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Conor Berndt

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AN EXPERIMENTAL STUDY OF A PASSIVE NO_x ADSORBER (PNA) FOR THE
REDUCTION OF COLD START DIESEL EMISSIONS

By

Conor T. Berndt

A THESIS

Submitted in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

In Mechanical Engineering

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2019

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This thesis has been approved in partial fulfillment of the requirements for the Degree of
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List of Abbreviations

dCSC™ – Johnson Matthey Diesel Cold Start Concept

DOC – Diesel Oxidation Catalyst

PNA – Passive NO_x Adsorber

CARB – California Air Resources Board

EPA – Environmental Protection Agency

NAAQS – National Ambient Air Quality Standards

HC – Total Hydrocarbons

NO – Nitric Oxide

NO₂ – Nitrogen Dioxide

NO_x – NO + NO₂

N₂O – Nitrous Oxide

CO – Carbon Monoxide

CO₂ – Carbon Dioxide

ATS – Aftertreatment System

ULN – Ultra-Low NO_x

H₂O – Water

O₂ – Oxygen

JM – Johnson Matthey

SCR – Selective Catalytic Reduction

SCR-F – Selective Catalytic Reduction Catalyst on a Diesel Particulate Filter

EGR – Exhaust Gas Recirculation

DPF – Diesel Particulate Filter

CPF – Catalyzed Particulate Filter

PM – Particulate Matter

CDA – Cylinder Deactivation

SwRI – Southwest Research Institute

LLC – Low Load Cycle

REAL – Real Emissions Assessment Logging

NI – National Instruments™

DAQ – Data Acquisition

VGT – Variable Geometry Turbo

AFR – Air-to-Fuel Ratio

GHG – Greenhouse Gas

PGM – Platinum Group Metals

Ar – Argon

Pd – Palladium

Pt - Platinum

Abstract

Medium and heavy-duty diesel engines contribute nearly a third of all NO_x emissions nationwide. Further reduction of NO_x emissions from medium and heavy-duty diesel engines is needed in order to meet National Ambient Air Quality Standards (NAAQS) for ambient particulate matter and ozone. Current diesel engine aftertreatment systems are very efficient at reducing NO_x emissions at exhaust temperatures above 200 °C, however at exhaust temperatures below 200 °C there are significant NO_x emissions at the tailpipe. Therefore, a reduction of diesel engine cold start and low speed/load operation emissions, where exhaust temperatures are below 200 °C, is needed. Utilizing a passive NO_x adsorber (PNA) to adsorb NO_x emissions at temperatures below 200 °C and reduce tailpipe NO_x emissions is part of the solution. In this research, over 200 hours of experimental testing was carried out on a Johnson Matthey Diesel Cold Start Concept Catalyst (dCSCTM), a passive NO_x adsorber with hydrocarbon trapping ability on an oxidation catalyst.

Storing NO_x emissions while the aftertreatment system downstream of the PNA is at temperatures below 200 °C needs to be supplemented by externally heating the aftertreatment system downstream of the PNA. This would reduce the time the aftertreatment system is at temperatures below 200 °C. The faster the aftertreatment system reaches operating temperature the less risk of substantial NO_x emissions at the tailpipe, because the storage capacity of the dCSCTM is finite. Methods such as electric heaters, fuel burners, engine calibration, engine hardware changes, and others to quickly reach desired aftertreatment temperatures are being researched. The EPA and CARB are preparing to monitor the emissions regulation compliance of medium and heavy-duty diesel engines by using on-board diagnostics, throughout the useful life of the engine. They are also investigating thermal and chemical catalyst poisoning in order to accurately age and predict the life of the aftertreatment system. Improving processes and reducing contaminants in fuels can reduce the risk of chemical catalyst poisoning.

A 2013 6.7L Cummins ISB (280 hp) diesel engine was used for a series of experiments to quantify the NO, NO₂, and NO_x storage and release performance of the dCSCTM. NO_x storage experiments were performed at a range of temperatures from 80 to 250 °C and NO_x release experiments were performed at temperatures from 200 to 450 °C. The portion of NO, NO₂, and NO_x that is converted and the portion that remains stored on the dCSCTM and the oxidation characteristics of the dCSCTM at these temperatures were also quantified.

Peak NO_x storage capacity of the dCSCTM was found to be at temperatures from 125 to 150 °C. Throughout the testing, a decrease in the total NO_x storage capacity was observed. However, the 200-second dCSCTM NO_x storage capacity remained constant throughout testing. The percentage of stored NO_x released was observed to be over 70% if the dCSCTM temperature ramped through 200 to 265 °C and/or reached 350 °C. These temperatures coincide with the desired operating temperatures of current aftertreatment systems. The dCSCTM also shows over 50% NO to NO₂ oxidation at temperatures from 200 to 400 °C and a peak oxidation performance of 90% at 300 °C. At temperatures of 150 °C and above, the dCSCTM oxidizes 90 to 100% of CO to CO₂. At 80 to 125 °C, the dCSCTM oxidizes 50 to 70% of the CO entering the substrate to CO₂.

1 Introduction

The purpose of this chapter is to give background information and the goals and objectives of the research conducted. Specifically, why the research is being conducted and what need does it fill. For decades, diesel engine aftertreatment system research has been continuously driven by increasingly stringent emissions standards. The Environmental Protection Agency (EPA) and California Air Resources Board (CARB) have worked in conjunction for years to develop new emissions standards, test cycles, compliance monitoring, useful life determinations, and advanced protocols to simulate real world deterioration of the components in the diesel engine aftertreatment system.

1.1 Background

The current heavy-duty diesel engine aftertreatment systems can reduce tailpipe emissions with very high efficiencies once they reach their operating temperature [1]. One such system from Cummins Emissions Solutions consists of (from upstream to downstream) a DOC, DPF, DEF injector, decomposition reactor, and SCR [2]. The DOC, or Diesel Oxidation Catalyst, oxidizes CO to CO₂, HC to CO₂ and H₂O, and NO to NO₂. The DPF, or Diesel Particulate Filter, filters the particulate matter (PM). The DEF, or Diesel Exhaust Fluid injector injects atomized DEF into the decomposition tube. The decomposition tube decomposes the atomized DEF into ammonia (NH₃) and water (H₂O), and mixes the NH₃ uniformly with the exhaust gas. The SCR, or Selective Catalytic Reduction, receives the NH₃-exhaust gas mixture and reduces the NO_x in the exhaust gas to nitrogen (N₂) and water (H₂O). There is a need to periodically actively regenerate the DPF due to excess PM by performing a late diesel injection [2]. The efficiency of the SCR catalyst has been increased to 90% at temperatures as low as 200°C [3]. However, when these systems are below 200 °C, during startup or low speed/load operation, their NO_x conversion efficiency is low. One of the goals of the EPA and CARB partnership is to reduce or even eliminate these NO_x emissions [3, 4, 5].

Currently, heavy-duty trucks contribute a third of the NO_x emissions produced in California and are projected to contribute a third nationwide by 2025 [3]. Further NO_x emissions regulations are required in order for the South Coast Air Basin to achieve the National Ambient Air Quality Standards (NAAQS) requirement for ambient PM and Ozone [3]. NO_x emissions are a precursor to PM, this makes them especially important to meeting the NAAQS PM requirement. The current NO_x reduction goal is an Ultra-Low NO_x (ULN) standard of 0.02 gNO_x/bhp-hr on the FTP and RMC-SET cycles [3]. The Federal Test Procedure (FTP) and Supplemental Emission Test Ramped Modal Cycle (RMC-SET) are the drive cycles currently used to certify medium and heavy-duty diesel engines [3]. The drive cycles command sequences of vehicle speed (chassis dynamometer) or engine load (engine dynamometer) and tailpipe emissions are measured. The tailpipe emissions measurements determine whether or not the specific drive cycle emissions regulations are met. Southwest Research Institute (SwRI) is working closely with CARB and the EPA to determine realistically achievable emissions levels for the drive cycles and the methods for doing so. “Per reference [3], SwRI has achieved 0.034 gNO_x/bhp-hr NO_x level over the FTP and a 0.038 g/bhp-hr NO_x level over the RMC-SET [3]”. The latest feasibility assessment from the CARB staff is that MY 2024 through 2026 heavy and medium-duty engines could be required to meet 0.05 to 0.08 gNO_x/bhp-hr on the FTP and RMC cycles [3, 6]. PM emissions standards will also see a reduction to 0.005 g/bhp-hr by MY 2024. MY 2027 will see an even further reduction in NO_x emissions levels [3, 6]. CARB and the EPA have reduction targets for greenhouse gas (GHG) and petroleum use as well. CARB Phase 2 GHG emissions standards will be implemented alongside the NO_x and PM regulations in 2021, 2024, and 2027. These Phase 2 GHG emissions standards require a 5.1% fuel efficiency improvement from the 2017 fuel efficiency levels, by model year 2027 [3].

A new “Low Load Cycle” (LLC) has been developed by SwRI to simulate the low speed and load of “urban tractor and vocational vehicle operations” [3, 7]. The current FTP and RMC-SET cycles fail to capture the low load and speed operation of medium and heavy-duty diesel engines. It is important to capture the low speed/load operation because

exhaust temperatures are low at these conditions: causing the current ATS to be ineffective [3, 7]. The LLC emissions requirements for NO_x will be between 1 to 3 times the FTP and RMC-SET requirements (0.05 to 0.24 gNO_x/bhp-hr) [3, 6].

During low speed/load operation, the ATS temperatures fall well below 200°C.

Increasing exhaust temperatures can be done via engine calibration, hardware, or external heat sources, and can ensure that the ATS temperature is above 200°C during startup and normal operation. In addition, improving ATS efficiencies at temperatures below 200°C can help reduce low speed/load emissions. This could involve improving the efficiency of current SCR systems at low temperatures; or employing a passive NO_x adsorber (PNA) to store NO_x emissions at low temperatures. Current ULN ATS solutions employ both the increase in exhaust temperatures and improving catalyst efficiencies at lower temperatures [1, 4, 5, 8].

The main goal of the ULN ATS is to reduce NO_x and HC emissions during low load/speed operation and cold start. Storing NO_x and HC emissions until the ATS is at operating temperature is a promising strategy. This can be achieved through the use of a PNA catalyst with zeolites to trap HC [1, 5, 8]. Figure 1.1 shows a schematic of proposed ULN ATS configurations compared to today's ATS systems [9]. The schematic was put together by Daimler Trucks to reflect the proposals from references [3, 5].

Figure 1.1 Possible ULN ATS Compared to Current ATS [9]

Both “Proposed Advance Technology” systems in Figure 1.1 include the utilization of a PNA to store NO_x emissions at temperatures below 200 °C [3, 5, 9]. PNA technology developed by Johnson Matthey to store HC, CO, and NO_x emissions at low temperatures and release them at high temperatures has been developed. The device consists of a PNA with HC trapping ability on an oxidation catalyst i.e. the Diesel Cold Start Concept (dCSC™) [1, 8]. The goal of this catalyst is to store emissions while the downstream ATS heats up. Externally heating the downstream ATS will reduce the time the PNA has to adsorb NO_x, HC, and CO emissions and improve ATS efficiency [4, 5, 9]. Once the downstream ATS is at its operating temperature, the dCSC™ will release these emissions to the downstream ATS to be reduced and oxidized [5, 8]. The ATS will have a complex control system that will require accurate thermal management in order to achieve desired tailpipe emissions [10].

The dCSC™ has a limited NO_x and HC storage capacity. Therefore, increasing exhaust temperatures quickly and keeping them above 200°C is still a primary goal of the ULN

ATS. As stated before, exhaust temperatures can be increased through engine calibration, hardware, or external heat sources like electric heaters. Late fuel injections are currently a common tool used to manage the ATS temperature; research is also being done to develop external heat sources such as electric heaters and fuel burners [3, 4, 5, 10, 11]. Figure 1.2 shows that a reduction in engine AFR increases exhaust gas temperatures [12]. Reducing AFR can be achieved by throttling, reducing boost, valve timing, EGR, and cylinder deactivation [4, 12]. Some of these are engine hardware changes while some of them are calibration changes will likely be needed. In Figure 1.2 the AFR was decreased through cylinder deactivation and late intake valve closing. A mixture of engine hardware and calibration changes. In this case the figure is reporting turbine outlet temperature which is at the inlet to the ATS. Cases where the turbine outlet temperature falls well below the curve are cases with high EGR rates [12].

Figure 1.2 Engine Turbo Outlet Temperature vs. AFR [11].

Another objective of the EPA's Cleaner Trucks Initiative and CARB is to “ensure in-use emissions reductions [4, 12].” One of the ways to do this is to properly determine the useful life of ATS components. This will ensure the compliance with regulations once the ATS is exposed to real world conditions. Current ATS aging procedures for certification

are not reflective of actual real-life deterioration factors [3]. Aging methods are extremely important to developing ATS components that will be required to perform throughout the useful life of the product. Properly aging the ATS with the correct deterioration factors will allow for more accurate ATS useful life estimates and service dates. Chemical poisoning is the primary cause for catalyst malfunction. This is usually caused by fuel contaminants that could be avoided through improved fuels and processes. Understanding all of the aging effects on the ATS is vital to achieving the goal of technology with a useful life of up to 1 million miles [3, 4].

CARB has proposed a program called Real Emissions Assessment Logging or REAL. REAL aims to utilize onboard data loggers to monitor compliance and enforce emissions regulations. They are investigating the feasibility of using NO_x sensors to monitor and determine emissions compliance. NO_x sensor data could be logged for future inspection or monitored in “real” time to detect emissions compliance issues [3].

The reduction of NO_x and PM emissions, ensuring the reduction of emissions through real-time monitoring, and advanced testing capabilities that are reflective of actual “real-world” situations are the overall goals of the EPA and CARB [3, 4].

1.2 Goals and Objectives

The goal of this research is to acquire experimental data on the dCSC™ device, characterize the device’s performance, and calibrate a high-fidelity 2D flow through model. This model would aid in the development of the ULN ATS and the overall goals the EPA and CARB. To achieve these goals, an engine test cell and test procedure had to be developed as well as a statistical test matrix. Determining the correct test cell instrumentation to acquire the data for the model was also needed. The specific objectives developed to achieve the research goals are as follows:

1. Perform a literature study on the dCSCTM, and other PNAs, related to experimental studies, in order to develop a set of objectives to achieve from the dCSCTM experimental data.
2. Determine the experimental data needed in order to calibrate the high-fidelity 2D flow through model to simulate the Johnson Matthey Cold Start Concept (dCSCTM).
3. Develop the engine test cell setup to perform experimental research on the dCSCTM.
4. Develop experimental testing procedures and a statistical test matrix.
5. Quantify the NO, NO₂, and NO_x storage performance of the dCSCTM at temperatures from 80°C to 250°C during the cold start period and NO_x release performance at temperatures from 200°C to 450°C.
6. Quantify the portion of the stored NO, NO₂, and NO_x that is converted and the portion that remains stored during the warm-up period.
7. Quantify the oxidation characteristics of the dCSCTM during the experimental testing.

1.3 Thesis Outline

This chapter gives background on the motivation for the research herein. The National Ambient Air Quality Standards (NAAQS) drive the CARB/EPA vehicle and engine emission standards for medium and heavy-duty diesel emissions. These standards drive research to be conducted and options to be explored. This research was to better understand the dCSCTM performance during storage and release experiments.

Chapter 2 is a literature review on the dCSCTM, related experimental studies, and similar technologies. These technologies are all directed towards meeting future Ultra-Low NO_x standards.

