
%term is often used for boundary layer transport. A simple total mole
%fraction constraint is used here to approximate that correction.
ys=yg+Ra1./ktc./cgt; %Uncorrected for Stefan flow (mole fraction)
ysc=ys./sum(ys); %Corrected for Stefan flow (mole fractions sum to 1)

%Update surface concentrations after both rxn. and m.t. accounted for
yH2s=ysc(1,1); yCOs=ysc(2,1); yC3H6s=ysc(3,1); yC3H8s=ysc(4,1);
yO2s=ysc(5,1); yNOs=ysc(6,1); yNH3s=ysc(7,1); yH2Os=ysc(8,1);
yCO2s=ysc(9,1); yN2s=ysc(10,1);

%%
%%
% adjust surface reactions to account for species that are generated, such as
%NH3 (VYP)
%Recalc. rxn. rates with adjusted surface concentrations
[Rrates] =
Rkin_vyp(A,Ea,Tgij(1,j),yCOs,yO2s,yCO2s,yC3H6s,yC3H8s,yH2s,yNOs,yNH3s,
yH2Os,xs);

%Recalc. net gen./sink rates for each gas species with adjusted surf.

```

```

%concs.
for n=1:ngs %Increment over gas species
    Rgengm(n,1)=sum(Rrates.*rxst(:,n));%Gen. rate for species n (mole/m^3 s)
end
%Recalc. net gen./sink rates for each solid species with adjusted surf.
%concs.
for p=1:nss %Increment over solid species
    Rgens(p,1)=sum(Rrates.*rxst(:,ngs+p));%Gen. rate for spec. p(mole/m^3 s)
end

%
ys=yg+Rgengm./ktc./cgt; %Uncorrected for Stefan flow (mole fraction)
ysc=ys./sum(ys); %Corrected for Stefan flow (mole fractions sum to 1)
%

%Update surface concentrations
yH2s=ysc(1,1);yCOs=ysc(2,1); yC3H6s=ysc(3,1); yC3H8s=ysc(4,1);
yO2s=ysc(5,1); yNOs=ysc(6,1); yNH3s=ysc(7,1); yH2Os=ysc(8,1);
yCO2s=ysc(9,1); N2s=ysc(10,1);

%%
%%

%Est. bulk gas concs. after integration time step
%ygn=(dt.*(ygij(:,j))./taug+Rgengm./cgt/eps)+yg)/(1+dt./taug);
ygn=(dt.*ygij(:,j))./taug+yg+ktc.*dt.*ysc)/(1+dt./taug+ktc.*dt);%Implicit form
ygn=ygn./sum(ygn); %Insure mole fractions are normalized

%Uncomment when solving energy balance equations(VYP)
%Est. bulk gas temperature after integration time step
%rhog=.029*Pg/Rgas2/Tg; %Gas density (kg/m^3)
%qt=htc*Ga/eps/rhog/Cpg; %Gas heat transfer time constant (1/s)
%Tgn=(Tg+dt*Tgij(1,j)/taug+qt*dt*Ts)/(1+dt/taug+qt*dt);%Implicit form
%Qt=htc*Ga*(Ts-Tg); %Net heat transferred from wall to gas (J/m^3 s)
%RTg=Qt/rhog/Cpg/eps+(Tgij(1,j)-Tg)/taug; %Gas heating rate (K/s)
%Tgn=Tg+RTg*dt; %Explicit form

%Est. solid surf. conc. after integration time step
xsn=xs+Rgens(1,1)*dt/ms; %Est. fraction of unutilized O2 storage

%Calc. net heat generation based on adjusted surface rxn. rates
%Qgenr=Rrates(:,1).*Hr(:,1); %Heat generation for each reaction (J/m^3 s)
%Qgent=sum(Qgenr); %Heat generation rate (J/m^3 s)
%Note: Convention used here is that negative heat generation is exothermic

```

```

%Calc. solid temperature change rate
%Cps=Cp_o+Cp_1*Ts-Cp_2/Ts^2; %Solid heat capacity (J/kg K)
%Qsext=ht_amb*Ga_ext*(Ts-T_amb); %Heat lost from solid to ambient (J/m^3 s)
%Qsnet=-Qgent-htc*Ga*(Ts-Tgn)-Qsext;%Net heat accumulation in solid (J/m^3
s)
%RTs=Qsnet/rhos/Cps/(1-eps); %Solid temperature change rate (K/s)

