MODELING, CONTROL, AND DIAGNOSIS OF A
DIESEL LEAN NO\textsubscript{x} TRAP CATALYST

DISSERTATION

Presented in Partial Fulfillment of the Requirements for
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* * * * *

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ABSTRACT

Diesel engines require the use of alternative catalytic methods to meet future emissions standards. One such alternative system is the bypass-regeneration, Lean NOx Trap (LNT), which is the focus of this work. A novel method of providing reductants for management of this system is presented, which is referred to as flame reforming. This method uses rich, premixed combustion of Diesel fuel to generate carbon monoxide, hydrogen, and light-chain hydrocarbons for LNT management. Through the development of a prototype flame reformer and experimental testing, this concept is demonstrated to offer advantages over traditional methods in cost and dynamic response.

A technique, which is referred to as exotherm analysis, is developed which allows the observation of chemical phenomena inside the catalyst using substrate temperature measurements. Through the proper analytical methods, it is demonstrated experimentally that the temperature rise in the catalyst can be correlated to the rate that key reactions are taking place, as well as the mass of NOx stored and the effects of sulfur poisoning. These key reactions include the reduction of stored oxidizers as well as the readsorption of oxygen by the catalyst. This technique is exclusive to the bypass-regeneration system because of the low gas flow rates involved.

A control-oriented model of the storage and regeneration process is also developed. This model is used to develop a complete LNT NOx management algorithm using the techniques of model-based control. This algorithm, which uses catalyst temperatures as the primary feedback signals, contains an adaptive engine-out NOx estimator as well as an adaptive catalyst-out NOx estimator. In this way, the algorithm automatically compensates for sulfur poisoning of the catalyst. The model also is used to develop a virtual LNT system simulator with all of associated control algorithms and adaptive estimators. With this tool, the
LNT management algorithm is evaluated for an intended Tier 2, Bin 5 emissions application. In addition, experimental validation of key sub-algorithms is conducted on an engine dynamometer. The simulated performance of the system suggests that the system and control algorithm are capable of meeting Tier 2 standards with fuel economy penalties of less than 1%. 

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Dedicated to a clean and sustainable future.
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FIELDS OF STUDY

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CHAPTER 1

INTRODUCTION

1.1 Introduction

The work comprising this dissertation deals solely with the control of emissions from direct-injection, compression ignition engines, which are commonly referred to as Diesel engines. Diesel engines have historically had a somewhat well-deserved reputation of being "dirtier" than their stoichiometric gasoline counterparts. This label was fostered by yesterday's Diesel engine's characteristic puff of soot during hard accelerations and the distinctive odor of the exhaust. With today's modern Diesel engine, these "dirty" traits are now largely beyond the limits of human detection. A properly calibrated Diesel engine will never emit the faintest hint of visible soot and the characteristic Diesel odor has been controlled with improved combustion and Diesel oxidation catalysts. Although these advances have helped the Diesel engine in the public eye, it has not warded off the ever tightening emissions standards. Unless these emissions regulations can be met by the Diesel engine, the Diesel and its proven efficiency gains will become a thing of the past.

1.2 Motivation - Passenger Cars

The motivation behind this work has many different levels, from something as abstract as the desire to be good stewards of our natural resources, to something as concrete as the need to meet federal emissions standards. When discussing the Diesel engine, it is inevitable that two conflicting characteristics emerge. The first is the proven potential for achieving superior fuel economy over gasoline engines. On the other
side, are the elevated emissions of the Diesel engine. Although the mass of emissions from a modern Diesel engine can be lower than the mass of emissions from a gasoline engine, the Diesel engine typically runs aground on the issue of NOx, especially with the structure of US emissions regulations.

1.2.1 Fuel Economy and the Diesel Engine

In the United States and elsewhere, there is a great push to decrease dependence on oil imports. The motivation behind this is to allow the nation to become more independent and less at the whim of events in other regions of the world. There are, of course, two sides to the equation for reducing oil imports, supply and demand. The current focus in the US is clearly on the supply side of the equation. When discussing mechanisms for decreasing foreign oil imports, the typical response of US lawmakers is to increase domestic production.

This approach completely ignores the demand side of the oil equation. In 1985, twenty years before the publication of this document, the Corporate Average Fuel Economy (CAFE) Standard was 27.5 miles per gallon. At the present time, in 2005, that standard still sits at 27.5 miles per gallon. In 1984, the light-duty truck standard was 20.0 miles per gallon, today it sits at 20.7 miles per gallon. The fact that the standards have not changed significantly in the past twenty years is somewhat upsetting, however, there is a third factor that makes the situation even more bleak. Since 1987, the fuel economy of the US vehicle fleet has steadily declined from a peak of 26.2 miles per gallon to an average of 24.7 miles per gallon from 2000 to 2004. Thus, despite regulations in place to foster improvements in fuel economy, the yearly fleet average has slowly sunk by 1.5 miles per gallon. This steady decline is a result of shifting consumer buying patterns that have significantly increased the number of light-duty trucks (pickups and SUVs) that are purchased. Since these vehicles are permitted a more relaxed fuel economy standard, it has had the effect of actually lowering the average fuel economy of new vehicles sold.

The Diesel engine offers a dual pronged approach to reducing foreign oil dependence. The first is the Diesel engine's inherent efficiency advantage. A comparably performing Diesel powered vehicle can be
expected to get 20% to 30% better fuel economy than an equivalent gasoline powered vehicle. Furthermore, a modern Diesel engine will accept BioDiesel blends with no required system modifications. Since BioDiesel is produced from domestic agricultural products, it has the added advantage of bolstering the national economy while decreasing the need for foreign oil. Thus, through increases in efficiency and by diluting the amount of actual crude oil required for the vehicle, it is possible to realize substantial reductions in oil imports. Obviously, there is not enough BioDiesel production capability to envision an America powered entirely by soybeans. But relatively low-cost, incremental gains such as these can offer no-compromise ways of improving the US oil and fuel economy situation.

1.2.2 Emissions Standards and the Diesel Engine

While the direction of the US fuel economy has been in the opposite direction intended, the direction of emission regulations reductions have been entirely the opposite case. At first, this sharp contrast might seem odd. Unlike fuel economy, however, emissions reductions are motivated by the public health. These reductions are largely dictated by ambient air quality standards which are set to ensure a certain levels of air quality. Fuel economy, on the other hand, does not directly have any impact on the public health. An SUV rated at 18 miles per gallon is capable of meeting the same emissions standards as a sedan that gets 30 miles per gallon. One can argue, of course, that the impact of the CO₂ emissions from the more inefficient vehicle is also of great concern to the public health because of its role in global warming. This, in fact, is the argument made by the state of California when they attempted to regulated CO₂ emissions in the same manner as CO, hydrocarbons, NOₓ, and particulate matter. This legislative move resulted in a suit being filed by a number of organizations representing the automotive industry that blocked the legislation. The basis of the suit was that a CO₂ regulation is tantamount to regulating fuel economy, which is under the domain of the Federal Government and not up to individual states. The ever amassing body of evidence supporting human-induced global warming is apparently not, at present, enough to spur legislative action.

The latest set of Federal emissions standards (Tier 2) make the use of Diesel engines extremely challenging. These standards will be reviewed comprehensively in the following chapter, but are presented
here in a qualitative sense. To give physical meaning to the magnitude of the emissions standards, consider the following. For a vehicle that achieves 30 miles per gallon, the Tier 2, Bin 5 standards can be converted into a percent mass of emissions emitted per mass of fuel consumed. Although this is not an direct comparison, it gives some concept of the magnitude of the emissions levels that must be met. The amount of NOx permitted is 0.0056% the fuel mass, NMOG is 0.0071%, CO is 0.33%, and PM is 0.00079% of the fuel mass. Although this is a slight tangent, consider the emissions of a typical push lawnmower, of which there are millions operating in the US. A 5 Hp mower operated for the average 3900 minutes/year results in the equivalent emissions of driving a Tier 2, Bin 5 vehicle over 40,000 miles per year. Thus, a typical suburban family has a distinct chance of emitting more hydrocarbon and NOx emissions during the summer mowing season than driving their multiple Tier 2, Bin 5 vehicles the entire year.

1.2.3 Emissions versus Economy

Based on the above, it is clear that the US passenger car emissions and fuel economy standards are not particularly favorable for Diesels to prosper. The emissions standards are such that they make Diesel engines quite difficult to certify to Tier 2 standards. Furthermore, the fuel economy standards are such that there is little legislative incentive to provide more efficient vehicles with a Diesel powertrain. It is this climate that has helped stifle the Diesel passenger car market in the US. Despite a soft domestic market for Diesel passenger cars, there are niche markets in the US and massive markets abroad. Because of this and the prospect of increased fuel prices in the near future, US automakers are reluctant to let the passenger car Diesel engine fall by the wayside.

1.3 Motivation - Heavy-Duty Vehicles

Fortunately for the Diesel engine, the US market for heavy-duty engines is far from soft. The vast majority of the US tractor trailer fleet is powered by large displacement in-line Diesel engines. The domination of the Diesel in the heavy-duty market can be distilled down to almost one simple fact. Fuel costs for a fleet operator are sizable given the great distances traveled for line-haul truck operators. The Diesel engine is a
necessity given the slim profit margins in the highly competitive trucking industry. The Diesel engine delivers on its promise as well, an 80,000 pound semi on the open road can get over 7 miles per gallon. When one considers that a 5,000 pound pickup truck with a gasoline engine will be lucky to break 20 miles per gallon, one sees the advantage of the Diesel quite dramatically. So despite equivalently aggressive emissions legislation for the heavy-duty industry, the Diesel engine has emerged as an essential tool in the trucking industry, which in is a major component of the US economy. As with the passenger car emissions standards, a review of the heavy-duty standards is provided in the following chapter.

1.4 Novel Approaches to the LNT Management Problem

Because of the funding mechanism of the work, it was possible, and even encouraged, to go off the beaten path in addressing the problems of LNT management for a Diesel engine. Because of this, a number of novel techniques were developed that have not yet been reported on in the literature.

1. Total Flow Bypass-Regeneration - The bypass flow regeneration system has been investigated by a number of researchers. Very little work has been done on bypass-regeneration where the entire exhaust is diverted around the regenerating catalyst.

2. Model-Based Control Methods for Bypass-Regeneration - The published work done on bypass-regeneration does not generally deal with control of the regeneration or regeneration scheduling. This work addresses these topics extensively.

3. Catalyst Temperature Measurements Analysis - No work has been published regarding the use of the catalyst exotherm measurements for witnessing the phenomenon occurring inside the catalyst.

4. Flame Reforming for LNT Management - The use of a rich combustor for LNT management has not been explored in any published work.
CHAPTER 2

LITERATURE REVIEW

2.1 Modern Engines

Before focusing on the various aftertreatment devices that are available for emissions reduction, it is necessary to provide a brief background on the engine types that currently are used or researched for transportation. Virtually all internal combustion engines today generically run on either gasoline or Diesel fuel. In actuality, most gasoline engines are capable of operating on significant percentages of ethanol, which is commonly blended into fuels. Similarly, Diesel engines are capable of running on fuel derived from biofuels, such as BioDiesel. All of the following engines are nearly identical mechanically, with the only difference being in the method of fuel introduction and the presence or absence of an ignition device. Despite the common mechanical structure, an array of combustion regimes has emerged for driving the internal combustion engine: stoichiometric, spark-ignited engines; lean, port-injected, spark-ignited engines; lean, direct-injection, spark-ignited engines; direct-injection, compression-ignition engines; and homogenous charge compression-ignition engines. Each of these is discussed briefly in the following sections. Because of the fundamental differences in the combustion, each technique has a different emissions characteristic and therefore requires a different approach to catalytic aftertreatment.

2.1.1 Stoichiometric, Spark-Ignited Engines

Stoichiometric gasoline engines, as their name implies, operate with an air-to-fuel ratio very close to the stoichiometric proportions. The control system on these engines cause the air-to-fuel ratio to oscillate slightly above and below stoichiometric. These engines are the workhorse of the US passenger car fleet.
and make up a large fraction of passenger vehicles worldwide. By operating at stoichiometric air-to-fuel ratio, a number of benefits are achieved. The primary benefit is that, in a near stoichiometric exhaust, the simultaneous reduction of NOx and oxidation of CO and HC is possible. Additionally, because of the premixed combustion, particulate matter is not formed in significant quantities. Lastly, the average exhaust temperature is relatively high (400°C to 600°C) because of the stoichiometric combustion, which generally leads to better catalyst performance.

The negative aspects of a gasoline engine are generally associated with cold-starts. Although a bit oversimplified, the challenge of meeting future emissions regulations is largely a problem of controlling the emissions during the first thirty seconds of engine operation. During the cranking phase, fuel is over injected in order to provide enough vaporized fuel for combustion to occur, which inevitably causes rich mixture excursions. To compound the problem, conventional catalysts are ineffective at cool temperatures. A third factor is that the exhaust gas oxygen sensors used for closed-loop control also require several seconds to reach operating temperature. The result of these three factors is that a sizable fraction of the vehicle hydrocarbon emissions typically occur during the first minute of operation.

2.1.2 Lean, Spark-Ignited, Gasoline Engines

There are two different varieties of lean spark-ignited engines, commonly referred to as lean-burn gasoline engines and direct injection gasoline engines. Lean-burn spark ignition engines are very closely related to the stoichiometric gasoline engine. Lean-burn engines are port fuel injected using conventional gasoline fuel injectors. The combustion chamber geometry is such that the air-to-fuel ratio around the spark plug is capable of ignition, despite an overall lean mixture. Lean-burn engines have an upper limit of air-to-fuel ratio of approximately 25:1. With proper calibration this engine is capable of operating in either lean or stoichiometric mode with little difficulty. Direct-injection spark-ignited (DISI) gasoline engines are distinctly different from the other two types of gasoline engines. They rely on an injector that injects high-pressure gasoline directly into the combustion chamber during the compression stroke, which is then
 ignited with a spark. In this way, considerably leaner mixtures can be combusted, up to an air-to-fuel ratio of 40:1.

Both of these engines offer improved efficiency when operating in the lean mode; however, the efficiency comes with a catch. In moving away from a stoichiometric air-to-fuel ratio, the exhaust has excess oxygen and is at a lower temperature. The excess oxygen does not impact oxidation reactions, such as CO and HC oxidation; however, it does have a strong impact on the NOx reduction reaction. In fact, the rate of NOx conversion in even slightly lean mixtures is virtually zero using conventional catalysts. Neither of the lean-burn gasoline engines produce relevant amounts of particulate matter when properly calibrated; therefore, the main issues with these engines are CO, HC, and NOx. Both of these engine types suffer the same type of cold start issues as the stoichiometric engine; however, certain aspects are improved.

2.1.3 Direct-Injection, Compression-Ignition Engines (Diesel Engines)

Modern Diesel engines are predominantly of the direct injection type, as opposed to the older technology indirect injection engine. These engines are commonly referred to as compression-ignition, direct-injection (CIDI) engines. CIDI engines have electronically controlled, high-pressure fuel injectors that inject fuel directly into the combustion chamber. Diesel engines are typically turbocharged to increase the power density of the engine to levels on par with stoichiometric gasoline engines. A Diesel engine generally operates lean because of particulate formation concerns, with a typical air-to-fuel ratio ranging from 17:1 to 90:1.

As with the lean gasoline engines, the major advantage of the Diesel engine is efficiency. A Diesel engine is considerably more efficient than all of its gasoline counterparts. However, as with the lean gasoline engines, this efficiency does not come for free. The issues of excess oxygen and low temperatures are even more of a problem for Diesel engines due to the much higher air-to-fuel ratios. However, Diesels introduce a new host of problems associated with the method of combustion. Diesel combustion can be coarsely grouped into two phases. After the injection event there is an ignition delay in which the fuel and air have
time to mix. This premixed fuel and air mixture soon ignite and burn rapidly, and for the most part, cleanly. The remaining fuel burns in a diffusion mode, in which it cannot combust until it is mixed with oxygen. This combustion mode leads to high levels of NO\textsubscript{x} but also to the formation of particulate matter. This leaves the Diesel automotive engineer with the task of controlling HC, CO, NO\textsubscript{x}, and particulate matter in a relatively cool, lean environment.

2.1.4 Homogenous Charge Compression Ignition Engines

Homogenous charge compression ignition (HCCI) is a combustion regime that is suitable for both Diesel-like fuels and gasoline-lie fuels. In this combustion regime, a pre-mixed fuel and air charge is initiated in the cylinder before the onset of combustion. Combustion is triggered through the fuel reaching the auto ignition point due to the temperature rise during the compression stroke. Work in this regime is focused on lean mixtures, which results in combustion that is very low in NO\textsubscript{x} and particulate matter. The downsides of this combustion regime are summarized in the following list.

1. Lack of Direct Combustion Control – In all other combustion regimes, the start of ignition is controlled via a spark or the timing of the fuel injection event. With pure HCCI, the start of combustion is controlled only by the fuel properties and the temperature and pressure history of the fuel and air charge. Thus, the primary controls on the combustion are the gas composition at intake valve closing and the temperature of the charge at intake valve closing.

2. Rapid Heat Release – The rate of heat release in HCCI combustion is very rapid because of the nature of the combustion. In theory, combustion starts uniformly in the cylinder and thus proceeds rapidly. In SI engines, the flame speed acts to slow the combustion down so that the heat release is spread over a number of crank angle degrees. In a direct injection Diesel engine, the combustion is limited by the mixing of the fuel spray with the air, and is thus kept under control. With HCCI, however, the rapid rate of heat release results in high cylinder pressures, which place mechanical limitations on the load that can be achieved in HCCI combustion.
2.1.5 Engine-Technology Summary

The following table provides a very general comparison of each combustion regime and the relative engine-out emissions. In general, the higher temperature and lower oxygen content makes emissions control more straightforward. As one can see, the CIDI engine is one of the most challenging, given its high O₂ levels, moderate temperatures, high particulate matter, and moderate NOₓ emissions.

<table>
<thead>
<tr>
<th>Combustion Regime</th>
<th>CO</th>
<th>THC</th>
<th>NOₓ</th>
<th>PM</th>
<th>O₂</th>
<th>Temp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stoichiometric., SI</td>
<td>high</td>
<td>mid</td>
<td>mid</td>
<td>low</td>
<td>low</td>
<td>high</td>
</tr>
<tr>
<td>Lean, PFI, SI</td>
<td>mid</td>
<td>mid</td>
<td>mid</td>
<td>low</td>
<td>mid</td>
<td>mid</td>
</tr>
<tr>
<td>Lean, DI, SI</td>
<td>mid</td>
<td>mid</td>
<td>mid</td>
<td>low</td>
<td>mid</td>
<td>mid</td>
</tr>
<tr>
<td>CIDI</td>
<td>low</td>
<td>mid</td>
<td>mid</td>
<td>high</td>
<td>high</td>
<td>mid</td>
</tr>
<tr>
<td>HCCI</td>
<td>high</td>
<td>high</td>
<td>low</td>
<td>low</td>
<td>mid</td>
<td>low</td>
</tr>
</tbody>
</table>

Table 1: General Characteristics of ICE Combustion Regimes

2.2 Past Aftertreatment Technologies

To understand the current state of the art in aftertreatment technology, it is helpful to follow the evolution of catalytic aftertreatment from its origins. The following subsections provide a brief review of the earliest aftertreatment systems for both gasoline and diesel engines.

2.2.1 Gasoline Oxidation Catalyst, Two-Way Catalysts

Gasoline oxidation catalysts were the first catalyst to be applied to motor vehicles. These catalysts were applied to gasoline vehicles in the 1970’s to reduce unburned hydrocarbon emissions and carbon monoxide emissions. These catalysts were first applied to carbureted engines and later on fuel injected engines. The operation of these catalysts was relatively simple: oxidize the available carbon monoxide and unburned hydrocarbons to harmless carbon dioxide and water. The catalysis was promoted using both base metals such as Cu and Ni as well as precious metals such as Pt, Pd, and Rh. It was rather quickly established that the precious metal based catalysts offered benefits in durability, stability, and conversion efficiency. The
obvious drawback in the two-way catalyst was the fact that it was indeed only a two-way catalyst, meaning CO and HC reduction. Efficient reduction of HC and CO in a two-way catalyst was only possible in a net lean or stoichiometric environment. This generally led to the biasing of engine calibrations to operate slightly lean of stoichiometric to maintain high conversion of HC and CO. This led to poor conversion efficiency for NOx emissions, which were acceptable under that era's emissions standards.

2.2.2 Early Gasoline Three-Way Catalysts with Two Beds

An early version of today’s three-way catalyst was employed to manage CO, HC, and NOx from stoichiometric gasoline engines. As noted above, it is difficult to support substantial oxidation reactions and reduction reactions unless the exhaust air-to-fuel ratio is very close to stoichiometric. In the era of carburetors, this tight of control was simply not possible; however, reductions in all three emissions were required to meet federal standards. This led to the use of a two-bed catalyst system, one for promoting reduction reactions and one for promoting oxidation reactions. The first bed of the catalyst was designed to operate in a rich environment to reduce NOx emissions. The second bed was an oxidation catalyst, designed to oxidize CO and HC emissions. The engine was tuned so that it would run slightly rich, allowing the first bed to reduce NOx emissions. In between the two beds, air was injected into the exhaust stream to make the air-to-fuel ratio lean. The second bed could then oxidize the CO and HC in the newly lean exhaust. This system was the first practical three-way system for gasoline engines. Various forms of this two-bed catalyst system persisted well into the 1990's, even after the advent of the modern three-way catalytic converter.

2.2.3 Early Diesel Catalysts

This subsection is quite short, as Diesel engines did not require the use of catalysts until the mid-1990s. The type of catalyst used at this time is, in essence, the exact same catalyst used today on Diesel engines, referred to as a Diesel oxidation catalyst. These catalyst are discussed in detail below; however, for now it
will simply be mentioned that they were used to control HC and CO emissions with low conversion efficiencies for PM and NOx.

2.3 Present Aftertreatment Technologies

The following subsections highlight the basic operation and limitations of the aftertreatment system that are currently used in production vehicles. This section covers three-way catalysts, hydrocarbon traps, Diesel oxidation catalysts, Diesel particulate filters, and hydrocarbon selective catalytic reduction. Of key relevance to this research are Diesel oxidation catalysts and Diesel particulate filters, since they are a key part of any Diesel aftertreatment system of the future. Understanding the operational needs and inherent limitations of these devices are critical for understanding how an LNT would fit into such an architecture. Lastly, it is worth noting that the three-way catalyst and the lean NOx trap share a great many characteristics, despite their different fields of use. On the simplest level, the LNT is nothing but a three-way catalyst with a NOx storage component in the formulation.

2.3.1 Modern Gasoline Three-Way Catalysts

The modern three-way catalyst (TWC) is applied to stoichiometric burning gasoline engines as well as lean gasoline engines, which operate in some driving conditions at stoichiometric air-to-fuel ratios. These catalysts are dubbed three-way catalyst for their ability to oxidize CO and HC while simultaneously reducing NOx emissions. In a narrow air-to-fuel ratio window around stoichiometric, the three-way catalytic converter has a high efficiency for CO, HC, and NOx. When lean gasoline engines operate lean, the catalysts serve primarily as oxidation catalyst for CO and HC with little impact on NOx emissions. Three-way catalysts are typically coated onto cordierite substrates and coated with combinations of Pt, Pd, and Rh. The precious metal coatings are supported by an alumina washcoat with a relatively large amount of ceria to stabilize the catalyst and provide oxygen storage. Three-way catalysts have also been successfully coated on metal matrix substrates for certain specialized applications.
2.3.1.1 Steady-state Conversion Efficiency

When discussing TWC technologies, one must realize that the TWC is a dynamic device due to the effect of oxygen storage and temperature. It is thus best to begin the discussion with the simplest case of steady-state conversion efficiency of a TWC that is well above its light-off temperature. When speaking of steady-state with a TWC, it is generally with respect to a steady-state engine-out air-to-fuel ratio. The following figure shows the steady-state conversion efficiency of a typical TWC over an air-to-fuel ratio sweep. These plots are typical for virtually any TWC and appear often in the literature.

Figure 1: Air-to-fuel ratio Sweep of a TWC (after [1])
As one can see from the figure, the conversion efficiency of each species has a strong dependence on air-to-fuel ratio. The reason for this is quite clear from the reaction mechanisms shown below. When operating rich, there is a large amount of reductants available to react with NO\textsubscript{x} in the form of CO and HC. This allows for the high conversion efficiency of NO\textsubscript{x}. In a rich exhaust, there is no net free oxygen, so the most readily available oxidizer is in the form of NO\textsubscript{x}. This explains why CO and HC conversions on the rich side of stoichiometric are quite poor under steady-state conditions. Conversely, on the lean side of stoichiometric, there is free oxygen. The oxidation of HC and CO is promoted by the net free oxygen. Therefore, the CO and HC are oxidized with the excess air and the NO and NO\textsubscript{2} are left largely untouched. This explains the high conversion efficiency of CO and HC and the nearly zero conversion efficiency of NO\textsubscript{x} just on the lean side of stoichiometry.

Near the stoichiometric air-to-fuel ratio, there is a narrow band in which the conversion efficiency is quite high for all three species. This is obviously where one would want to operate an engine for optimal elimination of all three species. Unfortunately, maintaining the air-to-fuel ratio in this narrow region in a real engine under real world driving conditions is not possible. Uncertainties in engine parameters, fuel dynamics, air dynamics, transport delays, and other factors make the air-to-fuel ratio control problem a challenging one.

As a side note, this plot also accentuates the plight of the lean-burn engine. In general, this figure represents the performance of any “ordinary” catalyst. NO\textsubscript{x} simply refuses to either decompose to N\textsubscript{2} and O\textsubscript{2} or to react with available reductants in an effective manner in the presence of excess oxygen. Either of the above are a thermodynamic possibility; however, no catalyst has been found that can facilitate either of these direct methods in an effective manner in the presence of excess oxygen. There are catalysts that can accomplish this feat by going through more indirect chemical paths, which are discussed in detail in later sections. The lean NO\textsubscript{x} trap is one such catalyst which uses an indirect path to lean NO\textsubscript{x} reduction.
2.3.1.2 Oxygen Storage in Three-Way Catalyst

One of the key features in the TWC catalyst that allow it to achieve such high conversion efficiencies is oxygen storage. TWCs are formulated to contain a relatively large amount of ceria in their washcoat. The presence of ceria (as well as palladium to a lesser degree) creates oxygen storage sites on the catalyst surface by the following reaction. The value of this reaction may not be immediately clear, but it has a profound effect on the operation of the TWC.

\[
O_2 + 2CeO_3 \leftrightarrow 4CeO_2 \quad (1)
\]

\[
O_2 + 2Pd \leftrightarrow 2PdO \quad (2)
\]

During the time engine-out air-to-fuel ratio is lean, a significant amount of oxygen is stored on the catalyst through the above mechanisms. As the engine transitions to a slightly rich air-to-fuel ratio, there is no longer oxygen available in the exhaust for the oxidation of CO and HC. In simplistic terms, the oxygen stored on the ceria acts as a buffer on the air-to-fuel ratio. It provides oxygen for the oxidation of CO and HC even though there is no oxygen available in the exhaust. Also, NO and NO\textsubscript{2} are reduced by the CO and HC as usual. Therefore, while the oxygen storage lasts, the “effective” air-to-fuel ratio can be thought of as stoichiometric. If one operates rich for a period of time, the oxygen storage will be depleted. Upon returning to slightly lean engine operation, the ceria will once again begin storing the available oxygen. With the gaseous oxygen sequestered on the catalyst, NO\textsubscript{x} is the main oxidizer in the exhaust for CO and THC reduction. This adsorption of O\textsubscript{2} and reduction of NO\textsubscript{x} again acts as an air-to-fuel ratio buffer until the oxygen storage reaches saturation. The goal of engine air-to-fuel ratio is to balance the lean and rich operation to effectively use the oxygen storage effect.

In looking at the pre and post air-to-fuel ratio measurements of a TWC operating in an stoichiometric engine, one can actually see signs of this air-to-fuel ratio buffering effect. The following figure illustrates this phenomenon. Note that when the inlet air-to-fuel ratio transitions to rich, the post catalyst air-to-fuel ratio drops and then remains at stoichiometric for a period of time before dropping to the inlet value. Upon
transitioning back to lean, the phenomenon repeats. An identical phenomenon is found in the LNT due to both oxygen storage and NOx storage.

![Figure 2: Oxygen Buffering in a TWC (after [2])](image)

### 2.3.1.3 Three-Way Catalyst Chemistry

The chemical reactions occurring in a warmed up three-way catalytic converter are complex. The following list summarizes some of the key reactions that are present. The list is not exhaustive, but provides a good feel for the complexities in the catalytic converter. The oxygen storage equations from above are not included; however, they play an important part in the process. Also, propene (C\textsubscript{3}H\textsubscript{6}) is used to represent a general hydrocarbon; however, engine exhaust contains a spectrum of hydrocarbons many of which participate in similar reactions. As mentioned above, all of these same reactions are present in the LNT.

Water-gas Shift:

\[ CO + H_2O \rightarrow CO_2 + H_2 \]  (3)
Steam Reforming:

\[ C_3H_6 + 3H_2O \rightarrow 3CO + 6H_2 \]  \hspace{1cm} (4)

CO₂ Reforming:

\[ C_3H_6 + 3CO_2 \rightarrow 6CO + 3H_2 \]  \hspace{1cm} (5)

Partial Oxidation:

\[ C_3H_6 + 3O_2 \rightarrow 3CO + 3H_2O \]  \hspace{1cm} (6)

Reactions with oxygen:

\[ CO + 1/2O_2 \rightarrow CO_2 \]  \hspace{1cm} (7)

\[ H_2 + 1/2O_2 \rightarrow H_2O \]  \hspace{1cm} (8)

\[ C_3H_6 + 4.5O_2 \rightarrow 3CO_2 + 3H_2O \]  \hspace{1cm} (9)

\[ NO + 1/2O_2 \rightarrow NO_2 \]  \hspace{1cm} (10)

Reactions with NOₓ:

\[ CO + NO \rightarrow CO_2 + 1/2N_2 \]  \hspace{1cm} (11)

\[ CO + 1/2NO_2 \rightarrow CO_2 + 1/4N_2 \]  \hspace{1cm} (12)

\[ H_2 + NO \rightarrow H_2O + 1/2N_2 \]  \hspace{1cm} (13)

\[ H_2 + 1/2NO_2 \rightarrow H_2O + 1/4N_2 \]  \hspace{1cm} (14)

2.3.1.4 System Considerations for Three-Way Catalysts - Temperature

One of the key system considerations for TWCs is their performance during cold starts. As with all catalyst, conversion efficiency depends greatly on temperature. A standard TWC has no appreciable
conversion efficiency below 200°C. The following figure shows typical conversion efficiencies as the catalysts warms up to operating temperature. These are commonly referred to as light-off curves. A catalyst is said to light-off once it reaches 50% conversion efficiency for a particular pollutant. This gives rise to the light-off temperature, which is the temperature at 50% conversion efficiency. Note that the light-off temperature is different for HC, CO, and NOx.

![Figure 3: Three-Way Catalyst Light Off (after [3])](image)

2.3.1.5 Results from the Literature for Three-Way Catalysts

There are numerous references in the public domain that report on the performance of three-way catalyst systems. The following two figures were chosen because they show a vehicle certified as ULEV and
compare it to the SULEV emission standards. The first graph, Figure 4, shows the cumulative non-methane hydrocarbons (NMHC) emissions during a FTP-75 cycle. Note that the vast majority of the emissions are generated during the first 100 seconds of the cycle due to the cold start. Similarly, the following plot shows the same trend for the NO\textsubscript{x} emissions.

The most striking feature that these plots show is that with this ULEV certified engine, it violates the SULEV emissions standard before it even starts moving. There is a few second period after the cycle starts that the engine simply idles. During this portion the cold ULEV engine with its cold catalysts has already put out more emissions then is allowed for the entire thirty minutes of the driving cycle for the SULEV standard. The ULEV catalysts operate at efficiencies of >95% once the engine and catalyst are hot, but the cold start emissions are the key. SULEV emissions regulations are such that the catalysts have to operate at virtually 100% efficiency once hot and must effectively deal with cold start emissions as well.
Figure 4: Cumulative Hydrocarbon Emissions for ULEV Vehicle (after [4])
2.3.2 Hydrocarbon Traps

Hydrocarbon traps are adsorption catalysts, which are used to capture unburned hydrocarbons during engine cold starts. As shown above, the first several seconds after a cold start a disproportionably large amount of emissions are emitted due to poor air-to-fuel ratio control during cranking and starting as well as the cold, inactive, catalyst. These hydrocarbon traps have been applied in various configurations on gasoline fueled vehicles meeting California SULEV emissions standards.

The basic hydrocarbon trap is an un-catalyzed device and is, therefore, capable of only hydrocarbon storage. The principle of operation is to store the unburned hydrocarbons during the initial starting phase of the engine. The storage mechanism used in the catalyst allows it to adsorb hydrocarbons at relatively...
low temperatures, thus it require no warm up time. As the engine exhaust heats the hydrocarbon trap, it continues to trap hydrocarbons. As the hydrocarbon trap temperature increases, its storage capacity for hydrocarbons decreases. As the trap capacity decreases, hydrocarbons from the saturated trap are released from storage into the exhaust. These released hydrocarbons must then be oxidized by a separate downstream catalyst.

A second variation of the hydrocarbon trap is the catalyzed hydrocarbon trap, which is sometimes referred to as an adsorber coated substrates (ACS). This aftertreatment device has both hydrocarbon storage components as well as a more standard catalytic coating for promoting oxidation reactions. A further extension is the application of three-way catalyst coatings in conjunction with the hydrocarbon storage components. Catalyzed hydrocarbon traps adsorb and release hydrocarbons in the same manner as above. However, due to the catalytic coating, the catalyzed hydrocarbon trap can oxidize the stored hydrocarbon as they are released or through surface reactions. Catalyzed traps are often coated in layers, with the hydrocarbon trapping washcoat applied first, and the three-way catalyst coating second. In this way, the released hydrocarbons must travel through the catalytic layer, which improves conversion rates.