Chapter 3 is an overview of the test cell setup: engine, dynamometer, instrumentation, emissions analyzers, and the methodology used to process the data. Also described is the

experimental test procedure developed to achieve the research goals, as well as the experimental test matrix. A test procedure was developed for varying engine conditions, steady-state dCSCTM temperatures, and temperature ramp rates.

Chapter 4 covers the results and the Summary/Conclusions from the experimental data. A more extensive description of the instrumentation and the data analysis calculations, time plots, control plots, and other data acquired can be found in Appendices A-H.

2 Literature Review

2.1 Ultra-Low NO_x Aftertreatment Systems

EPA and CARB are planning to reduce NO_x from medium and heavy-duty diesel engines in model years 2024 and 2027 [3, 4]. The ULN standard for 2027 has not been set, but could potentially be a 90% reduction from the current 0.2 to 0.02 gNO_x/bhp-hr on the FTP cycle. A study performed by SwRI achieved 0.034 gNO_x/bhp-hr over the FTP cycle on a 2014 MY 13.0L Volvo diesel engine [3]. Engine hardware changes to aide ATS thermal management and strategic control of ATS thermal management would improve the results of the reference [5]. Figure 2.1 shows the ULN ATS used on the engine at SwRI to achieve the 0.034 gNO_x/bhp-hr on the FTP cycle. The system features a PNA at the outlet of the engine exhaust.

Figure 2.1 ULN ATS used on a Volvo MY 13.0L Diesel Engine at SwRI [5]

The PNA in Figure 2.1 is followed by a diesel fueled mini-burner, DEF injector, SCR-F, SCR, and an ammonia slip catalyst (ASC). The diesel-fueled mini-burner was used as supplemental heat to achieve an SCR-F inlet temperature of 250-350°C [13]. The ASC compensates for slip of NH₃ from the SCR, leading to NH₃ emissions at the tailpipe. The ASC oxidizes NH₃ slip from the SCR into N₂ [14]. The PNA adsorbs NO_x, CO, and HC at low temperatures while the diesel-fueled mini-burner heats the rest of the ATS to its operating temperature (250-350 °C) [13]. Once the SCR is at its operating temperature, it can reduce the NO_x in the exhaust gas [15]. The ability of the PNA to store emissions is finite. Therefore, the mini-burner must heat the SCR to its operating temperature (250-

350 °C) before the PNA reaches its storage capacity. Instead of needing a separate DOC, the PNA serves as the DOC for the system as well. The PNA replaces the DOC with no added thermal mass to the ATS. This is the general architecture of the ULN ATS used at SwRI to conduct the ULN feasibility study on behalf of CARB and the EPA [5].

Another ULN ATS architecture being evaluated, shown in Figure 1.1, is to have a close-coupled SCR (ccSCR) or a LO-SCR in front of the PNA in Figure 2.1. Positioning this SCR in front of all of the other ATS components and as close to the engine as possible will allow it to heat up quickly. It would not reduce NO_x at its highest efficiency, but the amount of NO_x it does reduce would reduce the workload of the PNA to store NO_x during cold start. The LO-SCR would also supplement the ATS during hard acceleration events where a spike in tailpipe NO_x emissions is possible [16]. Multiple SCR's within the system would require complex dosing system with the ability to dose at low temperatures. Therefore, the dosing system must be externally heated so that it can effectively deliver DEF to the ATS [16].

Cold start is not the only operation in which NO_x emissions must be reduced. The development of the Low Load Cycle (LLC) will test the ULN ATS systems efficiency during low speed and load medium and heavy-duty diesel engine operation. Therefore, it is important that the ATS reaches operating temperature quickly, but also stays at operating temperature (above 200 °C). This will be achieved through properly packaging, positioning, and insulating the ATS to reduce thermal losses [16].

2.2 PNA Fundamentals

NO_x storage or adsorption is a viable strategy for controlling cold start NO_x emissions by using PNA technology that can adsorb NO_x emissions at temperatures below 200 °C. Common PNA formulations include ceria/alumina-supported Pd/Pt and zeolite supported Pd. Ceria/alumina-supported and zeolite supported Pd allows the PNA to store NO_x at temperatures below 200 °C as opposed to the alkaline earth oxide that is used on Lean NO_x Trap's. Zeolite supported Pd formulations have superior resistance to sulfur and HC

poisoning over the ceria/alumina and alkaline earth oxide Pd/Pt [17]. In addition to adsorption of NO_x the Pd zeolite's serve as an HC trap as well. The combination of an HC trap and NO_x adsorber, and good resistance to Sulphur and HC poisoning, makes the zeolite Pd PNA catalyst the best current option for cold start emissions control [1, 8, 17, 18].

Figure 2.2 illustrates NO adsorption on a PNA catalyst, from a flow reactor study at the University of Houston [19]. The gas mixture to the reactor was 80 °C and contained 400 ppm NO, 2% O₂, balance Ar. The gas mixture was comprised of all NO and no NO₂ because diesel engine outlet NO_x is 90-95% NO. The catalyst was fed with the gas for 5 minutes and the downstream NO, NO₂, and NO_x concentrations were measured. There is 400 ppm NO at the catalyst inlet, therefore a measurement less than 400 ppm of total NO_x at the catalyst outlet indicates NO storage or adsorption. The x-axis shows test time in seconds and the y-axis shows downstream PNA NO, NO₂, and NO_x concentrations in ppm. The downstream PNA NO_x concentrations are much lower than 400 ppm during the first 100 seconds. Indicating during the first 100 seconds, a large amount of NO is being adsorbed. During the 100 to 300 second time, the downstream PNA NO and NO_x concentrations are over 350 ppm which is less than 50 ppm lower than the 400 ppm at the PNA inlet. During these 200 seconds the PNA reaches its NO_x adsorption/storage capacity. There is a constant 0 ppm NO₂ concentration at the PNA outlet for the duration of the adsorption process that is occurring. The inlet gas temperature, 80 °C, is too low for the PNA to oxidize NO to NO₂. Therefore, 0% of the upstream NO is oxidized to NO₂ [19].

Figure 2.2 NO Adsorption Profile [19]

A NO_x desorption profile from the same study, is shown in Figure 2.3. The x-axis shows feed gas temperature in °C and the y-axis shows downstream PNA NO, NO₂, and NO_x concentrations in ppm. The y-axis starts at 0 ppm, to properly compare the NO, NO₂, and NO_x desorption profiles. In Figure 2.3 the PNA is being fed with the same feed gas as Figure 2.2 except for the 400 ppm NO. In this figure, the PNA has reached its NO_x peak storage capacity at 80 °C from the adsorption event in Figure 2.2. The temperature of the feed gas is increasing at a rate of 20 °C per minute from 80 to 500 °C. As the feed gas temperature increases, the downstream PNA NO, NO₂, and NO_x concentrations increase. The PNA inlet NO concentration is not increasing and the outlet concentration is increasing indicating NO_x is being desorbed from the PNA. The downstream PNA NO_x concentration reaches a peak as the feed gas temperature reaches 150 °C. The PNA continues to release NO_x until the feed gas temperature reaches 250°C. The presence of NO₂ downstream of the PNA indicates the PNA is oxidizing NO to NO₂. The $d_{200} = 52\%$

in the top right corner of Figure 2.3 indicates that by the time the feed gas temperature reached 200 °C, 52% of the adsorbed NO_x had been desorbed.

Figure 2.3 NO_x Desorption Profile [19]

Similar profiles are observed for the storage and release of other exhaust gas constituents: such as CO and HC. The presence of H₂O in the exhaust gas can inhibit the ability of the PNA to adsorb HC and NO_x. The presence of CO in exhaust gas can mitigate this inhibition [20].

The same experiment as Figure 2.2 was conducted three times in Figure 2.4. Of those three experiments, two were conducted with the addition of 5% H₂O in the feed gas and one was conducted with no H₂O in the feed gas. Of those two experiments containing 5% H₂O in the feed gas, one was “oxygenated” beforehand. The “oxygenation” consists of a 10% O₂ balance Ar feed gas to the reactor at 750°C for two hours. The data in Figure 2.4

illustrates the inhibition of water on NO_x adsorption by comparing the PNA NO_x adsorption profiles from the three experiments [19].

Figure 2.4 H₂O Effects on NO_x Storage Capacity [19]

The y-axis shows NO_x concentration in ppm and the x-axis shows time, in seconds. The addition of water in the exhaust will inhibit the PNA’s ability to store NO_x. Therefore, higher NO_x concentrations will be observed sooner at the PNA outlet with increasing H₂O concentrations. The oxytreatment attempts to reduce this water inhibition. At the 50 second time, the NO concentration downstream of the PNA with no H₂O in the feed gas and no oxytreatment was 200 ppm. The NO concentration downstream of the PNA that was fed with feed gas containing 5% H₂O and no oxytreatment was 375 ppm at the 50 second time. The NO concentration downstream of the PNA that was oxytreated and fed with feed gas containing H₂O was 345 ppm. Therefore, the “oxytreated” experiment, containing 5% H₂O in the feed gas, experienced less NO_x storage inhibition than the

experiment containing the 5% H₂O without oxytreatment. Therefore, it can be deduced that the oxytreatment reduced the inhibition effect of H₂O in the feed gas. In both the oxytreated and non oxytreated case, the 5% H₂O present in the feed gas caused the downstream PNA NO concentration to increase more rapidly than the experiment with no H₂O.

2.3 PNA, DOC, and Cold Start Concept Catalyst Performance

The Johnson Matthey Diesel Cold Start Concept (dCSC™), is a PNA with HC trapping ability on an oxidation catalyst [1, 8]. In reference [1], the dCSC™ was compared to a separate DOC and PNA to show the advantages of the dCSC™ which has coupling of DOC and PNA technologies [1].

The dCSC™, DOC, and PNA were exposed to 5% H₂O, balance air, at 750 °C, for 16 hours. The substrates were then fed gas containing 10% O₂, 5% CO₂, 5% H₂O, balance N₂ at 650 °C to clean the substrates of any stored emissions. All three substrates were then cooled to a temperature of 80 °C with the same feed gas composition. Once the substrates reached a steady state temperature of 80 °C, 200 ppm NO, 200 ppm CO, and 500 ppm decane (on a C₁ basis) was added to the feed gas for 100 seconds. At the conclusion of the 100 seconds, the temperature of the feed gas was increased from 80 to 650 °C at a rate of 100 °C per minute [1].

During this experiment, CO concentrations were measured downstream of the dCSC™, PNA, and DOC. Figure 2.5 shows the CO oxidation comparison between the dCSC™, DOC, and PNA. The dCSC™ is referred to in the plot legend as the CSC. At the 50 second point in the experiment, the downstream dCSC™ and PNA CO concentrations are around 50 ppm and the downstream DOC CO concentration is around 175 ppm. The amount of PGM on each substrate effects the CO oxidation capabilities of each substrate [1]. The PNA and dCSC™ contain a significantly higher amount of PGM than the DOC substrate. This is why the CO oxidation of the PNA and dCSC™ is greater than the DOC.

100 seconds into the experiment, the feed gas starts its temperature ramp from 80 to 650 °C. As soon as the feed gas temperature starts increasing, the downstream PNA and dCSC™ CO concentrations start decreasing. Both downstream PNA and dCSC™ CO concentrations reach 0 ppm before the feed gas temperature reaches 140 °C. The downstream DOC CO concentration does not start decreasing until the feed gas temperature reaches 140 °C and reaches 0 ppm once the feed gas temperature reaches 200 °C [1].

Figure 2.5 Downstream DOC, PNA, and dCSC™ CO Concentrations vs. Time and Temperature [1]

The dCSC™ and PNA show significantly higher CO oxidation than the DOC [1]. During the same experiment as Figure 2.5, downstream dCSC™, DOC, and PNA HC concentrations were measured. Figure 2.6 shows the HC concentrations downstream of the substrates. From time 0 to 100 seconds, the downstream HC concentrations of all three substrates are less than 50 ppmC (on C₁ basis), while the upstream HC concentration is 500 ppmC. Therefore, all three substrates show significant HC adsorption per reference [1].

At the 100 second point, the inlet gas temperature starts increasing from 80 to 650 °C. When the inlet gas temperature reaches 150 °C, the downstream DOC and PNA HC concentrations begin to increase indicating desorption of HC. The downstream dCSC™ HC concentration does not start increasing until the inlet gas temperature reaches 200 °C. At 220 °C inlet gas temperature of all three downstream substrate temperatures peak. The downstream PNA concentration peaks highest at 120 ppmC, the downstream DOC HC concentration peaks at 100 ppmC, and the downstream dCSC™ HC concentration peaks at slightly over 50 ppmC. The peak downstream dCSC™ HC concentration is less than half of the peak downstream DOC and PNA HC concentrations. This shows that the dCSC™ more effectively converts the stored HC than the DOC and PNA substrates. Once the inlet gas temperature reaches above 250 °C, all three substrates show 100% HC oxidation efficiency [1].

Figure 2.6 Downstream DOC, PNA, and dCSC™ HC Concentrations vs. Time and Temperature [1]

It was determined during further testing in reference [8] that during the temperature ramp in Figures 2.5 and 2.6 that N₂O is produced due to the HC lean NO_x reductions

occurring. Peak downstream substrate N_2O concentrations observed were 126, 74, and 30 ppm for the DOC, PNA, and dCSCTM substrates, respectively [8].

An additional experiment was run in reference [1] to characterize steady state NO to NO_2 oxidation activity of the DOC and dCSCTM. Figure 2.7 shows the steady state NO_2/NO_x ratio downstream of the DOC and dCSCTM substrates vs. temperature. The same feed gas containing 200 ppm NO, 200 ppm CO, 500 ppmC decane (C_1 basis), 10% O_2 , 5% CO_2 , 5% H_2O , balance N_2 was fed to the DOC and dCSCTM at temperatures from 200 to 550 °C, in 50 °C intervals. The gases were fed to the DOC and dCSCTM substrates for 30 minutes to ensure steady state NO to NO_2 oxidation was occurring [1].

The dCSCTM substrate shows slightly less NO to NO_2 oxidation than the DOC. Both the dCSCTM and DOC have peak NO_2/NO_x oxidation performance at a substrate temperature of 300°C. At 300 °C the dCSCTM converts 45% of the upstream NO to NO_2 and the DOC converts 55%. The NO oxidation of both is substantial from 250°C to 350°C. At substrate temperatures lower than 250 °C and higher than 350°C the NO oxidation decreases significantly [1].

Figure 2.7 Downstream dCSCTM and DOC NO_2/NO_x Ratio vs. Temperature [1].

Figure 2.8 shows the 200-second NO_x storage capacity of the Johnson Matthey Diesel Cold Start Concept (dCSC™) [8]. In addition to the experiments above, experiments were performed in reference [8] to quantify the NO_x storage capability of the dCSC™. In reference [8], multiple cold start concept substrates containing PNA catalyst with HC trapping ability and an oxidation catalyst were prepared. All of the experiments took place in a laboratory reactor. First, the substrates were hydrothermally aged at 650 °C for 2 hours with various feed gas compositions to reflect different air-to-fuel ratios.

NO_x adsorption experiments were performed with feed gas mixtures comprised to emulate exhaust gas from a diesel engine during cold start. The substrates were preheated to 500 °C in feed gas of 10% O₂, 5% CO₂, 5% H₂O, and a balance of N₂. The substrates were held at 500 °C to ensure desorption of any emissions from all of the active NO storage sites on the catalysts. The substrates were then cooled to low temperatures ranging from 80 to 250°C with the same feed gas composition. Once the substrates reached the temperature setpoint for the certain test, 200 ppm NO, 200 ppm CO, and 500 ppmC decane (on a C₁ basis) was added to the feed gas. The substrates were fed with this gas from 10 minutes to ensure complete saturation of all of the available NO_x storage sites [8].