%Calc. surf. temp. after integration time step
%Tsn=Ts+RTs*dt; %Est. Ts at new time (K)

yg=ygn; %Update gas concentrations to new values
%Tg=Tgij(1,j); %Update gas temperature to new value
%Ts=Tgij(1,j); %Update solid temperature to new value
xs=xsn; %Update Ce2O3 conversion to new value

end %End integration loop (index j) over ith inlet time interval

%Save final state of stage kij for the current time interval i.
%Tgsave(1,i+1)=Tgij(1,j); %Gas temp (K)
%Tssave(1,i+1)=Tgij(1,j); %Wall temp (K)

ygsave(:,i+1)=yg; %Gas comp. (-) original by stuart, which makes y at time=0 the
same for all stages
xssave(:,i+1)=xs; %Surface comp. (-)

%ygsave(:,i)=yg; %Gas comp. (-)
%xssave(:,i)=xs; %Surface comp. (-)
%Note: Current state is initial condition for the next time interval.

end %End time interval increment loop (index i) for stage kij

%Set inlet gas conditions for next stage based on previous stage output
%Tgin=Tgsave; %Exit temps. from previous stage
yggin=ygsave; %Exit comps. from previous stage

%Reset conditions in next stage back to zero time
Tg_q=Tg0_q; %Gas temp (K)
Ts_q=Tg0_q; %Wall temp (K)
yg=yg0; %Gas comp. (-)
xs=x0; %Wall comp. (-)

end %End stage increment loop (index kij)

%End integration section
%-----

```

```
%-----
%Results assessment section
%%
%simulated emissions, mole fractions
outdata_sim=ygsave'; %H2, CO, C3H6, C3H8, O2, NO, NH3, H2O, CO2, N2
%end of main script
```

```
function cat_mon_malibu1()
%Function that specifies the catalyst monolith properties used for the
%TWC and saves them as global variables.
```

```
%Initially created by C.S. Daw, 8/20/2016
```

```
% Modified by V.Y. Prihodko (VYP) 3/3/2017 for Pd-only TWC
```

```
%Outputs:
% nstages= no. of effective axial stages in the catalyst (-)
%Global output variables:
% Case= Name of the current case
% eps= hole (void) fraction in monolith (-)
% channel_density= channel density (1/m^2)
% Ga= channel wall surface area per unit volume (1/m)
% Dh= channel hydraulic diameter (m)
% cat_length= monolith length (m)
% cat_dia= monolith diameter (m)
% cat_volume= monolith volume (m^3)
% Ga_ext= external monolith surface area per unit volume (1/m)
% eps_wash= void fraction in the washcoat (-)
% Sh_o= Reference Sherwood number for gas-wall mass transfer (-)
% cNu_o= Reference Nusselt number for gas-wall heat transfer (-)
% cat_loading= active catalyst area per unit volume (1/m)
% O2_capacity= oxygen storage capacity of monolith (moles/m^3)
% rhos= monolith solid density (kg/m^3)
% rlam= monolith solid thermal conductivity (W/m K)
% Cp_o= reference value for solid heat capacity (J/kg K)
% Cp_1= 1st auxilliary coefficient for solid heat capacity (J/kg K^2)
% Cp_2= 2nd auxilliary coefficient for solid heat capacity (J*K/kg)
% Cpg= reference gas heat capacity (J/kg K)
% rlam_o= factor for gas thermal conductivity (W/m K)*1/(K^rlam_exp)
% rlam_exp= exponent for gas thermal conductivity (-)
% Pr= gas Prandtl number (-)
% T_amb= ambient temperature (K)
% ht_amb= external monolith heat tranfer coefficient (W/m^2 K)
```

```

%Define global variables to be set below
global Catcase eps channel_density Ga Dh cat_length cat_dia cat_vol;
global Ga_ext eps_wash Sh_o;
global cNu_o rhos rlam Cp_o Cp_1 Cp_2;
global cat_loading O2_capacity;
global Cpg rlam_o rlam_exp Pr;
global T_amb ht_amb;