Figure 6 shows the adsorption and release characteristics of a typical HC adsorber in a bench reactor. The reactor was equilibrated and then fed a mixture of 2% oxygen, 1% carbon monoxide, 0.33% hydrogen, 10% water, and 1500 ppm hydrocarbon mixture. The hydrocarbon mixture was removed after 60 seconds and the catalyst was slowly heated at a rate of 65°C/min. It is clear from the figure that the catalyst sample is adsorbing a fair amount of the hydrocarbons that entered the reactor, especially in the first several seconds of storage. The figure also clearly shows the slow release of the adsorbed hydrocarbons during the temperature programmed desorption. Note that in this test, no hydrocarbons were actually eliminated; they were simply stored and released at a later time.
2.3.2.1 Hydrocarbon Adsorber Reaction Mechanisms

The most popular type of hydrocarbon adsorbers uses zeolites to adsorb the hydrocarbons. Zeolites are microporous solids with crystalline structure. Because of their porous nature, they have the ability to adsorb various compounds, including hydrocarbons and water vapor. Zeolites are not novel to the field of catalysis, and are used in a variety of catalysis applications and industrial processes. \( \text{Ag}^+ \)-ZSM-5 is one particular zeolite formulation that has shown great promise in the literature for HC adsorbers. A given type of zeolite is good at adsorbing a certain range of hydrocarbons. Large pore zeolites are effective at trapping...
long chain hydrocarbons, while the converse is true for small pore zeolites. In addition, the exact trapping mechanisms for each hydrocarbon species is not well documented in the literature, and additional work is being conducted to understand the relevant phenomenon. A large number of zeolites have been screened for favorable properties as a hydrocarbon traps. These properties include the ability to store a large amount of hydrocarbon, the ability to store the specific types of hydrocarbon most present in a gasoline engine exhaust during cold start, the ability to sequester these hydrocarbons at relatively high temperature, a slow release of hydrocarbons once the desorption temperature is reached, and finally, it must be thermally rugged.

2.3.2.2 System Applications and Control

One key to successful implementation of a hydrocarbon trap system is to time the warm up of the hydrocarbon adsorber with the light-off characteristics of the catalyst that will oxidize the released hydrocarbons. Another key factor in managing a hydrocarbon trap system is that hydrocarbon traps are sensitive to thermal degradation, and must be located in an underbody position in the vehicle or protected from the exhaust heat in some fashion. This thermal limitation has caused a considerable problem in the design of successful systems. Two systems discussed below will highlight the key issues.

In one application, a catalyzed hydrocarbon trap is located near the end of the exhaust system. In this location, the exhaust gas is sufficiently cool that the catalyst will not be thermally degraded. The catalyst must be formulated so that the catalyst does not release hydrocarbons before it is active for their reduction. A second implementation is such that during cold starts, the exhaust is routed through the hydrocarbon adsorber using a bypass valve. Once the close coupled catalyst is at operating temperature, but before the hydrocarbon trap begins releasing hydrocarbons, the exhaust is rerouted through the main underbody catalytic converter. Once the main catalytic converter is at operating temperature, the hydrocarbons in the trap must be released upstream of the main catalyst so that they are oxidized. The first method above is used in the Nissan Sentra CA model, which is certified for California SULEV emissions. The second concept is used in the Toyota Prius, which is also certified California SULEV.
2.3.3 Diesel Oxidation Catalysts

Diesel oxidation catalysts (DOCs) are a specialized type of oxidation catalyst formulated to meet the requirements of Diesel engines. Specifically, these requirements are low temperature exhaust gasses with large amounts of excess oxygen. The catalysts are effective at oxidizing CO and HC from the exhaust with relatively high conversion efficiencies. It is also possible to reduce the mass of particulate matter slightly by oxidizing the soluble organic fraction (SOF) that clings to the soot particle. Surprisingly, it is also very possible to increase the mass of particulate matter emitted when using fuels with high levels of sulfur with an improperly used DOC. The mechanism for this formation will be discussed below.

2.3.3.1 Reaction Mechanisms in Diesel Oxidation Catalysts

The overall reaction mechanisms in a DOC are quite basic, in which reducible species are oxidized with gaseous oxygen into carbon dioxide, nitrogen, and water. DOCs are typically coated on cordierite substrates with an alumina washcoat. The catalysts consists of precious metals, with the principal component being platinum. Typical platinum loadings can range from a 30 gm/ft³ to over 100 gm/ft³. Commercial catalysts contain other proprietary compounds, which augment the oxidation ability and serve to stabilize the precious metals contained on the catalyst. In addition, some DOCs have hydrocarbon storage compounds to help reduce cold start emissions of Diesel engines. This hydrocarbon storage is sometimes achieved through the use of zeolites.

2.3.3.2 Performance of Diesel Oxidation Catalysts

The following graph, Figure 7, shows experimental data for a Diesel oxidation catalysts on a 2.5L direct injection engine. The results are from an engine fueled with 50% low sulfur Diesel and 50% virgin bioDiesel. As one can see, the catalyst has good conversion efficiency for HC and CO even at low temperatures. The first data point included in the data set was the lowest temperature possible given the engine/catalyst configuration, thus it ensures that the catalyst will function fairly well over the entire
operating range of the engine. The conversion efficiency for NOₓ is also shown on the right y-axis, and is substantially lower than the CO and HC conversion efficiency. The data for this figure was generated by the author and has not been published in open literature.

![DOC Conversion Efficiency](image)

**Figure 7: Diesel Oxidation Conversion Efficiency**

### 2.3.3.3 Particulate Reduction and Formation from Diesel Oxidation Catalysts

It is possible for DOCs to either improve or worsen particulate matter emissions from Diesel engines, depending on factors such as fuel sulfur content, catalyst formulation, and exhaust temperature. By their nature, Diesel oxidation catalysts are best suited for reducing gas-phase components. Because of this, DOCs are relatively ineffective at oxidizing the insoluble organic material of soot, which is mostly hard carbon material. However, DOCs have been shown to reduce the soluble organic material of a soot particle, which consists of long chain hydrocarbons stuck to a hard carbon nucleus. Through this effect, it
is possible to reduce the mass of soot emitted. This however, results in the same number of particles with a smaller diameter. These smaller particles are more easily inhaled which can pose a health risk. The following figure illustrates the general composition of a Diesel particulate.

Figure 8: Schematic of Diesel Particulate Matter (after [6])

The mechanism for increasing the mass of particulate matter comes from interaction of the catalysts with sulfur present in the Diesel fuel. The sulfur present in the fuel largely emerges from the exhaust manifold as SO₂, with only 1% to 3% of the sulfur released as SO₃. This SO₃ tends to hydrate in the exhaust with the available water vapor. Upon cooling, the hydrated SO₃ clings to the particulates and contributes to the total mass of particulate matter. A problem can occur if the DOC oxidizes a large amount of the SO₂ into additional SO₃. As before, this SO₃ hydrates to form SO₄ which contributes to particulate matter emissions. With certain catalysts under high exhaust temperatures, the 60% to 70% of the sulfur can be converted into
sulfate [7]. This can elevate particulate matter emissions substantially when using high sulfur fuels with highly active oxidation catalysts.

Figure 9 shows the potential increase in particulate matter emissions from this mechanism. For the low sulfur fuel cases, the DOC does an acceptable job at reducing the mass of PM emitted. However, as the fuel sulfur level is increased, the catalyst-out levels are substantially higher than the engine-out levels, almost doubling with 350 ppm sulfur fuel. This particular case is at a relatively high exhaust temperature of 518°C and represents the worst possible scenario. However, this increase at high temperature can partially offset the DOCs reduction in PM at the more common low temperatures. Sulfate formation can be avoided by using lower sulfur fuels and using a correctly formulated catalyst for the temperatures encountered in the particular configuration.

Figure 9: Effect of Fuel Sulfur on DOC PM Emissions (after [7])
2.3.3.4 Diesel Oxidation Catalysts – Results from the Literature

The following figure shows results of a DOC applied to a 2.5L passenger car Diesel engine. The results compare the performance of two different DOCs over three different driving cycles. The ECE cycle is a city driving cycle, and in this case, four consecutive ECE cycles are run. The results of the first two cycle (ECE1,2) and the third and fourth (ECE3,4) are grouped together. The tests were started with a cold vehicle, so one can see the change in conversion efficiency as the engine and catalyst warm up. Results for a EUDC driving cycle are also presented, which is a high-speed city driving cycle which results in higher exhaust temperatures.

As shown in the bottom of the figure, catalyst A is a platinum/alumina/zeolite catalyst, which has hydrocarbon storage capability. Catalyst C is a platinum/alumina catalyst, which is a basic oxidation catalyst formulation. From the driving cycle results, it is clear that the zeolite catalyst has significantly better performance on all parts of the test. The difference is most dramatic in the ECE1,2 section, in which the adsorption characteristics of the zeolite component really come into effect because of the cold start.
2.3.4 Particulate Filters

Particulate traps remove particulate matter from the engine exhaust. As Diesel engines are the only common engine with excessive particulate matter emissions, they are exclusively applied to Diesels. They
are commonly referred to as Diesel particulate filters (DPFs) or Diesel particulate traps. There are several types of DPFs made from different materials, different geometries, and different uses of catalytic materials.

The wall flow filter has emerged as the most popular filter geometry for high-efficiency applications. A wall flow filter is a conventional extruded substrate. On one end of the substrate, alternate channels are plugged; on the other end, the opposite channels are plugged. This forces the exhaust gas to migrate through the porous walls of the substrate. The pore size of the catalyst is such that a large portion of the soot particles become trapped on the surface of the upstream channels. In this manner, the exhaust particulates are contained. Wall flow filters are typically constructed from either cordierite or silicon carbide. Cordierite has the advantage of being cheaper and easier to manufacture as well as less restrictive to exhaust flow. Silicon carbide has the advantage of being more thermally robust. Thermal robustness is critical in DPFs, as they can experience high temperatures and temperature gradients during the soot removal process.

### 2.3.4.1 Active Diesel Particulate Filter Regeneration

DPFs also are routinely coated with catalysts or used in conjunction with a separate catalyst to improve their operation. In one implementation, the DPF itself is applied with a catalytic coating, in which the DPF is sometimes termed a catalytic Diesel particulate filter, or CDPF. The catalytic coating lowers the soot ignition temperature and also serves to oxidize hydrocarbons and carbon monoxide. In addition, the catalytic coating is used to oxidize additionally injected hydrocarbons to initiate filter regeneration. A second implementation of the DPF is a small oxidation catalyst located immediately upstream of a DPF. In this case, the upstream catalyst is designed to produce highly reactive soot reducing species, like NO₂, which then attack the soot trapped on the filter. The goal of this system is to make the DPF continuously regenerated. This configuration has been referred to as a continuously regenerating Diesel particulate filter, abbreviated CR-DPF. There are many other alternatives to DPF regeneration, including fuel additives to lower soot ignition temperature, fuel operated heaters, electrical heating, and even microwave regeneration.
2.3.4.2 Passive Diesel Particulate Filter Regeneration

The regeneration of a DPF can be classified as either passive or active. In a passive system, the trap is routinely purged without any modification of engine operation, addition of heat, or addition of fuel. This is the ultimate goal of a DPF system; however, it is often not achievable for a number of reasons. The problem of passive DPF regeneration is not if it will regenerate, but when. A vehicle driven in light city traffic for a long period of time will accumulate a large amount of soot; however, the low temperatures may not be enough to initiate a passive regeneration event. The problem occurs when this vehicle is then taken up to highway speeds and the exhaust temperature becomes much hotter. The soot in the DPF inevitably ignites, but due to the large amount accumulated high temperatures are generated and it is possible to destroy the trap.

2.3.4.3 Diesel Particulate Filters – Results from the Literature

Diesel particulate filters operate quite well in vehicle applications; however, as noted above, effectively controlling regeneration is still an ongoing issue. DPFs are capable of reducing the mass of emitted particulates by over 90% with some reports of filtering efficiencies of near 100%. Assuming that one has solved the practical issues of filter regeneration, these regeneration events must be appropriately timed. As soot builds on the DPF, the backpressure it creates on the engine creates a higher parasitic loss on the engine. The plot below for a passenger car application shows that the fuel penalty of a filter with 100 km worth of soot in it is less than 1%. As the distance traveled increases to 700 km, the fuel penalty increases to about 3.5%. From this, it seems that frequent regenerations are the best strategy. However, the extra fuel required to heat up the catalyst to start soot combustion is proportional to the amount of soot on the trap. If there is only a thin layer of soot coating the filter, it requires a much greater investment of fuel to initiate a regeneration event. From the figure, regeneration of 100 km worth of soot would exact a 7% fuel penalty whereas regenerating 700 km worth of soot would only cause a 1% fuel penalty.
These two tradeoffs create a minimization problem, which is shown on the figure. The optimal distance over which to initiate filter regeneration appears to be between 300 km and 500 km, which will lead to roughly a 3.5% increase in fuel consumption. In addition to the minimization problem, there is always a danger of actually destroying the DPF if too much soot is allowed to collect. If regeneration is initiated on a trap with a very high soot loading, the resulting exotherm can actually melt or crack the ceramic substrate. It is even possible for an overloaded DPF to become so hot that it melts a hole in the steel catalyst can.

Figure 11: Fuel Penalty Tradeoff for DPF Regeneration (after [9])
2.3.5 HC-SCR Catalysts

Hydrocarbon selective catalytic reduction (HC-SCR) catalysts are applied to lean-burn engines to reduce NO\textsubscript{x} emissions, with almost all of the applications being Diesel engines. These catalysts are also referred to in the literature as De-NO\textsubscript{x} catalysts or lean NO\textsubscript{x} catalysts (LNC). They are referred to as “selective” catalysts because they are used to selectively reduce NO\textsubscript{x} (instead of oxygen) under exhaust conditions that contain high levels of oxygen. In practice, this is difficult to achieve because the concentration of oxygen in lean exhausts is much greater than the concentration of NO\textsubscript{x}. Since these HC-SCR systems have been almost exclusively applied to Diesel engines, the following discussion will be presented in that context. To date, HC-SCR systems have not seen much application in the automotive industry due to their relatively low NO\textsubscript{x} conversion efficiencies; however, they were included in this section because there is still some active consideration of these systems, especially when used in conjunction with reformer technology.

HC-SCR systems can be grouped into two categories, passive and active. A passive system utilizes hydrocarbons that are available in the exhaust to reduce NO\textsubscript{x}. An active system adds supplementary hydrocarbons to the exhaust though in-cylinder post injection or through exhaust injection. In both systems, the added hydrocarbons are used as a reductant to selectively reduce the concentration of NO\textsubscript{x} over the catalyst. As one would expect, the active HC-SCR systems are capable of higher NO\textsubscript{x} conversion efficiencies when compared to their passive counterparts. Furthermore, two distinctly different types of HC-SCR catalysts have emerged with different properties. The first is copper exchanged zeolites with platinum (Pt-Cu/ZSM5) and the second is platinum on alumina (Pt-Al\textsubscript{2}O\textsubscript{3}) [10].

2.3.5.1 HC-SCR Reaction Mechanisms

The reaction mechanisms of HC-SCR are not as well understood as many of the other catalysts. This is largely due to the fact that there are many candidate reactions, and there is evidence that many of them play a predominant role in NO\textsubscript{x} reduction at the same time. [11, 12]. The basic concept is that the zeolite and/or platinum provide active sites for the storage of the relevant reducing species. Most reaction schemes
involve the hydrocarbon to be partially oxidized into a more active form. Because of this, the nature of the reductant is very important. HC-SCR systems tested with propene will demonstrate >80% of NOx; however, when the same test is repeated with Diesel fuel the efficiency will be much less. Early in the research of these catalysts, there was great hope that the bench reactor studies would directly extend to engine applications. Unfortunately, this has not come to pass for this technology. There has been recent attention in developing fuel reformer technology to generate more active species from Diesel fuel. If this technology becomes mature, then HC-SCR may be a viable technique for the future.

2.3.5.2 System Considerations for HC-SCR

The temperature windows of two HC-SCR catalyst formulations are shown in the following figure. In both cases, the systems are active systems, with Diesel fuel being injected in the exhaust stream with a supplemental injector. Note that the peak conversion of NOx is relatively low, 37% for the Pt-Zeolite catalyst and 27% for the Pt-Alumina catalyst. Another feature of the curves is the relatively narrow temperature window for the catalyst. In both cases, they only achieve greater than 20% conversion efficiency in a region of less than 100°C. The reason for the low efficiency at low temperatures is due to poor catalyst activity. Conversely, the reason for low efficiency at high temperatures is too much catalytic activity. At these higher temperatures, a large part of the reductant is used in the oxidation of the hydrocarbon with gaseous oxygen, which consumes reductant intended for the NOx reduction reaction.
2.3.5.3 HC-SCR - Results from the Literature

Although it is a fairly mature technology, the relatively low conversion efficiency and narrow temperature window have made it difficult to implement in many applications. It is perceived that, in general, the automotive industry does not want to invest the resources to bring a HC-SCR system to a production level, only to have the system be obsolete in a few years due to the ever-tightening NO\textsubscript{x} regulations. Unless a breakthrough occurs in the field, it is likely that HC-SCR will be shelved in favor of technologies such as urea-SCR and lean NO\textsubscript{x} traps. HC-SCR is not without advantages, as it is fairly sulfur tolerant.

The systems have been applied to prototype vehicles and their performance reported in the literature. The following figure is an excerpt from a 1999 paper reporting on the vehicle performance of HC-SCR. The results are for a 2.5L Diesel engine passenger car over the MVEG-B cycle. The left hand side of the figure
shows the four different system configurations that were tested. Note that in all cases, two different catalysts were used in series. This allows using catalysts with two different temperature operating windows. Also used are varying methods of hydrocarbon injection as well as in case D, active cooling of the exhaust. The highest conversion efficiency was achieved using system D, which resulted in a 28% NO\textsubscript{x} conversion efficiency. The same system, when operated using n-paraffin C14-C17 mixture as the reductant, achieved much better efficiency; however, it is not a practical system.

Figure 13: System Configuration Options for HC-SCR (after [13])

2.4 Near-Term Aftertreatment Technologies

The following catalysts are denoted as near term aftertreatment technologies. The word near-term is subjective, and thus a proper explanation of what is considered near-term is necessary. Technologies are considered near-term are those which have been successfully demonstrated in prototype vehicles or have seen extensive test bench using real engines under realistic conditions, yet have not been widely applied to production vehicles. In essence, they are the next likely step in the evolution of automotive catalysts. These near-term technologies include urea-SCR, lean NO\textsubscript{x} traps, and sulfur adsorbers. It must be
mentioned that lean NOx traps have in fact been applied to production lean gasoline engines. However, their use has not become mainstream; additionally, they have not yet been applied to Diesel engines, which is the focus of this work. For these reasons, they have been relegated to the near-term section of this chapter.

2.4.1 Urea Selective Catalytic Reduction

Urea selective, catalytic, reduction (urea-SCR) is a close relative to HC-SCR described above. It is an aftertreatment system for the reduction of NOx emissions in lean-burn engines. Although it is a viable option for lean gasoline engines, it has mostly been applied to Diesel engines. This is largely due to the fact that there are more promising techniques that can be applied to lean-burn engines (i.e. lean NOx traps) and that the NOx problem of the lean gasoline engine is not quite so desperate as with the Diesel. Urea-SCR catalysts require the injection of urea into the exhaust upstream of the urea-SCR catalyst. The urea rapidly decomposes in the hot exhaust as well as over the catalyst substrate to form gaseous ammonia. The gaseous ammonia is utilized by the catalyst to selectively reduce the NOx over the catalyst surface.

2.4.1.1 Urea-SCR Reaction Mechanisms

There are a number of different types of urea-SCR formulations that are viable candidates for future use. Some typical catalyst formulations are Pt/Al2O3, TiO2-WO3-V2O5, TiO2-and MoO3-V2O5; all of which are coated on cordierite substrates. These catalysts typically allow for ammonia to be stored on the catalyst surface. The stored ammonia is then used in the following reactions to reduce the NO and NO2 in the exhaust stream. In addition to the above mention urea-SCR catalyst, urea-SCR systems typically have other catalysts used in conjunction with the SCR catalyst. Other reactions included below show the decomposition of urea to ammonia and the oxidation of NO and ammonia [14].
NOx Reduction Reactions:

\[ 4NH_3 + 2NO + 2NO_2 \rightarrow 4N_2 + 6H_2O \]  \hspace{1cm} (15)
\[ 4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O \]  \hspace{1cm} (16)
\[ 4NH_3 + 3NO_2 \rightarrow 7/2 N_2 + 6H_2O \]  \hspace{1cm} (17)
\[ 4NH_3 + 6NO \rightarrow 5N_2 + 6H_2O \]  \hspace{1cm} (18)

Urea Decomposition Reactions

\[ NH_2 - CO - NH_2,_{(aq)} \rightarrow NH_2 - CO - NH_2,_{(s)} + xH_2O \]  \hspace{1cm} (19)
\[ NH_2 - CO - NH_2,_{(s)} \rightarrow NH_3,_{(g)} + HNCO,_{(g)} \]  \hspace{1cm} (20)
\[ HNCO,_{(g)} + H_2O,_{(g)} \rightarrow NH_3,_{(g)} + CO_2,_{(g)} \]  \hspace{1cm} (21)

Oxidation of NO:
\[ NO + 1/2O_2 \rightarrow NO_2 \]  \hspace{1cm} (22)

Oxidation of Ammonia:
\[ NH_3 + 3/2O_2 \rightarrow N_2 + 3H_2O \]  \hspace{1cm} (23)

Equations (15) through (18) are NOx reduction mechanisms in urea-SCR catalysts. They are ordered from the most rapid to least rapid under normal catalyst operating conditions. Reaction (17) and (18) are slow enough that they can be ignored in most situations, with the predominant reaction being (15) and (16). Reaction (15), in which one mole of NO and one mole NO2 reacts with ammonia to eliminate the NOx, is crucial to the successful operation of a urea-SCR system. As this reaction is the fastest, it is therefore very desirable to achieve an even ratio of NO and NO2. This topic will be revisited in a subsequent section.
2.4.1.2 Urea-SCR System Considerations

There are a number of considerations in the design and implementation of a successful urea-SCR system. There are a number of system configurations which have been proposed and evaluated in the literature to meet these challenges. One such system is shown below, which has been referred to as a VHSO system:

![System Diagram for a VHSO Urea-SCR System (after [15])](image)

The oxidation catalyst, denoted as the V-catalyst, is used primarily to convert NO into NO₂. As noted earlier, urea-SCR catalysts perform best when there is an equal molar concentration of NO and NO₂. Since Diesel engines primarily produce NO, it is helpful to use an oxidation catalyst to convert some of the engine out NO into NO₂. Note that the catalyst formulation must be selected appropriately for the expected exhaust conditions, as it is possible to convert too much NO to NO₂ and have the conversion efficiency suffer. The following plot shows a typical conversion curve of the oxidation catalyst for a particular
platinum loading. Note that the conversion of NO to NO₂ is strongly effected by temperature as well as the space velocity.

Figure 15: NO₂ Conversion of a Oxidation Catalyst (after [15])

The H-catalyst (hydrolysis catalyst) is used to convert the injected urea into gaseous ammonia. Because urea thermally decomposes at typical exhaust temperatures, it is possible that this catalyst is not required for certain systems. The S-Catalyst is where the selective reduction of NOₓ occurs using the ammonia produced upstream in the H-catalyst or through thermal decomposition. The final catalyst, the O-catalyst, is a clean-up oxidation catalyst that oxidizes the ammonia that “slips” through the S-catalyst. This catalyst is a safeguard against having the unpleasant odor and potentially dangerous effects of ammonia coming out of the tailpipe.
The left half of Figure 16 shows a typical conversion efficiency map for a urea-SCR system with respect to NO\textsubscript{2} to NO ratio. As mentioned earlier, the peak efficiency occurs at a NO\textsubscript{2}/NO ratio of 50\% due to the “partnering” of NO and NO\textsubscript{2} in a rapid reaction step. The right hand graph contains a map of conversion efficiency for the entire VHSO system with optimal urea injection. This plot contains the combined the performance of the O-catalyst in converting the NO to NO\textsubscript{2} in conjunction with the S-catalyst, which has strong dependency on this ratio. It also implicitly includes a calibration for the urea injection system. The most basic urea injection strategy is to inject urea based on the concentration of NO\textsubscript{x}, which is what is used in this context. This can lead to excessive ammonia slip due to the ammonia storage dynamics during dynamic catalyst situations.

2.4.1.3 Urea-SCR - Results from the Literature

The following figure shows the conversion efficiency of an aged urea-SCR system applied to a 2.0 L Diesel passenger car. The figure shows the conversion efficiency of the system on the US FTP-75 cycle, which is a highway driving cycle. The total NO\textsubscript{x} conversion over the entire cycle is 80\%. Additional tests for the European Union ECE test, a city cycle, yielded a conversion efficiency of 49\% and 73\% for the NEDC, a
highway cycle. The urea-SCR system was a VSO system with a 2.0 L V-catalyst, 4.6 L S-catalyst, and 2.0 L O-catalyst.

![Figure 17: Urea-SCR Effectiveness on a Passenger Car Application (after [16])](image)

**2.4.2 Lean NOx Traps**

The lean NOx trap, or LNT, is a catalyst that shows promise for reduction of NOx emissions from both lean gasoline and Diesel engines. The catalysts are typically coated on cordierite substrates much in the same was as three-way catalytic converters. The basic concept of a LNT is to chemically store NOx on the catalyst surface while the exhaust conditions are lean. When the exhaust condition is changed to rich, the adsorbed NOx is released and reduced using the available reductant in the rich exhaust. Providing this rich-lean cycling is not so much of a problem in a lean gasoline engine, as they are perfectly capable of running
rich. It does pose a problem for the Diesel engine, in which during normal operation the richest practical AFR is still quite lean. Because LNTs are the topic of this document, a much more detailed look at the catalyst is provided in the following sections.

2.4.3 Sulfur Traps

Sulfur traps are catalyst used to sequester the sulfur compounds in the exhaust gas of internal combustion engines. These sulfur compounds are present in both the fuel and the lubricating oil of the engine, both of which are combusted by the engine. Many of the most promising catalyst formulations are sensitive to the effects of sulfur, which has the general effect of degrading the performance of the catalyst. In the extreme case, catalysts such as lean NO\textsubscript{x} traps can be rendered nearly ineffective due the sulfur contamination. The nature of this deactivation will be discussed in the following chapter; however, the benefit of sulfur trap catalyst is clear.

The process of sulfur storage is similar to that of NO\textsubscript{x} storage; however, sulfur sorbate catalysts are designed to selectively store sulfur compounds at high efficiencies while letting NO\textsubscript{x} pass through untouched. It is also desirable to have the sulfur regeneration conditions to be easier to achieve then with a NO\textsubscript{x} storage catalyst. System design for sulfur catalysts is very important, because the sulfur must eventually be purged from the sulfur sorbate catalyst. If this sulfur is discharged through the NO\textsubscript{x} trap then the LNT simply adsorbs it and no net benefit is achieved. Instead, the sulfur must be purged and discharged around the LNT. The left-hand schematic in the following figure shows one such system that achieves this through reverse flow regeneration of the LNT and sulfur trap with a system of valves. The sulfur laden purge gasses are safely routed around the LNTs. The right-hand figure shows the benefit of using the sulfur storage catalyst in maintaining NO\textsubscript{x} storage efficiency using high sulfur fuel (389 ppm sulfur [17].) Note that the dashed line, the system without sulfur protection, is on a rapid decent towards poor efficiency.
2.4.4 Four-Way Catalysts

The four-way catalyst is a catalyst that is capable of eliminating all four of the regulated tailpipe emissions with good efficiencies. In reality, the four-way catalyst is nothing new, it is simply a combination of distinct aftertreatment technologies. For instance, a Diesel particulate filter can be coated with a lean NO\textsubscript{x} trap coating. With this coating, it performs as a NO\textsubscript{x} adsorber, it filters out soot, and also promotes CO and HC oxidation at high efficiencies. Similar situations arise if a wall flow DPF is coated with a HC-SCR or urea-SCR coating. These catalysts do not require any further elaboration since they are largely the sum of their parts.

2.5 Long-Term Aftertreatment Technologies

Long-term technologies are the systems that are currently under investigation, but have not been fully evaluated under real operating conditions. Only one technology is discussed here, which is non-thermal plasma technology.
2.5.1 Non-Thermal Plasma Techniques

Non-thermal plasma (NTP) aftertreatment is a promising aftertreatment technique that has seen a lot of attention for lean exhaust aftertreatment applications. NTP techniques involve generating a low-temperature plasma in the exhaust stream of a combustion engine. Generally, NTP catalysts concepts have been aimed at Diesel emissions because there are techniques that are better suited for emissions of gasoline engines. NTP techniques have been shown to effectively reduce all four regulated emissions species; however, the focus is on NO\textsubscript{x} and PM emissions because of the degree of difficulty in handling these two pollutants.

Generating non-thermal plasma in the exhaust stream has minimal immediate effect on NO\textsubscript{x} and particulate emissions; however, CO and HC emissions are generally reduced. In order for the non-thermal plasma to have a useful effect it must be used in conjunction with a downstream catalyst. As the exhaust gas passes through the plasma, reactive species are generated due to the impact of active electrons into the exhaust gas species. These species react with the hydrocarbons in the exhaust to promote more effective HC-SCR reactions over the downstream catalyst. Additionally, the plasma can be generated over the catalyst surface.

2.5.1.1 Non-Thermal Plasma Chemistry

The mechanisms behind non-thermal plasma catalysis are less understood than many of the above catalyst types. There is still a great deal of discussion in the literature of the exact mechanisms at work. The following discussion outlines only the key elements behind the operation of these systems which seem generally agreed upon by the research community. The following reaction list summarizes some of the important well known reactions that take place as the exhaust gas passes through the plasma [18].
Dissociation by electron impact:

\[ O_2 + e^- \rightarrow O + O + e^- \]  \hspace{1cm} (24)

Reaction of O radicals with hydrocarbons:

\[ O + HC \rightarrow RO, RO_2, OH, etc... \]  \hspace{1cm} (25)

*Aldehydes (RO):* primarily formaldehyde (CH\textsubscript{2}O) and acetaldehyde (CH\textsubscript{3}CHO)

*Peroxyl Radicals (RO\textsubscript{2})*

*Hydroxyl Radicals (OH)*

Reactions with NO\textsubscript{x}:

\[ NO + O \rightarrow NO_2 \]  \hspace{1cm} (26)
\[ NO + RO_2 \rightarrow NO_2 + RO \]  \hspace{1cm} (27)
\[ NO + OH \rightarrow HNO_2 \]  \hspace{1cm} (28)
\[ NO_2 + OH \rightarrow HNO_3 \]  \hspace{1cm} (29)
\[ CH_3O + NO_2 \rightarrow CH_3ONO_2 \]  \hspace{1cm} (30)

Formation of ozone:

\[ O + O_2 \rightarrow O_3 \]  \hspace{1cm} (31)

O radical formation (24) is a key in the process, as it proceeds to generate a number of reactive species. Through reactions with hydrocarbons present in the exhaust, (25), the oxygen radical creates a number of partial oxidation products in the aldehyde family as well as peroxyl and hydroxyl radicals. These are then capable of reacting with NO and NO\textsubscript{2} to form HNO\textsubscript{2} (nitrous acid) and HNO\textsubscript{3} (nitric acid) which remain in the gas phase, these are reactions (28) and (29). There is also ozone formation occurring (31), which has a similar effect as the oxygen radical in promoting partial oxidation of hydrocarbons.

The net result of the exhaust gas passing through the plasma is the conversion of most of the NO to NO\textsubscript{2} and the partial oxidation of the available hydrocarbons in the exhaust into more reactive species. Typically, downstream of the plasma generator the exhaust will be passed over a catalyst. These catalysts are often
very similar in formulation to the HC-SCR systems described above. In fact, in many cases the catalysts used in NTP catalysis are indeed catalysts designed for use in HC-SCR systems. The chemical reaction principles are similar to those discussed in the previous section; however, the available species for selective reaction with NO$_x$ are much more favorable than that of the HC-SCR system. As discussed earlier, the exact mechanism has not yet been universally agreed upon.

Non-thermal plasma can also be useful in eliminating particulate matter emissions. The following three reactions illustrate the fundamentals behind this reduction. In the reactions, soot is represented as atomic carbon. The reactions are fairly straightforward, in which carbon is oxidized by highly reactive oxidizers. These oxidizers are not generally present in large quantities in normal Diesel exhaust. It is imperative that the soot particles have ample exposure time to the reactive species so that the soot particles can be attacked. With the exception of NO$_2$, the oxidizers are short lived so it is imperative that the soot particles have a relatively long exposure time to the plasma. To accomplish this, researchers have developed devices that trap particulate matter inside the area of plasma generation.

Oxidation of Soot (carbon) by reactive species:

\[ C + O \rightarrow CO \]  \hspace{1cm} (32)

\[ C + OH \rightarrow CO + 1/2 H_2 \]  \hspace{1cm} (33)

\[ C + NO_2 \rightarrow CO + NO \]  \hspace{1cm} (34)

2.5.1.2 Non-Thermal Plasma Catalyst Experimental Results

There are very little published results showing the performance of NTP catalyst systems on actual engines or vehicles. One such published work shows data from a 2.2 L Diesel engine equipped with a silicon carbide particulate filter, a plasma generator, and De-NOx catalysts of various types (Ag-Al$_2$O$_3$, AgBa-Y-zeolite, and Pt-Al$_2$O$_3$.) The plasma generator was powered by a 220 VAC source and had a 350 W average power consumption over an MVEG cycle for the particular calibration used in the experiments.
Surprisingly, the system was relatively compact despite the relative immaturity of the technology. To give the reader a better idea of the nature of this system, a photograph is provided below.