The NO_x storage capacity of the substrates at temperatures of 80 to 250°C is characterized in Figure 2.8. The optimal temperature of the substrates to store NO_x emissions is observed from 125 to 175°C where the NO_x storage capacity peaks [8]. The storage capacity falls off from 125 to 80 °C. As feed gas temperature decreases from 125 to 80 °C, H₂O presence in the feed gas increases, this presence of water inhibits the NO storage sites from storing the NO in the feed gas. Storage capacity also decreases as temperature increases from 200 to 250°C. This is due to the NO storage sites becoming unstable above 200 °C [8].

Figure 2.8 200-Second dCSC™ NOx Storage Capacity vs. Temperature [8]

2.4 Summary

The dCSC™ device would integrate into the ULN ATS in Figure 2.1 as the PNA. Followed by an external heat source of some sort, to reduce the time the SCR and the rest of the ATS needs to reach operating temperature [11, 16]. The goal of the system is to meet ULN regulations for medium and heavy-duty diesel engines for 2024, 2026, and subsequent MY's. The EPA and CARB also plan for regulations over time to include emissions compliance for all use-cases, extended warranty requirements, accurate useful life determinations, and real time emissions logging capabilities [3].

Research has consisted of laboratory reactor studies on various substrates [1, 8, 19, 16], engine dynamometer studies on ULN ATS architectures [5, 13], engine hardware and calibration changes, [5, 16, 12], the development of new test cycles [7], and additional research studies to evaluate the feasibility and methods for achieving regulations laid out in reference [3].

The goal of this research is to acquire experimental data on the dCSC™ device, characterize the device's performance, and use the data to calibrate a high-fidelity 2D flow through model of the dCSC™. The model will be able to accurately predict outlet dCSC™ species concentrations, 2D temperature distributions, delta pressure, etc. This may be the first model of the dCSC™ and it will be very useful for the development of the ULN ATS, aiding the efforts being made by the EPA, CARB, and companies that need to meet future regulations.

3 Experimental Setup and Procedures

The experimental set-up was developed in order to carry out the experiments to gather the data needed to meet the objectives outlined in the Introduction. The test procedures and the experiments were then designed to get the data needed for the dCSCTM model and to determine the effect of the various variables on the storage, release, and oxidation of NO, NO₂, CO, and N₂O. The calculation procedures and equations used for analyzing the experimental data are also explained.

3.1 Experimental Setup

This section covers the general test cell layout, engine and dynamometer, fuel properties, exhaust heater, and ATS. The purpose of this section is to give background information on the experimental setup, engine, fuel properties, electric heater capability, and the aftertreatment system components.

3.1.1 Test Cell Layout

Figure 3.1 shows the layout of the Michigan Tech diesel engine aftertreatment test cell which was specifically modified to perform the dCSCTM research. Additions to the test cell included the Thermo Fisher 46i N₂O analyzer, a Cambustion fNOx400 NO_x analyzer, and a Cambustion HFR 400 Fast FID total hydrocarbon analyzer. The ambient air inlet and valve B were also added.

Figure 3.1 Test Cell Layout

The 2013 6.7L 6-cylinder Cummins ISB engine is coupled to a 500 HP dynamometer. The engine is controlled by the Calterm calibration tool provided by Cummins. A laminar flow element accurately measures the mass flow rate of air into the engine. A 25-kW heater from Watlow is in-line to control exhaust temperature to desired setpoints. See Appendix A for additional information on the exhaust heater. There are two NO_x sensors in the ATS. One sensor measures the engine outlet NO_x concentrations and the other measures downstream dCSC™ NO_x concentrations. See Appendix B for additional information on the NO_x sensors. The Pierburg 5-gas analyzer and N₂O analyzer can measure emissions upstream or downstream of the dCSC™. Appendices B.1 and B.4 have additional information on the Pierburg 5-gas bench and Thermo Fisher N₂O analyzer, respectively. Two fast response analyzers from Cambustion are part of the instrumentation. One of the analyzers measures NO and NO_x and the other measures HC. For more information on the Cambustion analyzers see Appendices B.2 and B.3. Each Cambustion analyzer has two channels, one upstream and one downstream of the dCSC™. There is a DEF injector downstream of the dCSC™ and upstream of the

SCR_F®. The SCR_F® is a Selective Catalytic Reduction catalyst on a Diesel Particulate Filter (DPF).

3.1.2 Engine and Dynamometer

As stated earlier, a 2013 6.7L inline 6-cylinder Cummins ISB engine, rated for 280 HP at 2400 rpm, was used to conduct the experimental testing. A list of engine specifications is shown in Table 3.1. The engine is coupled to a Dynamatic water-cooled eddy current dynamometer rated for 500 HP from 1700-7000 rpm. The dyno controls engine speed through a Digalog dynamometer controller.

Table 3.1 Engine Specifications

Model	Cummins ISB
MY	2013
Displacement	6.7 L, 408 in ³
Cylinders	6
Aspiration	Holset Variable Geometry Turbocharger
Bore & Stroke	107 x 124 mm
EGR System	Electronically controlled and cooled
CR	17.3 : 1
Firing Order	1-5-3-6-2-4
Fuel System	High pressure common rail, Bosch DI
Rated power and speed	280 HP at 2400 rpm
Rated torque and speed	660 lb-ft at 1600 rpm

3.1.3 Fuel Properties

A batch of summer blend #2 ultra-low sulfur diesel (ULSD #2) was purchased and stored at Krans Oil in Lake Linden for the dCSC™ testing. A fuel sample was sent to Paragon Laboratories in Livonia, Michigan for analysis and the results are shown in Table 3.2. For the complete analysis results from Paragon see Appendix C.

Table 3.2 ULSD #2 Fuel Properties used in Engine

Fuel Type	ULSD #2
Carbon (Wt%)	86.55%
Hydrogen (Wt%)	13.45%
API Gravity at 15.56 °C	34.5 °API
Density at 15.56 °C	0.8516 g/mL
Specific Gravity at 15.56 °C	0.8524
LHV	19669 BTU/lb 45.749
NLHV	18442 BTU/lb 42.895
Cetane	51.7
Air to Fuel Ratio (CH-based)	14.58
Hydrogen to Carbon Atomic Ratio	1.852

3.1.4 Exhaust Heater

A 25-kW heater was used to control exhaust gas temperatures to the desired setpoints for the dCSC™ testing. The heater and the heater controller were manufactured by Watlow. Controller PID's were tuned to eliminate temperature oscillations and they ensure temperature setpoint accuracy. Additional details on the exhaust heater and heater PID tuning are in Appendix A.

3.1.5 Aftertreatment System

The ATS consists of a Johnson Matthey dCSC™ upstream of an SCRF® previously used to conduct research at MTU [21, 22]. The dCSC™ was degreened before the experimental testing began. The dCSC™ was degreened by running the engine at 1660 rpm, 550 N-m, and with 32 mg/stroke of late fuel injection. The 25-kW heater was set to 700°C and the dCSC™ was held at temperatures between 650 and 700°C for 2 hours. This was done to emulate the hydrothermal aging done on the cold start concept technology testing in [1, 8]. The dCSC™ substrate specifications are shown in Table 3.3.

Table 3.3 dCSC™ Substrate Specifications

Material	Cordierite
Diameter (inch)	10.5
Length (inch)	6
Cell Geometry	Square
Total Volume (L)	8.51
Open Volume (L)*	7.72
Cell Density /in ²	400
Cell Width (in)	0.046
Open Frontal Area (in ²)	78.5
Channel Wall Thickness (in)	0.004
Wall Density (g/cm ³)	1.2
Porosity (%)	35
Number of Inlet Cells	31,415

*Total Volume minus No Flow Zone

3.2 Instrumentation

This section introduces the instrumentation used to record the data needed to meet the research objectives. Numerous thermocouples, pressure transducers, emission analyzers, and DAQ systems were utilized to gather the data needed.

3.2.1 Temperature Measurement

The dCSC™ substrate is instrumented with 32 thermocouples. These thermocouples are 16-inch Omega K-type MQSS series thermocouples with a 304 stainless steel sheath. The temperature data are used to monitor the 2D temperature distribution during testing.

Figure 3.2 shows the location of each thermocouple in the dCSC™.

Figure 3.2 dCSC™ Thermocouple Layout

3.2.2 Pressure Measurement

Intake air flow is monitored by an engine intake manifold pressure sensor and a laminar flow device upstream of the intake manifold. The laminar flow device's delta pressure is monitored with an Omega high accuracy oil-filled pressure transducer. The dCSC™ delta pressure is monitored with a similar transducer.

3.2.3 Emission Analyzers

Exhaust gas constituents are measured by a number of analyzers. A 5-gas analyzer from Pierburg measures O₂, CO₂, CO, NO_x, and total hydrocarbons. However, the sampling system is not conducive to measuring hydrocarbons; the sample lines are too long and the hydrocarbons get adsorbed on the sample lines. N₂O concentrations in the exhaust gas are measured by a Thermo Fisher 46i N₂O analyzer. Both the Pierburg 5-gas bench and Thermo Fisher N₂O analyzer are setup to measure either upstream or downstream dCSC™ NO_x concentrations. This is done by opening a pneumatic valve to either the upstream or downstream sample site and closing the other. There are two production NO_x sensors in the system to measure engine out and downstream dCSC™ NO_x.

concentrations. A Cambustion fNOx400 CLD is used to measure downstream dCSC™ NOx and NO concentrations. One of the fNOx400 channels was converted from NO measurement to NOx measurement. See Appendix B for additional details on all of the emission analyzers.

3.2.4 Data Acquisition Modules

National instruments NICDAQ modules are used to log temperatures, pressures, flow rates, Cambustion fNOx400 NOx concentrations, and numerous other signals. NI LabVIEW is used to monitor and log these signals as well as control the sampling system for the Pierburg 5-gas bench and the Thermo Fisher 46i N₂O analyzer. Electronic solenoids, controlled in LabVIEW, allow compressed air to open one-way valves to either an upstream or downstream dCSC™ sampling system, for these two analyzers.

3.3 Test Procedures and Experimental Conditions

This section lays out specific test procedures that were developed to conduct the experiments and the test conditions for those experiments. The procedures were developed by running test experiments before starting the research testing. During the test experiments, heater PID controls were tuned, engine controls were calibrated, and the overall setup was refined.

3.3.1 Test Procedure

Figure 3.3 shows engine load, engine speed, turbine outlet temperature, and the temperature of the thermocouple at the front and middle of the dCSC™ substrate (C1 Thermocouple), during a test. The Phases of every test are illustrated in Figure 3.3 as well.

Figure 3.3 dCSC™ Control Test

Prior to Phase I of the test, the engine is warmed up to a steady state coolant temperature. This ensures the engine-out emissions will be constant during Phases III and IV.

Phase I of the test, is called regeneration. During this Phase, the engine is set to 1660 rpm and 600 N-m and exhaust is routed to the aftertreatment system. With the aid of the heater, the dCSC™ will reach 500 °C and will be kept at that temperature for 10 minutes to clean the surface of the substrate and ensure the release of all emissions from the substrate [1, 8, 19]. When the 10 minutes is over, the exhaust is routed directly to the building exhaust and Phase II begins.

During Phase II (Cool Down) the building exhaust is allowed to pull ambient air through the heater to the aftertreatment system. This allows the temperature of the aftertreatment system to be controlled by the heater to the desired temperature for Phase III. During Phase II the engine is also set to the desired condition for the test. The engine will remain at this condition for the remainder of the test. Once the dCSC™ is controlled to the desired temperature for Phase III (Storage), the ambient air inlet to the aftertreatment

system is sealed off. Once the ambient air inlet is sealed off, the exhaust flow is routed to the aftertreatment system. At this time, Phase III (Storage) begins.

Phase III (Storage) is the portion of the test where dCSCTM emissions storage capacity is calculated. The dCSCTM is controlled to a desired constant temperature for Phase III by the 25-kW heater heating exhaust gas upstream of the dCSCTM. The Pierburg 5-gas bench and the Thermo Fischer 46i N₂O analyzer are both measuring downstream emissions for the entirety of Phases III & IV. Phase III is 40 minutes long to ensure that the dCSCTM emissions storage sites are saturated and steady state emissions can be measured. At the conclusion of Phase III, the 25-kW heater is set to heat the exhaust gas upstream of the dCSCTM so that the dCSCTM temperature will ramp up to a desired constant temperature for Phase IV. As soon as the temperature ramp begins, so does Phase IV.

Phase IV (Release) is the portion of the test where dCSCTM emissions' release performance is calculated. Once the dCSCTM temperature reaches the desired constant temperature, it is held there for 20 minutes in order to ensure the dCSCTM is finished releasing emissions and steady state emissions can be measured.

At the conclusion of Phase IV, the Pierburg 5-gas bench and the Thermo Fischer 46i N₂O analyzer are used to measure upstream dCSCTM emissions concentrations.

3.3.2 Engine Test Conditions

In order to re-create cold start conditions, the three low-load engine conditions shown in Table 3.4 were determined. These are the engine conditions used in Phases III and IV of each experiment, shown in Figure 3.3. The conditions allowed for low dCSCTM temperatures to be achieved during Phase III (storage phase) of tests. The use of condition 2 was vital to achieving a high dCSCTM temperature during Phase IV (release phase) of tests. Condition 2 was also used to achieve a higher temperature ramp rate of 40 °C/min from Phase III to Phase IV. The ramp rate was achieved by changing from engine condition 1 to 2 at the beginning of Phase IV. Engine condition 3 was needed in order to achieve dCSCTM temperature of 80 °C during Phase III of a test. Engine condition is set

before Phase III begins and remains at that condition for the entirety of Phases III and IV. The only exception to the previous statement is the test where a 40 °C/min temperature ramp rate was desired. During this test engine condition changes from 1 to 2 at the start of Phase IV, to achieve the temperature ramp rate of 40°C/min in the dCSC™. Table 3.4 also shows engine out or upstream dCSC™ emissions concentrations at each engine condition, measured by the Pierburg 5-gas bench. The air-to-fuel ratio at each engine condition was calculated from the measured fuel flow and air flow into the engine. They were measured with a Coriolis fuel mass flow rate meter and a laminar flow element instrumented to measure air mass flow rate. The H₂O concentration out of the engine was calculated using the AFR and the fuel properties from Table 3.2.

Table 3.4 Engine Test Conditions

Engine Parameter	Condition 1	Condition 2	Condition 3
Speed (rpm)	1000	1290	750
Load (N-m)	35	46	22
Exhaust Flow Rate (kg/min)	3.5	4.9	2.6
Turbine Outlet Temperature (°C)	140	180	110
Air-to-Fuel Ratio (AFR)	100	83	130
EGR (%)	0	0	0
O ₂ (%)	17.5	17.1	18.0
CO ₂ (%)	2.5	2.9	1.8
H ₂ O (%)	1.9	2.3	1.5
CO (ppm)	86	95	75
NO (ppm)	175	209	211
NO ₂ (ppm)	10	7	18
NO _x (ppm)	185	216	229

3.3.3 Experimental Test Conditions

Table 3.5 shows a list of desired dCSC™ temperatures for Phase III. These temperatures were decided upon based on findings from other dCSC™, PNA, and DOC research publications [1, 8, 17, 18, 24]. Refer to Chapter 2 Figure 2.8 for temperatures tested on the dCSC™ in reference [8]. These tests were all conducted with a dCSC™ temperature of 300 °C during Phase IV of the test.