%Define catalyst case
Catcase=char('Pd-only TWC');

%Monolith geometry
%%
%Pd-only properties. Used to calculate parameters used by model. (VYP)
wall_thickness=0.1263; %mm
channel_width_inside=0.9526; %mm
channel_width=channel_width_inside+wall_thickness; %mm
wetted_perimeter=3.09; %mm
Aw=0.1753; %washcoat cross sectional area, mm2
At=channel_width^2; %total cross-sectional area, mm2
Ac=channel_width_inside^2; %uncoated monolith cross-sectional area, mm2
Af=Ac-Aw; %flow area mm2

%%
eps=Af/At; %monolith void fraction (-) of coated monolith
channel_density= 1/(At/1000^2);%(number/m^2)
Ga=wetted_perimeter/At*1000; %geometric surface area, wall area/vol.
(m^2/m^3 or 1/m)
Dh=4*eps/Ga; %(m)

%BFR sample size
%cat_length=5/100; %(m)
%cat_dia=2/100; %(m)

%engine sample size
cat_length=13.4/100; %(m)
cat_dia=2*sqrt(100.1288/pi)/100; %(m) oval in shape with front area=100.1288
cm2

cat_vol=pi*cat_length*cat_dia^2/4; %(m^3)
Ga_ext=4/cat_dia; %external wall area/vol. (1/m)

%Monolith heat and mass properties
rhos=2500; %(kg/m^3) density of monolith substrate
rlams=1.5; %(special units in correlation to give W/m K)

```

```

Cp_o=1.071e3; %(J/kg K)
Cp_1=.156; %Units in correlation to give W/m K)
Cp_2=3.435e7; %Units in correlation to give W/m K)

[a_noble, MW_PGM] = Active_Site(0,1,0,0.25,208);
%determines the number of active sites in mol-site/(m3 of the converter)
%provided by Jian Gong and to be used with Jian Gong's kinetics [95]
% Inputs:
%   1. PtR: Rt ratio of PGM [-]
%   2. PdR: Rd ratio of PGM [-]
%   3. PhR: Rh ratio of PGM [-]
%   4. Disp: dispersion factor [-]
%   5. PGM: PGM catalyst loading [g/ft^3]
% Outputs:
%   1. a_noble: active sites density [mol-site/(m3 of the converter)]
%   2. MW_PGM: average molar weight of PGM [g/mole]

cat_loading=a_noble %mol-site/(m3 of the converter)

O2_capacity=0; %(moles/m^3)

%Mass transfer parameters
eps_wash=0.02; %(-)
Sh_o=3.657; %(-)

%Gas to wall heat transfer parameters
cNu_o=4.364; %(-) fully developed region with constant wall flux

%Exhaust properties
Cpg=1089; %(J/kg K)
rlam_o=2.269e-4; %(special units in correlation to give W/m K) [original
%by Zhiming]
rlam_exp=0.832; %(special units in correlation to give W/m K)

Pr=0.7; %(-)

%Ambient conditions
T_amb=298.15; %(K)
ht_amb=17; %J/m^2 K) % was 40

end
% end of cat_mon_malibu1() function

```

```

function [ngst,nsst,namgs,namss,rxst,A,Ea,Hr,rxo,MWg]=rxnparams_vyp()
%Sets reaction stoichiometric and kinetic parameters for TWC scheme
%
%Initially created by C.S. Daw, 8/20/2016

% Modified by V.Y. Prikhodko (VYP) 3/3/2017 for global kinetics from Jian Gong
[95]

global cat_loading

%Global inputs from function cat_mon_malibu1:
%cat_loading= %mol-site/(m3 of the converter)
%Outputs generated here:
%ngst= No. of tracked gas species
%nsst= No. of tracked solid species
%namgs= Character array with gas species names
%namss= Character array with solid species names
%rxst= Rxn. stoichiometric coefficients-Index1=Rxn. no.,Index2=Species no.
%A= Reaction pre-exp.factor (mole/mole-site s)- Index=reaction number
%Ea=Activation energy vector (J/mole)- Index=reaction number
%Hr=Heat of reaction (J/mole of unit reactant consumed)
%rxo= reaction order array (-) - Index1=Rxn. no., Index2=Species no.
%Kp=inhibition const. array (-)- Index1=K no., Index2=col 1=P1, col2=P2
%MWg=molecular wt. of each gas species (g/mole)