![Figure 19: Non-Thermal Plasma System Applied to a Diesel Engine (after [19])](image)

The resulting NO$_x$ conversion of this system on an MVEG cycle was 15% total, 30% on the highway portion, and 3% on the city portion. The fuel economy penalty attributed to the plasma generator was 5% and the penalty for additional HC injection was 3%, resulting in a total of 8%. The researchers also demonstrated the use of the plasma generator for DPF regeneration. It was shown that through generation of active oxidizers a non-catalyzed DPF could be made continuously regenerating. In this configuration, the plasma generator was moved upstream of the DPF. The authors noted a number of problems with the experiments, such as improper catalyst formulation as well as problems with NO$_x$ adsorption and subsequent release. To make this a practical system, these issues will obviously need to be addressed. However, in that it effectively demonstrated a NTP generator on a real vehicle with a realistic power consumption, it was quite successful.
Under more controlled circumstances, non-thermal plasma catalysts systems have demonstrated much more optimistic results. Typical laboratory efficiencies of over 60% can be demonstrated in synthetic Diesel exhaust for a temperature range of 150°C to 500°C which is the practical range of most Diesel engine applications. If these efficiencies can be matched in actual Diesel engines with the power consumption demonstrated in the above reference, then this technology will be very competitive with urea-SCR and lean NOx traps in the future. The following figure illustrates the promise of this technology for NOx reduction. It is hoped that the progress from the bench scale reactor studies will be backed up with similarly optimistic engine tests.

Figure 20: NOx Conversion of NTP Catalyst in Synthetic Diesel Exhaust (after [20])
2.6 Lean NO\textsubscript{x} Traps

Of the current and near-term NO\textsubscript{x} reduction techniques, there are only two that are capable of meeting the required 90% reductions required for future emissions legislation. The first is urea-SCR, which as been discussed earlier. The second is the lean NO\textsubscript{x} trap, which will be discussed in detail in this section.

2.7 Lean NO\textsubscript{x} Trap Catalyst Basics

Lean NO\textsubscript{x} traps (LNTs) are an aftertreatment technology that has shown promise for all lean-burn applications. LNTs are currently being used on production lean gasoline engines and are being researched for use on Diesel engines as well. As noted in the previous section, the basic concept of a LNT is to store NO\textsubscript{x} during lean exhaust conditions. When the catalyst is subsequently exposed to rich conditions, the stored NO\textsubscript{x} is released and the available reductants are used to reduce the NO\textsubscript{x} to harmless N\textsubscript{2}.

2.8 Basic Lean NO\textsubscript{x} Trap Chemistry

The following section is meant to give the reader a basic understanding of the chemical principles behind the operation of the LNT. The reaction scheme presented is essentially the minimum one needs to fully understand the operating principle. It is nonetheless not entirely the truth, and in fact, the absolute truth is not yet completely understood. In subsequent sections, more of the “truth” will be told; however, this section will cover the essentials. This simplified model of LNT operation is the starting point for many of the control-oriented models presented in the following chapter. More detailed chemical models, naturally, will require a more accurate view of the reaction mechanisms.

2.8.1 NO\textsubscript{x} Storage Phase

During the NO\textsubscript{x} storage phase of operation, the catalyst is receiving lean exhaust gas from the engine, or in certain applications, an upstream catalytic converter. The following table shows the basic reaction mechanisms. The first reaction is the oxidation of NO to NO\textsubscript{2} over the catalyst. This reaction is the key to
effective LNT operation, as the storage of NO on the trap is much slower than that of NO₂. For this reason it is necessary to convert as much NO to NO₂ as possible to achieve high storage rates of NOₓ. The second reaction is the storage of the NO₂ on BaCO₃ sites on the catalyst surface. Barium has emerged as the most popular storage material; however, other storage materials are possible.

NO Oxidation Reaction:

\[ NO + \frac{1}{2} O₂ → NO₂ \]  

(35)

NO₂ Storage Reaction:

\[ 2NO₂ + BaCO₃ + \frac{1}{2}O₂ → Ba(NO₃)₂ + CO₂ \]  

(36)

2.8.2 NOₓ Purge Phase

In the above section, it was illustrated how NOₓ is chemically stored on the surface of a LNT. Since the storage capacity of a LNT is finite, the stored NOₓ must periodically be purged from the trap and reduced to N₂. This process is called purging the trap or regenerating the trap. LNT regeneration occurs when the inlet exhaust air-to-fuel ratio drops below stoichiometric. In this sequence of reactions, the barium nitrate decomposes to barium oxide and thereby releases NO₂. The released NO₂ is then reduced by available reductants in the rich exhaust. If there is not sufficient reductants, then the NO₂ can be released out of the catalyst unreacted which, of course, is undesirable. The most active reductants are CO and H₂; however, other reductants are also useful to a lesser degree.

Desorption of NO₂:

\[ Ba(NO₃)₂ ⇒ BaO + 2NO₂ + \frac{1}{2} O₂ \]  

(37)

Reduction of NO₂:

\[ NO₂ ⇒ NO + \frac{1}{2} O₂ \]  

(38)

Reduction of NO to N₂ with available reductant:

\[ CO + NO ⇒ CO₂ + \frac{1}{2} N₂ \]  

(39)
\[ H_2 + NO \Rightarrow H_2O + \frac{1}{2}N_2 \]  
(40)

Carbonation of Barium:
\[ BaO + CO_2 \rightarrow BaCO_3 \]  
(41)

2.9 Advanced Lean NO\textsubscript{x} Trap Chemistry

The actual processes that occur in a lean NO\textsubscript{x} trap are not completely understood. There is still some debate on the exact mechanisms at work in the trap, as well as the interactions between certain intermediate reaction species. Of the primary debates is the actual nature of the NO\textsubscript{x} storage. Potential candidates for barium are a carbonate phase, an oxide phase, a peroxide phase, or an aluminate phase. In general, the two most popular candidates are an oxide phase or a carbonate phase. Indeed, it is also proposed that the barium cycles from carbonate to nitrate to oxide and back to carbonate during the storage and regeneration phase. In the following reaction mechanism it is assumed that the Ba moves from a carbonate phase, to a nitrate phase, to an oxide phase, and finally back to a carbonate phase. This scheme seems to have garnered the most support from the research community. From the standpoint of a control model, these differences are largely immaterial. The exact processes need not be known in order to model a system.

2.9.1 NO\textsubscript{x} Storage Phase

It is well accepted that NO\textsubscript{2} is the species that is stored on the Ba storage sites, and not NO. This has been demonstrated by preparing a catalyst with no NO oxidation properties. This catalyst is then exposed to simulated Diesel exhaust containing only NO. The result is that negligible amounts of NO will be stored. If the same procedure is repeated with NO\textsubscript{2}, appreciable amounts of NO\textsubscript{2} are stored. This supports the notion that NO\textsubscript{2} is the species that is trapped. This fact has a significant impact on the design of a practical catalyst to be used in a Diesel engine. Diesel engine’s typically only have 10% to 20% of their NO\textsubscript{x} as NO\textsubscript{2}, which indicates that it is necessary to convert NO to NO\textsubscript{2} to effectively store NO\textsubscript{x}.
The conversion of NO to NO$_2$ is fairly straightforward when there is excess oxygen, as in a Diesel engine exhaust. LNTs typically have precious metals and ceria in their formulations to catalyze this reaction. Figure 15 from before shows the basic concept of using a platinum catalyst to alter the amounts of NO and NO$_2$ in the exhaust. The figure is of a catalyst that has no NO$_x$ storage. A fixed concentration of NO is fed to the catalyst and the resulting NO$_2$ fraction is plotted for varying temperatures. Also included as an overlay are lines representing the equilibrium values of NO$_2$ to NO ratio. It is clear that at low temperatures the equilibrium favors there to be 100% NO. As the temperature increases, the equilibrium shifts to favor NO.

The effect of the catalyst is to try and make the NO$_2$ to NO ratio approach equilibrium. When the catalyst is at too low of a temperature, the reaction kinetics are not fast enough and the actual concentration does not reach equilibrium. At the higher exhaust temperatures the catalyst more active and is capable of approaching the equilibrium value of NO$_2$ to NO ratio. If one were to increase the exhaust flow rate, the region that was controlled by kinetics would increase, because of the lower residence time in the catalyst. Additionally, if a higher amount of platinum was loaded onto the catalyst, the region of kinetic controlled conversion would decrease because the catalyst would be more active at lower temperatures.

The following reaction scheme shows a more detailed look at the mechanisms in the NO$_x$ trap:

Surface Storage/Release on Platinum Sites:

\[
NO_{(g)} + S_1 \leftrightarrow NO - S_1 \tag{42}
\]

\[
NO_{2(g)} + S_1 \leftrightarrow NO_2 - S_1 \tag{43}
\]

\[
O_{2(g)} + 2S_1 \leftrightarrow O - S_1 \tag{44}
\]

Oxidation of stored NO to NO$_2$

\[
NO - S_1 + O - S_1 \rightarrow NO_2 - S_1 + S_1 \quad \text{rate limiting} \tag{45}
\]

Storage of Surface NO and NO$_2$ on Barium Sites

\[
2(NO - S_1) + 3(O - S_1) + BaCO_3 \rightarrow Ba(NO_3)_2 + CO_2 + 5S_1 \tag{46}
\]
\[ 2(NO_2 - S_i) + (O - S_i) + BaCO_3 \rightarrow Ba(NO_3)_2 + CO_2 + 3S_i, \text{ dominant reaction} \]  

Decomposition of Barium Nitrate

\[ Ba(NO_3)_2 \rightarrow BaO + 2NO + 1.5O_2 \]  

\[ Ba(NO_3)_2 \rightarrow BaO + 2NO_2 + O_2 \]  

Carbonation of Barium Sites:

\[ BaO + CO_2 \rightarrow BaCO_3 \]  

The first reaction set involves the surface storage of NO, NO\(_2\), and O\(_2\) on Pt sites. All of these species compete for the same Pt catalyst sites. The following reaction, (86), is the oxidation of surface NO to NO\(_2\) using surface O\(_2\). The third set of reactions involves the transfer of the surface stored NO\(_x\) from the platinum sites to the barium sites. It is useful to think of the Pt sites as “short-term” storage and the barium sites a “long-term” storage. The reaction involves the surface stored NO or NO\(_2\), surface stored O\(_2\), and the Ba storage site, which is in the form of BaCO\(_3\). As noted on the table, the storage of NO\(_2\) is the dominant reaction and in most cases the direct storage of NO on barium is negligible. These reactions are listed with a single arrow; however, the barium nitrate formation is an equilibrium problem. However, it is generally thought that the barium decomposes its NO\(_x\) into the gas phase; therefore, the reverse reaction is not entirely true. The fourth set of reactions is the decomposition of barium nitrate to release NO and NO\(_2\) under rich conditions. The fifth is simply the carbonation of barium oxide with capture CO\(_2\).

### 2.9.2 NO\(_x\) Regeneration Phase

The regeneration of NO\(_x\) proceeds along the same lines as the three-way catalyst mechanisms illustrated earlier. The only substantial difference is that there is NO\(_x\) being released from the surface in addition to any NO\(_x\) entering the catalyst from the gas phase. No additional discussion is necessary of these reactions.
2.10 Lean NO\textsubscript{x} Trap Experimental Reactor Results

The results from bench scale reactor studies can provide very useful results pertaining to lean NO\textsubscript{x} trap behavior. These devices allow the researcher to independently control the composition, temperature, and flow rate of the feedgas. They also allow for the use of specialized techniques such as infrared spectroscopy (IR) analysis, X-ray diffraction (XRD) analysis, and high-resolution transmission electron microscopy (HRTEM) analysis. These allows for a great deal of flexibility in the conditions the catalyst sample is exposed to as well as the analysis techniques. The drawback of this analysis is that it is very simplified, and the environment of an engine exhaust is quite a complex place. One must therefore be careful in directly extending these results to engine applications.

The following subsections will use the results of bench-scale tests to illustrate many of the key issues affecting lean NO\textsubscript{x} traps. These factors include:

- Catalyst Temperature
- NO\textsubscript{x} Surface Coverage
- Space Velocity (i.e. Residence Time)
- Feedgas NO\textsubscript{x} Concentration
- O\textsubscript{2} and CO\textsubscript{2} Concentration
- CO concentration
- Reductant Composition and Concentration
- Lean/Rich Duration and Level of Richness
- Exposure to Sulfur
- Substrate Geometry
- Catalyst Formulation

All of these factors play an important role in the modeling of lean NO\textsubscript{x} traps, their implementation, and also on their control.
2.10.1 Effect of Catalyst Temperature on Lean NO\textsubscript{x} Trap Behavior

Temperature, as in most chemical systems, plays a very important role in the performance of a LNT. It has been demonstrated that the storage mechanism at work in LNTs is active even at room temperature [21]. NO\textsubscript{2} fed to a catalyst at 25°C will be stored on the trap. Since NO cannot be converted in large amounts to NO\textsubscript{2} at low temperatures, it will pass through the trap untouched. It has also been demonstrated that at low temperatures the presence of CO and HC inhibits the storage of NO\textsubscript{2} by reducing it to NO [22]. Given the above considerations, the low temperature storage on NO\textsubscript{x} does not lead to any practical method of utilizing the available storage, since CO and HC are always present in an engine.

The upper temperature window is limited by the thermal decomposition of the stored NO\textsubscript{x} component. In a barium LNT, the Ba(NO\textsubscript{3})\textsubscript{2} becomes unstable at high temperatures and is incapable of storing a large quantity of NO\textsubscript{x}. Storage of significant NO\textsubscript{x} above 600°C is not possible on the barium trap. The decomposition reaction of Ba(NO\textsubscript{3})\textsubscript{2} to NO at 600°C with 7% O\textsubscript{2} leads to an equilibrium concentration of 2360 ppm NO [23]. Unless the inlet NO concentration was higher than this value no NO\textsubscript{x} would be stored. NO\textsubscript{x} levels this high are not common in today’s lean-burn engines, thus the trap has no usable storage. Similar results are found for other oxygen concentrations.

Another effect of temperature is the influence on NO to NO\textsubscript{2} conversion in the trap. As already discussed, NO is not readily stored on the LNT, it must first be oxidized to NO\textsubscript{2}. To achieve greater NO\textsubscript{2} conversion, one can increase the precious metal loading to create a more active catalyst or to decrease the space velocity. The situation in a LNT is unique, in that when NO\textsubscript{2} is formed it can be removed from the gas phase through storage. Therefore, the level of NO\textsubscript{2} is suppressed by the storage mechanism and NO\textsubscript{2} formation continues, which is beneficial for LNT operation.

2.10.2 Effect of NO\textsubscript{x} Surface Coverage on Lean NO\textsubscript{x} Behavior

NO\textsubscript{x} surface coverage is the number of sites currently storing NO\textsubscript{x} divided by the total number of sites available for the given conditions. It is essentially a measure of how “full” the catalyst is, a value of zero

57
denoting an empty traps and a value of one denoting a full trap. The surface coverage fraction, or fill ratio, has a profound effect on the ability of the NO\textsubscript{x} trap to store NO\textsubscript{x}. A catalyst with a low fill ratio can store a very large fraction of the NO\textsubscript{x} entering the trap; however, as the fill ratio approaches unity the amount of inlet NO\textsubscript{x} stored goes to zero. The reason for this is clear, since the probability of a NO\textsubscript{2} molecule finding an empty site is effected by the number of available sites.

2.10.3 Effect of Space Velocity on Lean NO\textsubscript{x} Trap Behavior

Space velocity has a major effect on any kinetically limited catalytic process. Lower space velocities, by definition, mean longer residence times; thus more chance for the chemical reactions to take place. The following figure shows the effect of space velocity and temperature on a lean NO\textsubscript{x} trap. In this case, the lean rich cycling times and NO\textsubscript{x} concentration was kept fixed while the space velocity was increased by increasing the flow of feedgas. The average NO\textsubscript{x} efficiency for the cycle drops with increasing space velocity. The first reason for this is obvious; a greater flow rate of gas with the same concentration of NO\textsubscript{x} delivers more mass of NO\textsubscript{x} per unit time. For a fixed lean rich cycling time this means the trap fills up more during storage and is thus less efficient at trapping NO\textsubscript{x}. The second reason is that the residence time in the catalyst is reduced and for the reasons mentioned above the storage efficiency is reduced.
2.10.4 Effect of Feedgas NO\textsubscript{x} Concentration on Lean NO\textsubscript{x} Trap Behavior

An increase in NO\textsubscript{x} concentration has the obvious effect of bringing a greater mass of NO\textsubscript{x} into the catalyst at for a given flow rate, but there are other effects as well. One of the primary effects is to increase the NO\textsubscript{x} storage capacity of the trap. To demonstrate this point, a basic model of chemical reaction engineering will be used, which is referred to as Langmuir-Hinshelwood (LH) kinetics.

Assuming that the NO\textsubscript{x} storage can be modeled by the following simple storage mechanism:
\[ A + s \xleftrightarrow[k_{d,a}]{k_{a,a}} A \cdot s \]

where:
- \( A \) = adsorbed species (NOx)
- \( s \) = a catalyst site
- \( k_{a,A} \) = adsorption reaction rate
- \( k_{d,A} \) = desorption reaction rate

Following the LH-kinetics model gives the following rate expressions:

\[
\begin{align*}
    r_{aA} &= k_{aA}c_A(1 - \theta_A) \\
    r_{dA} &= k_{dA}\theta_A
\end{align*}
\]

At equilibrium, these two are equal and it yields:

\[
\theta_A = \frac{K_A c_A}{1 + K_A c_A}
\]

\[
K_A = \frac{k_{aA}}{k_{dA}}
\]

The following two plots illustrate examples of this reaction scheme to highlight the importance in understanding LNT behavior. The figures were generated using fictitious values, so no units are provided. The left hand figure illustrates the effect of the adsorption rate constant and desorption rate constant with respect to the surface coverage at a constant concentration of \( A \). Note that as the storage capacity fills up (ie. \( \theta \) increasing) the rate of the forward reaction decreases rapidly, whereas the desorption rate constant increases. This simply expresses the fact that as the storage becomes more and more full it is increasingly difficult to get a species into storage. The right hand figure illustrates the point at hand. As the concentration of the gas species \( A \) (i.e. NOx) increases, the equilibrium storage capacity increases as well. There is another factor in this equation, which are the reaction rate terms. As shown in the figure, as the adsorption term becomes more dominant the curve saturates at a lower concentration. If the adsorption reaction rate for NOx is high enough, then even small concentrations in the gas phase will allow the catalyst
to adsorb the full capacity of NO\textsubscript{x} at equilibrium. Values for these reaction rates were not found in the literature; however, this simple example outlines the fundamental issues.

![Figure 22: Example of LH-Kinetics](image)

2.10.5 Effect of CO\textsubscript{2} and O\textsubscript{2} Concentration on Lean NO\textsubscript{x} Behavior

It has been noted that the composition of the feedgas during the trapping phase can have an impact on the quantity of NO\textsubscript{x} stored. In a lean-burn engine, especially a Diesel, the relative amounts of CO\textsubscript{2} and O\textsubscript{2} change drastically. These two components can have a direct impact on the maximum amount of NO\textsubscript{x} stored. In an engine, these two concentrations have an inverse relationship; however, in a bench reactor they can be independently controlled. The following figure shows the effect of these gasses on NO\textsubscript{x} storage. These results are from a single operating temperature meant to simulate the conditions in a lean engine exhaust. As the CO\textsubscript{2} level increases from 0% to 12%, the NO\textsubscript{x} storage drops by 25%. This is thought to be due to the fact that CO\textsubscript{2} is competing with NO\textsubscript{2}. As CO\textsubscript{2} levels increase they are more effective at occupying these sites, which eliminates storage sites for NO\textsubscript{2}. This effect of CO\textsubscript{2} is diminished in the presence or water vapor to roughly half of the result reported here.
The figure also shows that, in general, NO\textsubscript{x} storage increases with increasing O\textsubscript{2} levels. This is thought to be because that the conversion of NO to NO\textsubscript{2} requires oxygen to be present and also because the NO\textsubscript{2} storage step requires oxygen to be present. If there is more oxygen available, then it is more likely for a NO\textsubscript{2} molecule to end up adsorbed on an active site. Due to the inverse relationship between these two species in an IC engine, these two effects would be superimposed. At high load, the engine consumes produces high amounts of CO\textsubscript{2} and low amounts of O\textsubscript{2}, from below, this would have the effect of doubly lowering the NO\textsubscript{x} storage capacity of the trap. These effects have not been reported in the literature from engine testing. This is likely because an increase in load is accompanied by an increase in exhaust temperature, exhaust flow rate, and exhaust NO\textsubscript{x} concentration which mask the individual effects.

Figure 23: Effect of CO\textsubscript{2} and O\textsubscript{2} on NO\textsubscript{x} Storage (after [25])
2.10.6 Effect of CO on Lean NO\textsubscript{x} Trap Behavior

It has been shown that the CO reacts with NO\textsubscript{2} to form NO [22]. This reaction is very effective at temperatures above 140°C and has been shown to convert virtually all NO\textsubscript{2} to NO above this temperature. During this reaction, the CO is destroyed, so the process does not continue indefinitely. However, the presence of CO certainly has an effect on NO to NO\textsubscript{2} conversion. This would have the effect of inhibiting the storage process to some degree, which uses almost exclusively NO\textsubscript{2}.

2.10.7 Effect of Reductant Composition and Concentration on Lean NO\textsubscript{x} Trap Regeneration

The composition of the reductant, as well as the length of the regeneration phase, have an important effect on the NO\textsubscript{x} conversion efficiency and the reductant usage. It is important to realize that it is highly undesirable to have reductant wasted (i.e. not react with NO\textsubscript{x}) because it is wasted fuel energy and also because it can significantly raise the emissions of CO and unburned HC. Results from a bench reactor study of a commercial LNT is shown below. The LNT is subjected to a number of different reductants, including 2\% H\textsubscript{2}, 1\% CO, and 3330 ppm C\textsubscript{3}H\textsubscript{6} (propene). The regeneration times end up being quite lengthy due to the experimental conditions; however, the results still shed some light on the behavior in engine applications.

The first plot, Figure 24: Effect of Reductant Composition on LNT Regeneration, shows both the NO\textsubscript{x} conversion (■) and the amount of unused reductant (▲) for the various reductants listed above for four different regeneration times (t\textsubscript{R}). A general trend is clear for each of the reductants, as regeneration time increases NO\textsubscript{x} conversion increases. Another trend is also clear, in that as the regeneration time increases the amount of unused reductant increases. During the first several seconds of the regeneration process, nearly all of the reductant is consumed due to the high availability of trapped NO\textsubscript{x} sites to react with. However, as more and more stored NO\textsubscript{x} is liberated and reduced, the probability of the reductant reacting with stored NO\textsubscript{x} decreases and reductant starts to slip out of the catalyst unused.
The relative effectiveness of each of these reductants is quite different. The 2% H\textsubscript{2} case rapidly converts NO\textsubscript{x} and the amount of unused reductant does not increase substantially until a large amount of NO\textsubscript{x} has been reduced. After 70 seconds, the amount of unused H\textsubscript{2} in the exhaust begins increasing. A similar trend is evident for the CO mixture; however, the amount of NO\textsubscript{x} converted does not rise as fast. The case of the propene is more interesting than for CO and H\textsubscript{2}. From the onset of the regeneration a percentage of the propene is unused, and the percentage increases substantially as the regeneration time continues. In this particular case the propene shows fairly poor performance, regenerating less than 70% of the NO\textsubscript{x} after 200 seconds of regeneration.

![Figure 24: Effect of Reductant Composition on LNT Regeneration (after [22])](image-url)
The above results were all for a temperature of 300°C; however, the following figure from a separate reference shows the effect of temperature. In this study, the lean rich timing was fixed at 45 seconds lean and 1.5 seconds rich. This lean-rich timing is very similar to what one would expect in an engine application. Three different reductants were used, 3% CO, 2.25% CO/0.75% H₂, and 1% C₃H₆ all with the same lean rich timing. Note than in terms of stoichiometric reducing power, the 1% propene condition has three times the NO reduction potential as the 3% CO and 2.25% CO/0.75% H₂. This being said is generally outperformed by the CO/H₂ mixture.

The figure shows that at low temperature the CO/H₂ mixture is more effective; however, at higher temperatures the propene and CO have considerably higher conversion efficiencies. Note that in addition, the conversion efficiency with propene lags behind that of CO by approximately 50°C, but is otherwise very similar. The authors state that the higher conversion efficiency of the CO/H₂ mixture at low temperatures is due to the more reactive nature of the hydrogen. However, at higher temperatures this reactivity is a liability, as the H₂ is prematurely consumed by trapped oxygen on the catalyst surface. Therefore, at higher temperatures only the 2.25% CO is actively participating in the NOₓ reduction reactions.

The 50°C time lag between CO and propene is also due to the relative reactivity of each species. CO is by its very nature more reactive then propene; thus, it is expected that it be more effective at a lower temperature. Propene, being more complex, must first be activated by C-H bond breakage on precious metal sites. Because of this necessary reaction, the propene mixture with nine times the reduction power of the CO still performs worse. The authors note that the NOₓ efficiency curves of the CO and propene case look remarkably similar to the light-off curves of the total oxidation of CO and propene, which is an indication of the degree that the reductant is activated at certain temperatures by the precious metal sites.
Figure 25: Effect Reductant Composition and Temperature on Lean NO\textsubscript{x} Trep Regeneration (after [26])

Another interesting behavior is shown in Figure 26, which shows the conversion efficiency versus time for each of the above reductants at a temperature of 300°C. Note that in the case of the propene, that the NO\textsubscript{x} conversion efficiency has extremely large negative peaks. This corresponds to more NO\textsubscript{x} leaving the catalyst then entering the catalyst. This phenomenon is also evident in the other cases; however, none of the peaks are negative. These negative peaks happen during the transition between lean and rich operation. Once the gas mixture moves rich, NO\textsubscript{x} is released from the catalyst. If the there is not sufficient active reductant present to convert this NO\textsubscript{x}, then is simply passes unreacted out of the trap. Due to the necessary activation mechanism for propene, it appears that in the early stages of purge there is simply not enough activated reductant to treat all of the released NO\textsubscript{x}. This behavior also has a strong dependence on catalyst residence time and temperature. With higher residence times and temperatures, the NO\textsubscript{x} release is controlled much better.
2.10.8 Effect of Lean/Rich Duration and Richness on Lean NO\textsubscript{x} Trap Performance

The absolute and relative timing of the storage and purge phase of the LNT have a dramatic influence on the overall conversion efficiency. This is largely due the effect of NO\textsubscript{x} fill ratio shown earlier, in which as the trap fills up with NO\textsubscript{x} the trapping efficiency drops. From this, one expects that for a longer lean period one should expect a lower average NO\textsubscript{x} conversion. Additionally, if the regeneration length is not long enough, NO\textsubscript{x} can accumulate on the trap. This unpurged NO\textsubscript{x} acts as an offset surface coverage and can cause the average storage efficiency to suffer greatly.

The above effect is visible in Figure 27. A series of tests were conducted in which an LNT was run with fixed inlet conditions for a storage cycle of 300 seconds. Six different purge durations were used, each
with the same purge conditions. Each of the tests started with a completely regenerated trap, thus the origin of all of the curves are the same. Note that in the case of the longest purge time, 9 seconds, there is no degradation in the average storage efficiency of the trap. As the purge duration is decreased, the average storage efficiency drops considerably. For each of these sub nine-second cases, the conversion efficiency keeps decreasing over a number of storage cycles until it reaches a near steady-state value. This is due to the above phenomenon, in which all of NOx adsorbed from the previous cycle is not removed during the purge event. This means the trap starts the next storage cycle with some NOx already stored on the trap, which decreased the starting storage efficiency. This figure clearly shows the need to provide the correct regeneration conditions for these storage traps. The result is akin to a vehicle application in which the purge length is not long enough or the amount of reductants is not high enough. Over time, the efficiency of the system can drop considerably.

Figure 27: Effect of Lean and Rich Duration on Average Sorption Efficiency (after [27])
2.10.9 Effect of Sulfur Exposure on Lean NOx Trap Behavior

Sulfur compounds present in the feedgas of a LNT have a very detrimental effect on the storage process. In combustion engines, sulfur enters the exhaust through both the fuel and the lubricating oils used in the engine. It has been estimated that the sulfur resulting from combustion of the lubricating oil has the same effect as increasing the sulfur level of the fuel by 30 ppm. From this it is clear that sulfur free fuel is not entirely the answer to the LNT sulfur problem. Sulfur compounds entering the LNT are stored in a similar manner as NOx molecules to form BaSO4 and other compounds. Barium sulfate is unfortunately more stable than barium nitrate, thus they actually tend to accumulate on the trap even through the periodic NOx regeneration events.

The effect of three different sulfur compounds, sulfur dioxide (SO2), hydrogen sulfide (H2S), and carbonyl sulfide (COS) on the storage performance of a lean NOx trap sample are shown below. The plots show the time history of the LNT sample when expose to intermittent lean and rich cycles in which the lean in rich cycles contain 25 ppm of the sulfur compound. The plots from top to bottom show the effect of SO2, H2S, and COS. The samples are fed a simulated lean feedgas containing 400 ppm NO and are allowed to trap almost to saturation. As shown in the figure on the first trapping phase, the integral of the shaded area represents the mass of NOx stored. As the test progresses, the amount of NOx storage is clearly degraded by a large amount. The early tests show a gradual increase in NOx whereas in the later tests the outlet NOx concentration rises almost immediately. The effect of the different sulfur compounds appear to be nearly the same. In the next figure, Figure 29, these results are plotted in terms of sulfur exposure time and percent degradation of NOx storage capacity. The degradation is quite severe, after 100 minutes of sulfur exposure the samples showed virtually no NOx storage.
Figure 28: Effect of Sulfur Compounds on NOx Trap Performance (after [28])

Figure 29: NOx Storage Degradation from Sulfur Compounds (after [28])

70
The exact nature behind the effect of sulfur is still being investigated. Once recent study investigated the various mechanisms in which sulfur and NO\textsubscript{x} were stored on the catalyst [29]. The following figure summarizes the conditions and results for ten separate tests with identical catalyst samples. The following list outlines some of the important features:

- One effect that is clear from tests one and two is that oxygen need not be present for SO\textsubscript{2} storage to occur.

- Experiments five and seven indicate that the level of sulfur storage is 58% larger than the amount of NO\textsubscript{x} storage at saturation.

- Experiments five, six, and nine indicate that when the levels of NO\textsubscript{x} and SO\textsubscript{2} are comparable to that the sulfur storage is nearly the same as if there was no NO\textsubscript{x} in the feedgas. Also, NO\textsubscript{x} storage capacity is degraded by 60% with respect to the case when there is no SO\textsubscript{2} present.

- Experiments nine and ten show that when the level of NO\textsubscript{x} is considerably higher than the level of SO\textsubscript{2} that the amount of sulfur stored is reduced and the amount of NO\textsubscript{x} stored is slightly increased from the case of equal concentrations. This implies that the NO\textsubscript{x} is competing with the sulfur for storage sites.

<table>
<thead>
<tr>
<th>Experiment number</th>
<th>SO\textsubscript{2} content (ppm)</th>
<th>NO\textsubscript{x} content (ppm)</th>
<th>O\textsubscript{2} content (%)</th>
<th>Adsorption duration (s)</th>
<th>Amount of SO\textsubscript{2} adsorbed ($\times 10^{-5}$, mol mg$^{-1}$ of material)</th>
<th>Amount of NO\textsubscript{x} adsorbed ($\times 10^{-5}$, mol mg$^{-1}$ of material)</th>
<th>Desorption peaks of SO\textsubscript{2} (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100</td>
<td>0</td>
<td>7</td>
<td>2000</td>
<td>8.6</td>
<td>-</td>
<td>1000</td>
</tr>
<tr>
<td>2</td>
<td>100</td>
<td>0</td>
<td>6</td>
<td>2000</td>
<td>8.6</td>
<td>-</td>
<td>940</td>
</tr>
<tr>
<td>3</td>
<td>100</td>
<td>0</td>
<td>7</td>
<td>4000</td>
<td>16.9</td>
<td>-</td>
<td>410</td>
</tr>
<tr>
<td>4</td>
<td>200</td>
<td>0</td>
<td>7</td>
<td>2000</td>
<td>16.9</td>
<td>-</td>
<td>380, 1000</td>
</tr>
<tr>
<td>5</td>
<td>200</td>
<td>0</td>
<td>7</td>
<td>21 000</td>
<td>52.8$^*$</td>
<td>-</td>
<td>844, 1000</td>
</tr>
<tr>
<td>6</td>
<td>200</td>
<td>0</td>
<td>7</td>
<td>7000</td>
<td>50.2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>7</td>
<td>0</td>
<td>200</td>
<td>7</td>
<td>12 000</td>
<td>-</td>
<td>52.1$^*$</td>
<td>-</td>
</tr>
<tr>
<td>8</td>
<td>0</td>
<td>500</td>
<td>7</td>
<td>7000</td>
<td>-</td>
<td>52.1$^*$</td>
<td>-</td>
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<tr>
<td>9</td>
<td>200</td>
<td>200</td>
<td>7</td>
<td>7000</td>
<td>50.6</td>
<td>21.0$^b$</td>
<td>450, 1000</td>
</tr>
<tr>
<td>10</td>
<td>100</td>
<td>500</td>
<td>7</td>
<td>4000</td>
<td>13.8</td>
<td>22.4$^b$</td>
<td>430, 1000</td>
</tr>
</tbody>
</table>

$^*$ Saturation was obtained.

Figure 30: Tabular Results for the Effect of Sulfur on NO\textsubscript{x} Storage (after [29])
Using the temperature programmed desorption results from this series of experiments along with in situ diffuse reflectance infrared Fourier transform spectrometry (DRIFTS), the authors were able to speculate on the nature of the sulfur storage process. The key conclusions were that sulfur is stored in barium sulfates, but also on Pt-alumina as aluminum sulfates and possibly as ceria sulfates. It appears that the storage of sulfur as barium sulfates occurs rapidly, and is in direct competition with NO₃ storage. The storage on the alumina is a slower process. Among the support for these findings is that when a catalyst sample was allowed to saturate with NOₓ, it was still possible for the catalyst to trap SOₓ. Additionally, there was no evidence of the NOₓ being displaced by the sulfur so the conclusion is that the sulfur must be stored via a different mechanism (i.e. on ceria and alumina.) Conversely, if a catalyst sample was allowed to saturate with SO₂ it was not possible to store NOₓ on the catalyst. This implies that the sulfur is stored as barium nitrate and on the alumina and ceria, which is supported by experiments presented in later chapters of this work.