Table 3.5 Emissions Storage Test Plan

Engine Test Condition	Phase III (Storage) Emissions Temperature, °C
1	100, 125*, 150, 200, 225, 250
2	115, 150, 200, 250
3	80

The use of “*” next to a number in Tables 3.5-3.7 indicates that the test is a repeat of a test in one of the other two tables.

Based on downstream dCSC™ ATS operating temperatures, a list of desired dCSC™ temperatures was determined for Phase IV of the dCSC™ testing. This list of temperatures is referred to as the emissions release/conversion test plan in Table 3.6. The dCSC™ temperature during Phase III and engine condition for Phases III and IV is in Table 3.6 as well. Engine condition 1 and 150°C Phase III (storage) dCSC™ temperature was tested at 200-450°C Phase IV (release) dCSC™ temperatures. This was done in order to characterize the temperature of the dCSC™ vs. its ability to regain its NOx storage capacity.

Table 3.6 Emissions Release/Conversion Test Plan

Engine Test Condition & Phase III (Storage) Temperature, °C	Phase IV (Release) Emissions Temperature, °C
Condition 1 & 150	200, 250, 300*, 350*, 400, 450
Condition 2 & 150	300*, 350
Condition 1 & 125	300*
Condition 1 & 200	300*, 400

The use of “*” next to a number in Tables 3.5-3.7 indicates that the test is a repeat of a test in one of the other two tables.

Testing was completed to compare the release/conversion performance to temperature ramp rate. Two tests were run with the same Phase III and Phase IV temperature setpoints, but with different temperature ramp rates between the two. Details of these two tests are in Table 3.7. The first test was completed with a ramp rate of 20 °C/min and the second with a rate of 40 °C/min. In order to achieve the 40 °C/min ramp rate, the engine condition changes from condition 1 to 2 at the conclusion of Phase III and the start of Phase IV.

Table 3.7 Emissions Release/Conversion vs. Temperature Ramp Test Plan

Engine Test Condition & Phase III (Storage) Temperature, °C	Ramp Rate, °C/minute	Engine Test Condition & Phase IV (Release) Temperature, °C	Ramp Time, minutes
Condition 1 & 150*	20	Condition 1 & 350	10
Condition 1 & 150	40	Condition 2 & 350	5

A complete list of tests that were run can be found in Appendix D. A MATLAB vector containing the numbers 1 through 25 was randomized using the command ‘randperm’ to generate the test run order. In between each test in the run order, test 4, the control test, was run. The control test is performed at engine condition 1, 200 °C Phase III dCSC™ temperature, and a 300 °C Phase IV dCSC™ temperature.

3.3.4 ATS Thermal Management

Characterizing the dCSC™ performance at different temperatures is presented in Chapter 4. The data will be used to calibrate a model of the dCSC™ characteristics at different temperatures. Therefore, controlling the ATS temperature during the experiments is vital. Figure 3.4 shows the system (also shown in Figure 3.1) for controlling the temperature in the ATS.

Figure 3.4 ATS Thermal Management

The exhaust flow from the 2013 Cummins ISB engine can be routed to the ATS by closing valves C and B and opening valve A. The exhaust can also be routed directly to the building's exhaust by closing valve A and opening valve C. While valve A is closed, valve B can be opened to allow ambient air to be pulled through the ATS. This strategy is utilized to cool the ATS while also controlling the ATS temperature with the 25-kW heater. This allows the dCSC™ temperature to be controlled and stabilized at the desired temperature for Phase III of the test. This strategy also minimizes the possibility of the building exhaust vacuum pulling engine exhaust past valve A when it is closed. This is because the building exhaust will be able to pull ambient air through an open valve B rather than deadheading on valve A.

Figure 3.5 shows the dCSC™ temperatures and a calculated dCSC™ volume weighted temperature. Equation 3.7 and Appendix E describe how the volume weighted temperature is calculated. In Figure 3.5 the dCSC™ temperatures are measured by thermocouples C1, C2, and C18. The location of these thermocouples is shown in Figure 3.2. C1 and C4 are located on the centerline of the dCSC™ substrate. C1 is 32.4 mm from the upstream face and C4 is 30 mm from the downstream face of the substrate. C18 is 120 mm radially from the center of the dCSC™ and 30 mm downstream of C1, axially.

The thermocouple data in Figure 3.5 shows how the dCSC™ temperature is accurately and actively controlled during the experiment.

Figure 3.5 dCSC™ Exhaust Temperatures During a Control Test

3.4 Data Analysis Methods

The equations in this section were used in the postprocessing of the experimental data. The results from these equations were used to quantify the dCSC™ performance characteristics. Chapter 4 covers the results that were computed using these equations.

3.4.1 Adsorption and Desorption Calculations (Storage/Release)

The following equations were used to calculate the NO_x storage and release, N₂O production, and NO₂ to NO_x ratio at the dCSC™ outlet. Equation 3.1 is used to calculate the molar flow rate of the exhaust.

$$\dot{n}_{exhaust} = \frac{\dot{m}_{exhaust}}{M_{exhaust}} \quad 3.1$$

Where, $\dot{n}_{exhaust}$ is the molar flow rate of the exhaust. $\dot{m}_{exhaust}$ is the mass flow rate of the exhaust which is equal to the measured $\dot{m}_{air}$ plus the $\dot{m}_{fuel}$. The $M_{exhaust}$ is the molecular weight of the exhaust. The molecular weight of the exhaust used was 28.97 per reference [25]. After calculating the molar flow rate of the exhaust, the molar flow rate of NOx in the exhaust is calculated using Equation 3.2.

$$\dot{n}_{NOx} = \dot{n}_{exhaust} * \frac{C_{NOx}}{1,000,000} \quad 3.2$$

Where $\dot{n}_{NOx}$ is the molar flow rate of NOx, and C_{NOx} is the concentration of NOx in the exhaust. A more general form of Equation 3.2 is Equation 3.3, which can be used to calculate the molar flow rate of any exhaust gas constituent.

$$\dot{n}_X = \dot{n}_{exhaust} * \frac{C_X}{1,000,000} \quad 3.3$$

Where $\dot{n}_X$ is the molar flow rate of any exhaust gas constituent x and C_X is the exhaust gas concentration of that constituent, x. Using the molar flow rate of a species in the exhaust, in this case it is NOx, the species' storage, release, or production can be calculated using Equation 3.4.

$$n_{NOx\ Stored} = \sum_{i=t_i}^{t_f} (\dot{n}_{NOx\ In\ (i)} - \dot{n}_{NOx\ Out\ (i)}) * \Delta t \quad 3.4$$

Where, $n_{NOx\ Stored}$ is the moles of NOx stored. The sampling increment (Δt) is 0.5 seconds or 2 Hz. The summation for $n_{NOx\ Stored}$ is computed from the start of Phase III (t_i) to the time at which downstream dCSCTM NOx concentrations are equal to the upstream dCSCTM NOx concentrations (t_f). NOx storage in mass units can be computed by multiplying the moles of NOx stored ($n_{NOx\ Stored}$) by the molecular weight of NO₂ which is the definition of x = 2 (44.01). The molecular weight of NO₂ is used to calculate NOx stored because once NOx reaches the atmosphere the NO portion will be oxidized into NO₂. $\dot{n}_{NOx\ In\ (i)}$ is the molar flow rate of NOx into the dCSCTM and $\dot{n}_{NOx\ Out\ (i)}$ is

the molar flow rate of NOx out of the dCSCTM. Equation 3.5 is used to calculate the moles of N₂O produced.

$$n_{N_2O \text{ Produced}} = \sum_{i=t_i}^{t_f} (\dot{n}_{N_2O \text{ In } (i)} - \dot{n}_{N_2O \text{ Out } (i)}) * \Delta t \quad 3.5$$

Where, $n_{N_2O \text{ Produced}}$ is the moles of N₂O produced. $\dot{n}_{N_2O \text{ In}}$ is the molar flow rate of N₂O into the dCSCTM and $\dot{n}_{N_2O \text{ Out}}$ is the molar flow rate of N₂O out of the dCSCTM. N₂O molar flow rate is calculated using Equation 3.3 and the N₂O concentration (C_{N_2O}).

During Phase III of the experiments, the downstream dCSCTM NOx concentration increases from 0 ppm NOx to the upstream dCSCTM NOx concentration. The point at which the downstream NOx concentration is exactly 50% of the upstream concentration (where the ratio is 0.5) is referred to as dCSCTM 50% NOx storage capacity. The ratio of the dCSCTM downstream NOx concentration to the upstream NOx concentration (dCSCTM NOx inlet to outlet ratio) is calculated using Equation 3.6.

$$\frac{NOx_{out}}{NOx_{In}} = \frac{C_{NOx \text{ Out}}}{C_{NOx \text{ In}}} \quad 3.6$$

Where, $\frac{NOx_{out}}{NOx_{In}}$ is the ratio of the dCSCTM downstream NOx concentration to the upstream concentration. $C_{NOx \text{ Out}}$ is the downstream dCSCTM NOx concentration and $C_{NOx \text{ In}}$ is the upstream NOx concentration.

3.4.2 Calculation of NO₂ to NO_x Ratio (NO Conversion Efficiency)

Equation 3.7 is used to calculate NO₂ to NO_x ratio at the outlet of the dCSC™. This allows for the characterization of the NO_x oxidation characteristics of the dCSC™ during the steady state portions of Phases III and IV.

$$\frac{NO_2}{NO_x} = \frac{C_{NO_2 \text{ out}}}{C_{NO_x \text{ out}}} \quad 3.7$$

Where $\frac{NO_2}{NO_x}$ is the NO₂ to NO_x ratio at the dCSC™ outlet, $C_{NO_2 \text{ out}}$ is the concentration of NO₂ at the dCSC™ outlet, and $C_{NO_x \text{ out}}$ is the concentration of NO_x at the dCSC™ outlet. In Figure 3.6, the outlet concentration is greater for NO₂ than NO during Phase IV. This is because the substrate temperatures during these two phases are high enough to oxidize a large portion of the upstream NO to downstream NO₂.

Figure 3.6 Downstream dCSC™ NO, NO₂, and NO_x Concentrations during a 200 °C Phase III and 300 °C Phase IV

The NOx Storage is computed using the downstream NOx concentration versus time from the Pierburg CLD, Combustion CLD, NOx sensor, and two upstream NOx concentrations from the Pierburg and NOx sensor.

3.4.3 Calculation of dCSC™ Volume Weighted Temperature

dCSC™ volume weighted temperature is calculated using Equation 3.8.

$$T_{V.W.} = \sum_{i=1}^{24} (W_{T.C.(i)} * T_{T.C. (i)}) \quad 3.8$$

Where $T_{V.W.}$ is the dCSC™ volume weighted temperature, $W_{T.C.(i)}$ is the weight applied to each thermocouple, and $T_{T.C. (i)}$ is the thermocouple temperature reading. The weight applied to each thermocouple is calculated using Equation 3.9.

$$W_{T.C.} = \frac{V_{T.C.}}{V_{T.V.}} \quad 3.9$$

Where, $W_{T.C.}$ is the weight applied to each thermocouple reading. $V_{T.C.}$ is the volume that each thermocouple represents and $V_{T.V.}$ is the total volume of instrumented dCSC™. Appendix E is a detailed explanation of the dCSC™ volume weighted temperature calculation.

3.4.4 dCSC™ 2D Temperature Distribution

The top half of the dCSC™ is instrumented with 32 K-type omega thermocouples, as shown in Figure 3.2. The temperature data from thermocouples C1 through C20 are used to plot a 2D temperature distribution of the top half of the dCSC™. This plot is then mirrored across the centerline of the dCSC™ to illustrate the entire substrate temperature distribution. Thermocouples C22, 23, and C24 are instrumented on the bottom half of the dCSC™. The RMS Error in the plot title is computed using the difference between these three thermocouples and the mirrored 2D temperature distribution. A MATLAB code

was written to plot the temperature distribution using the command ‘contourf.’ The ‘contourf’ command plots each thermocouple reading at its axial and radial location within the substrate. The resulting distribution assumes a linear temperature gradient in between the thermocouple readings. Thermocouples C13-C16 were not used to create the 2D temperature distributions. Because it was assumed a maldistribution in the exhaust flow upstream of the dCSC™ caused this row of thermocouples to be at a higher temperature than the thermocouples radially inward of this row. Figure 3.7 shows the dCSC™ 2D temperature distribution during Phase III of a test where the temperature setpoint was 200°C.

Figure 3.7 Control Test 15 at minute 115, dCSC™ Temperature 200°C, Phase III 2D Temperature Distribution

The numbers in red indicate the actual thermocouple readings in the dCSC™. Each *1's in red font indicates a location in the dCSC™ where there is no thermocouple.

4 Results

This chapter presents the experimental data results from Phases III and IV. These two Phases are the portions of the testing where emissions storage, release, and oxidation were observed and analyzed. Section 4.1 discusses the emissions time plots during experiment Phases III and IV. Appendix F shows the measured emissions concentrations, engine parameters, delta pressures, and temperatures vs. time during a test. Appendix G shows the control parameters measured for each test such as upstream dCSC™ emissions concentrations, exhaust mass flow rate, intake air mass flow rate, etc.

Section 4.2 discusses the NO, NO₂, and NO_x storage/adsorption performance of the dCSC™ for a range of temperatures from 80 to 250 °C, during Phase III of the testing. Section 4.3 discusses the NO, NO₂, and NO_x release/desorption performance of the dCSC™ for a range of temperatures from 200 to 450 °C, during Phase IV of testing. Section 4.4 shows the dCSC™ NO to NO₂ oxidation characteristics. dCSC™ NO to NO₂ oxidation was calculated during Phases III and IV of testing, after the transient NO_x storage or release event. During NO_x release at the beginning of Phase IV, an N₂O concentration is observed downstream of the dCSC™ and section 4.5 discusses this production of N₂O. The dCSC™ CO storage/oxidation characteristics are discussed in section 4.6. Appendices H and I discuss the N₂O formulation and oxidation reactions in the dCSC™, respectively

dCSC™ 2D temperature distribution data were measured during Phases III and IV of testing and were plotted using the methodology described in 3.4.4. Section 4.7 presents the 2D temperature distribution plots of the dCSC™ temperatures. Throughout the figures in this chapter, the C1 thermocouple within the dCSC™ is referenced to represent the dCSC™ temperature. It was determined that additional thermocouples are needed to accurately capture the temperature gradient in the substrate, Appendix J discusses this.

Section 4.8 is the Summary and Conclusions of the results and Section 4.9 discusses recommendations for future work.

4.1 Test Phases III and IV Emissions Data

Figure 4.1 shows the NO, NO₂, NO_x, CO, and N₂O concentrations at the outlet of the dCSC™ during a test with temperatures of 115 °C during Phase III and 300 °C during Phase IV. The NO and NO_x are measured by the Combustion Fast Response CLD analyzer. NO₂ is calculated by subtracting the measured NO from the measured NO_x. CO is measured by the Pierburg 5-gas bench and N₂O is measured by the Thermo Fisher 46i N₂O analyzer. Before the start of Phase III, the dCSC™ has been controlled to 115 °C via the 25-kW electric heater. Once the temperature in the dCSC™ stabilizes at 115 °C, exhaust gas is routed to the dCSC™ and Phase III begins.