%Specify limits for species and reactions
ngst=10; %Total number of gas species
nsst=2; %Total number of solid species
nrt=13; %Total number of reactions considered
ninh=2; %No. of inhibition terms

%Allocate species index, stoichiometry, and rxn. parameter vectors/arrays
rxst=zeros(nrt,ngst+nsst); %Stoich.-Index1=Reaction no., Index2=Species no.
A=zeros(nrt,1); %Pre-exp. factors (mole/mole-site s)- Index1=Reaction no.
Ea=zeros(nrt,1); %Activation energies (J/mole)- Index1=Reaction no.
Hr=zeros(nrt,1); %Heat of reaction (J/mole reac. consumed)-Index1=Rxn. no.
rxo=ones(nrt,ngst+nsst); %Order-Index1=Reaction no., Index2=Species no.
Kp=zeros(ninh,2); %Array of inhibition constants
MWg=zeros(ngst,1); %Vector of gas molecular weights (g/mole)

%Define each tracked species
%Gases
nam1=char('H2');H2_ind=1;MWg(1,1)=2.02;
nam2=char('CO');CO_ind=2;MWg(2,1)=28.01;
nam3=char('C3H6');C3H6_ind=3;MWg(3,1)=42.08;

```

```

nam4=char('C3H8');C3H8_ind=4;MWg(4,1)=44.08;
nam5=char('O2');O2_ind=5;MWg(5,1)=32.0;
nam6=char('NO');NO_ind=6;MWg(6,1)=30.01;
nam7=char('NH3');NH3_ind=7;MWg(7,1)=17.03;
nam8=char('H2O');H2O_ind=8;MWg(8,1)=18.02;
nam9=char('CO2');CO2_ind=9;MWg(9,1)=44.01;
nam10=char('N2');N2_ind=10;MWg(10,1)=28.0;
namgs=char(nam1,nam2,nam3,nam4,nam5,nam6,nam7,nam8,nam9,nam10);
%Solids
nams1=char('CeO2');CeO2_ind=11;
nams2=char('Ce2O3');Ce2O3_ind=12;
namss=char(nams1,nams2);

%Define stoichiometric coefficients and kinetic params. for each rxn.
%Note: + coefficients for products, - coefficients for reactants

%rxn. 1- CO+0.5O2=>CO2, moles CO consumed/s m^3
rxst(1,CO_ind)=-1;rxst(1,O2_ind)=-.5;rxst(1,CO2_ind)=1;
A(1)=3.54e12*cat_loading;Ea(1)=110450;Hr(1)=-283.2e3;

%rxn. 2- C3H6+4.5O2=>3CO2+3H2O, moles C3H6 consumed/s m^3
rxst(2,C3H6_ind)=-1;rxst(2,O2_ind)=-4.5;rxst(2,CO2_ind)=3;rxst(2,H2O_ind)=3;
A(2)=5.92e13*cat_loading;Ea(2)=120530;Hr(2)=-1927.8e3;

%rxn. 3- C3H8+5O2=>3CO2+4H2O, moles C3H8 consumed/s m^3
rxst(3,C3H8_ind)=-1;rxst(3,O2_ind)=-5;rxst(3,CO2_ind)=3;rxst(3,H2O_ind)=4;
A(3)=9.404e14*cat_loading;Ea(3)=165160;Hr(3)=-2045.5e3; %165160

%rxn. 4- H2+0.5O2=>H2O, moles H2 consumed/s m^3
rxst(4,H2_ind)=-1;rxst(4,O2_ind)=-.5;rxst(4,H2O_ind)=1;
A(4)=1.67e12*cat_loading;Ea(4)=111450;Hr(4)=-242.0e3;