2.10.10 Effect of Substrate Geometry on Lean NOₓ Trap Behavior

Substrate geometry also plays an important part in the behavior of a lean NOₓ trap catalyst. The most popular substrate material for the LNTs is cordierite. Cordierite substrates can be manufactured with a wide range of cell densities, from 100 cells per square inch (cpsi) to 1200 cpsi with the latest manufacturing techniques. By moving to higher cell densities higher geometric surface area are possible, which can lead to better catalyst operation. The following figures show a comparison of several catalyst of identical dimensions but with varying cell densities. The figure clearly shows that the higher the cell density the better the performance of the LNT. The 800 cpsi case is capable of storing 25% more NOₓ for a similar weight of catalytic coating. The aspect ratio of the catalyst is also important for NOₓ conversion. Figure 32 shows three catalyst of nearly identical volume with identical cell densities. The longer catalyst with the smaller diameter performs markedly better than the other catalyst. This is thought to be due to the increased turbulence in the longer channels. As shown in these limited examples, the catalyst geometry can play an important part the behavior of LNTs.
Figure 31: Effect of Cell Density on Lean NOx Trap Performance (after [30])

Figure 32: Effect of Catalyst Aspect Ratio on Lean NOx Trap Performance (after [30])
2.10.11 Effect of Catalyst Formulation on Lean NO\textsubscript{x} Behavior

The effect of catalyst formulation will be touched on briefly just to illustrate the impact it has on the performance of an LNT. It was mentioned earlier that barium is the most popular choice as a NO\textsubscript{x} storage compound in the literature; however, many other compounds are effective as NO\textsubscript{x} storage agents. The following figure shows a comparison of a number of different catalysts all with different storage materials. The storage materials are all alkali metals or alkaline earth metals, and include barium, potassium, sodium, strontium, calcium, cesium, and magnesium. All of which demonstrate difference NO\textsubscript{x} storage efficiencies for the given evaluation cycle, which consists of a synthetic lean exhaust for one minute at a lean air-to-fuel ratio of 20 and a one minute rich with an air-to-fuel ratio of 13. Barium emerges as the best performer at low temperatures, whereas, potassium, and sodium perform well at higher temperatures. The selection of barium has to do with the expected range of engine temperatures expected as well as the relative ease at which sulfur can be removed from the catalyst.

![Figure 33: Effect of Storage Compound on Lean NO\textsubscript{x} Trap Behavior (after [24])](image-url)
As discussed above, lean NO\(_x\) traps also contain precious metals in their formulations. Naturally, amounts and types of precious metal loaded onto the catalyst play a large part in the performance. Platinum is one of the common precious metals used in lean NO\(_x\) traps to promote oxidation reactions. The following figure shows the effect of platinum loading on the efficiency curve of an LNT with identical trapping components. It is evident that the low temperature efficiency increases with increasing platinum content; however, there is little effect at higher temperatures. From this it is clear that the precious metal loading plays an important part in the overall performance of the LNT. This effect is due to improved NO to NO\(_2\) conversion in the catalyst which leads to better trapping.

Figure 34: Effect of Platinum Loading on Lean NO\(_x\) Trap Behavior (after [24])
2.11 LNT Models

Based on the previous sections, the complex chemistry of LNT has been illustrated. Because of this, any LNT model will need to be, to some degree, a simplification of the actual chemistry. A comprehensive review of the literature was conducted to find LNT models that are of the same general class as the models required in this work. These models would generally fall into the category of control-oriented models. The definition of a control-oriented model is not clearly defined, but is typically a model that is simple enough to be used for control validation, simulation studies, and/or implemented in real-time in an automotive engine controller. This classification excludes models, which require extensive computational time, such as models that include a large reaction set with reaction rate parameters. Although these models clearly have a place, they are typically too complex to serve the needs of control development. A selection of models relevant to this work is included in the following sections.

2.11.1 LNT Model 1: Yanying Wang et. al. (1999)

This LNT model was developed as a control model for use with lean gasoline engines [31]. As a substitute for all of the reaction mechanisms involved in LNT operation, this model relies on only a simple reaction scheme to provide the basic structure. All of the details of the reaction dynamics are hidden by using empirical equation fits from experimental data. The purpose of this model is for use in simulation and control studies of lean-burn engines. The assumed basic reaction scheme is the following:

- **Step I**: \( \text{NO} + \frac{1}{2} \text{O}_2 \leftrightarrow \text{NO}_2 \)
- **Step II**: \( \text{BaCO}_3 + 2 \text{NO}_2 \leftrightarrow \text{Ba(NO}_3)_2 \)
- **Step III**: \( \text{Ba(NO}_3)_2 \leftrightarrow \text{BaO} + 2 \text{NO}_2 \)
- **Step IV**: \( 2 \text{NO}_2 + 2 \text{CO/HC} \xrightarrow{\text{Pt/Rh}} \text{N}_2 + 2 \text{CO}_2 \)
- **Step V**: \( \text{BaO} + \text{CO}_2 \rightarrow \text{BaCO}_3 \)

Steps I and II are the familiar NO\(_x\) storage steps from earlier sections. Step III is the decomposition of barium nitrate under rich conditions. Step IV is the reduction of the release NO\(_2\) using CO and HC over a
platinum and rhodium catalyst. Finally, step V is the reformation of barium carbonate using captured CO$_2$. Although these reactions are overly simplified, they capture the overall dynamics well enough that they can lead to the formulation of an accurate model.

### 2.11.1.1 Model Dynamic Equations

The following table shows the equations used in the dynamic model. Equation (51) is the expression for the change in mass of NO$_x$ per unit time, which has three conditions based on air-to-fuel ratio. Note that $\rho$ is saturates between 0 and $c$, which prevents the stored mass from being negative or exceeding the maximum NO$_x$ capacity of the trap. The expression for $c$ is given by (52), which is simply a function of temperature. Figure 35 below shows the plot of this equation, note that NO$_x$ storage peaks at approximately 330°C.

\[
\frac{d\rho}{dt} = \begin{cases} 
  f_L(\rho, NO_x, c) & \lambda \geq 1 \text{ and } 0 \leq \rho \leq c \\
  f_R(\rho, CO) & \lambda < 1 \text{ and } 0 \leq \rho \leq c \\
  0 & \text{otherwise}
\end{cases} \tag{51}
\]

\[
c = \frac{1}{a + b \times TNT + c \times T^2 + d \times T^3 + e \times T^4} \tag{52}
\]

\[
e(\alpha, x) = \frac{\beta}{1 - e^{-\alpha}} \tag{53}
\]

\[
f_L(\rho, NO_x, c) = (1 - \beta) \times NO_x \times \mu \times e(\alpha, x) \tag{54}
\]

\[
f_R(\rho, CO) = \rho - \gamma \times CO \tag{56}
\]

\[
\beta = \text{fraction of NO}_x \text{ eliminated by HC-SCR reactions}
\]

\[
\mu = \text{maximum empty trap storage}
\]

\[
e(\alpha, x) = \text{trapping possibility function}
\]

\[
\gamma = \text{moles of CO to reduce 1 mole of NO}_x
\]

\[
\alpha(T) = \text{fifth order polynomial fit}
\]

\[
y = \text{outlet mass flow rate of NO}_x
\]

\[
x - \rho/c
\]

\[
\rho = \text{mass of stored NO}_x
\]

\[
NO_x = \text{mass flow rate of NO}_x \text{ into the catalyst}
\]

\[
c(T) = \text{maximum NO}_x \text{ storage capacity}
\]

\[
CO = \text{mass flow rate of CO into the catalyst}
\]

\[
f_L = \text{mass flow rate of NO}_x \text{ stored on the catalyst}
\]

\[
f_R = \text{mass flow rate of NO}_x \text{ reduced from the catalyst}
\]
The functions \( f_L \) and \( f_R \) are the mass flow rate of NO\(_x\) stored on the trap during the lean phase and the mass flow rate of NO\(_x\) leaving the trap during the rich phase. The function \( f_L \) is given by equation (97), and has a number of dependencies. The term \( \beta \) represents the amount of inlet NO\(_x\) destroyed via HC-SCR mechanisms, which is reported to be 15% to 20%. This amount of NO\(_x\) is destroyed outright and is thus not stored. Therefore, the LNT only has the opportunity to trap the \((1-\beta)\) times the inlet NO\(_x\) mass flow rate. The amount of NO\(_x\) that the LNT actually traps is represented by the two terms \( \mu \) and \( \varepsilon \). \( \varepsilon \) is the “trapping possibility function” and varies from one to zero. \( \mu \) is the maximum empty trap storage efficiency. These two factors multiplied together yield fraction of NO\(_x\) entering the trap (after the HC-SCR reaction) that is stored on the trap. The value of \( \mu \), although not given in the reference, would most likely be > 95% under most conditions. The shape of the trapping possibility function is shown below in Figure 36, which shows how it is parameterized by temperature. The purge phase of the model is quite a bit simpler, and is represented by equation above and is self-explanatory.

Figure 35: NO\(_x\) Capacity Curve for Model 1 (after [31])
2.11.1.2 Results for Model 1

An extensive review of the accuracy of this model is not included in the reference. However, the following four diagrams show that the agreement of the model with experimental data is good for the simple validation cycles used.
2.11.2 LNT Model 2: Mikael Larson et. al. (1999)

This model, like the previous model, was developed as a control model [32]. The authors actually went as far as to implement the model in a vehicle ECM to perform NOx trap catalyst management. The model is unusual as a control model in that it is spatially resolved in the direction of exhaust gas flow. It consists of ten non-symmetric catalyst cells, each with an identical model. The cells are in series with one another such that the outlet conditions of one cell are the inlet conditions of the following cell. The main purpose of the model was to predict the relative fullness of the NOx trap in order to purge it when required. Two different catalyst models are presented in this reference. The first model does not explicitly account for oxygen storage, but it proved to be unsatisfactory. In the second model, provisions were made to
incorporate oxygen storage sites in addition to NO\textsubscript{x} storage sites. Only the results of the second, more accurate model will be discussed here.

2.11.2.1 Model 2 Equations

This model is based on a simple reaction scheme as well. The following shows the model equations with relevant comments annotating each equation.

Assuming Langmuir kinetics for the NO\textsubscript{x} adsorption/desorption:

\[
\text{NO}_x + y\text{O}_2 + \text{Site} \rightarrow \text{NO}_x\text{ads} ; \quad r_{\text{ads}} = k_{\text{ads}} \cdot c_{\text{ads}} \cdot (1 - \theta_{\text{ads}})
\]

\[
\text{NO}_x\text{ads} \rightarrow \text{NO}_x + \text{Site} ; \quad r_{\text{ads}} = k_{\text{ads}} \cdot \theta_{\text{ads}}
\]

Reduction of stored NO\textsubscript{x} with reductant:

\[
\text{NO}_x\text{ads} + \frac{5}{6} \text{CH}_4 \rightarrow \frac{1}{2} \text{N}_2 + \frac{5}{6} \text{CO}_2 + \frac{5}{6} \text{H}_2\text{O} ; \quad r_{\text{red}} = k_{\text{red}} \cdot c_{\text{red}} \cdot \theta_{\text{red}}
\]

Reduction of stored oxygen with reductant:

\[
\text{O}_2\text{ads} + \frac{1}{3} \text{CH}_4 \rightarrow \frac{1}{3} \text{CO}_2 + \frac{1}{3} \text{H}_2\text{O} ; \quad r_{\text{red}} = k_{\text{red}} \cdot c_{\text{red}} \cdot \theta_{\text{red}}
\]

Oxidation of unburned fuel during lean operation:

\[
\text{CH}_4 + \frac{3}{2} \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O} ; \quad r_{\text{ox}} = k_{\text{ox}} \cdot c_{\text{ox}}
\]

NO\textsubscript{x} mass balance on cell:

\[
0 = m \cdot c_{\text{in,NO}_x} - m \cdot c_{\text{out,NO}_x} - r_{\text{ads}} + r_{\text{red}}
\]

Reductant mass balance on cell:

\[
0 = m \cdot c_{\text{in,CH}_4} - m \cdot c_{\text{out,CH}_4} - r_{\text{ads}} \cdot r_{\text{ox}}
\]

Mass balance of adsorbed NO\textsubscript{x}:

\[
\Delta \theta_{\text{ads}} / \Delta t = r_{\text{ads}} - r_{\text{ads}} - r_{\text{red}}
\]

Heat balance in cell with heat of reductant combustion:

\[
M \cdot c_p \cdot \Delta T / \Delta t = m \cdot c_p \cdot (T_{\text{in}} - T_{\text{out}}) + (-\Delta H_{\text{red}}) \cdot r_{\text{ox}}
\]

Storage of oxygen on ceria:

\[
\text{O}_2 + 2 \text{O}_{\text{ads}} \rightarrow 2 \text{O}_{\text{ads}} ; \quad r_{\text{o}} = k_{\text{o}} \cdot c_{\text{o}}
\]
To get a good fit of experimental data, the rate constants were changed from Arhenius types to mapped functions. This was necessary to get a better fit between the mass-transfer regime and the kinetic-controlled regime. The authors also site that using mapped functions results in faster calculations due to the relatively rapid operation of table lookup. The model used ten different cells, with the following size ratio, 5:8:10:11:11:11:11:11:11:11.

### 2.11.2.2 Model 2 Results

This reference provides a number of figures comparing the performance of the model to experimental data. The following figure shows the most difficult of the conditions, in which the model is being applied to a vehicle on a chassis dynamometer. The model does a fair job at predicting the output NO\textsubscript{x} emissions. The authors note that one of the main drawbacks with this (and any model) is that relying on estimates of engine out emissions introduces a large degree of error. Without NO\textsubscript{x} feedback, the engine management system is left with giving its best estimate of NO\textsubscript{x} emissions, which is unfortunately not always very accurate. Additionally, without knowing the quantity of reductant generated during the rich regeneration phase, it is difficult to ascertain how much NO\textsubscript{x} was purged from the trap. This leads to a significant problem, if one supplies excess reductant at each purge to ensure good NO\textsubscript{x} removal, the tailpipe carbon monoxide and hydrocarbons increase. Conversely, if one supplies too few reductants for each purge then not all of the NO\textsubscript{x} is purged and the NO\textsubscript{x} storage efficiency gets progressively worse until an equilibrium is reached.

Because this model comprised of ten different cells, it provides some interesting insight into what happens in the axial direction during storage. The following figure shows a simulation result from the reference. At the start of the trapping phase, the front part of the trap stores most of the incoming NO\textsubscript{x}. As the front cell begins to accumulate more and more NO\textsubscript{x}, NO\textsubscript{x} begins slipping through to the next cell. This process continues from cell to cell. By the end of the 750 seconds shown on the plot, the last cell is still starting to fill up and has not yet saturated. Careful attention to the purge event shows a similar trend, the last cell is the last one to be purged of NO\textsubscript{x}. It is important to keep in mind that a catalyst is not really a single lumped element, and that there are spatial effects to contend with. In the end, it must come down to whether or not
these spatial effects can be safely ignored in the use of the simpler single lumped model for the given application.

Figure 38: Chassis Dynamometer Validation of Model 2 (after [32])
2.11.3 LNT Model 3: Ahmed Kefti-Cherif et. al. (2000)

This LNT model is formulated to allow for adaptive updating of the model parameters during the operation of the model [33]. This feature of the model is quite important, as the performance of NO\(_x\) traps varies substantially with age. For a system to be able to deliver the required NO\(_x\) reduction over the life of the vehicle with the minimum fuel penalty, it must have an accurate model of the catalyst over the lifetime of the vehicle. This is simply not possible with a static model or with a model that attempts to predict the amount of catalyst degradation open loop.

2.11.3.1 Model 3 Equations

The following table contains the equations for the dynamic model proposed in this reference
\[ Q_i = V_g S_{cata} C_i = V_{cata} C_i \frac{V_g}{L} \]  (58)

\[ NS = V_{cata} N_{sc} \Theta \]  (61)

\[ NSC(T, C_{NOx}^{in}) = \frac{N_{sc}}{\left(1 + \left(\frac{k_1(T)}{k_2(T)} C_{NOx}^{in}\right)^{1/2}\right)^2} \]  (63)

\[ C_{red} = C_{CO} + C_{H2} + \left(1 + \frac{\gamma}{4}\right) C_{CH4} \]  (66)

\[ \frac{dNS}{dt} = \left(1 - \text{Eff}_p\right) \frac{Q_{NOx}^\text{in}}{Q_{NOx}^\text{in} + Q_{NOx}^\text{out}} \]  (59)

\[ Q_{NOx} = (1 - \text{Eff}_p) S_{cata} C_{NOx} \]  (60)

\[ \frac{dNS}{dt} = -\text{Eff}_p \frac{Q_{NOx}^\text{in}}{Q_{NOx}^\text{out} + Q_{NOx}^\text{out}} \]  (62)

\[ Q_{NOx}^\text{out} = (1 - \text{Eff}_p) S_{cata} C_{NOx} \]  (64)

\[ \text{Eff}_p = \frac{Q_{NOx}^\text{in} - Q_{NOx}^\text{out}}{Q_{NOx}^\text{in}} \]  (65)

\[ \text{Eff}_\text{p} = \frac{Q_{NOx}^\text{in} - Q_{NOx}^\text{out}}{Q_{NOx}^\text{in}} \]  (67)

\( Q_i \) = molar flow rate of component i
\( V_g \) = gas velocity
\( C_i \) = molar concentration of component i
\( S_{cata} \) = surface area of the catalyst
\( V_{cata} \) = volume of the catalyst
\( L \) = length of the catalyst
\( NS \) = NOx stored quantity
\( N_{sc} \) = NOx adsorption site concentration
\( \Theta \) = NOx fill ratio
\( k_1, k_2 \) = model fit parameters
\( C_{red} \) = Equivalent reductant concentration
\( \text{Eff}_p \) = Storage efficiency
\( \text{Eff}_\text{p} \) = Regeneration efficiency
\( Q_{NOx} \) = molar flow rate of NOx out of the catalyst
\( Q_{NOx}^\text{in} \) = molar flow rate of reductant out of the catalyst

Equation (58) is a generic equation for calculating the molar flow rate of a component based on concentration, flow velocity, and catalyst physical parameters. The following equation, (61), simply relates the current molar amount of stored NOx to the catalyst volume and NOx fill ratio. The equation for maximum NOx storage is given by (63), and shows dependence on temperature and concentration. This function would have the typical shape of NOx storage, with low storage at low and high temperatures and a peak storage at a midrange temperature. The authors introduce the concept of an “equivalent reductant” in their formulation, which is represented in equation (84). This equation uses the stoichiometric ratio of each species reacting with NO2 to normalize their effective NOx reduction potential. In this way a mix of reductants can be represented by a single concentration of equivalent reductant that has the potential to eliminate NO2 on a mole to mole basis.

The storage equations, which are active during lean operation, are deceptively simple. Equation (59) contains the storage efficiency term, which is dependent on temperature, gas flow velocity, inlet NOx
concentration, and fill ratio. The expression for Eff_s is not given explicitly in the reference; however, it would require a fair amount of experimental data in order to generate an accurate function. Equation (78) gives the molar flow rate of NO_x out of the catalyst. Similarly, the regeneration equations are active only during rich operation. Equation (62) represents that for a given flow rate of equivalent reducer, a certain amount of NO_x is regenerated from the catalyst based on the term Eff_p. The term Eff_p is dependent on temperature, gas flow velocity, and fill ratio. As with Eff_s, no functional form was given for Eff_p. Equation (82) gives the amount of equivalent reducer that slips unreacted from the catalyst which represents wasted fuel and added emissions of hydrocarbons and carbon monoxide. The model does not explicitly account for oxygen storage; however, given the generalized representation of Eff_p and Eff_s, the effect of oxygen storage could be incorporated. The authors do not explicitly mention this; however, they are certainly aware of the existence of oxygen storage acting in parallel with NO_x storage.

2.11.4 LNT Model 4: Yong-Wha Kim et. al. (2003)

This model is an extension of model number two discussed above [34]. The storage model relies on many of the same concepts; however, the mathematical formulation is changed slightly. This model was developed as a model for control evaluation and simulation for lean-burn gasoline engines.

2.11.4.1 Model 4 Equations

The following table shows the equation set used in the model. The first equation, (68), is the fundamental equation of NO_x storage which has three terms. The first term is somewhat unintuitive, but arises from the application of the chain rule when taking a derivative of \( m_{NO\text{x, stored}} = C_{LNT} \cdot x \). The other two terms represent the NO_x being stored on the trap during the lean phase and the NO_x being purged from the trap during the rich phase. Equation (87) is the expression for the NO_x exiting the trap, and consists of the NO_x not being stored by the trap during the lean phase as well as the NO_x that is released during the purge and is
not reduced by reductants. Equations (70) and (71) are the same functions discussed in the earlier model and need no explanation.

Equation (72) describes how NO\textsubscript{x} is released from the trap during the rich phase. It is a function of the oxygen storage fraction, inlet air-to-fuel ratio, air flow, and temperature. Figure 40 below shows the shape of this function for different air-to-fuel ratios at an undisclosed air flow and temperature. The general trend is that the release rate increases with decreasing air-to-fuel ratio. The higher the NO\textsubscript{x} storage fraction the faster the NO\textsubscript{x} release rate. The effect of oxygen storage is not shown on this graph; however, it is alluded to in the text of the reference. As oxygen storage fraction decreases, the rate of NO\textsubscript{x} release increases. This is because the reductants seem to preferentially target the oxygen storage first and the NO\textsubscript{x} storage secondly. Therefore the NO\textsubscript{x} release rate is not very high until the oxygen fraction is low.

Equation (91) describes the conversion efficiency of the NO\textsubscript{x} released during the purge event. It is clear from experimental results that not all of the NO\textsubscript{x} released from the trap is always reduced to N\textsubscript{2}, this term captures that effect. Figure 41 below shows the shape of this function for a particular airflow rate and temperature with varying air-to-fuel ratio and NO\textsubscript{x} storage fraction. In general, a higher air-to-fuel ratio gives a higher conversion efficiency. This again makes sense as if there is a richer mixture there is more reductant available to react with the released NO\textsubscript{x}. There is also a trend that as the NO\textsubscript{x} storage fraction decreases the conversion efficiency increases.

Oxygen storage is an integral part of this LNT model. Equations (74) and (75) are used to model the oxygen storage and were developed in another reference [31]. Figure 42 is a direct excerpt from the cited paper that describes the nature of the model. It is formulated in a very similar manner to the NO\textsubscript{x} trap model above so it requires no explanation other than that provided by the authors. Note that the equation for the tailpipe lambda was modified in the LNT formulation to include oxygen released during the NO\textsubscript{x} liberation process.
\[
\frac{dx}{dt} = -\frac{1}{C_{\text{LNT}}} \frac{dC_{\text{LNT}}}{dt} \cdot x + \eta_s \cdot \frac{\dot{m}_{\text{NOx, in}}}{C_{\text{LNT}}} - \frac{\dot{m}_{\text{NOx, r}}}{C_{\text{LNT}}}. \quad (68)
\]

\[
\dot{m}_{\text{NOx, r}} = (1 - \eta_s) \cdot \dot{m}_{\text{NOx, in}} + \dot{m}_{\text{NOx, r}} \cdot (1 - \eta_c). \quad (69)
\]

\[
C_{\text{LNT}} = C_m \cdot \exp \left[ -\left( \frac{T - T_m}{T_s} \right)^2 \right]. \quad (70)
\]

\[
\eta_s = \frac{e^{-\alpha x} - e^{-\alpha}}{1 - e^{-\alpha}} \quad (71)
\]

\[
k_r = \frac{\dot{m}_{\text{NOx, r}}}{C_{\text{LNT}}} = \frac{1 - e^{\mu x}}{1 - e^{\beta}} (1 - x_{\text{osc}}) f(\lambda, \text{MAF}, T) \quad (72)
\]

\[
\eta_c = \frac{e^{\gamma x} - e^{\gamma}}{1 - e^{\gamma}} f(\lambda, \text{MAF}, T) \quad (73)
\]

\[
\dot{\lambda}_o = \dot{\lambda}_i - \rho(\dot{\lambda}_i - 1) - (1 - \rho)\sigma(\dot{\lambda}_i - 1) \quad (74)
\]

\[
\sigma = \frac{0.21 \dot{m}_a \left( 1 - \frac{1}{\dot{\lambda}_i - \rho(\dot{\lambda}_i - 1)} \right)}{\varepsilon \dot{m}_{\text{NOx, released}}} \quad (75)
\]

\(x = \) current fraction of NOx capacity occupied \\
\(C_{\text{LNT}} = \) maximum NOx storage capacity of the trap \\
\(\eta_s = \) NOx storage efficiency \\
\(\dot{m}_{\text{NOx, in}} = \) mass flow rate of NOx into the LNT \\
\(\dot{m}_{\text{NOx, r}} = \) mass flow rate of NOx released from the trap during purge \\
\(\eta_c = \) NOx conversion efficiency during purge \\
\(C_m, T_m, T_s = \) model parameters for storage capacity function \\
\(\alpha(T, \text{MAF}) = \) temperature and space velocity sensitivity parameter \\
\(\beta = \) model parameter for NOx release function \\
\(x_{\text{osc}} = \) storage fraction of oxygen \\
\(\gamma = \) model parameter for conversion efficiency \\
\(\dot{\lambda}_i = \) inlet air-to-fuel ratio \\
\(\dot{\lambda}_o = \) outlet air-to-fuel ratio \\
\(\rho = \) contribution of oxygen from oxygen storage sites \\
\(\varepsilon = \) model parameter for oxygen storage function
Figure 40: NO\textsubscript{x} Release Rate Function of Model 4 (after [34])

Figure 41: NO\textsubscript{x} Conversion Efficiency Function for Model 4 (after [34])
2.11.4.2 Model 4 Validation and Results

The reference provides a few comparisons of the model against engine test cell results. The following figure shows the cumulative agreement of the model with experimental results for a series of three storage cycles and purges. The instantaneous agreement is very good during the storage phase and less so during purge phase. However, the cumulative results are quite generally quite for the set of data presented.
The authors also present some limited results on the tradeoff of the purge threshold, which is essentially how much of the lean NOx trap capacity is used before initiating a purge. As discussed above, the more NOx is stored on the trap the lower the average conversion efficiency. However, the more frequent the purge the higher the fuel economy penalty that is accrued. The following figure shows the results of such a simulation study for an unknown cycle. The figure contains data for three different purge thresholds, of which 0.37 grams represents 11% of the LNT storage capacity and 1.34 grams represents 35% of the NOx storage capacity. The tradeoff between NOx conversion and fuel economy penalty is clear.
2.11.5 LNT Model 5: M. van Nieuwstadt et. al. (2004)

The goal of this model is for assisting in control strategy development. This model includes modeling of NOx storage and release, oxygen storage and release, heat generation by internal reactions, sulfur poisoning, and desulphation modeling [35].

2.11.5.1 Model 5 Equations

The oxygen storage is modeled in such a way that it will adsorb or release as much oxygen as the feedgas allows up to the saturation limits. The oxygen flow rate out of the catalyst is the difference between what is adsorbed or released and what is coming in. This behavior is modeled mathematically by the equations
listed in (76) through (79). NOx storage is modeled in a slightly different way, since the adsorption is over a longer time scale. The rate of NOx adsorption is dependent on the amount of NOx stored in the catalyst, the temperatures, as well as the flow rate of NOx into the catalyst. The rate of NOx release is dependent on the amount of NOx stored, the temperature of the catalyst, as well as the oxygen deficiency of the inlet gas. The mathematical form is shown in equations (80) to (84). Temperature dynamics of the catalyst are modeled as an energy balance with a heat generation term that is related to the rate of oxygen storage depletion. This energy balance is listed as equation (85).

Provided that the temperature is high enough, the catalyst is assumed to adsorb all of the incoming sulfur. Sulfur poisoning is assumed to affect both the NOx storage and the oxygen storage, and thus the amount of sulfur is divided between the two via a function that depends on temperature. The amount of sulfur contaminating the oxygen and NOx storage sites are then subtracted out of the baseline oxygen and NOx storage. This models the effect of the sulfur making catalytic sites unavailable. Sulfur release during rich periods can be released as either SO2 or H2S. The fraction of sulfur released as SO2 is modeled as a function of the mass of oxygen stored. The sulfur dynamic equations are listed in equations (103) to (109).

Oxygen Storage:
\[
\frac{d}{dt} M_{ox} = I(F_{in}^{ox} > 0) S_{ox}(T, F_{in}^{ox}) + I(F_{in}^{ox} < 0) R_{ox}(T, F_{in}^{ox})
\]
\[
S_{ox}(T, F_{in}^{ox}) = F_{in}^{ox} \cdot S_{ox,T}(T) \cdot I(M_{ox} < C_{ox}(T))
\]
\[
R_{ox}(T, F_{in}^{ox}) = F_{in}^{ox} \cdot S_{ox,T}(T) \cdot I(M_{ox} > 0)
\]
\[
F_{in}^{ox} = F_{in}^{ox} - \frac{d}{dt} M_{ox}
\]

NOx Storage:
\[
\frac{d}{dt} M_{NOx} = I(F_{in}^{NOx} > 0) S_{NOx}(M_{NOx}, T, F_{in}^{NOx}) + I(F_{in}^{NOx} < 0) R_{NOx}(M_{NOx}, T, F_{in}^{NOx})
\]
\[
S(M_{NOx}, T, F_{in}^{NOx}) = (1 - M_{NOx} / C_{NOx}(T)) \cdot F_{in}^{NOx}
\]
\[
R(M_{NOx}, T, F_{in}^{NOx}) = (1 - M_{NOx} / C_{NOx}(T)) R_{NOx,T}(T)
\]
\[
R_{NOx,T}(T) = \frac{F_{in}^{NOx} \cdot R_{NOx,T}(T)}{R_{NOx}(M_{NOx}, T, F_{in}^{NOx})}
\]
\[ F_{\text{NOx}}^{\text{out}} = \left( F_{\text{NOx}}^{\text{in}} - \frac{d}{dt} M_{\text{NOx}} \right) \cdot I (F_{\text{NOx}}^{\text{LNT}} > 0) + \]
\[ \max(0, F_{\text{NOx}}^{\text{in}} - \frac{d}{dt} M_{\text{NOx}} + F_{\text{NOx}}^{\text{LNT}}) \cdot I (F_{\text{NOx}}^{\text{LNT}} < 0) \]
\[ F_{\text{NOx}}^{\text{out}} = F_{\text{NOx}}^{\text{LNT}} \cdot I (F_{\text{NOx}}^{\text{LNT}} > 0) + \]
\[ \min(0, F_{\text{NOx}}^{\text{LNT}} + F_{\text{NOx}}^{\text{in}} - \frac{d}{dt} M_{\text{NOx}}) \cdot I (F_{\text{NOx}}^{\text{LNT}} < 0) \]

Temperature Dynamics:
\[ \frac{d}{dt} \left( c_{\text{cat}} m_{\text{cat}} T_{\text{cat}} + c_{\text{air}} m_{\text{air}} T_{\text{air}} \right) = c_{\text{air}} F(T_{\text{in}} - T_{\text{cat}}) \]
\[ - h A (T - T_{\text{rao}}) + \max(0, - \frac{d}{dt} M_{\text{NOx}}) Q_{\text{LV}} \]

Sulfur Poisoning:
\[ \frac{d}{dt} M_{S,0x} = F_{S}^{\text{in}} \cdot S_{S,0x,T} (T) \cdot I (F_{\text{NOx}}^{\text{in}} > 0) \]
\[ F_{S}^{\text{in}} \cdot R_{S,0x,T} (T) \cdot S_{S,0x,T} (T) \cdot I (F_{\text{NOx}}^{\text{in}} < 0) \]
\[ \frac{d}{dt} M_{S,0x} = F_{S}^{\text{in}} \cdot (1 - S_{S,0x,T} (T)) \cdot I (F_{\text{NOx}}^{\text{in}} > 0) + \]
\[ F_{S}^{\text{in}} \cdot R_{S,0x,T} (T) \cdot (1 - S_{S,0x,T} (T)) \cdot I (F_{\text{NOx}}^{\text{in}} < 0) \]
\[ C_{\text{NOx}} (T) := C_{\text{NOx}} (T) - M_{S,0x} \]
\[ C_{\text{NOx}} (T) := C_{\text{NOx}} (T) - M_{S,0x} \]
\[ R_{S} = \max(0, - \frac{d}{dt} M_{S,0x}) + \frac{d}{dt} M_{S,0x} \]
\[ F_{\text{SO}_{2}}^{\text{in}} := R_{\text{SO}_{2},0x} (M_{\text{NOx}}) \cdot R_{S} \]
\[ F_{\text{H}_{2}S}^{\text{in}} := (1 - R_{\text{SO}_{2},0x} (M_{\text{NOx}})) \cdot R_{S} \]

\( c_{\text{NOx}} \) : order of the NOx release reaction.
\( c_{\text{NOx}} \) : order of the NOx storage reaction.
2.11.5.2 Model 5 Validation

No model validation was provided in the reference, as it was intended to present only a general methodology for LNT modeling.

2.11.6 Conclusions on Storage Models

As demonstrated in the previous chapter, the need for a simple, real-time model of a LNT results in many simplifications of the chemical behavior of the catalyst. For example, most of the models relied on some type of empirical storage efficiency term to model the storage behavior of the catalyst. This is not to say...
that the more fundamental studies are not of value. These studies provide guidance in selection of what dependencies to include, as well as the functional form of the empirical equations. Lastly, with the exception of one model, all of the models consisted of only a single catalyst element.

2.12 System Architecture

There are two distinct methods for providing the rich conditions for NO\textsubscript{x} regeneration of an LNT. The first method will be referred to as full-flow regeneration. In this technique, the entire flow rate of exhaust is brought to a rich air-to-fuel ratio for a brief time for NO\textsubscript{x} regeneration. The second method of NO\textsubscript{x} regeneration is what is referred to hereafter as bypass-regeneration. With this technique, a large portion of the exhaust is diverted around the catalyst being regenerated, such that only a fraction of the exhaust needs to be brought to a rich air-to-fuel ratio. A supplemental injection of reductant is required in the exhaust to bring the air-to-fuel ratio to rich conditions. Of these regeneration methods, the latter is the focus of this work. The following sections discuss the characteristics of these systems as reported in the literature. To illustrate the differences in these two systems, two examples are pulled from the literature, which offers reasonably comprehensive data regarding the performance of these systems.