During Phase III, NO and NO_x concentrations at the dCSC™ outlet start at 0 ppm and increase until they reach the upstream dCSC™ concentration of NO and NO_x, indicating NO and NO₂ storage. At a temperature of 115 °C, there is zero NO to NO₂ oxidation occurring in the dCSC™ and the upstream NO_x is comprised of 99% NO. Therefore, 0 ppm NO₂ is measured at the dCSC™ outlet. CO concentrations downstream of the dCSC™ start at 0 ppm and increase until they reach approximately 40 ppm. The upstream dCSC™ CO concentration during this test was approximately 85 ppm. This indicates a storage and oxidation of CO on the dCSC™. After the dCSC™ has finished storing emissions and the concentrations have reached steady state, steady state concentrations are recorded.

During Phase IV, dCSC™ temperature increases from 115 to 300 °C. As the temperature is increasing and reaches approximately 200 °C, the NO and NO_x concentrations start increasing, indicating NO_x release. The concentrations peak at approximately 450 ppm as the dCSC™ temperature reaches 250 °C and then decrease to a steady state concentration. Once the dCSC™ temperature reaches approximately 220 °C, the NO₂ concentration starts increasing, and the dCSC™ is now at a high enough temperature to oxidize some of the stored NO to NO₂ while releasing it. The NO₂ concentration peaks as the temperature reaches 265 °C and then decreases to a steady state concentration of approximately 110 ppm. The NO_x concentration returns to its initial value of

approximately 150 ppm, and the NO concentration reaches a steady state concentration of about 40 ppm. The steady state NO₂ concentration is more than double the NO concentration, indicating over half of the NO entering the substrate is being oxidized to NO₂. These steady state concentrations from each test are used to compute the downstream dCSC™ NO₂/NO_x ratio at each Phase IV temperature. As soon as the dCSC™ temperature starts increasing, the CO concentration downstream of the dCSC™ starts to decrease and reaches 0 ppm by the time the temperature reaches approximately 150 °C. The dCSC™ is then oxidizing all the upstream CO to downstream CO₂. A concentration of N₂O is observed at the dCSC™ outlet as the temperature approaches 200 °C. This concentration increases from 0 ppm to a peak of approximately 14 ppm as the dCSC™ reaches 230 °C and then decreases back to 0 ppm. The concentration of N₂O at the dCSC™ outlet is due to a small occurrence of HC lean NO_x conversion occurring within the dCSC™, this is supported in reference [1].

Figure 4.1 NO, NO₂, NO_x, CO, and N₂O Concentrations Downstream of the dCSC™ during a 115 °C Phase III and a 300 °C Phase IV, at Engine Condition 1

4.2 NO, NO₂, and NO_x Storage Performance

NO_x concentrations upstream of the dCSCTM were measured using both the NO_x sensor and the Pierburg CLD. NO_x concentrations downstream of the dCSCTM were measured using the NO_x sensor, Pierburg CLD, and a Cambustion CLD. Referring to Equation 3.4, a NO_x concentration at the inlet (upstream) and outlet (downstream) of the dCSCTM is needed to compute the NO_x stored. In this case there are two NO_x concentration measurements made at the inlet (upstream) and three NO_x concentration measurements made at the outlet (downstream). The upstream dCSCTM NO_x concentration is constant throughout Phases III and IV of each of the tests as the engine condition remains constant. The NO_x sensor monitors the upstream dCSCTM NO_x concentration for the entire test. The Pierburg CLD measures the upstream dCSCTM NO_x concentration at the conclusion of Phase IV of each of the tests.

The two upstream dCSCTM NO_x concentrations (Pierburg and NO_x Sensor) are compared in Figure 4.2. Figure 4.2 includes upstream dCSCTM NO_x concentration data for all of the tests completed. Therefore, tests completed at all three engine conditions described in Chapter 3. The y-axis of the plot is NO_x in ppm and the x-axis is the order in which each test was run. The upstream NO_x concentration changes slightly from test to test due to factors such as test cell environmental conditions and engine condition. The Pierburg CLD measurement in Figure 4.2 is consistently slightly higher than the NO_x sensor measurement. The Pierburg CLD upstream dCSCTM NO_x concentration measurement is used to calculate NO_x stored. During Phases III and IV of testing, dCSCTM NO_x storage and release are calculated, respectively.

Figure 4.2 Upstream dCSC™ NOx Concentrations vs. Test Order

In order to calculate dCSC™ NOx storage and release, a downstream dCSC™ NOx concentration measurement is needed. Figure 4.3 shows the downstream dCSC™ NOx concentrations from the three different instruments during Phase III and IV of an experiment.

Before the start of Phase III, the dCSC™ temperature is controlled to 115 °C with a feed of room air that has been heated by the 25-kW Watlow heater. Once the dCSC™ temperature is stabilized at 115 °C, the feed is changed from heated ambient air to heated exhaust gas containing approximately 200 ppm of NOx. The exhaust gas temperature is also controlled by the 25-kW Watlow heater. The downstream dCSC™ NOx concentration starts at 0 ppm and increases to reach the upstream dCSC™ NOx concentration. The measured concentration of each of the three instruments measuring downstream dCSC™ NOx concentrations varies from instrument to instrument. The Pierburg NOx measurement increases first followed by the Cambustion CLD and NOx Sensor, respectively. Therefore, computing NOx stored with each of the three downstream NOx concentrations yields three different NOx stored values.

During Phase IV, the feed of exhaust gas is being heated from 115 to 300 °C. An increase in downstream dCSC™ NOx concentrations is not observed until the exhaust gas temperature reaches 200 °C. By the time the exhaust gas reaches 265 °C, the downstream dCSC™ NOx concentrations have peaked and are decreasing to reach the upstream dCSC™ NOx concentration. Therefore, the majority of the NOx release occurs from 200 to 265 °C.

Figure 4.3 Downstream dCSC™ NOx Concentrations vs. Time during a 115 °C Phase III and 300 °C Phase IV, at Engine Condition 1

NOx storage was computed for each of the three NOx concentration measurements downstream of the dCSC™. Figure 4.4 shows total NOx storage for the tests with a 200 °C temperature during dCSC™ test Phase III from each downstream NOx measurement. Note that there is space between the points on the figure because these tests were not conducted with a 200 °C Phase III storage temperature.

The total NOx stored for the first eight control tests is approximately 0.6 g.NOx/L.Sub. During the last six control tests the total NOx stored was reduced to approximately 0.35 g.NOx/L.Sub. This is likely due to a decrease in the number of active NO storage sites on the dCSC™ substrate, or in the effectiveness of the sites, as more tests are completed.

Engine out NO_x is composed of 90 to 95% NO, only a 5 to 10% of the NO_x is NO₂. Therefore, most of the NO_x stored by the dCSC™ is NO. The activity of the NO storage sites directly affects the total NO_x storage. However, it is still possible for some NO₂ to be stored on the dCSC™.

From reference [19], H₂O can greatly inhibit NO_x storage. Ambient air flows through the dCSC™ during Phase II of testing to control the dCSC™ to the Phase III temperature setpoint. It was investigated as to whether or not the relative humidity in the test cell had an effect on the NO_x storage. During the first control test the relative humidity in the test cell was measured to be 36% and during the last test it was measured to be 28 %. From the first control test to the last control test total NO_x stored decreased by 46%. The relative humidity during the last test was 8% lower than it was during the first test. This indicates that relative humidity of the test cell did not affect the total NO_x storage. There was no trend showing that relative humidity in the test cell increased as NO_x stored decreased. The relative humidity in the test cell was recorded for each test (Appendix G, Figure G.12) and the engine out H₂O concentrations are shown in Table 3.4.

There are significant reductions in control test total NO_x storage from approximately 0.6 to 0.5 g.NO_x/L.Sub. and 0.5 to 0.4 g.NO_x/L.Sub. at the 15th test and the 35th test, respectively. These two transitions occur from control test 7 to 8 and control test 17 to 18 and have been labeled with a black dashed line in Figure 4.4. The time the dCSC™ was at 500 °C and exposed to engine exhaust while the engine was at 1660 rpm and 600 N-m was quantified at the start of the 15th and 35th tests. At the start of the 15th test the dCSC™ had been at 500 °C and exposed to exhaust gas from the diesel engine at 1660 rpm and 600 N-m for a total of 5 hours and 30 minutes. At the start of the 35th test the dCSC™ had been exposed to these conditions for 9 hours and 10 minutes. This high-temperature high load exposure is likely the reason for the reduced activity of the NO storage sites.

Figure 4.4 Control Test 200 °C Phase III dCSC™ Total NOx Stored vs. Test Order

Figure 4.5 shows the data from Phase III (storage) from two control tests, control test 7 and control test 23. Control test 7 was the 14th test to be run and control test 23 was the 48th test run. Figure 4.5 shows downstream dCSC™ NOx concentrations from the Pierburg CLD, during the 200 °C Phase III, for both tests. It also shows total NOx stored, computed from the downstream NOx concentrations. The total NOx stored from control test 23 is 0.32 g.NOx/L.Sub. while the total NOx stored from control test 7 is 0.55 g.NOx/L.Sub. This is a significant decrease in the total NOx storage capacity of the dCSC™ from the 14th to the 48th test run.

The initial rate of storage appears to be similar from 79-81 minutes, which refers to the initial bulk diffusion of reactants. Bulk diffusion of reactants is when the NO is reacting with the NO storage sites on the outer surfaces of the substrate, which are the easiest storage sites to reach, as discussed in reference [23]. The pore diffusion of reactants is when the NO in the feed gas has to diffuse through the substrate to reach active NO storage sites that are not as accessible as the bulk diffusion storage sites. Reactants go to

these sites after the easiest (bulk diffusion) NO storage sites have been saturated, as discussed in reference [23]. At a time of 81 minutes, the two NO_x traces split and test 23's downstream dCSC™ NO_x concentration increases more rapidly towards the upstream NO_x concentration than test 7's. This indicates a decrease in the activity of the pore diffusion NO storage sites on the dCSC™, which causes the decrease in NO_x storage capacity.

Figure 4.5 Control Test 200 °C Phase III NO_x Storage Comparison, at Engine Condition

1

Over 200 hours of testing was completed on the dCSC™. The total NO_x storage capacity of the dCSC™ appears to decrease over time due to a reduction of the active pore diffusion NO storage sites. However, the bulk diffusion NO storage sites appear to remain active. dCSC™ NO_x storage capacity was computed for the first 200 seconds of each test. Figure 4.6 shows the total NO_x stored during the first 200 seconds of the 200 °C Phase III control tests. The 200-second NO_x storage capacity of the dCSC™ over the first 15 tests is roughly 0.35 g.NO_x/L.Sub. The 200-second NO_x storage capacity over

the last 15 tests is slightly less at 0.3 g.NOx/L.Sub. Indicating that the majority of the dCSC™ bulk diffusion NO storage sites remain active.

Figure 4.6 Control Test 200 °C Phase III 200-second dCSC™ NOx Storage Capacity vs. Test Order

The 200-second NOx storage capacity of the dCSC™ at Phase III test temperatures of 80 to 250 °C was computed. The NOx measurements used were the Pierburg CLD, upstream and downstream measurements. Figure 4.7 shows the 200 second NOx storage capacity of the dCSC™ versus the average volume weighted temperature calculated by the equations in section 3.4.3.

Consistent with references [1] and [8], the range of temperatures at which the dCSC™ stores the largest quantity of NOx is 125 to 150 °C. The storage capacity slightly decreases as the temperature decreases from 125 °C. This is because as the temperature is decreasing, the water concentration in the exhaust is increasing. The higher presence of water in the exhaust inhibits the ability of the NO storage sites on the dCSC™, as is

discussed in references [1, 8, 19]. At temperatures above 200 °C the NO storage sites on the dCSC™ become unstable and less able to store NOx [1, 8].

The black curve in Figure 4.7 is a 3rd order polynomial fit of the tests performed at engine condition 1. There are two points in Figure 4.7 at 150 °C and 0.65 g.NOx/L.Sub. that were performed at engine condition 2 (exhaust flow rate – 4.9 kg/min), where the exhaust flow rate is 1.5 kg/min more than engine condition 1 (exhaust flow rate – 3.5 kg/min). Therefore, during the 200-second period, the dCSC™ NO storage sites were exposed to a more molecules of NO than the tests at engine condition 1, and thus store a larger mass of NOx.

Figure 4.7 200-second dCSC™ NOx Storage Capacity vs. Temperature at all Engine Conditions

During Phase III of each test, the ratio of downstream dCSC™ NOx concentration to the upstream concentration (dCSC™ NOx inlet to outlet ratio) begins at 0 and increases to 1. The time it takes for the ratio to reach 0.5 (dCSC™ 50% NOx storage capacity) is

dependent upon the temperature of the dCSC™. Figure 4.8 shows time in minutes for the ratio to reach 0.5 at different dCSC™ temperatures.

The data in Figure 4.8 refers to the tests in three groups, tests 1-15, tests 15-30, and tests 30-50. The groups are arranged in chronological order in which the tests were run. Tests 1-15 show the largest amount of time before the dCSC™ 50% NO_x storage capacity is reached, while tests 15-30 show a reduction in time and tests 30-50 show an even further reduction in time. The reduction in time to the 50% NO_x storage capacity with increasing number of tests run is another indication that the pore diffusion NO storage sites are becoming less active.

Figure 4.8 50% dCSC™ NO_x Storage Capacity vs. Temperature

4.3 NO, NO₂, and NO_x Release Performance

NO_x release is calculated during Phase IV of each test. During this phase, the dCSC™ temperature increases from the temperature setpoint during Phase III to the temperature setpoint for Phase IV. As the dCSC™ temperature increases, the downstream dCSC™ NO_x concentration increases from the initial value to a peak and then decreases to the

initial value, which indicates a NO_x release. The NO_x released in g.NO_x/L.Sub. is calculated during this time using Equation 3.4.

Figure 4.9 shows the NO_x released by the dCSC™ at different Phase IV (release) average volume weighted temperatures. The average volume weighted temperature of the dCSC™ is calculated using the equations in section 3.4.3. The dCSC™ NO_x storage capacity is highest at Phase III (storage) temperatures of 125 to 150 °C and decreases as temperature increases from that range. Tests run with Phase III temperatures of 200 to 250 °C showed lower total NO_x storage capacity. The dCSC™ can only release NO_x that it has first adsorbed or stored. Therefore, the NO_x released is dependent upon the NO_x stored during Phase III, which is dependent upon the Phase III dCSC™ temperature. In addition, dCSC™ NO_x storage capacity has shown to decrease with increasing number of tests run.

Figure 4.9 dCSC™ Total NO_x Released vs. Temperature

The tests with 150 °C Phase III storage temperatures were followed by Phase IV release temperatures of 200 to 450 °C. This was done to determine the percentage of NO_x stored that is released at different temperatures. Figure 4.10 shows the percentage of NO_x stored during Phase III that is released during Phase IV. The black line is a curve fit through the percentage of stored NO_x released points during the tests with a 150 °C Phase III

(storage) temperature. With a 150 °C Phase III temperature, as Phase IV (release) temperature increases, the percentage of NO_x stored released also increases.

Two of the tests with a 300 °C average volume weighted release temperature, show a percentage of stored NO_x released lower than 30%. These two tests had a storage temperature of 250 °C. Therefore, the temperature increase during Phase IV was from 250 to 300 °C. The rapid NO_x release of the dCSC™ has been found to occur from 200 to 265 °C in reference [8]. Therefore, the NO_x release event for these two tests, which occurs from 250 to 300 °C, does not pass through the rapid NO_x release temperature range. However, there is a secondary rapid NO_x release centered around 350 °C per reference [8]. A test was conducted with 250 °C Phase III storage temperature and a 350 °C Phase IV release temperature that shows over 90% of the stored NO_x released. Therefore, in order to release a high percentage of the stored NO_x, the release temperature ramp must ramp from 200-265 °C or reach at least 350 °C. The 250 to 350 °C temperature ramp is 60% more efficient at releasing NO_x than the 250 to 300 °C temperature ramp.