%rxn. 5- CO+NO=>CO2+0.5N2, moles CO consumed/s m^3
rxst(5,CO_ind)=-1;rxst(5,NO_ind)=-1;rxst(5,CO2_ind)=1;rxst(5,N2_ind)=0.5;
A(5)=2.154e9*cat_loading;Ea(5)=52374;Hr(5)=-373.6e3;

%rxn. 6- C3H6+9NO=>3CO2+3H2O+4.5N2, moles C3H6 consumed/s m^3
rxst(6,C3H6_ind)=-1;rxst(6,NO_ind)=-
9;rxst(6,CO2_ind)=3;rxst(6,H2O_ind)=3;rxst(6,N2_ind)=4.5;
A(6)=8.242e9*cat_loading;Ea(6)=80063;Hr(6)=-2741.8e3;

%rxn. 7- H2+NO=>H2O+0.5N2, moles H2 consumed/s m^3
rxst(7,H2_ind)=-1;rxst(7,NO_ind)=-1;rxst(7,H2O_ind)=1;rxst(7,N2_ind)=0.5;
A(7)=4.642e8*cat_loading;Ea(7)=69237;Hr(7)=-332.4e3; %

```

```

%rxn. 8- CO+H2O=>CO2+H2, moles CO consumed/s m^3
rxst(8,CO_ind)=-1;rxst(8,H2O_ind)=-1;rxst(8,CO2_ind)=1;rxst(8,H2_ind)=1;
A(8)=1.800e5*cat_loading;Ea(8)=56720;Hr(8)=-41.2e3;

%rxn. 9- C3H6+3H2O=>3CO+6H2, moles C3H6 consumed/s m^3
rxst(9,C3H6_ind)=-1;rxst(9,H2O_ind)=-3;rxst(9,CO_ind)=3;rxst(9,H2_ind)=6;
A(9)=6.430e6*cat_loading;Ea(9)=53620;Hr(9)=373.8e3;

%rxn. 10- 2Ce2O3+O2=>4CeO2, moles Ce2O3 consumed/s m^3
rxst(10,Ce2O3_ind)=-2;rxst(10,O2_ind)=-1;rxst(10,CeO2_ind)=4;
A(10)=2.943e0;Ea(10)=5296;Hr(10)=-280.91e3; %CHECK Hr

%rxn. 11- NH3+1.25O2=>NO+1.5H2O
rxst(11,NH3_ind)=-1;rxst(11,O2_ind)=-
1.25;rxst(11,NO_ind)=1;rxst(11,H2O_ind)=1.5;
A(11)=3.000e13*cat_loading;Ea(11)=139300;Hr(11)=-165.8e3; %

%rxn. 12- NO+2.5H2=>NH3+H2O
rxst(12,NO_ind)=-1;rxst(12,H2_ind)=-
2.5;rxst(12,NH3_ind)=1;rxst(12,H2O_ind)=1;
A(12)=7.390e9*cat_loading;Ea(12)=44720;Hr(12)=-378.7e3; %

%rxn. 13- NH3+1.5NO=>1.25N2+1.5H2O
rxst(13,NH3_ind)=-1;rxst(13,NO_ind)=-
1.5;rxst(13,N2_ind)=1.25;rxst(13,H2O_ind)=1.5;
A(13)=1.5e10*cat_loading;Ea(13)=121400;Hr(13)=452.4e3; %

end
%end of rxnparams_vyp() function

function [Re,cNu,htc,Sc,Sh,ktc] = mhttp(T_gas,z,velocity,MWg)
%Estimates current values of mass and heat transfer properties in gas boundary
%layer.