2.12.1 Full-Flow Regeneration

Full-flow regeneration systems are by far the most popular regeneration method in the literature. A series of papers reporting on recent work sponsored by the United States Dept. of Energy serves as the most recent and comprehensive look at such a system for passenger car applications [36, 37, 38]. The system under investigation in this series of publications is shown in Figure 45. The system includes a close-coupled pre-catalyst, a large, underbody lean NO\textsubscript{x} trap, and a large, ceramic Diesel particulate filter at the back of the system.
The system discussed in the references is applied to a 1.9L Diesel engine rated at 100 kW. The engine is installed in a 1540 kg compact station wagon with a five speed manual transmission. Two separate catalyst configurations are investigated; however, one emerges as the better system and consists of a 1.34 L pre-catalyst (which has a LNT formulation); a 2.5 L, underbody LNT; and a 4.1 L silicon carbide DPF. This system uses a combination NO\textsubscript{x}/AFR sensor before and after the underbody LNT for use in the control strategy. With this vehicle and engine, a 82\% NO\textsubscript{x} reduction and a 83\% reduction and PM matter are required to hit the targeted Tier 2 Bin 5 emissions standards.

In this system, the engine is used to generate the rich conditions required for NO\textsubscript{x} regeneration. As described in the references, this includes a combination or modification of fuel and air parameters. The fuel parameters that can be adjusted for this three-injection system include rail pressure, post-injection timing, post-injection quantity, main injection timing, main injection quantity, pilot injection timing, and
pilot injection quantity. On the air side, the relevant actuators include boost pressure modification through the VGT, intake air throttling, and EGR valve position. It is noted in the references that fuel parameter modifications are the most desirable due to their ease of control. The air control, on the other hand, can excite unwanted dynamics due to the coupling of the air and exhaust systems through the EGR and the turbocharger.

The rich-calibration developed in the references involves using a significantly delayed post-injection. By adjusting the timing of the post-injection, it was determined that a value of 65º after TDC provided a good compromise between generation of carbon monoxide while minimizing hydrocarbons, smoke, and oxygen. In addition to post-injection timing, the rail pressure was increased to improve the opacity. For one operating point provided in the reference, a lambda of 0.95 was achieved with O₂ levels of 3.0%, CO levels of nearly 1.2%, and THC emissions of approximately 4000 ppm. To balance the torque due to the increase in post-injection fuel quantity, it was also necessary to reduce the quantity of the main injection. The fuel-only method described above was found to work well at mid to high loads; however, at low loads it requires very large post-injection quantities since the exhaust is quite lean. This results in unacceptable fuel economy penalties as well as NVH problems. To overcome this, a two-stage method is implemented in which the air mass is first reduced by increasing the mass of EGR. Once a stable condition is reached, the fuel-injection parameters are modified as described above.

Using the above mechanisms for rich exhaust generation leaves a substantial amount of free oxygen in the exhaust. This gives rise to the need for a pre-catalyst, which is a feature of virtually every full-flow regeneration architecture. One of the critical roles of this catalyst is to eliminate the gaseous oxygen from the exhaust during the rich phase. It is important to note the magnitude of the oxygen concentration in the exhaust stream. In the experimental case provided in the references, this is typically on the order of 3.0%. If one considers only CO for the moment, this amount of oxygen will consume all of the CO in the rich exhaust gas. Clearly, the oxygen would not consume just CO, as there is a fair amount of hydrocarbons as well as some hydrogen in the exhaust. However, it can be assumed that CO and H₂ will be consumed preferentially due to their higher reactivity. Thus, after the exhaust is reduced of oxygen in the pre-catalyst,
it will have significantly less of the desired CO and H₂ than the engine-out measurements indicate. This catalytic combustion of reducing species results in a substantial exotherm on the pre-catalyst.

A sulfur poisoning regeneration strategy is also discussed in the references. The method used to create sulfur regeneration conditions is an extension of the previously described method of providing NOₓ regeneration conditions. For sulfur regeneration, an exhaust lambda of 0.97 to 0.98 is targeted for a duration of six minutes. To achieve the desired reduced level of air flow, the intake system is throttled using an electronically controlled throttle body. After the reduced air rate is established, a post-injection strategy similar to the NOₓ regeneration strategy is employed. This strategy leads to pre-turbine temperatures in excess of 800°C, which is a durability concern for the turbocharger. The inlet to the underbody LNT is in the range of 650°C to 700°C for the steady-state condition provided in the reference. During the regeneration process, which lasts for approximately five minutes, the tailpipe emissions of CO are approximately 0.3% and the emissions of hydrocarbons are approximately 250 ppm. Although not discussed in the paper, this level of emissions would be an order of magnitude higher than the Tier 2 emissions standards. This leads to a regulatory gray area. If all things were considered, this amount of emissions would need to somehow included in the emissions results for a standard test cycle, in which a sulfur regeneration event is unlikely. A similar gray area exists for DPF regenerations, which can result in elevated levels of hydrocarbons in particular. Both of these events also adversely effect the real-world fuel economy of the vehicle but are generally not captured by the regulatory cycles.

A long-term durability study was conducted on the aftertreatment system to determine the ability of the system to meet the 50,000 mile intermediate life standards required by the Tier 2 regulations. Desulfurization was conducted every 100 hours, however, it was noted that in practice, this would have to occur somewhat more frequently to ensure the emissions standards were met at all times. The composite FTP results ranged from 0.07 g/mile to 0.025 g/mile for the system with an aging level equivalent to 50,000 miles, some of which are above the target value of 0.05 g/mile standard. THC emissions for the aged system varied from about 0.10 g/mile to 0.23 g/mile, which is significantly greater than the 0.10 g/mile
standard. CO emissions were acceptable in all cases. With the exception of a filter cracking problem midway through the test series, particulate emissions were also below the standard.

Unfortunately, the fuel economy impact of the system is not discussed in the references. In a government sponsored LNT study, a rich engine calibration was developed for LNT management with engine-based regeneration. With this calibration, the instantaneous fuel consumption of rich calibration was 40% to 80% that of the normal, lean operation. A table of the lean and rich parameters are provided in Table 2. Note the differences in the total fuel quantities of the main and post injection for the lean and rich calibrations. Also shown is the required lean-rich timing, which can be used to calculate the fuel economy penalty for steady-state operation at the particular operating condition. For the 300°C case, the fuel required for LNT management from this method of LNT management results in a 7% increase in fuel consumption. At 350°C, the LNT regenerations increase the fuel consumption by 12%. There have been advances in both LNT technology as well as rich engine calibrations since this work was published, however, it clearly demonstrates the scale at which such regeneration methods can affect the fuel economy of a Diesel vehicle.
2.12.2 Bypass-Regeneration

The most recent and comprehensive published work regarding bypass flow regeneration involved the application of a dual-catalyst bypass system on a medium-duty pickup truck [40 and 41]. The engine in the vehicle is a 6.6 L Diesel engine and the vehicle mass is 6568 lb. The aftertreatment system configuration is shown in Figure 46. With this particular system, there is a close-coupled oxidation catalyst located at the exhaust manifold. In the under floor location, there are two parallel DOC + LNT combinations with downstream bypass valves. After the dual legs rejoin, there is an oxidation catalyst and a DPF at the very rear of the system. Also include in the system are two supplemental fuel injectors, which provide reductants for LNT regeneration and a burner which assists in the thermal management of the system.
Figure 46: Bypass-Regeneration System (after [40])

Starting from the initial stock engine calibration of the vehicle, a 99% reduction in NO\textsubscript{x} and a 88% reduction in particulate matter was required. After performing a recalibration of the engine, the NO\textsubscript{x} emissions were reduced by 65%, which resulted in a more realistic reduction requirement from the NO\textsubscript{x} adsorber system of 94 %, but a more rigorous PM reduction requirement of 97%. Considerable effort was required in optimizing the temperature of the system, through use of the burner, engine calibration, and insulation of the exhaust components. This was necessary to get the NO\textsubscript{x} adsorber catalysts into a more favorable temperature region.

The method of regeneration is to first use the burner to increase the temperature of the LNT if necessary. Once the LNT system is at an appropriate temperature, the downstream bypass valve is closed which directs all of the flow through the opposite catalyst. The supplemental fuel injector then injects fuel into the system based on an estimate of how much NO\textsubscript{x} is predicted to be in the system. There is no mention of the flow rate of exhaust that is present in the regenerated system, however, it is implied in the references that some exhaust flow is present to carry the reductant through the DOC and LNT.
The authors originally attempted to use a time-based storage-regeneration cycle, however, this proved to be ineffective. A second method is suggested which uses an engine-out NO₅ map to integrate the NO₅ out and make a more accurate decision on NO₅ regeneration. Cold-start UDDS NO₅ emissions were over 0.140 g/mile and hot start UDDS NO₅ emissions were less than 0.04 g/mile. Hot-start UDDS THC emissions were between 0.20 and 0.30 g/mile and cold-start UDDS THC emissions were around 0.50 g/mile. The NO₅ emissions proved to be acceptable. The NMOG emissions were still a challenge considering the Tier 2, Bin 5 target of 0.09 g/mile; even when it is factored in that the methane should account for roughly 60% of the THC mass.

It must be noted, that majority of the bypass-regeneration systems are sized such that the regeneration requires a significant portion of the storage time. This results in the system catalyst volume being increased to nearly double the required size, since only half of the system is working at any given time. This shortcoming is not addressed in the literature, but it only arises due to under sizing of the reductant delivery system. If the reductant delivery system is sized appropriately, it is possible to regenerate the LNT at the maximum rate that the chemical kinetics will permit. If the catalyst is at a reasonable temperature, this can be on the order of ten seconds.

2.13 Reductant Delivery Systems for Bypass-Regeneration

Since the bypass-regeneration system does not rely on the engine to provide reductants, an external reductant delivery system is required. This device can be as simple as a supplemental fuel injector or as elaborate as a non-thermal plasma reformer in series with a partial oxidation catalyst. Since the reductant delivery system is a key component to the system, a review of the current methods reported in the literature is provided in the following subsections. In later chapters, experimental results from the author will be presented regarding supplemental fuel injection as well as a novel technique developed by the author, which is referred to as a flame reforming.
2.13.1 Supplemental Fuel Injection

Supplemental fuel injection is the most basic method of providing reductants for LNT regeneration, and is the method described in the earlier section on the bypass-regeneration system. Because of this earlier discussion, no further discussion is warranted.

2.13.2 Catalytic Reformers

With the emergence of fuel cells as a major research topic in the automotive community and elsewhere, it is a natural extension to apply hydrogen production methods researched for fuel cells to LNT management. There are a number of different processes for fuel reformation, all with slightly different advantages and disadvantages. A recent paper on a compact autothermal reformer will be discussed to illustrate the general behavior of such devices [42]. Of particular concern in the reformation of heavy fuels is the formation of carbonaceous deposits on the catalyst surface. It is possible to select operating conditions that minimize the formation, but long-term usage is still a concern. Typical start up times reported in the reference are of the order of 6-8 minutes, and require supplemental heating to achieve operating temperature. When fully warmed up and operating, the temperature of the device is above 700°C. For one operating condition presented with Diesel fuel, the steady-state H2 concentration is 36% and the efficiency from fuel into to H2 and CO out is 81%. Another reference, although providing minimal information on the reformer, provides some experimental results of the reformer applied to a Diesel LNT system [43]. The partial oxidation reformer used generated a 33% H2, 18% CO, 6% CO2, 42% N2, and < 1% THC mixture from naphtha. This mixture was demonstrated to achieve good NOx regenerations down to 150°C for a 14 L LNT on a 5.9 L engine. Because of the low flow rate of the reformer, regeneration of the large catalyst volume required nearly two minutes of reformer operation time.
2.13.3 Plasma-Based Reformers

There is a considerable history in the literature of a plasma-based reformer that is suitable for use with Diesel fuel. This plasma device was developed by MIT and then licensed to Arvin-Meritor in the field of Diesel aftertreatment. The device can be used in a number of different configurations, such as in conjunction with a catalytic reactor with water injection for promoting water-gas shift reactions. As reported by MIT, one prototype of the device can process 0.3 g/s to 0.5 g/s of Diesel fuel and require 300 W to 600 W of electrical energy. 30% hydrogen yields are obtained in three seconds with 90% yields achieved after 90 seconds. Hydrogen yields without the catalytic reactor or water injection drop to 64%. The overall power conversion efficiency, which is the heating value of the products over the heating value of the reactants is 56% for the case without the catalytic reactor [44]. A table summarizing the operation for different cases is shown in Table 3.

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Electrical power input (W)</th>
<th>O/C ratio</th>
<th>H₂O/C ratio</th>
<th>Fuel flow rate 0.001 kg/s</th>
<th>Fuel power 1000 W</th>
<th>Hydrogen yield (%)</th>
<th>Energy consumption (MJ/kg)</th>
<th>Power conversion efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empty reactor no water</td>
<td>270</td>
<td>1.32</td>
<td>0</td>
<td>0.26</td>
<td>11</td>
<td>0.64</td>
<td>13</td>
<td>56</td>
</tr>
<tr>
<td>Ceramic catalyst no water</td>
<td>190</td>
<td>1.51</td>
<td>0</td>
<td>0.48</td>
<td>20</td>
<td>0.75</td>
<td>4</td>
<td>64</td>
</tr>
<tr>
<td>Honeycomb reactor no water</td>
<td>230</td>
<td>1.21</td>
<td>0</td>
<td>0.34</td>
<td>14</td>
<td>0.91</td>
<td>6</td>
<td>74</td>
</tr>
<tr>
<td>Honeycomb reactor with water</td>
<td>150</td>
<td>1.24</td>
<td>1.8</td>
<td>0.31</td>
<td>13</td>
<td>1.22</td>
<td>3</td>
<td>87</td>
</tr>
</tbody>
</table>

Table 3: Performance of the MIT Plasmatron for Reformation of Diesel Fuel (after [44])

After the device was licensed to Arvin-Meritor, two papers have been published regarding its application of LNT bypass-regenerations systems [45, 46]. These papers report a fuel reformer output of 21% H₂, 20% CO, 3% CO₂, with 2% HC with a catalytic reactor. Hydrogen production without the catalytic reactor falls to less than 8%. Some basic trapping and regeneration experiments were conducted in [45] which compared the regeneration performance of the reformer and of straight Diesel injection. For identical fuel
quantities, it was determined that the reformer has overall better regeneration performance than Diesel injection, with the most marked differences occurring below 200°C. Fuel penalties on the order of 3% were required for a NO\textsubscript{x} efficiency of around 90%. The time response of the device was such that its 0 to 90% output time is about 10 seconds, although this measurement is obscured by the slow dynamics of the hydrogen measurement system. In [46], the fuel reformer is applied to LNT sulfur regeneration. The device demonstrates the ability to effectively regenerate sulfur poisoned catalysts, requiring an 800 second time to regenerate the 15 L catalyst.

2.14 Diesel Engine-Out NO\textsubscript{x} Models

An engine-out NO\textsubscript{x} model is an important part of the control algorithm that is presented in a later chapter, thus, engine-out NO\textsubscript{x} models are of interest. To provide some background into the type of model that would lend itself to such a use, the following reference is provided for discussion [47]. The model is developed with the specific purpose of being used for aftertreatment control, and therefore is capable of being implemented in real time in an automotive powertrain controller. The model is formulated based on the dominant reaction mechanisms for NO\textsubscript{x}, which includes the well known Zeldovich mechanisms. Based on these mechanisms, the rate of NO formation in the cylinder is determined by the concentration of oxygen, nitrogen, and NO in the cylinder as well as a number of rate constants. In this equation, the concentration of oxygen is that in the post-combustion gasses. This requires the development of a model which predicts the concentration of oxygen in the exhaust. With this estimate of post-combustion oxygen concentration, the NO\textsubscript{x} formation equation can be integrated into a isothermal continuously-stirred, tank reactor to model the combustion chamber. This leads to an expression of a dynamic exhaust NO concentration model.

Model parameters were identified using the first bag data from an EPA-75 test on a 4.5 L engine. The performance of the model was then compared to data collected on different EPA 75 tests with the same vehicle, as well as a seconds vehicle with an identical powertrain. 1\textsuperscript{st} data over an entire EPA-75 cycle was found to be 1290 ppm over the almost 1800 second cycle. Unfortunately, no data was presented in terms of
cumulative mass of NOx error, which would be of greater value for the LNT. However, the model appears to do a fair job at predicting the instantaneous NOx emissions of the vehicle.

2.15 Conclusions

Based on the contents of this chapter, it is clear that there is a substantial body of published literature to draw from for the study of the LNT. There are a number of aspects, however, that are missing which are to be addressed in this work. The first of these issues is the modeling of bypass-regeneration, which until now, has not been reported in the literature. Bypass-regeneration involves the same reactions as engine-based regeneration; however, there are great differences in the residence times and concentrations of reductants. A typical bypass-regeneration has a much higher concentration of reductants and a much lower space velocity than engine-based regeneration. The second area that is addressed in the following chapters is a more versatile method of LNT regeneration. Two reformer methods were reviewed in this chapter; however, both of these lack some key desirable features. The last element that is missing from the literature is a control algorithm for bypass-regeneration systems, of which there is nothing substantial reported in the literature. It is these three goals that the remaining chapters hope to address.
CHAPTER 3

EXPERIMENTAL METHODS AND EQUIPMENT

3.1 Introduction

The work presented in this document relies heavily on experimental data. This chapter explains the relevant equipment and procedures used for the collection of the data. Several sections detail the experimental hardware used to collect the data, which was taken entirely on the same 2.5 L engine on an engine dynamometer. For reference, the types of sensors used to make the key measurements are documented. Following a description of the off-the-shelf hardware, the fuel atomization device that is used in the research is described in some detail. This device uses a patent-pending process to generate sub-micron droplets of diesel fuel for use as a reductant in the LNT. Lastly, there is discussion of some of the analytical methods used in the research that are specific to the LNT as well as some specific applications of the catalyst exotherm measurements.

3.2 Catalyst Test Bed

The catalyst system under investigation throughout the duration research project was a dual-catalyst, full-bypass-regeneration system. A picture of the experimental setup, with a single catalyst installed, is shown in Figure 47. The exhaust enters the system from the left hand side of the photograph, where it encounters the split between the two catalyst paths. Upstream of each catalyst is a solenoid-actuated butterfly valve that closes to divert the exhaust away from the catalyst. Numerous ports are available at relevant locations for UEGO sensor measurements, gas sampling lines, and thermocouples. Two different types of LNT catalyst were used in the research. Unfortunately, no information on the catalyst formulation is available.
3.3 Test Engine

All of the experimental results presented are conducted on a 2.5L direct-injection Diesel engine coupled to a DC dynamometer. The specifications of the engine are summarized in Table 4. This engine is used in a number of light-duty applications in small to mid-sized SUVs and mini-vans, and is typical of the engines used in European vehicles of this class for meeting EURO III emissions. The fuel used throughout the testing was a low sulfur Diesel fuel donated by BP. The fuel, ECD-1, is a commercial fuel available in the US with a maximum fuel sulfur level of 15 ppm. To minimize the unknown quantity of sulfur entering the exhaust through combusted lubricating oil, the engine crankcase ventilation system was not vented into the intake system during the sulfur poisoning investigations.
<table>
<thead>
<tr>
<th>Cylinder Configuration</th>
<th>Inline, four-cylinder</th>
</tr>
</thead>
<tbody>
<tr>
<td>Displacement</td>
<td>2499 cm³</td>
</tr>
<tr>
<td>Valvetrain</td>
<td>4 per cylinder, DOHC</td>
</tr>
<tr>
<td>Max Power</td>
<td>100 kW</td>
</tr>
<tr>
<td>Peak Torque</td>
<td>250 ft-lb @ 2000 rpm</td>
</tr>
<tr>
<td>Compression Ratio</td>
<td>17.5:1</td>
</tr>
<tr>
<td>Air Induction</td>
<td>Waste-gated turbocharger w/ Intercooler</td>
</tr>
<tr>
<td>Emissions Compliance</td>
<td>Euro III</td>
</tr>
<tr>
<td>Fuel Injection System</td>
<td>Bosch Common-Rail Direct Injection (CP3)</td>
</tr>
</tbody>
</table>

Table 4: Test Engine Specifications

3.4 Instrumentation

Throughout the duration of the project, the sensor set evolved as the measurement needs changed. Table 5 provides the specifications of the major instrumentation used in the research project.

<table>
<thead>
<tr>
<th>Gas Sampling</th>
<th>Horiba MEXA 7500</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dual sampling lines</td>
</tr>
<tr>
<td></td>
<td>Heated, wet HC and NOₓ measurements</td>
</tr>
<tr>
<td></td>
<td>Chilled, dry CO, CO₂, and O₂ measurements</td>
</tr>
<tr>
<td>Air-to-fuel ratio Measurement</td>
<td>ETAS LA3 and LA4 UEGO Sensors</td>
</tr>
<tr>
<td>Gas Temperature Measurements</td>
<td>OMEGA type-K thermocouples, 1/16” stainless steel sheath, ungrounded</td>
</tr>
<tr>
<td>Catalyst Substrate Temperature Measurements</td>
<td>OMEGA type-K thermocouples, .050” stainless steel sheath, ungrounded</td>
</tr>
<tr>
<td>Gas flow meters (CO, Air, CO₂)</td>
<td>Variable area flow meters</td>
</tr>
<tr>
<td>Gas flow controller (SO₂)</td>
<td>Hot-film, mass flow controller</td>
</tr>
<tr>
<td>Data Acquisition System</td>
<td>National Instruments ATMIO-16E connected to a SCXI-1100 chassis with the two 32-channel AI cards and one 32 channel DIO card.</td>
</tr>
<tr>
<td>Engine Air Flow</td>
<td>Bosch HMF5 production hot film air flow meter, custom calibrated on flow bench</td>
</tr>
<tr>
<td>Dynamometer</td>
<td>General Electric 200/150 Hp DC Dyno Dyne-Systems dyno and throttle controller</td>
</tr>
</tbody>
</table>

Table 5: Instrumentation Specifications

As discussed in later chapters, much of the work focused on the analysis of catalyst bed temperature measurements. These temperature measurements were made using fine sheathed thermocouples with a
sheath outer diameter of 0.050". These thermocouples were inserted down the substrate channels to depths from 0.5" to 5.5" at 0.5" depths, giving 6 measurement locations in the 6" long catalyst substrate. Typically, two or three sets of six thermocouples were inserted into the catalyst in this manner.

In order to access the catalyst for instrumentation, the inlet cone of the catalyst was cut off of the catalyst almost flush with the catalyst face. A rolled stainless steel sleeve was then welded just short of half way around the circumference of the can. This sleeve had ports available for inserting three sets of thermocouples as well as a gas sampling port for the emissions analyzer and a port for a gas temperature sensor which measures the gas temperature immediately in front of the catalyst. After the thermocouples were installed in the catalyst can, an inlet cone was placed in the proper position on top of the catalyst and large steel band clamps were used to compress the rolled sleeve around the catalyst and the inlet cone. The band clamping and sleeve provided mechanical rigidity to the catalyst, while a high temperature RTV sealant was used to seal the seam around the interface of the sleeve, the catalyst, and the cone. This method of instrumenting the catalyst proved to be convenient, as it allowed the catalyst to be opened for inspection or to make a change in the catalyst configuration. Figure 48 shows two photographs of the instrumented catalyst and method of packaging.

Figure 48: Photographs of Catalyst Thermocouple Instrumentation
3.5 Data Acquisition and Control

For data acquisition and control, the test bed computer was used. This PC is equipped with a National Instruments data acquisition card which also allows simple control tasks to be performed. For the research, a "Virtual Instrument" data acquisition program was written using National Instruments LabView software. This program allows the acquisition of numerous channels of data, provides real-time displays of measurements, and performs limited data processing to display real-time calculated results. Through this interface, all of the relevant measurements could be observed first-hand.

The program also performs all of the control tasks required for the test program. This includes actuating the exhaust diverter valves, actuating the solenoid valves for the gas cylinders during regenerations, and supplying the atomizer fuel command. In addition to this low level control, the program is also used to conduct test sequences. For this function, a test procedure file could be loaded at the start of the acquisition. This file would specify the duration of the LNT trapping phase as well as the duration of each of the phases of regeneration. A number of different test procedures were developed that were used to generate repeatable, automated results.

3.6 Fuel Atomization Requirements for Lean NOx Trap Management

The unconventional LNT management methods explored in this research dictate some specific requirements for the fuel preparation system. Of critical importance is that the atomization device be capable of producing a fine spray of droplets, specifically Diesel fuel, which is typically difficult to atomize. The need for a fine droplet spray is motivated by a number of factors:

1. The fuel spray is directed into a confined space into a mixture of gasses at atmospheric pressure. For this reason, a spray with low penetration (i.e. small droplets and/or low velocity) is required to prevent wall wetting.
2. The fuel spray is directed into a space in which the temperature can be below the upper boiling range of Diesel fuel. Under certain conditions, the temperature can be well below even the lower boiling point of Diesel fuel. Under these circumstances, it is important to minimize the chance for contact with the walls of the system. Figure 49 shows a distillation curve for BP Amoco ECD-1 fuel, which is the fuel used for all of the experimentation in this research.

3. The fuel spray is conveyed to the catalyst using a relatively low speed flow of gasses, which are typically air or combustion products. This requires a spray which stays in suspension.

4. Under certain circumstances, the fuel spray is ignited to produce combustion gasses or heat for the management of the catalyst. The preferred style of combustion in this operating mode is premixed combustion. To achieve a well mixed fuel-air charge in a minimal space, it is beneficial to have small droplets.

5. During the combustion process, it is beneficial to have as small of droplets as possible. Small droplets facilitate ignition of the mixture and have rapid evaporation dynamics in the flame zone. Both of these factors improve the quality of the combustion.
Figure 49: Distillation Curve of BP ECD-1 Low Sulfur Diesel Fuel

The above requirements dictate only what the output of the atomization device should be. However, there are a number of more practical considerations that must be evaluated since this system is intended for a vehicle system. These considerations are summarized in the following list:

1. **Low Cost** - Any system employed on a production vehicle must meet this requirement.

2. **Low-Pressure Fuel Supply** - Although modern Diesel engines have an on-board high-pressure fuel system, this system is integrated onto the engine. It would be problematic to extend high-pressure lines that are anchored to the engine to the body or frame of the vehicle, since they are not rigidly connected. A system that is capable of operating off of the existing low-pressure fuel supply system would be preferable.
3. Compact Size - The atomization device must be compact to allow packaging of the system in modern vehicles.

4. Good Transient Response - To meet the demands of the LNT management, the fuel system must possess good dynamic response.

5. Minimal Auxiliary Requirements - Depending on the atomization technique, pressurized air or electrical power are required. Electrical power is already available on-board any vehicle, thus pressurized air would be less desirable from a system standpoint.

3.7 The OSU Atomizer

For various reasons, the conventional methods of atomization (high-pressure, air blast, ultrasonic, etc.) are undesirable for LNT management. The atomization method selected for this study is a patent pending method developed at the Ohio State University Center for Automotive Research. This method has been developed by the Advisor of this research and the author. Early work on the atomizer identified it as an effective method for preparation of Diesel fuel for premixed combustion with system requirements compatible with an automotive platform. Because of this prior successful experience, it was selected as the atomization technique for the duration of the research.

3.7.1 Atomization Technique

The OSU atomizer relies on a thermal process for the atomization of the liquid. A basic design will comprise of a length of stainless steel capillary tubing affixed to a resistive heating element using a thermally conductive bonding medium. Fluid is directed through the capillary tubing and, due to the heating element, increases in temperature. As the fluid traverses the length of the tube it increases in temperature and undergoes a phase change from liquid to a mixture of liquid and vapor that is predominantly comprised of vapor. Because of the phase change and the heating, the density of the fluid
decreases substantially from the entrance to the exit of the capillary tube. For a fixed inner diameter tubing, this decrease in density results in a substantial increase in velocity, to the point where the fluid can become choked at the exit of the tube. When this high velocity flow is ejected into ambient conditions, it entrains a substantial amount of the ambient gas in the spray. The process of entrainment is key to the atomization, as it isolates small parcels of the fuel vapor so that it condenses into a small droplet without combining with nearby droplets.

3.7.2 Atomized Fuel Properties

Using this atomization technique, a sub-micron spray of Diesel fuel is produced provided the method is properly controlled. The quality of atomization is qualitatively illustrated in Figure 50 which shows 2 mL of Diesel fuel atomized into a 2 L glass flask at room temperature and pressure. The evolution of the fuel spray over 15 minutes is demonstrated in the series of time lapse photographs. The quality of the atomization is excellent, considering that the typical residence times of the fuel spray for LNT management will be on the order of a few seconds.
The OSU atomizer is capable of operating at various fuel flow rates up to its design limit. Figure 51 shows one version of the atomizer operating from a very low flow rate (0.044 g/s) up to its maximum flow rate of approximately 1 g/s. The atomization quality of the fuel spray is maintained across the entire range of flow rates.
3.7.3 Atomizer System Requirements

As stated above, the ability to produce a fine spray of Diesel droplets only satisfies part of the requirements, as the atomization method must integrate well into a vehicle. Since the OSU atomizer is a thermal device, it does not require a source of high-pressure air as would an air-blast atomizer. A second attractive feature is that it does not require a high-pressure fuel supply, which is typical of pressure-based atomization techniques.
The only significant drawback of the atomizer is that, in its present form, it requires a moderate power input when atomizing fuel. Based on the implementation described above, it is clear that a fair amount of heat is required for the atomization of the fuel. This power consumption, for a typical design, is approximately 600 W per gram per second of fuel. Although this is not a prohibitive power demand since the atomizer is only used intermittently for LNT management, it is certainly an issue that must be addressed. The most effective method of addressing the power requirement is through the recovery of waste heat from the vehicle. By preheating the incoming fuel to a point below the desired exit temperature of the atomizer, it is possible to significantly offset the power consumption of the device. With appropriate integration, it is possible to envision a device in which the bulk of the fuel heating is done from waste heat, while the electrical heating is only used to fine-tune the exit temperature of the fuel spray. With this system, it is foreseeable that the electrical demand could be reduced by greater than 75%.

3.7.4 Atomizer Physical Embodiment

For the purpose of this research project and others, a new generation of atomizer was developed based on the need for a fully stand-alone atomizer and control system. The goal of this atomizer design was to provide a compact and rugged package using off-the-shelf components. Of great importance was that all of the components used be suitable for the prototype to be implemented on a vehicle without the need for any additional hardware beyond what is already standard. For this design, Diesel glowplugs are used as heating elements, as they are both rugged and are reasonably compact resistance heaters. A single glowplug provides approximately 150 W of heat with a 13.0 VDC supply voltage. For the atomizer, four glowplugs are used in parallel to allow the atomizer to deliver up to 1 g/s of atomized Diesel fuel. Fuel control is accomplished using a small fast-acting, 12 VDC solenoid valve. Through pulse-width modulation, it is possible to accurately control the flow of fuel through the device. The atomizer developed for the research, is shown in Figure 52, is housed in a stainless steel welded package that allows it to be integrated into a wide range of applications.
3.7.5 Atomizer Control System

The control system developed for the atomizer is based on an Infineon C164CI micro-controller that was pre-packaged with all of the necessary peripherals onto a 22.5 x 55.5 mm DIP-40 package (Phytec DIP-Modul-164.) The micro-controller was configured with and Infineon configuration utility (D.A.V.E.) which provided skeleton C-code based on the specified configuration of the available timers, interrupts, capture-and-compare channels, etc. This skeleton C-Code served the foundation for the control algorithm for the atomizer. As is typical, the C164CI micro-controller itself does not have the ability to interface directly with external systems, and thus requires some supporting circuitry. An existing, in-house PCB board design was upgraded for use with the atomizer, which provided the necessary power supplies for the C164CI as well as basic driver circuits to allow the digital and PWM outputs of the boards to drive moderate impedance loads.

In addition to the existing PCB board, a driver board was also required to meet the specific needs of the atomizer for control. This board was designed using a board layout utility (EAGLE) and fabricated using
an external PCB board fabrication shop. The board dimensions are 3" x 5" and it is a dual layer design. This board, referred to as the interface board, had the following functions:

1. High Current Driver - A high-side MOSFET based IC power switch is used to supply the commanded power to the atomizer. This IC also provides a current signal used for feedback control of the atomizer. A large heat sink is located on the board to dissipate the heat from the high-current switch.

2. Solenoid Valve Driver - A high-side MOSFET based IC power switch is used to actuate the fuel control valve.

3. Thermocouple Conditioner - A type-K thermocouple conditioner is located on the board which conditions the feedback thermocouple from the atomizer.

4. Control Gain and Set-Point Potentiometers - External potentiometers are used on the board to allow fine tuning of the controller gains and set-point.

5. Hour Meter - An hour meter is also on the interface board, which serves to keep track of the operating time of the device.

6. Communication Ports - The interface board contains three DB-9 connectors which allow communication with the handheld controller, a PC through a serial interface, or to a CAN network (CAN is a serial communications protocol is used extensively in the automotive industry.)

7. Other Miscellaneous Functions - Functions such as power distribution, signal routing to communications ports, inductive load snubbing, low-pass filtering, and fusing are also implemented on the board.

The entire control system, including the micro-controller, driver board, and interface board, is packaged in an enclosure, as shown in Figure 53.
The control algorithm developed for atomizer control is a feed-forward PI control with three distinct operating modes. The first operating mode is a power-down state, in which the controller is active but the atomizer is not being powered. Because it is necessary to preheat the atomizer for a few seconds prior to fuel injection, a second state is provided which is referred to as standby. In standby mode, the controller warms up the atomizer to a ready state, but fuel injection is prohibited. This mode maintains the atomizer in a ready state but requires only a small amount of electricity. The third mode is the injection mode, in which fuel is injected. Once a threshold temperature has been reached in standby mode, it is possible to toggle between standby and injection mode rapidly. Because the algorithm incorporates feedforward control, it is possible to rapidly increase fuel flow in a near step-wise fashion. Fuel control is accomplished using a high frequency solenoid valve operating with a PWM waveform in which the duty cycle dictates
the fuel flow. Also included in the control algorithm are a number of fault detection schemes which check for basic faults, such as loss of a feedback signal.