Figure 4.10 dCSC™ Percent of Stored NO_x Released vs. Temperature

4.4 NO to NO₂ Oxidation Characteristics

The dCSC™ oxidizes NO to NO₂ through the catalytic oxidation reaction show in Equation 4.1 below.

During Phases III and IV of testing, after the transient NO_x storage and release periods, steady state emissions are measured. The Cambustion CLD measures NO and NO_x downstream of the dCSC™. Subtracting the NO from the NO_x measurement yields NO₂. This NO₂ value and the Cambustion NO_x value are used to calculate the NO₂ to NO_x ratio at the dCSC™ outlet.

Figure 4.11 shows the NO to NO₂ oxidation performance of the dCSC™ at different temperatures. As temperature increases, the NO to NO₂ oxidation reaction rate increases and more of the NO passing through the substrate is oxidized to NO₂. Therefore, as the dCSC™ temperature increases from 100 to 300 °C, the NO₂/NO_x ratio increases. Which indicates that the NO to NO₂ oxidation is increasing. At temperatures below 300 °C Equation 4.1 has an equilibrium towards the right side of the equation. From 300 to 450°C, the NO₂/NO_x ratio decreases, meaning less of the NO passing through the substrate at these temperatures is oxidized to NO₂. This is because Equation 4.1 has an equilibrium which shifts to the left side of the equation at these higher temperatures which is discussed in reference [27]. Therefore, the dCSC™ NO to NO₂ ratio is decreasing as temperature increases beyond 300 °C.

Figure 4.11 Downstream dCSC™ NO₂/NO_x Ratio vs. Temperature

4.5 N₂O Production

N₂O concentrations were measured downstream of the dCSC™ substrate during Phases III and IV of testing. While the dCSC™ is releasing NO_x, after a Phase III storage temperature of 150 °C or less, there is a low level of NO_x conversion to N₂O observed. This production of N₂O in the dCSC™ is a result of the HC lean NO_x reduction that occurs on the substrate, as discussed in reference [1]. The oxidation of adsorbed HC and NO, once the dCSC™ is approximately 200 °C and above, potentially results in the formation of N₂O [28]. Equation H.1 and H.2 in Appendix H describes the reactions that produce N₂O [28].

Figure 4.12 shows the N₂O concentration at the dCSC™ outlet during an 80 °C Phase III and a 300 °C Phase IV, at engine condition 3. At the beginning Phase IV, while the dCSC™ is releasing NO_x and HC, there is N₂O production. The N₂O concentration increases to a peak of 12 ppm and then decreases to a constant concentration of 0 ppm at the 300 °C Phase IV temperature.

Figure 4.12 N_2O Concentration vs. Time during an 80 °C Phase III and a 300 °C Phase IV, at Engine Condition 3

4.6 CO Storage/Oxidation Performance

Figure 4.13 shows the CO concentration at the dCSC™ outlet, during a 125 °C Phase III and 300 °C Phase IV test at engine condition 1. During Phase III the downstream dCSC™ CO concentration increases from 0 ppm to a constant value of 35 ppm. The CO concentration upstream during this test is 85 ppm. The difference between the upstream 85 ppm CO concentration and downstream 35 ppm CO concentration is stored/oxidized by the dCSC™. During the start of Phase IV, as the dCSC™ temperature is increasing from 125 to 300 °C, the CO concentration decreases to 0 ppm. As the dCSC™ temperature increases, the CO oxidation capability of the dCSC™ increases and oxidizes all the CO to CO_2 .

Figure 4.13 Downstream dCSC™ CO vs. Time during a 125 °C Phase III and 300 °C Phase IV, at Engine Condition 3

Figure 4.14 shows the dCSC™ CO storage/oxidation efficiency of the 125 °C Phase III and 300 °C Phase IV test. During Phase III, the storage/oxidation efficiency starts at 100% and then decreases to 55% towards the end of Phase III. At the start of Phase IV the dCSC™ temperature increase from 125 to 300 °C. As dCSC™ temperature increases the CO storage/oxidation increases to 100%. As dCSC™ temperature increases all of the upstream CO is oxidized to downstream CO₂.

Figure 4.14 dCSCTM CO Storage/Oxidation Efficiency vs. Time during a 125 °C Phase III and 300 °C Phase IV, at Engine Condition 1

Figure 4.15 shows the steady state CO oxidation of the dCSCTM at different average volume weighted temperatures during Phases III and IV. The data in Figure 4.15 are from all the testing completed. At 150 °C, there is 100 % CO oxidation for the tests completed at engine condition 1. The 150 °C tests at engine condition 2 showed 90-99% CO oxidation. This is because at engine condition 2 (exhaust flow rate – 4.9 kg/min), the exhaust flow rate is 1.5 kg/min more than engine condition 1 (exhaust flow rate – 3.5 kg/min). Therefore, the dCSCTM is exposed to more molecules of CO at engine condition 2 than at engine condition 1. At temperatures above 150 °C the dCSCTM CO oxidation is 100%. The CO oxidation % decreases from 150 to 100 °C because the CO to CO₂ oxidation reaction rate is decreasing as temperature decreases. Also, the CO storage ability of the dCSCTM is being inhibited by H₂O in the exhaust at these low temperatures. However, from 100 to 80 °C the CO oxidation percentage increases. This is because the test at 80 °C was performed at engine condition 3 (exhaust flow rate – 2.6 kg/min) where the exhaust flow rate is 0.9 kg/min less than engine condition 1 (exhaust flow rate – 3.5 kg/min) where the 100 °C test was completed. Therefore, the dCSCTM is exposed to fewer molecules of CO at engine condition 3 than at engine condition 1. At temperatures

from 80 to 125 °C the dCSC™ showed 55 to 70% CO oxidation and 90 to 100% CO oxidation at temperatures from 150 to 400 °C.

Figure 4.15 Downstream dCSC™ CO Oxidation % vs. Temperature

4.7 2D Temperature Distributions

Figure 4.16 shows the dCSC™ 2D temperature distribution for Phase III of control test 13 using the analysis methodology in Section 3.4.4. The temperature setpoint for the dCSC™ during Phase III of a control test is 200 °C. Each row of thermocouples (radial location) shows less than 6 °C temperature difference from the front to the back of the substrate. From the center of the dCSC™ to the outermost radius there is a 13 °C temperature difference between the furthest downstream thermocouple locations in each

Figure 4.16 Control Test 13 at minute 113, dCSC™ Temperature 200 °C, Phase III 2D Temperature Distribution

¹ *Engine Condition/Test Number/Storage Temperature (°C)/Release Temperature (°C)/Indicates # of times the specific test has been run (02 = 2nd time running test). -TR1 indicates 20 °C/min ramp rate. -TR2 indicates

Figure 4.17 shows the dCSC™ 2D temperature distribution for a test with a 115 °C Phase III temperature. Differing from Figure 4.16, each row of thermocouples (radial location) shows less than 3 °C temperature difference from the front to the back of the substrate. From the center of the dCSC™ to the outermost radius there is a 6 °C temperature difference between the furthest downstream thermocouple locations in each row. Figure 4.16 showed larger temperature gradient's because the temperature setpoint was 200 °C, 75 °C higher than Figure 4.17, and room temperature is approximately the same.

Figure 4.17 Test 9 minute 103, dCSC™ Temperature 115 °C, Phase III 2D Temperature Distribution

At the start of Phase IV, the dCSC™ temperature increases from the Phase III temperature setpoint to the Phase IV temperature setpoint. Figure 4.18 shows the dCSC™ 2D temperature distribution during this temperature increase. In this case it is plotted for

control test 13, where the temperature is increasing from 200 to 300 °C, at minute 119 when the dCSC™ temperature is approximately 250 °C. During this temperature increase there is a 20 °C temperature difference between the C1 and C4 thermocouples (front and back). There is also a 20 to 30 °C temperature difference from the center row of thermocouples to the outermost radius of the substrate.

Figure 4.18 Control Test 13 at minute 119, dCSC™ Temperature Approximately 250°C, Phase IV Heating (from 200 to 300 °C) 2D Temperature Distribution

Figure 4.19 shows the dCSC™ 2D temperature distribution during a temperature increase from 115 to 300 °C during Phase IV. The 2D distribution is plotted at minute 119 when the temperature is approximately 250 °C. During this temperature increase within the dCSC™ there is a 30 °C temperature difference between the C1 and C4 thermocouples (front and back). This is 10 °C higher than in Figure 4.18 because the temperature ramp

starts at 115 °C in Figure 4.19 rather than 200 °C in Figure 4.18. Therefore, the dCSC™ temperature ramps an additional 75 °C in Figure 4.19 which makes the temperature gradient larger. There is also a 30 °C temperature difference from the center row of thermocouples to the outermost radius of the substrate, which is on the higher end of the same gradient in Figure 4.18.

Figure 4.19 Test 9 minute 112, dCSC™ Temperature Approximately 175 °C, Phase IV Heating (from 115 to 300 °C) 2D Temperature Distribution

Figure 4.20 shows the dCSC™ 2D temperature distribution at test minute 149 of control test 13, when the dCSC™ has reached the 300 °C Phase IV temperature setpoint. Each row of thermocouples (radial location) shows less than 3 °C temperature difference from the front to the back of the substrate. From the center of the dCSC™ to the outermost radius there is a 26 °C temperature difference between the furthest downstream thermocouple locations in each row. This is twice the temperature difference from Figure

4.16. This is expected because the temperature setpoint is 100 °C higher in Figure 4.20 than 4.16, but the room temperature is approximately the same, providing a larger temperature gradient.

Figure 4.20 Control Test 13 at minute 149, dCSC™ Temperature 300 °C, Phase IV
 Release 2D Temperature Distribution

Figure 4.21 shows the dCSC™ 2D temperature distribution at test minute 140 of test 9, when the dCSC™ has reached the 300 °C Phase IV temperature setpoint. The temperature gradients between the thermocouples in each row, and between the rows, is within 1 °C of the temperature gradients in Figure 4.20. This is because the temperature setpoint is the same for Phase IV of both tests and test cell temperature is approximately the same. The RMS error for the dCSC™ 2D temperature distributions never exceeds 5 °C.

A literature review was conducted to determine data and fundamentals of PNA devices that are available. An engine test cell and test procedure were developed as well as a statistical test matrix. The test cell instrumentation needed to acquire the data for the high-fidelity 2D flow through model of the dCSC™ was determined. Data analysis methods were developed to determine the dCSC™ performance characteristics from the experimental data. Over 200 hours of testing was completed on the Diesel Cold Start Concept Catalyst (dCSC™) with a 2013 Cummins ISB 6.7L 280 hp diesel engine.

The goal of the dCSC™ is to store NO, NO₂, CO, and HC emissions at temperatures below 200 °C where the current ATS is ineffective and release them at temperatures above 200 °C when the downstream ATS has increased its temperature. A list of conclusions from the experimental results are as follows.

1. Consistent with reference [8], the dCSC™ shows significant low temperature NOx storage capability, with peak NOx storage occurring from 125 to 150 °C.
2. Once the dCSC™ temperature has been at 500 °C while being exposed to exhaust gas from the diesel engine at 1660 rpm and 600 N-m for 5 hours and 30 minutes the 200 °C total NOx storage capacity reduces from approximately 0.6 to 0.5 g.NOx/L.Sub. After 9 hours and 10 minutes at these conditions the 200 °C dCSC™ total NOx storage capacity reduces from 0.5 to 0.4 g.NOx/L.Sub.
3. However, during the first 200-seconds of Phase III of testing, the 200 °C dCSC™ NOx storage capacity remained nearly constant at 0.3 g.NOx/L.Sub.
4. The ability of the dCSC™ to regain NOx storage capacity is dependent upon the release temperatures. If the dCSC™ temperature ramped through the 200 to 265 °C range, rapid NOx release was observed and the substrate released over 70% of the NOx stored on the substrate. At a release temperature of 350 °C, another rapid NOx release temperature range was observed and 70 to 90% of the NOx stored was released. This conclusion is supported by the data in reference [8].
5. The 250 to 350 °C temperature ramp is 60% more efficient at releasing NOx than the 250 to 300 °C temperature ramp.
6. The rapid NOx release temperature range of the dCSC™ occurs at temperatures above 200 °C. This is well within the operating temperature range of the aftertreatment system after the cold start period.
7. N₂O production was measured as a result of the HC lean NO reduction that occurs on the dCSC™, this is supported by the data in reference [1]. A peak N₂O concentration of 12 ppm was measured during a dCSC™ temperature ramp from an 80 °C Phase III to a 300 °C Phase IV. This indicates the upstream NO is

converted to downstream N_2O during the temperature ramp at the beginning of Phase IV, where NO_x release is observed.

8. At temperatures from 200 to 400 °C, the dCSCTM shows 50% or greater NO to NO_2 oxidation. NO to NO_2 oxidation peaks at approximately 75% at 300 °C.
9. The dCSCTM also showed 50 to 70% CO oxidation at temperatures of 125 °C and below. At temperatures of 150 °C and above the dCSCTM oxidizes 90 to 100% of the CO emissions entering the substrate.
10. The RMS error of the dCSCTM 2D temperature distributions is less than 5 °C.

4.9 Future Work

Modeling of the dCSCTM substrate will take place now that the experimental data has been acquired. This model will be used to predict downstream dCSCTM emissions concentrations at specified conditions. In conjunction with the species model an accurate thermal model of the device will be developed from all of the temperature data acquired herein.

In order to improve the temperature measurements, it is recommended that an additional row of thermocouples be instrumented within the dCSCTM substrate. Details of this recommendation are in Appendix J.

Additional experimental research with accurate methods to measure upstream and downstream dCSCTM HC is needed. This needs to be done in order to calibrate the HC storage, release, and oxidation performance of the dCSCTM.

The NO_x storage capacity of the dCSCTM is finite, therefore, the faster the more robust downstream ATS reaches its operating temperature of over 200 °C, the better.

Experimental research must be done to determine a reliable method for increasing the ATS temperature downstream of the dCSCTM as quickly as possible. Electric heaters, fuel burners, engine calibration, engine hardware, etc. have all been brought up as viable options [5, 11, 12, 13].