%Initially created by C.S. Daw, 8/27/2016
%Updated by C.S. Daw, 10/10/2016

%Inputs:
% T_gas=Gas temperature (K)
% z=axial position relative to entrance (m)
% velocity= gas velocity in monolith channels (m/s)
% MWg= vector of gas molecular weights (g/mole)

%Outputs:

```

```

% Re= gas Reynolds number (-)
% cNu= gas-to-wall h.t. Nusselt number (-)
% htc= gas-to-wall heat transfer coefficient (W/m^2 K)
% Sc= gas-to-wall Schmidt number for each species (-)
% Sh= gas-to-wall Sherwood number for each species (-)
% ktc= gas-to-wall mass transfer coefficient for each gas species(1/s)

%Global variables from function cat_mon
global Ga Dh Sh_o cNu_o rlam_o rlam_exp Pr
% Ga= channel wall surface area per unit volume (m^2/m^3 or 1/m)
% Dh= channel hydraulic diameter (m)
% Sh_o= Reference Sherwood number for gas-wall mass transfer (-)
% cNu_o= Reference Nusselt number for gas-wall heat transfer (-)
% rlam_o= factor for gas thermal conductivity (W/m K)*1/(K^rlam_exp)
% rlam_exp= exponent for gas thermal conductivity (-)
% Pr= gas Prandtl number (-)

%Gas B.L. heat transfer properties.
%Assumes hydrodynamic properties of air.

rlamg=rlam_o*(T_gas^rlam_exp); %thermal conductivity-(W/m K)

density=0.029*1.01325e5/8.314/T_gas; %density (kg/m^3)

viscosity=18.27e-6*411.15/(T_gas+120);
viscosity=viscosity*(T_gas/291.15)^1.5; %viscosity (kg/m s)

Re=density*velocity*Dh/viscosity; %Reynolds no. (-)
cNu=cNu_o*(1+.095*Re*Pr*(Dh/z))^0.45; %h.t. Nussel no. (-)
htc=cNu*rlamg/Dh; %h.t. coefficient (W/m^2 K)

%Gas B.L. mass transfer properties.
%Except for diffusivity, all other assumed properties are for air.
DN2o=.177e-4; %(m^2/s) Diffusivity of N2 at 298K
phi=sqrt(1./MWg+1/29)./sqrt(2/29); %Correction factors for different MWs
diff=phi.*DN2o.*(T_gas/298)^1.5;%Diffusivity of each gas species(m^2/s)
(Diffusivity is proportional to T^(3/2) and P^(-1))
Sc=viscosity./(density.*diff); %Schmidt no. for each gas species (-)
Sh=(Sh_o.*(1+.095.*Re.*Sc.*Dh./z).^0.45); %Sh no. for each gas species (-)
ktc=Sh.*diff.*Ga./Dh; %m.t. coeff.*transfer area for each gas species (1/s)

end
%end of mhttp() function

```

```

function [Rrate] =
Rkin_vyp(A,Ea,Ts,yCO,yO2,yCO2,yC3H6,yC3H8,yH2,yNO,yNH3,yH2O,xs)
%Calculates surface kinetic reaction rates for specified conditions.
%Inputs:
%A = Arrhenius pre-exponential factors for each rxn. (mol-site/(m3 of the
converter))
%Ea = Activation energy for each rxn. (J/mole)
%K = Inhibition factors
%Ts = Surface temperature (K)
%yCO,yO2,yC3H6,yC3H8,yH2,yNO,yH2O = reactant gas mole fractions (-)
%xs = coverage fraction Ce2O3 in ceria (-)

%Output:
%Rrate = rates for each rxn. (moles of reactant or product/m^3 s)

%Initially created by C.S. Daw, 8/20/2016

% Modified by V.Y. Prikhodko (VYP) 3/3/2017 for global kinetics from Jian Gong
[95]

Rgas=8.314; %Ideal gas constant (J/mole K)

%Calc. K factors used in inhibition terms
K1=4.314*exp(485/Ts);
K2=1.289*exp(-166/Ts);
K3=2.147e-4*exp(10163/Ts);
K4=8.699e5*exp(-3685/Ts);

%Calc. inhibition terms
G1=(1+K1*yCO+K2*yC3H6)^2*(1+K3*yCO^2*yC3H6^2)*(1+K4*yNO);
G2=exp(-(-41034+44.19*Ts-5.553e-3*Ts^2)/(Rgas*Ts));

%Calc. rxn. rate constants
kr=A.*exp(-Ea./Rgas./Ts); %(Moles/m^3 s)

%Calc. rxn. rates
%rxn. 1- CO+0.5O2=>CO2,(moles CO/m^3 s)
Rrate(1,1)=kr(1)*yCO*yO2/G1;