3.8 Analytical Methods

Conventional analytical methods were used for interpreting the data. Based on the list of instrumentation in Table 5, it is clear that there is no unusual instrumentation that requires any special elaboration. Despite this, it is worth describing the method used in determining the amount of stored NO\textsubscript{x} that accumulates in the LNT during a storage phase, since it is not a direct measurement.

The measurement of the NO\textsubscript{x} stored in the LNT requires integrating the mass flow rate of NO\textsubscript{x} into the trap and the mass flow rate of NO\textsubscript{x} flowing out of the trap. In order to measure the absolute quantity of NO\textsubscript{x} trapped in the catalyst, it is critical to start with a trap that has been fully depleted of stored NO\textsubscript{x}. Any NO\textsubscript{x} that remains stored in the catalyst will not be counted in the integral and will thus constitute an error in the measurement. For this reason, a prolonged purge event is always conducted before the start of a storage measurement. The precise definition of a "prolonged purge" would be a purge that lasts of significant duration that there is no longer any exothermic activity in the catalyst.

The chemiluminescent NO\textsubscript{x} analyzer used for the research is calibrated in concentration of NO and the majority of NO\textsubscript{x} emitted by a Diesel engine is in the form of NO. For this reason, the mass flow rate of NO\textsubscript{x} entering the catalyst is based on a flow rate of NO. The mass flow rate of NO is calculated based on total exhaust gas flow rate (air plus fuel) as well as the calculated molar mass of the exhaust gas based on standard methods [48]. Up until this point, the method is fairly straightforward. The main difficulty arises in the fact that during a saturation storage, the outlet NO mass flow rate (or concentration) never reaches the value of the inlet NO mass flow rate (or concentration.) If one were to simply integrate the inlet and outlet values, one could arrive at a NO\textsubscript{x} storage value that were, in theory, infinite. Although it would be convenient to have such a LNT, it is an incorrect method of analyzing the data.
The phenomenon is illustrated in Figure 54 using a selected set of engine data. The figure shows the calculated NO flow rate versus time for a saturated storage cycle. Note that, at the end of the storage period, the catalyst outlet flow rate is not equal to the catalyst inlet flow rate. This "missing" NO\textsubscript{x} is due mainly to reactions in the catalyst which eliminate NO\textsubscript{x} using available hydrocarbons, referred to here as De-NO\textsubscript{x}. Even though it is not observable, the most reasonable assumption is that this NO\textsubscript{x} removal mechanism is constant over the entire storage cycle. This De-NO\textsubscript{x} factor can be calculated and applied to the engine-out NO\textsubscript{x} for use in the NO\textsubscript{x} inlet integration. By using this new catalyst inlet value, labeled "Modified Catalyst In" in the figure, as the artificial catalyst inlet value, it is possible to calculate an accurate value of the mass of NO\textsubscript{x} stored. In the figure, Area 1 denotes the area integration that would give NO\textsubscript{x} stored, Area 2 would be the NO\textsubscript{x} emitted, and Area 3 would be the NO\textsubscript{x} that was eliminated via the HC reduction reaction.

Figure 54: Example of NO\textsubscript{x} Emissions Calculations
When calculating the amount of NO\textsubscript{x} stored during a storage that is not completely to saturation, it is necessary to assume that the De-NO\textsubscript{x} mechanism is constant based on the most recent De-NO\textsubscript{x} value calculated during a saturated storage at an identical operating condition. Experimental evidence indicates that the De-NO\textsubscript{x} adjustment is reasonably constant for a constant operating condition, but changes from operating point to operating point and with increasing sulfur poisoning.

3.9 Exotherm Analysis

In the process of data collection for the storage model, it was discovered that thermocouples imbedded in the catalyst substrate show consistent behavior during the LNT regeneration that correlates with factors such as the timing of reductant breakthrough and the amount of stored NO\textsubscript{x} in the catalyst. The initial discovery was made with only two thermocouple measurements, each 0.5" from the front and back of the catalyst. After the initial discovery, a subsequent set of six thermocouples was imbedded in the channels of the catalyst substrate at 0.5" increments through the 6" long substrate. A photograph of the measurement method is provided in Figure 48. With this measurement set, it is clear that information regarding the spatial and temporal progress of the regeneration of the catalyst is being sensed, as well as information on the amount of NO\textsubscript{x} and oxygen stored on the LNT at the time of the regeneration event. The process of using these temperature measurements to provide useful information regarding the catalyst is referred to hereafter as exotherm analysis.

3.9.1 Theoretical Foundation

The mechanism at work in exotherm analysis lies in the nature of the reactions that take place in the LNT during regeneration. Many of the dominant reactions are exothermic surface reactions, thus, they can be observed through the increase in temperature of the catalyst surface as well as the gas temperature. During a typical regeneration event in a bypass-regeneration system, a relatively low flow rate flow of gas with a high concentration of reductants will be passed through the catalyst. As this gas enters the catalyst, it is used preferentially at the front of the catalyst for the reduction of surface stored NO\textsubscript{x} and oxygen. Since the
reduction of these stored oxidizers is exothermic, there is a rise in temperature of the substrate and gas mixture. As the front sections of the catalyst become depleted of stored oxidizers, reductant begins to reach the downstream sections of the catalyst. These sections behave just as described, consuming reductant at a rapid rate while stored oxidizers are present, and then allowing the supplied reductants to slip rearward as the oxidizers are depleted. By monitoring the temperature of a particular section of catalyst, it is possible to monitor the progress of the reactions in that area of the catalyst. The resulting temperature rise during the phase of NO\textsubscript{x} and oxygen depletion is referred to as the rich exotherm. A similar temperature rise happens when oxygen is reintroduced to the catalyst after regeneration. This temperature rise is referred to as the lean exotherm. If one considers a small section of catalyst, one can write the following energy balance on the cell.

\[ m_{in} h_{in} + \dot{Q}_{\text{reac}} = m_{out} h_{out} + \dot{Q}_{\text{cond}} + m_s c_s \frac{dT_s}{dt} + m_g c_g \frac{dT_g}{dt} \]  

(93)

Where:

\( m_{in} \) = mass flow rate of gas into the catalyst section

\( h_{in} \) = enthalpy of gas entering the catalyst section

\( \dot{Q}_{\text{reac}} \) = rate of heat release due to chemical reactions in the cell

\( m_{out} \) = mass flow rate of gas out of the section

\( h_{out} \) = enthalpy of gas exiting the catalyst section

\( \dot{Q}_{\text{cond}} \) = rate of heat loss of the catalyst section to the surrounding substrate

\( m_s \) = mass of the catalyst section

\( c_s \) = specific heat of the catalyst substrate

\( T_s \) = temperature of the catalyst section
\( m_g = \) mass of the gas in the catalyst section

\( c_g = \) specific heat of the gas in the catalyst section

\( T_g = \) temperature of the gas in the catalyst section

Considering the magnitude of these parameters in relation to each other as well as the actual physical process, the following assumptions are made:

1. The enthalpy terms on both sides can be neglected, since the gas flow rates are very low and the temperature rise across the catalyst cell is relatively small (on the order of 40ºC).

2. The mass of gas in the catalyst section is small compared to the mass of the catalyst. These terms will be assumed to be lumped into the corresponding catalyst substrate terms.

3. The conduction term, \( \dot{Q}_{\text{cond}} \), can be neglected. Provided that the location of the hypothetical catalyst section is near the center of the catalyst, there is little chance for heat loss in the catalyst. Firstly, the substrate is a thin wall ceramic with a relatively high thermal resistance; secondly, the catalyst section is surrounded on all sides by catalyst of nearly the same temperature, which minimizes the conduction due to the low thermal gradient

Based on these assumptions, equation (93) becomes equation (94).

\[
\dot{Q}_{\text{reac}} \propto C_1 \frac{dT_s}{dt} \quad (94)
\]

Where:

\( C_1 = \) a constant representing the \( m_s c_s \) term from above.
At various stages in the regeneration process, different reactions contribute to the heat generated in the catalyst section. For this level of analysis, the exact reaction mechanisms can be ignored and only the net result of the reaction considered. During the rich phase of the regeneration, the dominant exothermic reactions are the reduction of surface stored oxygen and the reduction of surface stored NOx. During this phase, there will also be an exotherm due to the oxidation of any gaseous oxidizers that are present in the rich regeneration gasses. Since these reactions generally all happen at the same time in the catalyst, it is not possible to discern the individual temperature rise from the reduction of oxidizers. (It is possible, however, to arrive at these values through appropriate analysis and experimental methods.) The rich phase leaves the oxygen storage in the catalyst in a depleted state. Upon the reintroduction of oxygen containing gas, the oxygen is re-adsorbed generating a rise in temperature that is related to oxygen storage. This exotherm is referred to as the lean exotherm.

Using a concept of a heating value for each of the reactions described above generates the following equation set.

\[
\dot{m}_{O_2,g} \cdot H_{rxn}^{O_2,g} = C_1 \frac{dT_{s,O_2,g}}{dt} \tag{95}
\]

\[
\dot{m}_{O_2,des} \cdot H_{rxn}^{O_2,des} = C_1 \frac{dT_{s,O_2,des}}{dt} \tag{96}
\]

\[
\dot{m}_{NOx,des} \cdot H_{rxn}^{NOx,des} = C_1 \frac{dT_{s,NOx,des}}{dt} \tag{97}
\]

\[
\dot{m}_{O_2,ads} \cdot H_{rxn}^{O_2,ads} = C_1 \frac{dT_{s,O_2,ads}}{dt} \tag{98}
\]

\[
\frac{dT_s}{dt} = \frac{dT_{s,O_2,g}}{dt} + \frac{dT_{s,O_2,des}}{dt} + \frac{dT_{s,NOx,des}}{dt} + \frac{dT_{s,O_2,ads}}{dt} \tag{99}
\]

Where:
$\dot{m}_{O_2,g} = \text{mass flow rate of gaseous oxygen reduced}$

$H_{rxn}^{O_2,g} = \text{heating value of gaseous oxygen reduction}$

$\dot{m}_{O_2,des} = \text{mass flow rate of oxygen desorbed}$

$H_{rxn}^{O_2,des} = \text{heating value of oxygen desorption reaction}$

$\dot{m}_{NO_x,des} = \text{mass flow rate of NOx desorbed}$

$H_{rxn}^{NO_x,des} = \text{heating value of oxygen desorption reaction}$

$\dot{m}_{O_2,ads} = \text{mass flow rate of oxygen readsoorbed}$

$H_{rxn}^{O_2,ads} = \text{heating value of oxygen readsoorption reaction}$

One last manipulation is made on equations (95) through (98) to get them into a form suitable for using the exotherm information in the context of experimental data. This step is simply combining the $C_1$ term with the heat of reaction terms to yield an equation with a single constant, which can be easily identified from experimental results. The result of this last simplification is found in equations (100) through (103). The values of these new constants can be experimentally determined for a given catalyst without the need to know the physical properties of the catalyst and the heat of reaction of the precise reactions involved.

$$\dot{m}_{O_2,g} = D_{O_2,g} \frac{dT_s}{dt}$$ (100)

$$\dot{m}_{O_2,des} = D_{O_2,des} \frac{dT_s}{dt}$$ (101)

$$\dot{m}_{NO_x,des} = D_{NO_x,des} \frac{dT_s}{dt}$$ (102)
\[ \dot{m}_{\text{O}_2,\text{ads}} = D_{\text{O}_2,\text{ad}} \frac{dT_x}{dt} \]  

(103)

Where:

\[ D_X = \text{combined mass/specific heat/heat of reaction constant for reaction X} \]

3.9.2 A Sample Exotherm

A typical exotherm is shown in Figure 55. The depth of the measurement from the front of the catalyst is shown in the legend. The front section of the catalyst is the first to see at temperature rise, with each section in turn having an increase in temperature. The dashed vertical lines in the figure, labeled A through D, denote the phases of the regeneration. In region A to B, the catalyst is being supplied with 100% carbon monoxide gas. In region B-C, the catalyst is supplied with a short duration flow of carbon dioxide. The carbon dioxide is a buffer between the CO and the air that is injected in the next phase. If the air injection happens immediately after the CO injection, there is some mixing of the CO and air and the front temperature measurement can get distorted due to the temperature rise. This is not necessary, but is simply a convenience for the demonstration. Note that there is a small exotherm in the \( \text{CO}_2 \) phase, which is presumed to be from further formation of barium carbonate beyond what was formed in the rich phase. The final region, from C to D, is the air injection phase. In this phase, air is injected into the catalyst and the lean exotherm from the adsorption of oxygen is measured. As with the \( \text{CO}_2 \) phase, the air injection phase is not necessary for the operation of an LNT. It will be demonstrated in later chapters, however, that this phase can yield some important results and is therefore warranted in many circumstances.
3.9.3 Temperature Measurement System Time Response

One important consideration that needs addressed for this measurement technique is the time response of the sensor. Sheathed thermocouples are used for the measurements, which are essentially very fine diameter thermocouples housed in a thin-walled stainless steel tube. The size of the thermocouple is such that it restricts gas flow through the channel it is placed. The thermocouples are insulated from the stainless steel house by a thermally conducive ceramic material. The desired temperature measurement is the temperature of the catalyst substrate on the other side of the substrate wall. A schematic of the situation is shown in Figure 56. Note that there are a number of thermal resistances separating the thermocouple junction from the desired temperature. Of these thermal resistances, the most critical is the contact resistance between the outside of the thermocouple sheath and the inner wall of the catalyst channel that the
The thermocouple is located within. The only control over this contact resistance was through the proper selection of thermocouple sheath diameter for a snug fit. The diameter that was selected was such that it required the use of pliers to insert a thermocouple down the catalyst channel. It is worth noting that if such a measurement system were to be applied on a vehicle, there could be great improvements in this contact resistance. This improvement would increase the response time of the measurement.

A measurement of the response time of the thermocouples was made to verify that the measurement dynamics were faster than the phenomenon being measured. To measure this somewhat difficult to quantify value, a cross section of a catalyst was fitted with a number of thermocouples at a depth of 1 inch. The channels in which thermocouples were located were sealed with a high temperature silicone sealant to prevent the unwanted entry of fluid. The catalyst section, which was not installed in an exhaust system, was heated using a electric heat gun to a temperature about 40°C above ambient, which is a typical

Figure 56: Schematic of Temperature Measurement Method
magnitude for an exotherm. The catalyst is then subjected to a close approximation of a step input in substrate wall temperature. The step change in wall temperature is introduced by dumping a large volume of cold water on the catalyst, which rapidly cools the catalyst substrate to the temperature of the water. Since the channels containing the thermocouples are sealed, they only communicate with the change in temperature via the temperature of the wall in the adjacent channels. This, of course, is the exact temperature that we are trying to measure with the method, since it is the location of the chemical reactions during the operation of the LNT.

The results from the above described system identification experiment are shown in Figure 57. The average time constant of the measurement, assuming a first order response, is 1.1 seconds. Although this is somewhat slow, it is expected given the nature of the measurement. The minimum time constant of the exotherm temperature rises, as measured by the thermocouples, is 2.2 seconds. A more typical value would be 4 to 8 seconds. Therefore it is necessary to exercise some caution in interpreting dynamic measurements of the catalyst temperatures. This, of course, does not affect the steady-state value of the temperature, thus it does not impact the interpretation of absolute magnitudes of the temperature rise. It is these steady-state measurements which play the most dominant role in the developed control algorithms.
3.9.4 Exotherm Derivatives

Based on Equation (94), it is clear that the rate of temperature rise is proportional to the rate of the chemical reactions occurring in the vicinity of the temperature measurement. However, to use this relation it is necessary to take the derivative of the temperature signal. Since the temperatures rise of the catalyst is relatively slow, on the order of 10°C per second, noise in the thermocouple signal is of great importance. With a proper filter, it is possible to extract the temperature derivatives through the noise. To accomplish the filtering, a fourth order digital low pass filter is used for noise removal with the cut-off frequency at 5 Hz. Since the filtering is applied in post-processing, a bi-directional filtering process is used to cancel the phase lag induced by the filter. After the digital signal processing, the filtered time-domain signal was
differentiated. Typical results are shown in Figure 58. The figure shows the derivatives at each of the six measuring locations.

In some respects, this way of viewing the temperature data provides more insight than the time-domain signal. It is clear, in this particular case, that the reductant flow rate is low enough that each section of the catalyst uses most of the incoming reductant before allowing it to slip back to the downstream sections. This is indicated by the fact that the reaction rate \( (\text{i.e. temperature derivative}) \) of a catalyst section does not begin increasing until the preceding section's reaction rate begins to taper off. The bottom section of the figure shows the post-catalyst air-to-fuel ratio at the inlet and outlet of the catalyst. As shown in the figure, reductant slip, which is indicated in a drop in the post-catalyst AFR, does not occur until the last exotherm derivative has peaked and began to decrease. More discussion on the behavior of the catalyst exotherm derivatives is included in subsequent chapters. Overall, the application of the derivative measurements seem limited largely to laboratory measurements, due to the difficulty in extracting the signal. A non-causal filter can be used in post-processing, however, this is not the case in real time.
3.10 Exotherm Applications

The exotherm measurement technique described above can be used for a number of practical purposes both in the vehicle and in the lab. A sample of these applications is provided in the following subsections. Many of these techniques make up the fundamental measurement set that the control algorithm developed in later chapters rely upon for feedback. Most of the exotherm applications rely only on the magnitude of the temperature rise, thus, the somewhat sluggish dynamics of the measurement do not have an impact.
3.10.1 NO\textsubscript{x} Storage Estimation

The most basic application of the exotherms is the estimation of the amount of the mass of NO\textsubscript{x} regenerated from the catalyst during a regeneration event. Assuming that the catalyst is fully purged of NO\textsubscript{x} during a regeneration, this value is the amount of NO\textsubscript{x} stored during the storage period that led up to the regeneration event. Figure 59 shows data from regenerations for three different operating conditions at various temperatures and exhaust flow rates. For each operating condition, the length of the storage cycle is varied so that the mass of NO\textsubscript{x} stored varies over many different levels. The magnitude of the rich exotherm at each of the six measurement locations is determined and all of these temperatures are summed to give a single value, referred to as the maximum exotherm sum.

Since the rich exotherm includes a temperature rise due to both oxygen storage and NO\textsubscript{x} storage, it is necessary to subtract out the exotherm magnitude that is due to oxygen storage. The contribution of the exotherm due to oxygen storage, with this data, is the projected value of a linear fit of the data at NO\textsubscript{x} mass stored equal to zero. Each of the three data sets shown in Figure 59 is at a different catalyst temperature, and therefore has different levels of oxygen storage. Once normalized by oxygen storage, it is apparent that the plotted results lie very nearly on a straight line crossing through the origin. In this form, there is a linear relationship between the maximum exotherm sum and NO\textsubscript{x} storage that can be extended to different operating points. For these points, the average error is 8.9% in using the temperature to predict NO\textsubscript{x} storage.
This method cannot be applied directly to a vehicle formulated as such. The problem lies in the reliance upon normalizing by the temperature rise associated with the oxygen storage during the rich regeneration. Due the fluctuating operating conditions encountered in the vehicle it would simply not be possible to perform the same type of test performed in the laboratory, where progressively more and more NOx was stored. Fortunately, if a lean phase is provided after the regeneration, it is possible to measure oxygen storage in the catalyst via the lean exotherms. Knowing these parameters, it is possible to correct the rich exotherm for the temperature rise and perform the same type of correlation as above. As discussed in a later chapter, it is necessary to have an adaptive model that tracks the oxygen storage capacity of the catalyst. In this way, effects of catalyst aging on oxygen storage can be compensated for as the catalyst changes.

Figure 59: Temperature Rise Sum Correlation to NOx Stored
3.10.2 Catalyst Deactivation by Thermal Damage

Due to their temperature instability, LNTs are susceptible to deactivation at high temperatures, especially under lean conditions. During normal operation in a Diesel engine, this is not much of an issue due to the relatively low temperature exhaust gas. However, during the require sulfur regeneration events, the required temperatures for desulphation get dangerously close to the temperature that will damage the catalyst. During the testing program conducted for this research, temperatures in excess of 750°C were reached due to a hardware glitch that caused reductant to be injected at the improper time. This reductant caused a large exotherm in the catalyst raising the temperature of the substrate to the point that the NO\textsubscript{x} storage was diminished from 3.2 grams to 1.9 grams after the thermal incident. Figure 60 shows the exotherms of the damaged catalyst for a full storage cycle plotted against the maximum temperature that section of the catalyst reached during the overheating. The sections of the catalyst that were only heated to 600°C showed little or no degradation when compared to there typical values before the overheating. However, the sections that were heated over 650°C show considerable reduction which increases linearly with the maximum temperature.
3.10.3 Sulfur Poisoning Detection

Perhaps the most valuable static exotherm application is for the detection of sulfur poisoning of the LNT. Desulphation of the LNT is unavoidable, there is simply too much sulfur present in the fuel and lubricating oil to completely avoid the issue of sulfur poisoning, even with low sulfur fuels and lubricants. Therefore, it is certain that desulphation is required; however, it is extremely undesirable for a number of reasons discussed earlier. One particularly troubling problem is that desulphation tends to damage the catalyst, such that it does not recover to its un-poisoned condition. Because of the many negatives associated with desulphation, it should be conducted as infrequently as necessary to keep that catalyst function at the required NOx conversion efficiency.
3.10.3.1 Underlying Concept of Sulfur Detection

The method of sulfur detection is fairly straightforward when using the exotherm measurements. Sulfur is stored similarly to NOx in the LNT; therefore, it is expected that it will accumulate towards the front of the trap. As the total level of sulfur increases, its influence should be witnessed further and further towards the rear of the catalyst. The effect of sulfur poisoning is to prevent NOx storage by occupying the base metal storage sites or through deactivation of the precious metals that catalyze the NOx storage reaction. Either of these two factors will cause less NOx storage in a sulfur poisoned area of the catalyst. Moreover, since the sulfur poisoned area of the catalyst is allowing more NOx through to the downstream sections of the catalyst, these sections should see an increase in NOx storage. The first symptom of sulfur poisoning, lower than expected mass of NOx in the poisoned area, would be detected by a lower than expected exotherm towards the front of the catalyst. The second symptom of sulfur poisoning, more NOx stored at the rear of the catalyst than expected, is also detectable by the exotherms through a higher than expected exotherms.

3.10.3.2 Sulfur Poisoning Protocol

Artificial sulfur poisoning was used to accelerate the process of sulfur poisoning of the catalyst. This was accomplished using a bottle of SO2 gas that was bled into the exhaust through a mass flow controller. The SO2 injection point was at the exit of the turbocharger, which allowed sufficient length for mixing to occur. This method of artificial sulfur poisoning was very similar to that of the following reference, which offers justification of the method [49]. Each sulfur poisoning "stage" consisted of a sulfur poisoning cycle followed by an evaluation cycle. SO2 injection only occurred on the sulfur poisoning cycle, which consisted of twenty, 2-minute NOx storage events, with each one followed by a complete purge. The evaluation cycle consisted of a saturation storage so that the maximum NOx storage of the catalyst could be calculated. Both the poisoning stage and the evaluation stage were conducted at an engine operating point of 2000 rpm and 90 ft-lb. The flow rate of added sulfur into the trap was 2.25 grams per hour, which results in 0.75 grams of SO2 reaching the catalyst per sulfur poisoning cycle. For the fuel flow rate of the
engine at this operating point, this amounts to about ten times more sulfur than the amount that is being
delivered via the low sulfur fuel. There is, unfortunately, no way of quantifying the amount of sulfur that is
entering via the lubricating oil. However, the PCV hose was disconnected from the intake manifold, which
should minimize the amount of combusted oil entering the catalyst.

3.10.3.3 SO$_2$ Effect on Efficiency and Trap Capacity

In order to evaluate the efficiency degradation of the catalyst in a way that correlated to the intended use of
the catalyst, it was decided to measure the degradation over a fixed time interval that resulted in a starting
efficiency on par with that required for meeting upcoming emissions standards. This time interval was the
two-minute trapping sequence during the SO$_2$ poisoning stages. This trapping duration resulted in a de-
greened catalyst trapping efficiency of less than 94% for the two minute cycle. By the end of the sulfur
poisoning, this efficiency was degraded to 82%. Figure 61 shows the progression of the efficiency
degradation with increasing sulfur loading. In regenerations 0 through 19 (i.e. SO$_2$ cycles one and two), no
added sulfur was injected, thus the initial drop and plateau is the de-greening of the catalyst. After this
point, sulfur was added continuously. To a first approximation, the efficiency decreases linearly with
increasing sulfur.
The evaluation cycles in between the sulfur poisoning stages allowed for the determination of the maximum NO\textsubscript{x} storage at the operating point tested. Figure 62 shows the calculated maximum trap capacity for each of the evaluation cycles. Note that there is an initial rapid decrease in capacity, from evaluation cycle 1 to cycle 4. After this initial decrease, the maximum NO\textsubscript{x} storage remains fairly constant for the remainder of the evaluation cycles. At first glance, this does not seem to correlate with the results of Figure 61, which shows a constant degradation in storage efficiency. To reconcile this apparent conflict, one must acknowledge that there are a number of ways that sulfur can impact the catalyst, with two being the most dominant. The first is through occupation of NO\textsubscript{x} storage sites by sulfates, which prevent NO\textsubscript{x} storage and result in a loss of storage capacity. A little bit of this is evident in the plot from cycles 4 to 10, but it can not explain the constant degradation in two-minute storage efficiency over these tests. The second factor is that sulfur can interfere with the precious metal sites that are required to facilitate the NO\textsubscript{x}
being adsorbed onto the catalyst. This would not affect the total trap capacity very much, but the efficiency of the storage process would be degraded. Indeed, this is the phenomenon that explains the loss of efficiency with little or no loss in total trap capacity.

Proof that the above mechanism of sulfur degradation is correct can be found in the time-domain NO$_x$ data from the catalyst while it is filling with NO$_x$ during the storage to saturation. Consider, for example, evaluation 4 and evaluation 8 from Figure 62. The calculated mass of stored NO$_x$ for both cases is nearly identical, at 3.48 grams and 3.44 grams respectively. However, the average two-minute trapping efficiencies of these two cases are 91% and 84%, which results in a 1.8 times increase in NO$_x$ emissions over the two-minute period. Figure 63 shows the storage efficiency of the two cases in two different forms. The left hand plot shows the trapping efficiency over the first two minutes, which would correspond to the time period that the average efficiencies are calculated for on the SO$_2$ cycles. Note that the case with higher sulfur exposure has a lower efficiency over the first two minutes. The second plot is a different representation of efficiency, in which it is plotted against the fill ratio of the catalyst. It is clear that, over the entire capacity of the trap, that the sulfur poisoning decreases the storage efficiency. Even with the degraded efficiency, the poisoned trap can store the same amount of NO$_x$, but it takes longer for it to get filled to saturation.
Figure 62: Maximum Trap Capacity at 2000 rpm, 90 ft-lb

Figure 63: NOx Storage Efficiency for Evaluations 4 and 8
3.10.3.4 SO₂ Effect on Exotherm Magnitudes

As suggested earlier, the catalyst exotherm measurements can be used to detect the level of sulfur poisoning in the catalyst. Figure 64 shows the average of the exotherms during the two-minute trapping sulfur poisoning phases for four of the nine sulfur poisoning cycles. The behavior that was hypothesized to occur is the exact behavior measured during the experiments. As shown in the figure, the exotherms in SO₂ cycle 1, with the exception of the very front exotherm, decrease as one moves further back into the catalyst. This implies that the amount of NOₓ stored at the front of the catalyst is greater than at the rear, which is what one would expect. The reason that the front exotherm is slightly lower than the second measurement location is because the particular LNT had already been used, and thus, had already been exposed to some unknown amount of sulfur. Cycle three, shown in the figure, is the first cycle in which sulfur is being injected, and thus constitutes a lightly poisoned catalyst. Note that the next two cases, the sixth and ninth sulfur storage, have a distinctively different character to them. With increasing sulfur exposure, the exotherm at the front continues to be depressed while the exotherms in the middle and back of the catalyst tend to increase. This implies that less NOₓ is being stored in the front of the catalyst, which increases the amount of NOₓ seen by the rear of the catalyst.
Figure 64: Average Rich Exotherms for Four Selected Sulfur Cycles

Figure 65 shows the lean exotherm magnitudes over the same four sulfur poisoning cycles. The fact that there is only a slight decrease in the exotherms implies that the oxygen storage capacity is not affected greatly by the SO$_2$ exposure. It is likely that the sulfur poisoning mechanism that is affecting the NO$_x$ storage efficiency is also impacting the oxygen storage efficiency as well, since they are both catalyzed by the same precious metal sites. The difference is that the concentration of oxygen in the exhaust is so high that the catalyst has a chance to fill to capacity with oxygen. This uptake of oxygen likely lasts only a few seconds, even with the inhibiting effects of the sulfur.
Another way of looking at the exotherm magnitudes is to normalize the exotherm magnitudes by some baseline condition. The baseline condition, in this case, is selected to be that of the first sulfur storage case. This represents the "healthy" condition of the trap. By subtracting the baseline out of each of the cases, the relative changes from the healthy exotherm signature will be more apparent. Figure 66 shows the data processed in this manner. The plot shows that as sulfur exposure is increased, the depression in temperature at the front of the catalyst becomes larger, approaching 10 degrees C. At the same time, the increase in temperature in the back of the catalyst increases by over 5 degrees C. The magnitude of this difference is large enough that a successful fault detection algorithm should be able to be created from these observations. Another way of looking at the average effect of the sulfur poisoning is to perform a linear fit on the six temperatures, which is shown in Figure 67. Note that there is a significant slope change in the data, which is caused by the change in NOx storage distribution.
In this work, a rigorous fault-diagnosis routine is not developed. In lieu of a fault diagnosis routine, an adaptive catalyst storage model is developed in later chapters. This method allows the control strategy to cope with a large amount of sulfur poisoning and still meet the emissions reduction goals. It also serves as a convenient sulfur poisoning detection algorithm, since the variation of the adaptive parameters are due directly to catalyst efficiency degradation. Based on the strong signatures that arise from sulfur poisoning, it is reasonably certain that an algorithm could be developed.

Figure 66: Rich Exotherms for Four Selected Sulfur Cases Normalized by a Baseline
3.10.4 Exotherm Derivatives

Extracting the temperature derivatives directly from the exotherm measurements is difficult, due to the high level of noise present in the experimental measurements. The noise in the unfiltered sample has a low amplitude, but the frequency is such that it completely masks the derivative of the temperature rise that is being sought. By heavily low pass filtering the signal, it is possible to salvage the desired signal from the noise. Since the temperature rise a reasonably low-bandwidth process, there is little loss in the filtering process. Also, since the data is filtered off-line, use of a bi-directional filter is possible which minimizes phase distortion.
Figure 68 through Figure 72 show the exotherm derivatives at a single engine operating point with varying flow rates of reductant. In this case, the reductant is bottled carbon monoxide and the flow rates vary from 0.4 g/s to 2.0 g/s. At the lower flow rates, the derivatives at each measurement location are distinct and separate from one another. Since the temperature derivatives are proportional to the reaction rates in the catalyst, one can infer that each measurement location is able to use the majority of the reductant that it is receiving without letting it slip rearward. As the reductant flow rate increases, the separation of the temperature derivatives decreases. At the highest flow rate, the peaks overlap substantially, which is an indication that the reductant supply is greater than what an individual section can utilize for stored oxidizer reduction. Also shown in the figures is the pre and post catalyst UEGO signals. Note that the timing of the post-catalyst UEGO drop is, in general, near the point that the last temperature measurement derivative begins to decrease.

Figure 68: Temperature Derivatives for CO Regeneration at 0.4 g/s
Figure 69: Temperature Derivatives for CO Regeneration at 0.8 g/s
Figure 70: Temperature Derivatives for CO Regeneration at 1.2 g/s
Figure 71: Temperature Derivatives for CO Regeneration at 1.6 g/s
3.10.5 Laboratory Catalyst Evaluation

In the above applications, the context for exotherm analysis is for in-vehicle methods. However, this overlooks a great many applications that would be suitable for laboratory use. Of particular interest would be quantities related to the rate of reaction of the various reactions that occur in the catalyst. Being able to quickly ascertain the maximum rate of reaction of a catalyst using inexpensive sensors could facilitate the evaluation of catalysts. For the evaluation of catalyst durability, the method allows real-time, non-destructive, spatial measurements of the effect of degradation in terms of reaction rates, NO\textsubscript{x} storage, and oxygen storage. Furthermore, it allows this measurement to be conducted in real engine exhaust. This technique would be helpful in the following research areas: catalyst aging studies, durability studies, catalyst formulation evaluation, and catalyst benchmarking. Features of the method include the following:
non-destructive, inexpensive, real-time, spatial information is acquired, and temporal information is acquired. Many of these properties are taken advantage of in upcoming chapters for the purpose of regeneration model parameter determination.

3.11 Conclusions

In the previous sections, the basic experimental setup and measurement system was provided. The experimental setup that was used for all of the work consisted of basic instrumentation that is available in virtually any automotive test cell. This is important, as it ensures that the method does not rely on expensive, non-standard measurement techniques. By relying on standard measurement systems, the methods become practical for widespread use in the industry. Additionally, the fundamental theory behind exotherm analysis was presented as well as a number of practical applications for exotherm analysis. This technique will be used in the remaining chapters as a basis for an adaptive LNT management algorithm, which relies on the catalyst temperature measurements as the primary feedback sensor.
CHAPTER 4

REDUCTANT DELIVERY SYSTEMS AND SYSTEM INTEGRATION

4.1 Introduction to Reductant Delivery Methods

The traditional method of reductant generation for an LNT is through rich engine operation. The main goal of the bypass-regeneration system is to avoid this method of regeneration, since it has a number of drawbacks. The most basic method of reductant generation for the bypass system is the use of straight Diesel fuel to regenerate the catalyst. Although this method has good performance under certain operating conditions, it can not be applied at low temperatures because of the low activity of the catalyst. A second method that has been reported in the literature is the use of catalytic fuel reformers, which have received a great deal of attention with the recent popularity of fuel cells. This technique is an excellent source of reductants, but has liabilities in cost and dynamic response. A third technique is the use of plasma reformers, which can be used either stand-alone or in conjunction with a catalyst bed to increase yields of hydrogen. This method also suffers the drawback of increased cost, significant power consumption, and poor dynamic response.