References

1. Chen, H., Mulla, S., Weigert, E., Camm, K. et al., "Cold Start Concept (CSC™): A Novel Catalyst for Cold Start Emission Control," *SAE Int. J. Fuels Lubr.* 6(2):2013, doi:10.4271/2013-01-0535. (2013)
2. "Modular Aftertreatment System," *Cummins Inc.* [Online]. Available: <https://www.cummins.com/components/aftertreatment/modular-aftertreatment-system>. [Accessed: 09-Nov-2019].
3. CARB, "California Air Resources Board Staff Current Assessment of the Technical Feasibility of Lower NOx Standards and Associated Test Procedures for 2022 and Subsequent Model Year Medium-Duty and Heavy-Duty Diesel Engines," CARB staff white paper, (2019).
4. "Cleaner Trucks Initiative," *EPA*, 21-Feb-2019. [Online]. Available: <https://www.epa.gov/regulations-emissions-vehicles-and-engines/cleaner-trucks-initiative>. [Accessed: 10-Nov-2019]. (2019)
5. Sharp, C., Webb, C., Neely, G., Sarlashkar, J. et al., "Achieving Ultra Low NOx Emissions Levels with a 2017 Heavy-Duty On-Highway TC Diesel Engine and an Advanced Technology Emissions System - NOx Management Strategies," *SAE Int. J. Engines* 10(4):2017, doi:10.4271/2017-01-0958. (2017)
6. Emission Standards, Available from: www.dieselneta.com.
7. "Low Load Cycle (LLC)," Emission Test Cycles: Low Load Cycle (LLC). [Online]. Available: <https://www.dieselneta.com/standards/cycles/llc.php>. [Accessed: 12-Nov-2019]. (2019)
8. Chen, H., Liu, D., Weigert, E., Cumaranatunge, L. et al., "Durability Assessment of Diesel Cold Start Concept (dCSC™) Technologies," *SAE Int. J. Engines* 10(4):2017, doi:10.4271/2017-01-0955. (2017)
9. Alissa Recker, "Fuel Contaminants, Effects on Aftertreatment, and Their Limits on NOx Stringency and Extended Useful Life", *presentation, University of Wisconsin Madison symposium on technologies to meet ultra-low NOx standards*. <https://www.erc.wisc.edu/symposium2019.php>. (2019)

10. Naseri, M., Aydin, C., Mulla, S., Conway, R. et al., "Development of Emission Control Systems to Enable High NO_x Conversion on Heavy Duty Diesel Engines," *SAE Int. J. Engines* 8(3):2015, doi:10.4271/2015-01-0992. (2015)
11. Culbertson, D., Pradun, J., Khair, M., and Diestelmeier, J., "Development of Robust Electric Heating System for Medium Duty Diesel Vehicles," *SAE Technical Paper* 2017-01-0937, doi:10.4271/2017-01-0937. (2017)
12. Magee, Mark E. "Exhaust Thermal Management Using Cylinder Deactivation and Late Intake Valve Closing." MS Thesis, Purdue University, May, (2014)
13. Sharp, C., Webb, C., Neely, G., Carter, M. et al., "Achieving Ultra Low NO_x Emissions Levels with a 2017 Heavy-Duty On-Highway TC Diesel Engine and an Advanced Technology Emissions System - Thermal Management Strategies," *SAE Int. J. Engines* 10(4):2017, doi:10.4271/2017-01-0954. (2017)
14. J. M. S. E. Control, "Ammonia slip catalysts," *JM Stationary Emissions Control*. [Online]. Available: <https://www.jmsec.com/air-pollution-solutions/selective-catalytic-reduction-scr/ammonia-slip-catalysts/?L=0>. [Accessed: 10-Nov-2019].
15. W. A. Majewski, "Selective Catalytic Reduction," *Selective Catalytic Reduction* [Online]. Available: https://www.dieselnets.com/tech/cat_scr.php. [Accessed: 10-Nov-2019]. (2005)
16. Sharp, C., Webb, C., Yoon, S., Carter, M. et al., "Achieving Ultra Low NO_x Emissions Levels with a 2017 Heavy-Duty On-Highway TC Diesel Engine - Comparison of Advanced Technology Approaches," *SAE Int. J. Engines* 10(4):2017, doi:10.4271/2017-01-0956. (2017)
17. Zheng, Y., "Low-Temperature Pd/Zeolite Passive NO_x Adsorbers: Structure, Performance, and Adsorption Chemistry." *The Journal of Physical Chemistry C* **121**(29): 15793-15803. (2017)
18. Chen, H. Y.; Collier, J. E.; Liu, D. X.; Mantarosie, L.; Duran-Martin, D.; Novak, V.; Rajaram, R. R.; Thompsett, D. Low Temperature NO Storage of Zeolite Supported Pd for Low Temperature Diesel Engine Emission Control. *Catal. Lett.* 2016, 146, 1706–1711. (2016)

19. S. Malamis, M.P. Harold, W.S. Epling, "Coupled NO and C₃H₆ Trapping, Release and Conversion on Pd-BEA: Evaluation of The Lean Hydrocarbon NO_x Trap," in press, Ind. Eng. Chem. Res. (2019)
20. Vu, A.; Luo J.; Li, J.; Epling, W.S.; Effects of CO on Pd/BEA Passive NO_x Adsorbers. Catal. Lett. 2017, 147, 745-750. (2017)
21. "An Experimental Investigation of the Effect of Temperature and Space Velocity on the Performance of a Cu-Zeolite Flow-through SCR and a SCR Catalyst on a DPF with and without PM Loading," Vaibhav Kadam, MS Thesis, Michigan Technological University, (2016)
22. "An Experimental Investigation into NO₂ Assisted Particulate Oxidation With and Without Urea and Active Regeneration of Particulate Matter in a SCR Catalyst on a DPF," Erik Gustafson, MS Thesis, Michigan Technological University, (2016)
23. "Catalyst Fundamentals," Catalyst Fundamentals. [Online]. Available: https://www.dieselnet.com/tech/cat_fund.php#rate. [Accessed: 11-Nov-2019].
24. Pihl, J., Majumdar, S.S., NO adsorption and desorption phenomena on a Pd-exchanged zeolite passive NO_x adsorber, CLEERS Workshop, September 19, (2018)
25. Heywood, John B., Internal Combustion Engine Fundamentals. New York: McGraw-Hill, (1988)
26. James Sanchez, "EPA's Cleaner Trucks Initiative", *presentation, University of Wisconsin Madison symposium on technologies to meet ultra-low NO_x systems*. <https://www.erc.wisc.edu/symposium2019.php> (2019)
27. W.A. Majewski, "Diesel Oxidation Catalyst," *Diesel Oxidation Catalyst* [Online]. Available: https://www.dieselnet.com/tech/cat_doc.php. [Accessed: 6-Dec-2019]. (2018)
28. Malamis, S., Ambast, M., Harold, M.P., Epling, Coupled NO and C₃H₆ trapping, release and conversion on Pd-BEA, W., CLEERS Workshop, September 19, (2018)

Appendix A. Heater PID Tuning

Tuning of the heater PID controller was needed in order to achieve zero steady state temperature error. 10 °C temperature oscillations were observed when attempting to hold the temperature constant, as shown in Figure A.1. The C1, C2, C3, and C4 thermocouples are on the centerline of the dCSC™ substrate spaced evenly from front to back, respectively.

A.1 Watlow Heater Temperature Data Showing Oscillating Response

By tuning the heater controller all temperature oscillations were eliminated. As shown in Figure A.2, the dCSC™ thermocouple data achieve steady state readings.

A.2 Watlow Heater Temperature Response Data After Tuning

Appendix B. Emissions Instrumentation

B.1 Pierburg 5-Gas Bench

The Pierburg 5-Gas bench was utilized to measure exhaust gas concentrations of CO, CO₂, NO, NO₂, and O₂. In addition, the bench is setup to measure exhaust gas concentrations from two different locations within the ATS. With the control of solenoid valves, air pressure regulates one-way valves open or closed. By opening one valve and closing another, it is possible to switch from upstream dCSC™ sampling to downstream sampling in seconds. A list of the measuring methods for each exhaust gas constituent is in Table B.1.

Table B.1 Pierburg 5-Gas Bench Analyzer Types

Exhaust Gas Constituent	Detection Method	Notes:
O ₂	Paramagnetic	
CO ₂	IRD	
CO	IRD	
NO	Chemiluminescence	
NO ₂	NO ₂ to NO converter, Chemiluminescence	
Total Hydrocarbons	Flame Ionization (FID)	Not able to measure with current sampling system.

NO₂ is not directly measured, it is first converted from NO₂ to NO and then measured with the Pierburg Chemiluminescence detection system. Due to the long lengths of sample line from the ATS, total hydrocarbons could not be measured with the Pierburg FID.

B.2 Combustion Fast NO and NO_x CLD

Cambustion's fNO400 CLD Fast Response NO measuring system was used to measure NO and NO_x downstream of the dCSC™. In order to measure total NO_x, a NO₂ to NO converter was placed in line with channel 2 of the fNO400 system. Figures B.1 and B.2 illustrate the Cambustion sampling system. Figure B.1 shows the sampling locations of both Cambustion channels (Fast NO and Fast NO_x), a production NO_x sensor, and the downstream sample location for the Pierburg 5-gas bench and Thermo Fisher N₂O analyzer.

B.1 Downstream dCSC™ NO_x Sample Locations.

Figure B.2 shows the NO₂ to NO converter placed directly in line with the Cambustion fNO400 channel 2 sampling system. Fittings were fabricated in order to allow the converter to be mounted in between the sample probe and sample head.

B.2 Cambustion fNO400 CLD NO_x Channel Setup

The Cambustion fNO400 CLD Fast Response system has a 4 ms response time of the CLD output from 90% to 10% NO concentration. This is in response to a step input at the sample source. Insitu calibration is achieved via flooding the entire sampling system with calibration gas.

B.3 Cambustion HFR 400 Fast FID

A Cambustion HFR 400 Fast FID measured total hydrocarbon concentrations in the exhaust. Similar to the fNO400 CLD system the HFR 400 has two measuring channels, insitu calibration, and a 4 ms 10-90% response time of the FID output for a step input at the source. The FID fuel is pure hydrogen (H₂).

B.4 Thermo Fisher 46i N₂O IRD

The range of this analyzer is 0 to 50 ppm with a 60 s 10-90% response time to a step input. This system samples in parallel with the Pierburg 5-gas bench. It was initially a concern that CO₂ might cause an interference while measuring N₂O. In Figure B.3, it is shown that the N₂O analyzer does measure a concentration of N₂O when exposed to a constant CO₂ concentration. However, the CO₂ concentration during testing is constant, therefore the interference is constant. By taking an upstream dCSC™ measurement with

the N₂O analyzer, the constant CO₂ interference can be accounted for. The N₂O measurement upstream of the dCSC™ is subtracted from the N₂O measurements downstream of the dCSC™. The N₂O analyzer was logged in LabVIEW.

B.3 N₂O Analyzer CO₂ Concentration Interference

B.5 NO_x Sensors

Two production NO_x sensors are setup to measure engine out NO_x and downstream dCSC™ NO_x concentrations. The error of these sensors is +/- 10 ppm or 10%, whichever is greater. The sensors' output were logged using Cummins Calterm Software. In order to ensure the NO_x sensors were on at all times, the ATS temperature sensors were clamped in a heater to keep them above 200 °C during testing. If these sensors dropped below 200 °C, the NO_x sensors would shut off to protect them from condensation.

Appendix C. Paragon ULSD #2 Fuel Analysis Results

Table C.1 Paragon ULSD #2 Fuel Analysis Results

ANALYTICAL RESULTS

Workorder: 224870 MICH TECH-080618

Lab ID: 2248700001	Date Collected: 11/27/2017 00:00	Matrix: Diesel					
Sample ID: #2 ULSD	Date Received: 8/6/2018 15:42						
Sample Desc:	PO: CC ON FILE						
Parameters	Qualifier	Result Units	Dilution Factor	Reporting Limit	Result Qualifier Min Max	Analyzed	By
Elemental Analysis							
Analytical Method: ASTM D5291 D [A]							
Carbon (Wt%)		86.55 % m/m	1	0.05		8/10/2018 15:01	PRS
Hydrogen (Wt%)		13.45 % m/m	1	0.05		8/10/2018 15:01	PRS
Individual Parameters							
Analytical Method: ASTM D4052 [A]							
API Gravity at 15.56°C		34.5 °API	1	0.1		8/13/2018 10:28	VUA
Density at 15.56°C		0.8516 g/mL	1	0.0001		8/13/2018 10:28	VUA
Spec. Grav. at 15.56°C/15.56°C		0.8524	1	0.0001		8/13/2018 10:28	VUA
Analytical Method: ASTM D240 [A]							
Gross Heating Value (BTU/lb)		19669 BTU/lb	1	175		8/8/2018 09:54	AJB2
Gross Heating Value (MJ/kg)		45.749 MJ/kg	1			8/8/2018 09:54	AJB2
Net Heating Value (BTU/lb)		18442 BTU/lb	1	175		8/8/2018 09:54	AJB2
Net Heating Value(MJ/kg)		42.895 MJ/kg	1			8/8/2018 09:54	AJB2
Analytical Method: ASTM D613 [A]							
Cetane No.		51.7	1			8/9/2018 13:08	PRS
Stoichiometric Ratios							
Analytical Method: SAE J1829							
Air/Fuel Ratio (CH-based)		14.58	1	0.01		8/13/2018 12:46	PRS
H/C Atomic Ratio		1.852	1	0.001		8/13/2018 12:46	PRS

Appendix D. Experimental Testing Matrix

Table D.1 Experimental Testing Matrix

Run Order	Test Name	Engine Condition	Phase III Storage Temp. (°C)	Phase IV Release Temp. (°C)	Temp. Ramp (°C/minute)
22	C1/01/S100/R300	1	100	300	N/A
6	C1/02/S125/R300	1	125	300	N/A
3	C1/03/S150/R300	1	150	300	N/A
16	C1/04/S200/R300	1	200	300	N/A
11	C1/05/S225/R300	1	225	300	N/A
7	C1/06/S250/R300	1	250	300	N/A
17	C1/07/S200/R350	1	200	350	N/A
14	C1/08/S250/R350	1	250	350	N/A
8	C2/09/S115/R300	2	115	300	N/A
5	C2/10/S150/R300	2	150	300	N/A
21	C2/11/S200/R300	2	200	300	N/A
19	C2/12/S250/R300	2	250	300	N/A
15	C1/13/S150/R200	1	150	200	N/A
1	C1/14/S150/R250	1	150	250	N/A
23	C1/15/S150/R300	1	150	300	N/A
2	C1/16/S150/R350	1	150	350	N/A
4	C1/17/S150/R400	1	150	400	N/A
18	C2/18/S150/R300	2	150	300	N/A
13	C2/19/S150/R350	2	150	350	N/A
9	C1/20/S125/R300	1	125	300	N/A
20	C1/21/S200/R300	1	200	300	N/A
10	C1/22/S150/R350 - TR1	1	150	350	20
12	C1/23/S150/R350 - TR2	1	150	350	40
24	C3/24/S080/R300	3	80	300	N/A
25	C1/25/S150/R450	1	150	450	N/A

*Engine Condition/Test Number/ Phase III Storage Temperature (°C)/Phase IV Release Temperature (°C)/Indicates # of times the specific test has been run (02 = 2nd time running test). -TR1 indicates 20 °C/min ramp rate. -TR2 indicates

Appendix E. Calculation of dCSC™ Volume Weighted Temperature

First, the total volume of instrumented dCSC™ is calculated using Equation D.1.

$$V_{T.V.} = \pi * r_{T.V.}^2 * L_{T.V.} \quad \text{E.1}$$

Where $V_{T.V.}$ is the instrumented dCSC™ total volume, $r_{T.V.}$ is the outermost radius of the instrumented dCSC™, and $L_{T.V.}$ is the total length of the instrumented dCSC™. The radius of cylindrical volume that each thermocouple represents is calculated by Equation D.2.

$$r_W = \sqrt{\frac{r_{O.T.}^2 + r_{T.C.}^2}{2}} \quad \text{E.2}$$

Where r_W is the radius of cylindrical volume that the thermocouple represents. $r_{O.T.}$ is the radial location of the next outer thermocouple and $r_{T.C.}$ is the radial location of the thermocouple being weighted. The axial length of dCSC™ substrate each thermocouple represents is calculated using Equation D.3.

$$L_{T.C.} = \frac{L_U}{2} - \frac{L_D}{2} \quad \text{E.3}$$

$L_{T.C.}$ is the axial length of substrate that the thermocouple represents. L_U is the axial length of substrate to the next thermocouple or dCSC™ edge upstream and L_D is the axial length of substrate to the next thermocouple or dCSC™ edge downstream. Equation D.4 is then used to calculate the dCSC™ volume that each thermocouple represents.

$$V_{T.C.} = (\pi * r_W^2 * L_{T.C.}) - V_{I.T.C.} \quad \text{E.4}$$

$V_{T.C.}$ is the dCSC™ volume each thermocouple represents and $V_{I.T.C.}$ is the volume represented by the next inner radial thermocouple. Equation D.5 is used to calculate the weight applied to each thermocouple reading.

$$W_{T.C.} = \frac{V_{T.C.}}{V_{T.V.}} \quad \text{E.5}$$

$W_{T.C.}$ is the weight applied to each thermocouple reading. $V_{T.C.}$ is the volume that each thermocouple represents and $V_{T.V.}$ is the total volume of instrumented dCSC™. From Equation D.5 and the thermocouple readings, Equation D.6 was developed to calculate the dCSC™ volume weighted temperature.

$$T_{V.W.} = \sum_{i=1}^{24} (W_{T.C.(i)} * T_{T.C. (i)}) \quad \text{E.6}$$

Where $T_{V.W.}$, is the volume weighted temperature of the dCSC™ substrate and $T_{T.C. (i)}$ is the reading of each thermocouple used in the calculation. $W_{T.C.(i)}$ is the weight applied to each corresponding thermocouple reading. The thermocouples' used in Equation D.6 are C1-20 and C25 – C28.