%rxn. 2- C3H6+4.5O2=>3CO2+3H2O,(moles C3H6/m^3 s)
Rrate(2,1)=kr(2)*yC3H6*yO2/G1;

%rxn. 3- C3H8+5O2=>3CO2+4H2O, (moles C3H8/m^3 s)
Rrate(3,1)=kr(3)*yC3H8*yO2/G1;

```

```

%rxn. 4-  $\text{H}_2 + 0.5\text{O}_2 \Rightarrow \text{H}_2\text{O}$ , (moles  $\text{H}_2/\text{m}^3 \text{ s}$ )
Rrate(4,1)=kr(4)*yH2*yO2/G1;

%rxn. 5-  $\text{CO} + \text{NO} \Rightarrow \text{CO}_2 + 0.5\text{N}_2$ , (moles  $\text{CO}/\text{m}^3 \text{ s}$ )
Rrate(5,1)=kr(5)*yCO*yNO/G1;

%rxn. 6-  $\text{C}_3\text{H}_6 + 9\text{NO} \Rightarrow 3\text{CO}_2 + 3\text{H}_2\text{O} + 4.5\text{N}_2$ , (moles  $\text{C}_3\text{H}_6/\text{m}^3 \text{ s}$ )
Rrate(6,1)=kr(6)*yC3H6*yNO/G1;

%rxn. 7-  $\text{H}_2 + \text{NO} \Rightarrow \text{H}_2\text{O} + 0.5\text{N}_2$ , (moles  $\text{H}_2/\text{m}^3 \text{ s}$ )
Rrate(7,1)=kr(7)*yH2*yNO/G1;

%rxn. 8-  $\text{CO} + \text{H}_2\text{O} \Rightarrow \text{CO}_2 + \text{H}_2$ , (moles  $\text{CO}/\text{m}^3 \text{ s}$ )
Rrate(8,1)=kr(8)*(yCO*yH2O-yH2*yCO2/G2)/G1;

%rxn. 9-  $\text{C}_3\text{H}_6 + 3\text{H}_2\text{O} \Rightarrow 3\text{CO} + 6\text{H}_2$ , (moles  $\text{C}_3\text{H}_6/\text{m}^3 \text{ s}$ )
Rrate(9,1)=kr(9)*yC3H6*yH2O/G1;

%rxn. 10-  $\text{Ce}_2\text{O}_3 + .5\text{O}_2 \Rightarrow 2\text{CeO}_2$  (moles  $\text{Ce}_2\text{O}_3/\text{m}^3 \text{ s}$ )
Rrate(10,1)=kr(10)*xs*yO2;

%rxn. 11-  $\text{NH}_3 + 1.25\text{O}_2 \Rightarrow \text{NO} + 1.5\text{H}_2\text{O}$ 
Rrate(11,1)=kr(11)*yNH3*yO2/G1;

%rxn. 12-  $\text{NO} + 2.5\text{H}_2 \Rightarrow \text{NH}_3 + \text{H}_2\text{O}$ 
Rrate(12,1)=kr(12)*yNO*yH2/G1;

%rxn. 13-  $\text{NH}_3 + 1.5\text{NO} \Rightarrow 1.25\text{N}_2 + 1.5\text{H}_2\text{O}$ 
Rrate(13,1)=kr(13)*yNH3*yNO/G1;

end
%end of Rkin_vyp function

```

VITA

Vitaly Y. Prikhodko came to the USA from Russia in 1997 as a high school exchange student. After completing high school, he began studying computer science and business at Maryville College, Maryville, Tennessee. In May 2002 he received a Bachelor of Art degree from Maryville College. Upon completion of his undergraduate studies he worked at the Oak Ridge National Laboratory's National Transportation Research Center for a year, and in 2003 he enrolled in the graduate studies program at the University of Tennessee, Knoxville. Vitaly received his Master of Science degree in Mechanical Engineering from the University of Tennessee in August 2007. After one year post-master appointment at ORNL, he returned to graduate school at the University of Tennessee to pursue his PhD degree in Mechanical Engineering. He was hired as a full staff employee at ORNL in 2011 and completed his PhD studies in August 2018.