The catalytic and plasma methods were described in the literature review. The first method, Diesel fuel injection, is discussed in the following sections, with experimental results generated by the author. In addition to these three methods, a fourth method was developed during the project which appears to be a novel concept. This concept, referred to as flame reforming, involves using rich combustion to produce the desired carbon monoxide, hydrogen, and lighter chain hydrocarbons. This method offers exceptional dynamic response and low cost at the expense of decreased efficiency when compared to the other
Furthermore, the method offers a number of synergies to the management of the aftertreatment system.

### 4.2 Diesel Fuel Regeneration

Regeneration with straight Diesel fuel would be the preferred method of regeneration, as it has the highest possible efficiency of any method considered. In all of the other methods, some of the energy content of the fuel is lost in the conversion of Diesel fuel to other species. With Diesel fuel regeneration, the entire energy in the fuel is available for the reduction of stored NOx. The experimental setup used for the Diesel LNT regenerations relied on the OSU atomizer for fuel delivery. The atomizer delivered the atomized fuel in the center of the exhaust pipe directed at the front face of the catalyst. This configuration allowed the Diesel fuel droplets and/or vapor to mix with the carrier gas flow in the inlet cone before entering the catalyst. Because of the relatively high density of Diesel vapor and the even higher density of the liquid droplets, the volume of Diesel fuel is generally not high enough to carry itself through the catalyst. This results in the Diesel fuel collecting in the inlet cone during the injection period. When the exhaust gas flow resumes through the catalyst, the fuel is rapidly pushed through the catalyst. Because of the high flow rate of exhaust gas, the fuel only has a brief time reduce the NOx in the LNT. This results in poor NOx regeneration and high levels of hydrocarbon slip under all conditions.

A solution to the above problem is to use a low flow rate of gas to push the Diesel fuel through the catalyst, which is referred to as carrier gas. The preferred source of this carrier gas, for both efficiency and system cost, would be from the exhaust stream. This could be implemented by allowing position control of the bypass valve such that it could remain slightly opened to allow a low flow of exhaust through the catalyst. Alternatively, an two-position type valve could be used in which the valve was not completely sealed in the closed position, or through the use of a control valve similar to a conventional EGR valve. This solution of using exhaust gas is attractive because the engine exhaust is already partially depleted of oxygen. The oxygen in the carrier gas consumes some of the fuel that is intended for regeneration, which is an undesired
effect. Additionally, the exhaust gas is at a high temperature, and therefore less dense. Therefore, for a
given volume of gas, there will a much lower mass of oxygen in the exhaust gas.

The above solution was not implemented for the series of tests evaluating the performance of Diesel fuel
for regeneration. Instead, a flow of atmospheric air was used as a carrier gas. Air was used because it
allowed for precise control and measurement of the amount of carrier gas entering the catalyst. The air was
introduced at the location of the butterfly valve. In this position, the air can scavenge out most of the
Diesel vapor after the fuel injection. This scavenging effect was found to reduce the hydrocarbon
emissions upon reintroduction of the exhaust gas flow. If this technique was used in-vehicle, it would
require either a small air pump or perhaps the use of pressurized air from the compressor of the
turbocharger.

Two different catalyst configurations were used in the Diesel regeneration experiments. The first is simply
an LNT with no additional catalysts. For reasons discussed below, this configuration was augmented by a
1.25 L oxidation catalyst located immediately in front of the LNT. The distance between the rear face of
the DOC and the front face of the LNT is approximately 0.5". A schematic of these two systems is
provided in Figure 73.
4.2.1 LNT Diesel Regenerations

The first set of Diesel regeneration experiments was performed on an LNT with no oxidation catalyst. The regeneration parameters that were evaluated were the fuel flow rate, fuel injection duration, and carrier air flow rate. This was necessary because there is a trade-off between the fuel flow rate and the carrier gas flow rate. From a control standpoint, it is preferable to have as low of transport delay as possible from the point of injection to the rear of the catalyst. This makes the closed-loop control of the process much easier to implement. If one considers the same situation from an efficiency standpoint, it is desirable to have as low of a carrier flow as possible, since it unnecessarily consumes reductant that would otherwise be used for NOx reduction. In terms of fuel rate, a low flow rate of fuel would be desirable because it slows down the regeneration process, making it easier to control. A high flow rate of fuel shortens the regeneration period, which is beneficial from a systems standpoint. Naturally, a compromise between all of these competing factors must be found. Note that these factors apply equally to the DOC-LNT system discussed in the following sections.
A study of air rate and fuel rate variation was completed at three different fuel settings and three different air rates. Some of the results are shown in Figure 74. The figure shows the results of some of the regeneration parameter sweeps in which fuel flow rate, air flow rate, and injection duration are varied. The x-axis is simply the number of different sets of parameters that were evaluated. For each set of parameters, three to five regenerations were performed to yield good results. The y-axis of the figure shows the minimum concentration of NO\(_x\) after the regeneration event. For reference, the inlet NO\(_x\) concentration was approximately 275 ppm. In the first group of experiments, labeled A, there is only a slight increase in the recovery NO\(_x\). Based on the regeneration parameters, all of these cases were expected to be good, which is indicated by the circles in the legend. At the end of this set of parameter changes, there were two trials which, on the basis of the UEGO signal, were expected to be bad. This is generally because the amount of fuel injected is too little. These points are denoted by asterisks and, as shown in the figure, do not have increase recovery NO\(_x\). Because of the way that the parameters are varied, the next set of parameters led to an excess of fuel, thus they would expected to have good NO\(_x\) recovery. However, in each of the experiment sets, the regeneration performance of the "expected very good" points are worse than the last few points of the previous set. In most of the cases, there is a step increase in the recovery efficiency after the points which were expected to be bad. The cause of this deactivation was coking of the Diesel fuel on the catalyst substrate. It was found that in the "expected bad" cases, that the temperature rise of the front of the catalyst was fairly low because of the regeneration parameters. This appears to promote coking of the catalyst substrate due to the deposition of Diesel fuel on the catalyst substrate.
Attempts were made to recover the efficiency through exposing the catalyst to high temperatures. These attempts had no effect on the performance of the catalyst. The catalyst was then removed from the test rig and disassembled for inspection. Just as suspected, the face of the catalyst was covered with black coke deposits. The coking was so thick around the periphery of the catalyst that it was blocking the channels of the catalyst. A photograph of the coked catalyst is shown in Figure 75. The coking was removed with a lengthy cleaning with compressed air. The cleaning removed all visible traces of the coking from the catalyst, such the entrance and exit of the catalyst were the same color. The catalyst was then remounted in the can and installed on the engine for a follow-up test. The performance of the trap was helped very little by the cleaning, thus it was hypothesized that the surface of the catalyst must be masked by a thin layer of carbon, preventing the adsorption of NOx. After this experience, it was decided to try an alternative system with a DOC located in front of the LNT.

Figure 74: Loss of Efficiency During Diesel Regenerations
4.2.2 DOC + LNT Diesel Regenerations

Based on the above experience with the LNT only system, a 1.25L oxidation catalyst was added directly in front of the LNT. This shielded the more sensitive LNT from the possibility of condensing Diesel fuel and coking. Moreover, the DOC could endure a higher temperature rise, which allowed higher flow rates of carrier air without fear of overheating the front part of the LNT. By using a higher air rate, it was ensured that the coking problem encountered with the LNT only system would not occur. Indeed, during the testing
of this system, no coking was observed on the front of the DOC and no degradation of efficiency was witnessed.

4.2.2.1 Impact of Temperature on DOC + LNT Diesel Regenerations

The temperature of the catalyst has a dramatic impact on the regeneration performance with Diesel fuel. Figure 76 through Figure 80 shows the exotherm measurements for Diesel fuel regenerations at average temperatures of 250°C, 285°C, 310°C, 340°C, and 380°C. In the first case, there is very little regeneration activity in the catalyst, as indicated by the low temperature rise in the second through sixth thermocouple. On the other hand, the front exotherm shows a steady, steep increase in temperature. This is a result of the oxygen in the carrier gas flow oxidizing some of the Diesel fuel at the front of the catalyst. If the system were warmer, the Diesel oxidation catalyst located immediately upstream of the DPF would have served this function. However, the oxidation catalyst that was used did not have very good low temperature activity. It is to have a more active Diesel oxidation catalyst to adsorb this large exotherm, which is potentially dangerous for the LNT. As the temperature increases, the magnitude of this temperature rise decreases as the oxidation catalyst becomes more active and removes more of the gaseous oxidation from the carrier gas.

In the subsequent figures, the catalyst temperature is higher and the exotherms begin to look more favorable as the rate of the temperature rise increases substantially. Although the catalyst can be regenerated as low as 285°C, it is not practical to do so for a number of reasons. The first reason is that it would take a prohibitive amount of time to complete the regeneration. The regenerations for the three lowest temperatures do not reach completion before the regeneration fuel is shut off to prevent thermal damage to the catalyst. Regenerations of greater than thirty seconds begin to have a considerable impact on the control, especially on driving conditions with high average NOx levels. The second factor is that a significant amount of hydrocarbons slip through the catalyst unreacted at low temperatures, which is discussed further in the following subsection. As shown in Figure 79, once the catalyst reaches a
temperature of about 340°C, Diesel regeneration begins to become practical with respect to the duration. At 385°C, the regeneration of the catalyst looks nearly identical to that of a carbon monoxide regeneration.

Figure 76: Exotherms for Diesel Regeneration at 250°C
Figure 77: Exotherms for Diesel Regeneration at 285°C
Figure 78: Exotherms for Diesel Regeneration at 310°C
Figure 79: Exotherms for Diesel Regeneration at 340°C
4.2.2.2 Hydrocarbon Slip

Even if the LNT is at an appropriate temperature, hydrocarbon slip is always an issue when using Diesel for regeneration. Because the regeneration gas is extremely rich, slipping even a small volume of regeneration gas results in a relatively large mass of unburned hydrocarbon entering the exhaust. In this context, the relative is defined in comparison to the 0.075 g/mile hydrocarbon standard, which affords very little room for hydrocarbon slip. Figure 81 shows the pre-catalyst and post-catalyst UEGO signals for a LNT during a Diesel fuel regeneration. Once the post-catalyst UEGO transition occurs, the fuel injection is stopped. Despite this, there is a significant drop in the post-catalyst UEGO signal, which is due to the transport delay from the injection point and the post-catalyst measurement location. This results in an increase in hydrocarbon emissions an order of magnitude greater than the engine-out concentration. Furthermore,
because the slip is primarily Diesel fuel, it is not handled as effectively by an oxidation catalyst. Even after the transport delay is compensated for, some of the reductant still slips through the catalyst.

![Air to Fuel Ratio for Diesel Regeneration](image)

**Figure 81: UEGO Response for a High Temperature Diesel Fuel Regeneration**

### 4.2.3 Conclusions for Diesel Fuel Regeneration

Considering the above experimental data and substantially more that was not presented, it is concluded that Diesel fuel regeneration is not practical for an intended Tier 2 aftertreatment system with the catalyst used in the investigation. Although it offers the lowest theoretical fuel economy penalty and has very low system cost, it has a number of problems that make it unattractive. These problems are summarized below:

1. **Long Regeneration Time at Low Temperatures** - The performance below 350°C is poor with regard to the time required for regeneration. With the system tested in the lab, complete
regeneration at very low temperatures was impossible due to the temperature increase at the front of the LNT rising to levels that are damaging to the LNT.

2. High Hydrocarbon Slip at Low and Middle Temperatures - The hydrocarbon slip from the catalyst at low to middle temperatures is also poor. Because of the stringent hydrocarbon standards the vehicles must meet for Tier 2 emissions, it is necessary to very tightly control hydrocarbon emissions.

3. Minimal Fuel Economy Advantage - Although the fuel cost of a Diesel regeneration may be half that of another regeneration technique, the amount of fuel used in regeneration of a bypass system is small compared to the engine's fuel consumption. Therefore, this seemingly large advantage turns into a rather small advantage in terms of fuel penalty.

There are a few possible scenarios in which Diesel regeneration might be a valid method:

1. High Exhaust Temperature Applications - If the exhaust temperature could be maintained above approximately 350ºC, then this method would prove acceptable. Although this is clearly not the case for passenger vehicles, it may be the case for some stationary engines or certain heavy-duty vehicles.

2. Applications with Less Stringent Hydrocarbon Standards - If the hydrocarbon standards for the given application were not as stringent, it might allow the use of Diesel fuel regenerations.

3. Improved Catalyst Formulations - The LNTs used for the Diesel regeneration studies were procured in 2001, thus, they are far from state of the art formulations. Additionally, if the catalyst were designed from the start to be used for Diesel regeneration, it is likely that some of the above problems could be reduced or eliminated.

4. As a Secondary Method - There are many driving conditions in which the catalyst temperatures would be in the range of which Diesel fuel regeneration can be successfully conducted. If the
negative aspects can be tolerated under these conditions, then it is the most fuel efficient way to regenerate the LNT. Therefore, it could be used as a secondary method.

4.3 Flame Reforming

The idea of a "flame reformer" appears to be a novel concept for LNT management. The term is coined to describe a combustion device which purposefully runs at a rich air-to-fuel ratio to produce carbon monoxide, hydrogen, and lighter chain hydrocarbons than the original fuel. The principal advantage of this method is that it can have extremely fast dynamics and a low system cost when compares to other methods of reforming. The concept flame reforming is discussed in great detail in the following sections, with experimental results presented on the ability of a flame reformer to successfully regenerate an LNT.

4.4 Theoretical Flame Reformer Output

It is possible to calculate the upper bound theoretical output of a flame reformer assuming ideal combustion and equilibrium in the exhaust products. This calculation was made based on the methods presented in [48]. With this analysis, the products of the reaction are assumed to be CO₂, H₂O, CO, H₂, and N₂ and the equilibrium constant between H₂O, CO, CO₂, and H₂ via the water gas shift reaction is assumed to be 3.5. With these assumptions, the composition of the flame reformer output is described by a simple set of equations containing such parameters as the H/C ratio of the fuel and the fuel-air equivalence ratio. The result of the calculation is shown in Figure 82. From the theoretical results, it is clear that reasonable amounts of both hydrogen and carbon monoxide could be expected from this method. At a fuel-air equivalence ratio of 1.5, 12% CO and 4% H₂ can theoretically be produced.

Figure 83 and Figure 84 show the theoretical mass flow rate outputs of CO and H₂ from the flame reformer for fuel and air inputs specified by the x and y axes. The bold lines clipping the contour lines represent fuel-air equivalence ratios of 1.0 (upper line) and 2.0 (lower line) which are the limits over which such a device would be expected to operate. Note that for a Diesel fuel input of 1.0 g/s, approximately 1.8 g/s of
CO could theoretically be produced, along with 0.04 g/s of H₂. Through the heating values and mass flow rates of the inlet fuel, number 2 Diesel, and the useful outputs, CO and H₂, it is possible to calculate an efficiency map for the theoretical reformer. This efficiency map is shown in Figure 85. Since this is ideal combustion, it is intuitive that the efficiency varies from 0 at stoichiometric to 50% at phi = 2. From this theoretical investigation, the feasibility of the flame reformer concept is demonstrated.

Figure 82: Theoretical Flame Reformer Output
Figure 83: Theoretical Flame Reformer Carbon Monoxide Output
Figure 84: Theoretical Flame Reformer Hydrogen Output
Although a theoretical flame reformer is a good thought experiment, reduction to practice is the true test. A prototype flame reformer was designed and constructed for evaluation for LNT management. The target of the design was to be able to process 0.5 g/s of fuel, which will result in enough carbon monoxide and hydrogen to regenerate the 2.5L LNTs used in the research in an acceptable time. Beyond this target, the design was intended to be reasonably compact and to be compatible with the systems on a conventional vehicle, despite the fact that it is a first generation prototype.
4.5.1 Flame Reformer Design

An annotated picture of the prototype flame reformer is shown in Figure 86. The prototype design is housed in a length of 2.5" OD x .050" wall stainless steel tubing that is ten inches in length. At one end of the tube, a prototype version of the OSU atomizer is located which injects fuel in three locations tangentially to the radius of the tube. The air is introduced in a similar tangential fashion, such that it causes a significant swirling motion inside the flame reformer. In having the fuel and air directed against each other, it is possible to achieve counter-flow mixing, which provides good mixture preparation prior to combustion. Approximately two inches downstream of the introduction of the air and fuel, a Diesel glowplug is located which serves as an ignition source. The glowplug serves a second function as a buffer body flame anchor to foster good combustion. After the ignition source, there is approximately 5 inches of empty tube which serves as a combustion chamber before the combustion gasses exit though the 0.5" OD tube at the end of the flame reformer.

Figure 86: Annotated Flame Reformer Photograph
4.5.2 Flame Reformer Output

The flame reformer was tested over a range of fuel and air flow rates to evaluate its operating regime as well as the output of the device. Because of the high levels of CO emissions and unburned fuel, it was not possible to directly measure the output of the device with direct emissions sampling. Instead, the reformer output was diluted with a fixed flow rate of air and this diluted sample was measured and the actual output of the reformer was back calculated knowing the inlet flows.

The upper operating regime of the device is limited mainly by thermal considerations. Heat is dissipated from the device by natural convection and radiation, thus it is susceptible to overheating at high combustion loads. The problem of overheating was localized at the 0.5” exit tube, since it has a high velocity, high temperature gas passing through it and a relatively low surface area to promote heat dissipation. If higher outputs were required, then the implementation of a slightly different design would alleviate this problem. The lower operating regime was not definitively established, since the fuel flow rates were low enough not to be practical for LNT regeneration and the tests were not conducted. Overall, the burner readily ignites and had acceptable performance with air flow rates of 2 to 7 scfm.

The emissions data from all of the test conditions were found to lie on the same characteristic curves when plotted versus fuel/air equivalence ratio. The relevant components for LNT management are shown in Figure 87 through Figure 90. Note that the concentration of H2 was not measured directly, but was estimated based on standard analysis methods presented in [48]. The results for CO and H2 agree with the theoretical results up to a fuel/air equivalence ratio of around 1.3, where the CO and H2 begins to plateau. This effect is due to the increasing presence of unburned fuel in the output, which contains the "missing" carbon and hydrogen that would go into the formation of CO and H2 in ideal combustion. Also note that there is a non-negligible concentration of O2 in the flame reformer output which must be accounted for. This unwanted oxygen will consume CO and H2 when it is exposed to a catalyst.

As will be discussed in later chapters, the presence of the hydrocarbons in the flame reformer output will require special consideration in the application of the method to LNT management. The hydrocarbons,
based on qualitative observations, have been reduced in chain length from pure Diesel and are better used by the LNT than straight Diesel. However, a fraction of the hydrocarbons generally will slip through the catalyst unreacted and contributed to the HC emissions of the vehicle. It is likely that the HC emissions could be improved somewhat with a different flame reformer design, but this is left for future work.

Figure 87: Prototype Flame Reformer CO Concentration
Figure 88: Prototype Flame Reformer H$_2$ Concentration
Figure 89: Prototype Flame Reformer THC Concentration
Based on these curve fits of the experimental data, it is possible to construct a flame reformer output map that relates inlet fuel mass flow and air mass flow to an output mass flow of a particular species. These maps are provided in Figure 91 through Figure 94. Note that maximum CO mass flow rate of 1.06 g/s occurs at the peak fuel flow rate in the plot, which, as expected, is lower than the 1.8 g/s predicted by the theoretical calculations above. Maximum hydrogen production is .017 g/s, which again, occurs at the maximum fuel flow rate on the map. Looked at in a different way, the flame reformer produces 1.06 g CO / g fuel and .017 g H₂ / g fuel at maximum efficiency. It is also worth pointing out that, although the mass flow rate of hydrogen is quite low because of its low molecular weight, the heating value is an order of magnitude higher than carbon monoxide. Because of this, a small mass of hydrogen has a substantial reducing ability.
Figure 91: Prototype Flame Reformer Output Summary
Figure 92: Prototype Flame Reformer CO Map
Figure 93: Prototype Flame Reformer H₂ Map
An obvious criticism this method of this reductant production is the loss of efficiency that comes from destroying better than half of the input fuel energy in combustion. The efficiency of the flame reformer was calculated based on equation (104). In this definition of efficiency, only CO and H\textsubscript{2} are considered in the numerator as desired products of the process. Although hydrocarbons can be used for LNT regeneration, they are not as desirable as CO and H\textsubscript{2} and are included as a loss in efficiency. Additionally, it is necessary to adjust for the effect of oxygen which will consume reductant. This is done by reducing the concentration of CO based on CO-O\textsubscript{2} stoichiometry. The result of this calculation is shown in Figure 95. Based on this definition of efficiency, the peak conversion is around 28% and at a fuel-air equivalence ratio of 1.55. Referring to Figure 91, this corresponds to the point where the CO and H\textsubscript{2} emissions begin to plateau, which makes intuitive sense.
\[
\eta_{FR} = \frac{\dot{m}_{CO,\text{out,adj}} \cdot Q_{HHV,CO} + \dot{m}_{H_2,\text{out}} \cdot Q_{HHV,H_2}}{\dot{m}_{\text{fuel,in}} \cdot Q_{HHV,fuel}} 
\]

(104)

Where:

\( \eta_{FR} \) = efficiency of flame reformer

\( \dot{m}_{CO,\text{out,adj}} \) = adjusted mass flow rate of CO out of the reformer

\( Q_{HHV,CO} \) = HHV of CO = 10.1 MJ/kg

\( \dot{m}_{H_2,\text{out}} \) = mass flow rate of H\(_2\) out of the reformer

\( Q_{HHV,H_2} \) = HHV of H\(_2\) = 142.0 MJ/kg

\( \dot{m}_{\text{fuel,in}} \) = mass flow rate of fuel into the reformer

\( Q_{HHV,fuel} \) = HHV of fuel = 46.1 MJ/kg for Diesel
4.5.3 Flame Reformer Particulate Matter Emissions

Unfortunately, characterization of the soot emissions was not possible with the current facilities; therefore, the only results that can be provided are qualitative. Visually, there was soot formation at the lower air-to-fuel ratios. At higher air-to-fuel ratios, there was no visible soot formation, however, a damp paper towel placed in the burner output gasses revealed the presence of soot. Regardless of the type of hydrocarbon fuel, one would expect to get various amounts of soot for rich combustion, even in a premixed flame. Diesel fuel, of course, is certainly not an exception to this rule, and the presence of droplets, even if very small, would only augment the production of soot. Given the low flow rate of fuel, it is not clear if the soot emissions would have a major impact on the cumulative particulate matter emissions of a vehicle.
If it turns out that particulate matter is a problem, there are at least three methods of alleviating the problem. The first method is to locate the Diesel particulate trap downstream of the LNT system. It would then be capable of trapping any particulate matter from the burner, just as it does for the engine-out particulate matter. This method would require the use of some external DPF regeneration method, perhaps with the flame reformer, since the DPF could not be regenerated through the LNTs using the engine. The second method would be to place the DPF before the LNT, which, if coated with a catalytic coating, could take the place of the oxidation catalyst which might be in this position. This method has the advantage of allowing engine-based regeneration, as well as the reduction of trapped soot by NO₂. Furthermore, this method allows the flame reformer used for the LNT management to be used for DPF regeneration with no additional hardware. The final method would be to fit the flame reformer with a small Diesel particulate filter. Given the low flow rates and low soot loadings, the filter could be made quite small. Regeneration would clearly not be an issue, since the flame reformer is capable of generating temperatures in excess of 1000°C, which is well above the ignition point of soot. From a system synergy standpoint, the second option would be preferred, however, the third option allows for more flexible placement of the DPF.

4.6 Flame Reformer Model

Based predominantly on the data described above, a model for the flame reformer was constructed for use in the LNT simulator. The model consists of the steady-state maps shown above as lookup tables. To account for the dynamics of the flame reformer startup and shutdown, a simple first order time constant is applied to match the experimental data. This implementation, although quite basic, provides the level of detail required. In addition to the flame reformer maps, the model also allows the flame reformer to function in a mode where it is not combusting. In this mode, the flame reformer is delivering unburned fuel and air rather than combustion products.
4.7 Flame Reformer for LNT Management - Experimental Results

A series of tests was conducted to determine the ability of the flame reformer to successfully regenerate the NO\textsubscript{x} from an LNT. The test setup was much the same as for the Diesel or carbon monoxide experiments, in which the regeneration gas is injected upstream from the catalyst with the exhaust flow entirely diverted. For these experiments, the LNT was preceded by a 1.25 L oxidation catalyst. The catalyst was mainly in place for convenience, as it served as a buffer between the flame reformer and LNT in the case of problems with the flame reformer. It has the added benefit of oxidizing any free oxygen in the flame reformer gas stream which tends to distort the front exotherm of the LNT by generating a constant temperature rise. In a vehicle application, it would not be necessary to have the DOC ahead of the LNT, provided that the front exotherm measurement was not required and the thermal considerations were not necessary. The goals of the tests were:

1. Evaluate the ability of the flame reformer to regenerate the LNT at all temperatures.

2. To assess the fuel required by the flame reformer for LNT regeneration.

3. To collect data for modeling of the flame reformer regeneration process.

Successful NO\textsubscript{x} regenerations were achieved with flame reformer down to a temperature of 225°C, which is roughly the lower limit one would expect in a warmed-up vehicle during normal driving conditions. Regenerations are possible at lower temperatures, but with the particular catalyst used in the experiments, the reaction rate at low temperatures is low, even for carbon monoxide only regenerations. This low reaction rate results in long regenerations with low reductant flows and high amounts of HC slip. This problem would have to be addressed with the catalyst formulation. This long regeneration behavior was present even for bottled carbon monoxide gas regenerations, and therefore seems to be a deficiency of the catalyst rather than of the flame reformer.

The flame reformer shows an interesting behavior in the hydrocarbon slip during regeneration. The hydrocarbon slip will remain at a low value while the catalyst is consuming all of the reductant that it is
supplied. As the oxidizer stores of the catalyst are depleted and the reductant supply is greater than the usage, the HC slip increases rapidly to the inlet concentration from the flame reformer. This phenomenon is shown in Figure 96. The top plot shows the hydrocarbon slip during the regeneration while the bottom shows that the timing of the end of the post catalyst AFR plateau corresponds to the start of the rise in hydrocarbon emissions. In general, carbon monoxide slip would occur shortly after hydrocarbon slip. The data for the figure was a regeneration that at 320ºC. To summarize this effect, there are two levels of reductant slip that can be expected. The first level, which is lower than the second, occurs regardless of the state of the stored oxidizer. The hydrocarbons that comprise this source of slip are hypothesized to be hydrocarbons that are not reactive enough to participate in the stored oxidizer reactions for the current temperature and space velocity conditions. The second level of hydrocarbon slip is essentially the amount of hydrocarbons that the flame reformer is putting out. Once the oxygen stores are eliminated, the hydrocarbon passes through the catalyst mostly untouched. Under closed-loop control, this second mode of hydrocarbon slip should not be encountered. The first mode, however, is unavoidable.
The ratio of the average hydrocarbons during the AFR plateau and the hydrocarbon concentration representing the inlet concentration (i.e. with the oxidizer mostly depleted) varies considerably with temperature. At higher temperatures, the level during the AFR plateau is less than 10% of the inlet concentration while at lower temperatures it could be as much as 60%. This demonstrates that the ability of the catalyst to utilize the hydrocarbons in the flame reformer output improves dramatically with increased temperature. This type of behavior is expected, given the dependence of catalytic reactions on temperature. This phenomenon led to the definition of reactive and non-reactive hydrocarbons for LNT regeneration. The ratio of the average low-level plateau THC concentration and the high-level plateau concentration of THC is the non-reactive fraction of the hydrocarbons. The fraction of reactive hydrocarbons is one minus the non-reactive hydrocarbon number. A plot of the reactive hydrocarbon ratio is shown in Figure 97. The general trend is an increasing of the amount of reactive hydrocarbons, where above approximately 350ºC.
more than 95% of the hydrocarbons are able to be used by the catalyst. The higher the reactive fraction, the better the ability of the LNT to use the hydrocarbons that are present in the reformer output.

![Flame Reformer Reactive Hydrocarbons](image)

Figure 97: Flame Reformer Reactive Hydrocarbons

Given the dependence of the flame reformer hydrocarbon output on the fuel-air equivalence ratio, there is a significant increase in hydrocarbons with increasing equivalence ratio. Since a significant portion of the hydrocarbons supplied by the flame reformer are unused at low temperatures, it is important to consider this in the selection of the flame reformer operating point during a regeneration. A flame reformer operating point with low hydrocarbon emissions would be required for regenerations at low temperatures. This requires a lower flow of fuel, which in turn creates a lower flow rate of reductants. However, since the rate at which the catalyst consumes reductants is limited at low temperatures, this is not much of a limitation.
Beyond the ability to partially mitigate THC emissions with the selection of the flame reformer operating point, they can be further controlled using a clean-up oxidation catalyst. A clean-up catalyst is an oxidation catalyst located at the back of the LNT system. During a regeneration, reductant slip is mixed with the lean exhaust and can be partially oxidized by the clean-up catalyst. Figure 98 shows the maximum hydrocarbon emissions after the clean-up oxidation catalyst for three different fuel rates at a constant flame reformer air input. In all of these cases, the catalyst was over regenerated; therefore, the hydrocarbon slip from the catalyst is approximately equal to the raw output of hydrocarbons from the fuel reformer. As the temperature of the catalyst increases, the ability of the clean-up catalyst to control the hydrocarbon emissions increases. By the time the catalyst reaches 345°C, virtually all of the hydrocarbon slip from the catalyst is removed. Also note that in the case of the lower fuel flow rate, the concentration drops to zero at a earlier temperature, which is beneficial. Since a regeneration can be fairly quick, this elevated amount of hydrocarbons will only be emitted for a few seconds during the regenerations. Furthermore, this is a worst-case scenario, in which the catalyst is over regenerated.
4.8 Comparison of Regeneration Methods

The four regeneration methods discussed in this chapter each have a number of advantages and disadvantages. A comparison of these methods is made to demonstrate the method developed during this research project, flame reforming, is a viable alternative to the other methods. Each of the methods will be evaluated in the following areas:

1. Dynamic Response - This includes both initial start-up time as well as the warmed-up response time.
2. Efficiency of Reductant Production - This is simply the fraction energy content remaining in the reductant from the original fuel. This includes electrical energy usage, as electrical energy production in a vehicle is a relatively inefficient process in terms of fuel consumption.

3. System Integration - This attempts to factor in the ability of a system to fit into an existing vehicle in terms of packaging as well as the need for auxiliary components.

4. System Costs - This is the relative cost of one method to another. Although this is difficult to put an exact number, it must be addressed given the importance of cost in automotive manufacturing.

5. Synergy with Other Systems - The ability of the system to provide other synergistic benefits to other systems in the vehicle. An example of this would be the ability of a flame reformer to function as a heater for rapid catalyst light-off during cold starts.

6. Scalability - The regeneration system must also be scalable for application to different size LNTs. For passenger car application, the LNT can be on the order of 2.5 L. For a Diesel bus application, the LNT may be as large as 14 L.

The factors listed above are the main motivating forces behind the development of the flame reformer. The following table summarizes the author's evaluation of each of the technologies ability to meet the six criteria above, based on the material available in the literature. From this qualitative comparison, the clearest advantages of the flame reformer compared to the other systems are dynamic response, system cost, and system synergies. The dynamic response and scalability of the system is critical secondary impact on the cost of the system. With poor dynamic response, the regenerated system must be brought offline longer to wait for the reductant deliver system to ramp up. If the system scales poorly to higher flow rates, then it becomes difficult to apply to large catalyst systems for heavy-duty vehicles. These factors results in the regenerated LNT being brought offline for a long period of time, in some cases, approaching the storage time of the second catalyst. This can lead to significant increases in the catalyst volume requirement, since the entire system is not being used for a significant period of time.
Table 6: Comparison of Reductant Delivery Systems for LNT Management

<table>
<thead>
<tr>
<th>Dynamic Response</th>
<th>Diesel Injection</th>
<th>Catalytic Reformers</th>
<th>Plasma Reformers</th>
<th>Flame Reformers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Efficiency of Reductant Production</td>
<td>very high (&gt; 0.1 sec.)</td>
<td>very low (≈ 20 sec)</td>
<td>very low (≈ 10 sec)</td>
<td>high (&gt; 1 sec)</td>
</tr>
<tr>
<td>System Integration</td>
<td>easy</td>
<td>moderate</td>
<td>difficult</td>
<td>moderate</td>
</tr>
<tr>
<td>System Cost</td>
<td>lowest</td>
<td>high</td>
<td>high</td>
<td>low</td>
</tr>
<tr>
<td>System Synergies</td>
<td>very few</td>
<td>few</td>
<td>few</td>
<td>many</td>
</tr>
<tr>
<td>Scalability</td>
<td>high</td>
<td>low</td>
<td>low</td>
<td>moderate</td>
</tr>
</tbody>
</table>

4.9 LNT System Design

Based on the knowledge gained over the course of the research project, it is possible to design an LNT system around the flame reformer that offers advantages over the system that was evaluated in the laboratory. This chapter covers the qualitative aspects of designing a system and the supporting components for a system that could be implemented in practice. It is this improved system that will be used in the remaining sections to apply the control and diagnostics techniques that have been developed and alluded to thus far. This section covers the sizing of the components, the physical layout of the system, the required auxiliary systems, and the necessary sensor set.

4.9.1 Target Application

In order to facilitate comparison with conventional, engine-based LNT management, the selected target vehicle is based on the vehicle from a series of published papers on engine-based regeneration. The series of papers, discussed in the literature review, describe the performance of an LNT system on a 1.9 L Diesel engine in a 1540 kg vehicle. The aftertreatment system consists of a 1.34 L close-coupled LNT, a 2.5 L
underbody LNT, and a 2.5 L DPF at the rear of the system. Regeneration of both the LNT and the DPF were accomplished using engine based methods.