Appendix F. Emissions Timeplots During Testing

F.1 Control Test dCSC™ Delta Pressure during Test Phases I-IV

F.2 Control Test dCSC™ Temperature during Test Phases I-IV

F.3 Downstream dCSC™ CO Concentration during a 200 °C Test Phase III and 300 °C Phase IV, at Engine Condition 1

F.4 dCSC™ CO Storage/Oxidation Efficiency during a 200 °C Test Phase III and 300 °C Phase IV, at Engine Condition 1

F.5 Downstream dCSC™ CO₂ Concentration during a 200 °C Test Phase III and 300 °C Phase IV, at Engine Condition 1

F.6 Downstream dCSC™ CO₂ Concentration during a 200 °C Test Phase III and 300 °C Phase IV, at Engine Condition 1

F.7 Downstream dCSC™ NO, NO₂, and NOx Concentrations during a 200 °C Test Phase III and 300 °C Phase IV, at Engine Condition 1

F.8 Downstream dCSC™ NOx Sensor Concentrations during a 200 °C Test Phase III and 300 °C Phase IV, at Engine Condition 1

F.9 Downstream dCSC™ Combustion CLD NO, NO₂, and NOx Concentrations during a 200 °C Test Phase III and 300 °C Phase IV, at Engine Condition 1

F.10 Downstream dCSC™ NOx Concentrations during a 200 °C Test Phase III and 300 °C Phase IV, at Engine Condition 1

F.11 Engine Load and Speed, Turbo Outlet Temperature, and C1 Thermocouple Temperature during a 200 °C Test Phase III and 300 °C Phase IV, at Engine Condition 1

F.12 Downstream dCSC™ Brake Specific NOx during a 200 °C Test Phase III and 300 °C Phase IV, at Engine Condition 1

Appendix G. Control Plots

Appendix G shows control plots for the various lab instrumentation and testing conditions monitored during testing. Test run order refers to the order in which the tests were run. Certain engine and test cell conditions were measured with lab instrumentation and are also measured with sensors on the engine or calculated by the Cummins Calterm calibration tool. The values measured with lab instrumentation were logged with NI LabVIEW DAQ hardware and software. These values are referred to in the plot legend as LabVIEW. The values measured with sensors on the engine or calculated by Calterm are referred to in the plot legend as Calterm.

G.1 Engine Condition vs. Test Order

G.2 Upstream dCSC™ NO/NOx Ratio vs. Test Order

G.3 Upstream dCSC™ NOx Sensor NOx Concentration vs. Test Order

G.4 Upstream dCSC™ NOx Sensor O₂ Concentration vs. Test Order

G.5 Upstream dCSC™ Pierburg NO Concentration vs. Test Order

G.6 Upstream dCSC™ Pierburg NO₂ Concentration vs. Test Order

G.7 Upstream dCSC™ Pierburg NO_x Concentration vs. Test Order

G.8 Upstream dCSC™ Pierburg CO Concentration vs. Test Order

G.9 Upstream dCSC™ Pierburg CO₂ Concentration vs. Test Order

G.10 Upstream dCSC™ Pierburg O₂ Concentration vs. Test Order

G.11 Test Cell Barometric Pressure vs. Test Order

G.12 Test Cell Relative Humidity vs. Test Order

G.13 Average Test Cell Temperature during Test vs. Test Order

G.14 dCSC™ Delta Pressure vs. Average Volume Weighted Temperature

G.15 Engine Intake and dCSC™ Delta Pressures vs. Test Order

G.16 AFR Calculated from Fuel and Air Flow Rates vs. Test Order

G.17 AFR Calculated from O₂ and CO₂ vs. Test Order

G.18 Comparison of all AFR Calculations vs. Test Order

G.19 Upstream dCSC™ NOx Sensor O_2 Concentration vs. Test Order

G.20 Engine Turbo Outlet Temperature vs. Test Order

G.21 Engine Inlet Air Density vs. Test Order

G.22 Coriolis Fuel Flow Meter (LabVIEW) and Calculated (Calterm) Fuel Flow Rate vs. Test Order

G.23 Laminar Flow Element Engine Intake Air Mass Flow Rate vs. Test Order

G.24 Engine Exhaust Mass Flow Rate Measured (LabVIEW) and Calculated (Calterm)
vs. Test Order

G.25 Engine Air Mass Flow Rate Measured (LabVIEW) and Calculated (Calterm) vs.
Test Order

G.26 Engine Intake Boost (Calterm) vs. Test Order

G.27 Engine EGR Position (Calterm) vs. Test Order

G.28 Engine EGR Flow Rate (Calterm) vs. Test Order

G.29 Engine Coolant Temperature (LabVIEW and Calterm) vs. Test Order

G.30 Engine Variable Geometry Turbo Position (Calterm) vs. Test Order

G.31 Engine Accelerator Pedal Position (Calterm) vs. Test Order

G.32 Engine Load vs. Test Order

G.33 Engine Speed vs. Test Order

G.34 Engine Out H₂O Concentration Calculated from LabVIEW Flowrate AFR vs. Test Order

G.35 Engine Out H₂O Concentration Calculated from Calterm Flowrate AFR vs. Test Order

G.36 Engine Out H₂O Concentration Calculated from Pierburg Engine Out CO₂ Concentration vs. Test Order

G.37 Engine Out H₂O Concentration Calculated from Pierburg Engine Out O₂ Concentration vs. Test Order

Appendix H. N_2O Formulation Reactions

The following equations are used to describe the N_2O formulation reactions within the dCSCTM per reference [19, 28]. Equation H.1 describes the NO reduction reaction that results in N_2O production.

Where NO forms N_2O and O_2 . Equation H.2 describes the reaction between C_3H_6 and NO_2 causing a formulation of CO, H_2O , and N_2O .

Appendix I. CO, HC, and NO Oxidation Reactions

The following equations describe the oxidation reactions within the dCSC™. The equations were found in reference [27]. Equation H.1 defines the HC oxidation reaction.

Where 1 HC atom is oxidized with 1 O₂ atom to form carbon dioxide, CO₂, and water vapor, H₂O. Equation H.2 describes the oxidation reaction of CO.

Where 2 CO atoms are oxidized with 1 O₂ to form 2 CO₂ atoms. Equation H.3 describes the oxidation reaction of NO.

Where 1 NO atom is oxidized with ½ of an O₂ atom to form 1 NO₂ atom.

Appendix J. Additional Substrate Thermocouples

Additional substrate temperature instrumentation is needed in order to capture temperature gradient. Figure H.1 shows the dCSC™ radial temperature gradient measured during a steady state temperature condition of 250 °C. It is recommended for future testing to add rows of thermocouples at the locations indicated in Figure I.1.

J.1 Recommended Additional Thermocouples to Measure Temperature

Appendix K. Copyright Documentation

K.1. Figure 1.1 Possible ULN ATS Compared to Current ATS

Conor Berndt <ctberndt@mtu.edu>

Tue, Oct 29, 2019 at 4:33 PM

To: alissa.recker@daimler.com

Dear Alissa,

I am writing to request permission to reference a figure from your presentation "Fuel contaminants, effects on aftertreatment, and their limits on NO_x stringency and extended useful life" - from the UW Symposium. The figure is shown below.

The figure would appear in my thesis titled: "AN EXPERIMENTAL STUDY OF A PASSIVE NO_x ADSORBER (PNA) FOR THE REDUCTION OF COLD START DIESEL EMISSIONS."

Is there a paper this figure appears in? Otherwise I would reference the presentation in the figure caption and text.

Thank you for your time,

Conor Berndt

Mechanical Engineering - Graduate Student

Michigan Technological University

Email: ctberndt@mtu.edu

Phone: (906) 221-6485

MEEM B008

Conor Berndt <ctberndt@mtu.edu>

Wed, Nov 6, 2019 at 1:12 PM

To: alissa.recker@daimler.com

Hi Alissa,

I was wondering if you received my first email? Please let me know if you have any questions.

Thanks,

Conor Berndt

Mechanical Engineering - Graduate Student

Michigan Technological University

Email: ctberndt@mtu.edu

Phone: (906) 221-6485

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[Quoted text hidden]

alissa.recker@daimler.com <alissa.recker@daimler.com>

Thu, Nov 7, 2019 at 1:06
PM

To: ctberndt@mtu.edu

Hi Conor,

Sorry for the delayed response. Yes, you can use it. It's really just a simple schematic of some of the proposals we've been seeing from CARB and Southwest Research. You can find more of them in the CARB White Paper:

https://ww3.arb.ca.gov/msprog/hdlownox/white_paper_04182019a.pdf

Thanks,

Alissa Recker

Catalyst Kit Engineer

ATS Performance TP/PNF

Daimler Trucks Powertrain Engineering NAFTA

Cell: +1 313 452-3926

Desk: +1 313 592-5689

[Quoted text hidden]

If you are not the addressee, please inform us immediately that you have received this e-mail by mistake, and delete it. We thank you for your support.

**K.2. Copyright Permission for Thesis Figure 1.2 Turbine Outlet
Temperature vs. AFR**

Conor Berndt <ctberndt@mtu.edu> Tue, Oct 29, 2019 at 3:31 PM

To: gshaver@purdue.edu

Dear Dr. Shaver,

I am writing to request permission to use Figure 2.2 from Mark Magee's masters thesis "Exhaust Thermal Management

Using Cylinder Deactivation and Late Intake Valve Closing" as a reference for my own masters thesis at Michigan

Technological University.

My thesis will be titled "AN EXPERIMENTAL STUDY OF A PASSIVE NOX ADSORBER (PNA) FOR THE REDUCTION

OF COLD START DIESEL EMISSIONS".

Any assistance in obtaining permission to use the figure would be greatly appreciated.

Thank you for your time and consideration,

Conor Berndt

Mechanical Engineering - Graduate Student

Michigan Technological University

Email: ctberndt@mtu.edu

Phone: (906) 221-6485

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Shaver, Gregory M <gshaver@purdue.edu> Tue, Oct 29, 2019 at 3:33 PM

To: Conor Berndt <ctberndt@mtu.edu>

Dear Conor,

I approve. I assume you would add a citation to Mark's thesis in the caption?

Greg

[Quoted text hidden]

Conor Berndt <ctberndt@mtu.edu> Tue, Oct 29, 2019 at 3:34 PM

To: "Shaver, Gregory M" <gshaver@purdue.edu>

Greg,

Thank you very much. Yes, I would cite Mark's thesis in the figure caption and where mentioned in the text.

Kind regards,

Conor Berndt

Mechanical Engineering - Graduate Student

Michigan Technological University

Email: ctberndt@mtu.edu

Phone: (906) 221-6485

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Magee Master's Thesis

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[Quoted text hidden]

Shaver, Gregory M <gshaver@purdue.edu> Tue, Oct 29, 2019 at 3:36 PM

To: Conor Berndt <ctberndt@mtu.edu>

Sounds good, Conor. Best wishes finishing up.

Cheers,

[Quoted text hidden]

Conor Berndt <ctberndt@mtu.edu> Tue, Oct 29, 2019 at 3:36 PM

To: "Shaver, Gregory M" <gshaver@purdue.edu>

Thank you!

Conor Berndt

Mechanical Engineering - Graduate Student

Michigan Technological University

Email: ctberndt@mtu.edu

Phone: (906) 221-6485

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[Quoted text hidden]

K.3. Copyright Permission for Thesis Figure 2.2 NO_x Adsorption/Storage, Figure 2.3 NO_x Desorption/Release, and Figure 2.4 Effects of H₂O on NO_x adsorption

Conor Berndt <ctberndt@mtu.edu> Fri, Oct 25, 2019 at 9:48 AM

To: mharold@uh.edu, samalamis@uh.edu

Hi,

I am writing to request permission to reference figures from the attached presentation from the 2018 CLEERS

conference. They would appear in the Literature Review Chapter of my master's thesis titled "AN EXPERIMENTAL

STUDY OF A PASSIVE NO_x ADSORBER (PNA) FOR THE REDUCTION OF COLD START DIESEL EMISSIONS".

The figures I would like to reference are the NO_x adsorption, NO_x desorption, and water inhibition of NO_x storage

figures.

Please let me know if you have any questions,

Thank you for your time,

Conor Berndt

Mechanical Engineering - Graduate Student

Michigan Technological University

Email: ctberndt@mtu.edu

Phone: (906) 221-6485

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2018CLEERS_SamMalamis_Web.pptx

3109K

Harold, Michael P <MPHarold@central.uh.edu> Fri, Oct 25, 2019 at 11:25 AM

To: Conor Berndt <ctberndt@mtu.edu>

Cc: "Malamis, Sotirios A" <samalamis@uh.edu>

Dear Conor,

That will be fine. Or you could reference the paper that is related to that presentation which will be accepted soon. It

is

S. Malamis, M.P. Harold, W.S. Epling, "Coupled NO and C₃H₆ Trapping, Release and Conversion on Pd-BEA:

Evaluation of The Lean Hydrocarbon NO_x Trap,” in press, Ind. Eng. Chem. Res. (2019).

The paper should appear by mid November on the IECR website.

Best wishes,

11/6/2019 Michigan Technological University Mail - 2018 CLEERS Presentation
Reference

<https://mail.google.com/mail/u/0?ik=8713e930df&view=pt&search=all&permthid=thread-a%3Ar-7940216985565214836&simpl=msg-a%3Ar22165828...> 2/2

Mike Harold

[Quoted text hidden]

Conor Berndt <ctberndt@mtu.edu> Mon, Oct 28, 2019 at 2:06 PM

To: "Harold, Michael P" <MPHarold@central.uh.edu>

Cc: "Malamis, Sotirios A" <samalamis@uh.edu>

Dear Mike,

Thank you very much! I will use the paper citation you have provided to cite the figures.

I appreciate the timely response.

Conor Berndt

Mechanical Engineering - Graduate Student

Michigan Technological University

Email: ctberndt@mtu.edu

Phone: (906) 221-6485

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K.4. Copyright Permission for Thesis Figure 2.1 ULN ATS used on a Volvo MY 13.0L Diesel Engine at SwRI

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Instructor name	Dr. Jeffrey D. Naber		

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Author/Editor	Society of Automotive Engineers.	End Page	381
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