4.9.2 Physical System Layout

The layout of the proposed system consists of a dual-leg bypass-regeneration system with a 0.625 L pre oxidation catalyst and a 1.25 L LNT. A 2.5 L cordierite DPF is included after the two systems rejoin, which is catalytically coated to serve as a clean-up catalyst. Routing of the flame reformer to the LNTs or the DPF is accomplished using a two way valve. Routing of the flame reformer to the required leg of the LNT system is accomplished in the design of the exhaust bypass valve system. The total catalyst volume of the proposed system is 6.25 L, which is identical to that of the engine-based system from the literature. In addition, the volume of LNT is reduced by 1.34 L and is replaced by a similar volume of oxidation catalyst, which is less expensive. In addition, a cordierite substrate is traded for the silicon carbide substrate, which again, is less expensive. This trade-off is warranted by the fact that the flame reformer will be used for DPF regeneration, which will be less thermally punishing than the engine-based method. This allows for the more fragile cordierite trap to be used, which is also less restrictive. The lower back pressure from the less restrictive DPF can lead to gains in fuel economy.

4.9.3 Feasibility of Catalyst Temperature Measurements

The sensor set of the LNT system consists only of catalyst temperature measurements. In basing a control and diagnostics algorithm on temperature measurements, one must be certain that it would be possible to implement the measurement in practice. Without extensive cost and durability studies, it is not possible to come to a certain conclusion. Despite this, a case is made that points towards the likelihood that such a measurement set could be cost effectively applied. The following subsections review some of the considerations for the temperature-based sensor set.
4.9.3.1 Cost and Durability

The cost of the sensor set only needs to be at or below the cost of the sensors that are eliminated from the traditional sensor set. If the costs of the sensors for research are any indication, the cost of a thermocouple is much less than for a UEGO sensor. A single sheathed thermocouple costs less than $30 and a high performance IC conditioning circuit can be purchased for less than $10, giving $40 per thermocouple. Obviously, the actual costs at volume are much less, but this should serve as a reference point. On the other hand, the cost of a research-grade UEGO sensor is on the order of $2000 if it is purchased for research, and a NOx sensor costs around $12,000. Given that a thermocouple is essentially two base-metal wires of different materials welded together and a gas sensor is a complicated solid state device, it seems that there would indeed be a significant difference in cost.

The measurement device is not restricted to only thermocouples, and RTDs would be a particularly attractive measurement technique. Thermocouples are susceptible to electrical noise and require an amplifier with cold-junction compensation to account for the dissimilar metal junctions in transitioning from the thermocouple metals to the copper contacts that are used in electrical connections and wiring. Because of these reasons, commercial exhaust gas temperature sensors for automotive applications typically use RTDs. Additionally, RTDs have already been applied to commercial automotive grade temperature sensors, which sets a precedent for their ability to survive in the field.

4.9.3.2 System Cost

There is no doubt that the cost of the exhaust hardware for implementing a bypass-regeneration system is more that of an engine based regeneration system. The need for a diverter valve and actuator in the exhaust and the flame reformer add a non-negligible cost to the vehicle. These costs will be offset somewhat by savings in other aspects of the system. As described above, the elimination of exhaust gas sensors would go a long way towards offsetting this cost, and maybe even overcome the entire cost.
Additional savings would be realized in the elimination of the need for a calibration effort, which is substantial considering the complexity of Diesel engine calibration.

It is also felt that the bypass-regeneration system, with the ability to rapidly light off the catalysts using the flame reformer, has a reasonable chance at reducing the required NO\textsubscript{x} reduction over the cycle because of significant gains during cold start. Any efficiency improvement that can be obtained by the system results in a decreased cost of the catalysts, since the size or precious metal loadings can be reduced. Given the high cost of precious metals, a small reduction in precious metal requirements translates to a significant cost savings.

4.9.4 System Synergies

The presence of the flame reformer gives rise to a number of synergies that make this particular implementation attractive. It is always difficult to justify a new system concept unless it is drastically better in terms of cost and efficiency. The proposed system would, as will be shown in subsequent chapters, offer advantages in fuel economy and emissions performance over the traditional system. The cost, on the other hand, would likely not be that drastically different than the traditional system. It is true that higher cost sensors are replaced with inexpensive sensors, but the system hardware would surely be more expensive due to the presence of the diverter valves and the flame reformer. Even at the same cost and better efficiency, it is likely that further justification is needed to overcome the "inertia" of the previous method. Possible justification comes in the ability of the system to provide other attractive features. These features are discussed in the following subsections.

4.9.4.1 Rapid Catalyst Light-Off

In order to meet Tier 2 emissions standards, light-off of the aftertreatment system becomes critical for both NO\textsubscript{x} and hydrocarbon emissions. The effect on the cumulative emissions released during the cold-start can be such that they can eliminate any chance of meeting the emissions target. The most straightforward
approach to improving cold start emissions is to rapidly heat up the catalyst. Since the proposed system is equipped with a flame reformer for LNT management, it is, without any added cost, equipped with a Diesel fueled heater with a heat output of tens of kilowatts. The flame reformer, with its near instantaneous heat deliver, could serve as an important tool for lower cumulative emissions during the cold start. Any reduction in emissions during the cold start reduces the NOx reduction required on the rest of the cycle.

4.9.4.2 Key-Off NOx Regeneration

Another feature that becomes possible with the flame reformer is the possibility of a key-off regeneration function. It has been demonstrated the LNTs are capable of storing NOx at low temperatures, particularly when it is the form of NO2. To make the most of this phenomenon, it would be preferred that the LNT is completely depleted of NOx at vehicle startup. Since an LNT can not be regenerated when it is at a low temperature, this goal must be accomplished at the end of the previous trip. Since the regeneration strategy is engine-independent, it is possible to perform a regeneration immediately after the shutdown of the engine. Thus, at key-off, the flame reformer could regenerate the catalysts to prepare them for the next trip. This would help reduce the NOx emission during the light-off period. Although this method seems trivial, when cycle NOx reductions on the order of 95% are required, which seems likely in the future, the efficiency during the cold start becomes crucial. Even a small gain in efficiency can result in substantial improvements overall, since a large percentage of the total NOx is emitted during the cold start. This implementation would require an electric air delivery system for the flame reformer.

4.9.4.3 Sulfur Regeneration

Because the flame reformer is used to provide the rich gasses, the fuel economy penalty for a SO2 regeneration should be reduced over traditional methods. The key advantage to the flame reformer is that it does not need to operate in a continuous fashion, as does engine-based sulfur regenerations. Sulfur regeneration requires a long duration exposure to hot, rich gasses. The long exposure time is only required because the rate of sulfur decomposition is relatively slow. At any given time, only a small fraction of the
reductant provided by the engine-based method is actually used for sulfur removal, the rest simply passes through the catalyst which is both wasted fuel and increased emissions. By using the flame reformer, it is possible to heat up the catalyst to regeneration temperature with a continuous flow of hot combustion products. The catalyst can then be provided pulses of extremely rich combustion gas. The key to this method is to provide only pulses of gas. When the flame reformer is not active, these ultra rich combustion gasses will remain in the catalyst, reacting with the sulfur that is stored on the catalyst. In the event that the catalyst cools down below the desired temperature or a fresh batch of reductants are needed, the flame reformer sends another pulse of combustion gasses to the catalyst. This method of regeneration is, in principle, very similar to taking the poisoned catalyst and putting in an enclosed oven in a hydrogen and CO rich atmosphere. Because of this regeneration mechanism, the fuel economy penalty associated with sulfur regeneration should be very low. Additionally, the presence of a clean-up catalyst further minimizes the increase in hydrocarbon and CO emissions.

**4.9.4.4 DPF Regeneration**

Another important synergy of the flame reformer is the ability to provide heat for DPF regeneration. Any aftertreatment system that targets Tier 2 emissions for a Diesel engine will require a high efficiency DPF. DPFs, with a high enough exhaust temperature, can be regenerated passively through the use of a pre-oxidation catalyst that converts NO to NO₂. The NO₂ then continuously regenerates the soot out of the filter. Unfortunately, the conditions for continuously regenerating the trap are not met for every vehicle's duty cycle, thus every vehicle must be capable of performing active particulate filter regeneration. This can be accomplished using engine-based methods; however, this imposes additional, expensive engine calibration requirements while also having adverse effect on fuel economy.

Fuel-operated heater assisted DPF regeneration has been suggested and implemented by a number of researchers. It has proven to be very effective and efficient in the research to date, but due to the added cost of a combustor, it has not been applied in many applications. As with the catalyst heater, this DPF regeneration function is already present in the flame reformer. In certain catalyst configurations, it would
be possible to perform very controlled regenerations of the DPF since the exhaust flow could be reduced or eliminated using the bypass valves. This allows the heat from the flame reformer to be applied directly to the DPF rather than mixing with the exhaust gas and thus diluting the energy addition by heating up the exhaust gas. In this way, a larger percentage of the fuel energy can go towards heating the Diesel particulate filter.

4.10 Conclusions

In this chapter, experimental results for Diesel fuel-based regeneration were presented as well as for a new method of LNT management, referred to as flame reforming. The regeneration performance of Diesel fuel was acceptable at mid to high temperatures, however, hydrocarbon slip proved difficult to control. In addition, the inclusion of a Diesel oxidation catalyst before the LNT was required to prevent coking on the face of the catalyst. With the proper regeneration parameters, the data suggested that coking could be minimized such that an oxidation catalyst is not required. Motivated primarily by the hydrocarbon emissions and the poor low-temperature performance, the flame reformer was developed for reductant generation. This method of reductant generation proved capable of regenerating the catalyst across a wide range of temperatures, as well as offering a number of other synergies. A qualitative comparison to the other technologies was made based on results available in the literature. Based on this comparison, the flame reformer offered particular advantages in system cost, dynamic response, and system synergies.
CHAPTER 5

LEAN NOx TRAP STORAGE MODELS

5.1 Storage Model Goals

Because of the many different levels of modeling and uses for models, it is necessarily to clearly define the intended purpose of the LNT storage models that were developed in this research. There were two different storage models developed over the course of this research, both sharing a common structure. The first model, which is based on the work of the project sponsor [34], was a single lump model with NOx storage as the single state. The model was simple enough that it could be implemented in an engine controller for providing estimates of the state of the catalyst. Partway through the project, this model was no longer capable of meeting the needs of the project. Specifically, the requirements were for a spatially resolved model that would support the work in exotherm analysis. To meet this need, a six-lump distributed model was developed from the original single-lump model using the same set of model equations. This model, like its predecessor, is intended to be implemented in an engine controller in real time. Because of this need, it must remain as simple as possible while maintaining the required accuracy. As demonstrated in later chapters, the selected model framework allows the model to be adapted online using available measurements. This results in a model that learns the behavior of the catalyst and adjusts itself to match the current state of the catalyst. This is critical for a LNT, since the behavior changes considerably with sulfur poisoning and aging.
5.2 Model Data Collection

Data collection for storage model development and validation was performed at a range of operating points that corresponded to the typical driving conditions encountered in a passenger vehicle of the class that would have the 2.5 L engine that was used for the experiments. To this end, data was collected at 1500, 2000, 2500, and 3000 rpm at load points of 30, 60, 90, 120, and 150 ft-lb. The data required for the storage model is a NOx storage event from a completely empty trap to a completely full trap. These storage cycles would vary from 40 minutes at low-load, low-speed to less than a minute at high-load, high-speed. This large variance in time is due to the drastically different NOx flow rates at these operating conditions. For each of these tests, the pre and post-catalyst NOx emissions are measured as well as other relevant data. From this data, it is possible to determine the required storage model parameters that are described in the following sections. For much of the early data, simultaneous, two-point NOx sampling was not possible due to the lack of a second NOx sampling line. For this data, the tailpipe NOx was measured for the majority of the time with the sampling location being toggled to the front of the catalyst periodically to measure the catalyst inlet concentration. Since catalyst inlet concentration does not vary quickly over reasonable time periods, the average inlet NOx concentration was used for the inlet NOx.

5.3 Single-Lump Model

The input to the storage model is the mass flow rate of NOx into the catalyst and the temperature of the catalyst bed. For this model, the temperature of the bed is assumed to be the average of the inlet and outlet catalyst temperatures. The mass flow rate of NOx is reduced by the de-NOx efficiency factor in Equation (105). This de-NOx efficiency factor is needed to account for NOx that is destroyed by the reaction with hydrocarbons without having a change to be stored. The storage model contains a single state, which represents the mass of NOx stored in the LNT. This state is represented by Equation (106). The mass flow rate of NOx out is represented by a simple relationship, in Equation (107), to the trapping efficiency factor, $\eta_{\text{trap}}$. The equation set presented as Equations (105) through (107) would be linear if it were not for the
various parameters in the model, which depend on inputs and states such as temperature and catalyst fill ratio, which is a scaled mass of NO\textsubscript{x} stored. The dependencies and functional form of these parameters and the supporting equations are outlined in the following subsections.

**Model Equations:**

\[
\dot{m}_{\text{NO}_x,adj} = \dot{m}_{\text{NO}_x,in} \cdot \eta_{\text{DeNO}_x} \tag{105}
\]

\[
\dot{m}_{\text{NO}_x,st} = \eta_{\text{trap}} \cdot \dot{m}_{\text{NO}_x,adj}, \text{ hence } m_{\text{NO}_x,st} = \int \dot{m}_{\text{NO}_x,st} \, dt \tag{106}
\]

\[
\dot{m}_{\text{NO}_x,\text{out}} = (1 - \eta_{\text{trap}}) \cdot \dot{m}_{\text{NO}_x,adj} \tag{107}
\]

**Additional Equations:**

\[
\eta_{\text{trap}} = \eta_{\text{max}} \cdot \eta_{\text{st}} \tag{108}
\]

\[
\theta = \frac{m_{\text{NO}_x,st}}{M_{\text{NO}_x}} \tag{109}
\]

**Where:**

\(\dot{m}_{\text{NO}_x,adj} = \) NO\textsubscript{x} mass flow rate adjusted for De-NO\textsubscript{x} effect

\(\dot{m}_{\text{NO}_x,in} = \) inlet NO\textsubscript{x} mass flow rate (the model input)

\(\eta_{\text{DeNO}_x} = \) de-NO\textsubscript{x} efficiency factor

\(\dot{m}_{\text{NO}_x,st} = \) rate of change of the mass of stored NO\textsubscript{x}

\(m_{\text{NO}_x,st} = \) mass of stored NO\textsubscript{x}

\(\eta_{\text{trap}} = \) NO\textsubscript{x} trapping efficiency

\(\eta_{\text{st}} = \) normalized NO\textsubscript{x} trapping efficiency, which is a function of \(\theta\) and \(T\)

\(\eta_{\text{max}} = \) maximum NO\textsubscript{x} trapping efficiency

\(\dot{m}_{\text{NO}_x,\text{out}} = \) NO\textsubscript{x} mass flow rate out of the catalyst
\[ \theta = \text{catalyst fill ratio} \]

\[ M_{NOx} = \text{maximum NOx storage capacity} \]

### 5.3.1 De-NO\textsubscript{x} Efficiency Factor

As described earlier, the de-NO\textsubscript{x} efficiency factor is needed to account for the steady-state reaction of hydrocarbons with NO\textsubscript{x} without the NO\textsubscript{x} having a chance to be stored on the catalyst. An example of this effect was shown in Figure 54. Based on the data set used for the modeling, a clear dependence on the catalyst temperature was found which fit the data satisfactorily. It is suspected that higher levels of hydrocarbons would promote the de-NO\textsubscript{x} reactions as would lower exhaust flow rates. These factors also correlate well with temperature on the experimental engine (low exhaust temperature = high hydrocarbons = low exhaust flow rate), so that only the dominant factor was included. The experimental data points and the functional fit of the data are shown in Figure 99. The solid line represents a fit of the experimental data points. The dashed line was included based on engineering judgment to limit the curve fit at extremely low temperatures. The model, in general, is not calibrated at temperatures below 200ºC, thus this does not a represent major uncertainty.

The functional forms of the curve fits are as follows:

\[ \eta_{DeNOx} = b_1 \cdot e^{b_2 \cdot T} \quad \text{for high temperatures} \quad (110) \]

\[ \eta_{DeNOx} = \frac{b_1}{1 + e^{-(T-b_3)/b_3}} \quad \text{for low temperatures} \quad (111) \]
5.3.2 NO\textsubscript{x} Trapping Efficiency

The trapping efficiency of NO\textsubscript{x} is one of the key parameters in the model. The trapping efficiency is characterized by two terms, as shown in Equation (108). The first parameter, $\eta_{mx}$, is the maximum trapping efficiency of the catalyst. For the moderately aged LNT used for data collection for the model, the trapping maximum trapping efficiency was always extremely high, nearly 100%, after a regeneration regardless of the operating conditions. Typically, the NO\textsubscript{x} analyzer would read 0 ppm of NO\textsubscript{x} for a brief time at the beginning of a full storage. Unfortunately, the resolution of the NO\textsubscript{x} measurement system at such low level is not sufficient to resolve the NO\textsubscript{x} accurately. For these reasons, $\eta_{mx}$ was set at a constant value of 0.99, which agreed well with the data.
The second parameter, $\eta_{st}$, is the perhaps most critical parameter in the model. Because of the $\eta_{mx}$ factor described above, $\eta_{st}$ is a non-dimensional trapping efficiency and ranges from 0 to 1. Based on the experimental data, it was found that $\eta_{st}$ was a very strong function of the fill ratio of the catalyst and a weak function of temperature. There is no doubt that there is some dependency on exhaust gas flow. With smaller catalyst volumes, it is expected that the exhaust flow rate dependence would be amplified and would require consideration. Including this factor, or others, is possible by regressing the shape factor in the storage efficiency function by more variables than just temperature. To parameterize $\eta_{st}$, a nonlinear fitting routine was used to fit the parameters in Matlab. The functional form of the function is shown in Equation (111). The shape of $\eta_{st}$ is shown in Figure 100, which shows that the trapping efficiency tends to be more favorable at lower temperatures.

$$\eta_{st} = \frac{e^{b_1} \theta}{1 - e^{b_1}}$$  (112)
5.3.3 Maximum NO\textsubscript{x} Storage Capacity

The maximum NO\textsubscript{x} storage capacity parameter is simply the maximum NO\textsubscript{x} that can be stored at a particular operating condition. As expected, temperature was the dominant factor in the trap capacity and was used exclusively to generate a fit of the experimental data. The functional form of the curve fit is listed as Equation (113). Figure 101 shows the resulting fit of the experimental data. NO\textsubscript{x} storage capacity shows a maximum around 300ºC, tapers off gradually at low temperatures, and tapers off more rapidly at high temperatures.

\[
M_{NOx} = \frac{1}{b_1 + b_2 \cdot T + b_3 \cdot T^2 + b_4 \cdot T^3}
\] (113)

Figure 100: Effect of Temperature on Storage Efficiency Function Shape
5.3.4 Single-Lumped Model Validation

The single-lump model was validated against data not used in the calibration process. Figure 102 and Figure 103 show the agreement between the model and the experimental results for at 1500 and 2000 rpm for engine loads of 30, 60, 90, and 120 ft-lb. Over all of the cases, the output at saturation agrees very well, indicating that the De-NO\textsubscript{x} model is accurate. On the whole, the trajectory of the NO\textsubscript{x} traces agree well with the experimental data, particularly at the lower NO\textsubscript{x} levels where the engine most typically will operate. In later chapters, it will be demonstrate how this model can be adapted online to match the current state of the catalyst. In essence, the model parameters are adjusted to optimize the agreement of the model over the driving conditions encountered. This allows a simple model to be used with acceptable accuracy.
Figure 102: Storage Model Validation for Single-Lump Model at 1500 rpm
5.4 Multi-Lump Model

The multi-lump model consists of six identical catalyst elements positioned in series. The decision to move to a multi-lump model resulted in the demands of the regeneration model. The input of the first element is catalyst inlet NOx mass flow rate. This element stores a certain amount of the NOx and then passes the rest to the next element. Each element continues in this fashion, with the outlet of one being the inlet of the
next. The NO\textsubscript{x} leaving the last element of the series is the NO\textsubscript{x} exiting the catalyst. Despite being a distributed lump model, the equations for each cell are virtually identical to the equation set presented for the single lump model. This modified equation set is listed as equation (114) through (120). The parameter $\eta\text{DeNO}_x$ remains unchanged from the previous model and $M_{NOx}$ is simply the previous maximum NO\textsubscript{x} storage capacity divided by the number of cells.

**Model Equations:**

\[
m^1_{NOx,in} = \dot{m}^{cat}_{NOx,in} \cdot \eta_{DeNOx} \tag{114}
\]

\[
\dot{m}^x_{NOx,in} = \dot{m}^{x-1}_{NOx,out} \text{ for } x = 2 \text{ through } 6 \tag{115}
\]

\[
\dot{m}^x_{NOx,sto} = \eta^x_{trap} \cdot \dot{m}^x_{NOx,in}, \text{ hence } m^x_{NOx,sto} = \int \dot{m}^x_{NOx,sto} \, dt \tag{116}
\]

\[
\dot{m}^x_{NOx,sto} = (1 - \eta^x_{trap}) \cdot \dot{m}^x_{NOx,in} \tag{117}
\]

\[
\dot{m}^{cat}_{NOx,sto} = \dot{m}^6_{NOx,sto} \tag{118}
\]

**Additional Equations:**

\[
\eta^x_{trap} = \eta^x_{mx} \cdot \eta^x_{st} \tag{119}
\]

\[
\theta^x = \frac{m^x_{NOx,sto}}{M^x_{NOx}} \tag{120}
\]

**Where:**

Superscript $x$ denotes the catalyst cell number

Superscript "cat" denotes the whole catalyst

$\dot{m}_{NOx,adj} = \text{NO}x \text{ mass flow rate adjusted for de-NO}x \text{ effect}$

$\dot{m}_{NOx,in} = \text{inlet NO}x \text{ mass flow rate to catalyst of cell}$

$\eta_{DeNOx} = \text{de-NO}x \text{ efficiency factor}$

$\dot{m}_{NOx,sto} = \text{rate of change of the mass of stored NO}x$
\[ m_{\text{NOx, st}} = \text{mass of stored NOx} \]

\[ \eta_{\text{trap}} = \text{NOx trapping efficiency} \]

\[ \eta_{\text{st}} = \text{normalized NOx trapping efficiency} \]

\[ \eta_{\text{mx}} = \text{maximum NOx trapping efficiency} \]

\[ \dot{m}_{\text{NOx, out}} = \text{NOx mass flow rate out of the catalyst or cell} \]

\[ \theta = \text{catalyst fill ratio} \]

\[ M_{\text{NOx}} = \text{maximum NOx storage capacity} \]

### 5.4.1 Trapping Efficiency

Although the representation of the trapping efficiency for the multi-lump model remains unchanged from single-lump model, the curve fit parameters are substantially different. The trapping efficiency of the catalyst needs to be considerably lower for each cell since the cells are working in series. This results in both a change of the efficiency function scaling parameter, \( \eta_{\text{mx}} \), as well as the shape of the efficiency function curve. Figure 104 shows the resulting fill ratio and temperature dependence of the efficiency function for the multi-element model. Note that, in comparison to Figure 100, the efficiency curves are nearly linear with respect to fill ratio. This is interesting, in that a typical reaction engineering model is to model adsorption rate of a species with a linear dependence on the amount of the species adsorbed on the catalyst. When broken into smaller pieces, this representation appears to be very near the case for the LNT.
Figure 104: Effect of Temperature on Multi-Element Model Storage Efficiency Function

5.4.2 Multi-Lump Model Validation

The multi-lump model was derived from the single-element model, and thus it agrees almost exactly with it. For this reason, the validation of the multi-lump model is redundant with the single-lump model and will not be presented. The reader is referred back to Figure 102 and Figure 103 for this comparison.

5.5 Catalyst Thermal Model

A thermal model was developed for use with the multi-lump storage model, since it is necessary to provide spatially resolved catalyst temperatures for the regeneration model. The thermal model for the multi-lump model consists of six states with two inputs. The states correspond to the temperatures of the six catalyst
element. The inputs to the model are the inlet gas temperature and the inlet gas flow. The model uses a simple network of first order systems, in which the time constant of the first order system are based on the mass flow rate of exhaust through the catalyst. The input temperature to the catalyst drives the front catalyst section's first order system, and the output of this system drives the second catalyst section. This continues through the catalyst in the same manner, with the output of one element serving as the input to the next element.

\[
\frac{dT_e}{dt} = \frac{1}{\tau_{th}} \left( T_{\text{prev}} - T_e \right)
\]

(121)

\( T_e \) = temperature of the catalyst element

\( T_{\text{prev}} \) = temperature of previous element or inlet exhaust gas temperature

\( \tau_{th} \) = thermal time constant which depends on exhaust flow rate

Although this model structure is simple, it proved capable of capturing the dominant temperature dynamics of the catalyst well. The identification of system came from performing step changes in catalyst temperature and flow rate by performing step changes in load. For the experiments, three catalyst temperatures were recorded in the pre-LNT DOC and six were recorded in the LNT. From each of these cases, the time constant which minimized the absolute error in all of the temperature measurements was calculated iteratively and tabulated with the average exhaust flow rate over the period of interest. Figure 105 shows the resulting curve fit used for this time constant parameter. This plot points out the sluggish temperature dynamics of the catalytic converter. At idle, the time constant of a 1" segment of the catalyst is about 12 seconds. The system under investigation is comprised of 9, 1" segments in series. Because of this, the temperature dynamics of the catalyst substrate are very slow with respect to the speeds that the exhaust gas temperature can change.
Figure 105: Time Constants for Temperature Model

Figure 106 and Figure 107 show the results of the model for a step down in load followed by a step up in load. The temperatures shown in the figure are the inlet temperature of the catalyst, the front DOC temperature, rear DOC temperature, front LNT temperature, and rear LNT temperature. The solid lines are the measured data and the dashed lines are the model output. The agreement is generally good, with Figure 107 showing that the maximum temperature error of -17 °C, with the error typically being much less. The lower half of Figure 106 shows the change in the thermal time constant, which is a result of the exhaust flow rate change during the step. Figure 108 and Figure 109 show the same results for a case with a larger step in temperature but with a lower engine speed. The agreement of the model is similar to the previous one, with the exception of the maximum error increasing somewhat. Overall, however, the performance of the model was satisfactory considering its simplicity and the intended purpose. An identical model was used for the pre-LNT catalysts as well as the clean-up catalyst. The sensor set that the control algorithms
are based on include catalyst temperatures, so this model is used only in the plant model to represent the general behavior of the catalyst in simulation. Because of this, the error in the temperature model does not affect the validation of the control algorithm which is conducted in later chapters.

Figure 106: Thermal Model Results, Low Temperature Step Change, High Engine Speed
Figure 107: Thermal Model Error, Low Temperature Step Change, High Engine Speed
Figure 108: Thermal Model Results, High Temperature Step Change, Low Engine Speed
The storage model also includes a simple static model of the conversion efficiency of carbon monoxide and hydrocarbons over the LNT. The main goal of the model is to provide an accurate estimation of NO\textsubscript{x} emissions, but it is also desirable to include the oxidation of CO and HC for the sake of completeness. As shown in Figure 110, the data is fit using a sigmoid function and is a function of only temperature. As is typical, the oxidation of hydrocarbons occurs at a lower efficiency than for carbon monoxide and the low temperature activity of the catalyst is better for carbon monoxide. Also shown on the plot is the steady-state conversion efficiency used for the de-NO\textsubscript{x} reaction, which was discussed in an earlier section. The steady-state conversion efficiency of NO\textsubscript{x} is dwarfed by the conversion of CO and THC. This exemplifies the difficulty of supporting NO\textsubscript{x} reduction in a lean environment.
5.7 Conclusions

Of the two storage models that were developed, the multi-element model is the one that is discussed in the remainder of this document. The single-lump model has been used in some extensive batch simulations evaluating the general behavior of systems designs and catalyst volumes. For this purpose, the interest is in trends and the fast running single lump model allows for a large number of simulations to be conducted in a relatively short time frame. However, for doing control algorithm investigations and more detailed work, it is necessary to use the multi-element formulation so that the NO\textsubscript{x} storage distribution throughout the catalyst is modeled rather than just one single mass of stored NO\textsubscript{x}. The following diagram shows all of the components that are active during the storage period for the LNT during a simulation. The only component
not discussed above is the bypass valve model, which is simply a block which routes the exhaust through catalyst 1, catalyst 2, or both.

Figure 111: Schematic of Storage Model Components
6.1 Regeneration Model Goals

The regeneration model was developed primarily for use in simulation of control and diagnostic algorithms. Although it would be possible to integrate it into an ECU for some type of control function, with eighteen states it would be a stretch that it would be acceptable based on the computational time required. The goal of the model is to simulate the reduction of stored oxygen and NO\textsubscript{x}, the readesorption of oxygen, and the resulting temperature rise from these events. Furthermore, the model predicts the mass flow rate of reductant slip out of the catalyst. In addition to the regeneration model, there are a number of additional sub-models which are necessary to form the full regeneration model.

6.2 Storage Model Structure and Equations

The regeneration model is only active during the regeneration of the LNT and is initialized using the states from the storage model. In turn, the regeneration model hands off the states back to the storage model at the end of the regeneration event. The core of the storage model is six identical storage cells, which represent six equally spaced sections of the catalyst. It is not by coincidence that the number of cells corresponds to the number of thermocouples used for exotherm analysis in the catalyst. The model relies heavily on the temperature measurements for calibration of model parameters. The three states of the model for each cell are the mass of stored oxygen, mass of stored NO\textsubscript{x}, and the catalyst temperature. Two
of these states, temperature and mass of stored NO\textsubscript{x}, are initialized at the start of the regeneration using the corresponding states from the storage model. The third state, mass of stored oxygen, is initialized at the start of the regeneration based on the temperature of the catalyst cell. The initialization of the oxygen storage is accomplished using a static function of temperature and assumes that the oxygen storage is saturated from the previous lean phase.

As reductant enters the first catalyst cell, it first goes towards reducing the stored oxygen. The amount of reductant that can be consumed by the oxygen storage is, of course, not infinite. Therefore, if the mass flow rate of reductant exceeds the amount of reductant that the stored oxygen can utilize, it is passed on to reduce the NO\textsubscript{x} stored in the element. The NO\textsubscript{x} storage has a similar rate limit, and any reductant not used for NO\textsubscript{x} reduction exits the catalyst cell. This process happens in turn to each of the catalyst cells until the last cell, where the reductant exits the catalyst as reductant slip. When the lean phase of the regeneration is entered, oxygen is supplied which goes towards restocking the oxygen storage. Just as with the oxygen and NO\textsubscript{x} desorption process, the oxygen adsorption process is rate limited and unused oxygen slips to the next cell, or in the case of the last cell, out of the catalyst. The temperature of the cell depends on the mass of reductant or oxygen used in each of the three processes described above. The regeneration process is modeled to be adiabatic. Since all of the reactions are exothermic, the temperature always increases during a regeneration event.

With a basic verbal description of the storage cell behavior, it is now possible to formalize the model with the set of equations numbered (122) to (133). The inputs to the model are the mass flow rate of equivalent reductant and the mass flow rate of free oxygen. The concept of equivalent reductant is described below, but is a way of capturing the effect of different reductants by normalizing their reductive ability to that of carbon monoxide. Because of this simplification, the regeneration model only needs to have one set of constants.
State Equations:

\[ m_{O_2} = B_1 \cdot \dot{m}_{\text{red}, O_2} \quad \text{if } \dot{m}_{O_2, \text{in}} = 0 \quad (122) \]

\[ \dot{m}_{O_2, \text{in}} = B_3 \cdot \dot{m}_{\text{ads}, O_2} \quad \text{if } \dot{m}_{O_2, \text{in}} > 0 \quad (123) \]

\[ \dot{m}_{\text{NO}_x} = B_2 \cdot \dot{m}_{\text{red}, \text{NO}_x} \quad (124) \]

\[ \hat{T} = C_1 \cdot (B_1 \cdot \dot{m}_{\text{red}, O_2}) + C_2 \cdot (B_3 \cdot \dot{m}_{\text{ads}, O_2}) + C_3 \cdot (B_2 \cdot \dot{m}_{\text{red}, \text{NO}_x}) \quad (125) \]

Supporting Equations:

\[ \dot{m}_{\text{red}, O_2} = \dot{m}_{\text{red}, \text{in}} \quad \text{if } \dot{m}_{O_2, \text{in}} = 0 \quad \text{and} \quad \dot{m}_{\text{red}, \text{in}} < A_1(T) \cdot m_{O_2} \quad (126) \]

\[ \dot{m}_{\text{red}, O_2} = A_1(T) \cdot m_{O_2} \quad \text{if } \dot{m}_{O_2, \text{in}} = 0 \quad \text{and} \quad \dot{m}_{\text{red}, \text{in}} \geq A_1(T) \cdot m_{O_2} \quad (127) \]

\[ \dot{m}_{\text{ads}, O_2} = \dot{m}_{O_2, \text{in}} \quad \text{if } \dot{m}_{O_2, \text{in}} > 0 \quad \text{and} \quad \dot{m}_{O_2, \text{in}} < A_3(T) \cdot (M_{O_2, \text{max}}(T) - m_{O_2}) \quad (128) \]

\[ \dot{m}_{\text{ads}, O_2} = A_3(T) \cdot (M_{O_2, \text{max}}(T) - m_{O_2}) \quad \text{if } \dot{m}_{O_2, \text{in}} > 0 \quad \text{and} \quad \dot{m}_{O_2, \text{in}} \geq A_3(T) \cdot (M_{O_2, \text{max}}(T) - m_{O_2}) \quad (129) \]

\[ \dot{m}_{\text{red}, \text{NO}_x} = \dot{m}_{\text{red}, \text{in}} - \dot{m}_{\text{red}, O_2} \quad \dot{m}_{\text{red}, \text{in}} - \dot{m}_{\text{red}, O_2} < A_2(T) \cdot m_{\text{NO}_x} \quad (130) \]

\[ \dot{m}_{\text{red}, \text{NO}_x} = A_2(T) \cdot m_{\text{NO}_x} \quad \dot{m}_{\text{red}, \text{in}} - \dot{m}_{\text{red}, O_2} \geq A_2(T) \cdot m_{\text{NO}_x} \quad (131) \]

Outputs:

\[ \dot{m}_{\text{red}, \text{out}} = \dot{m}_{\text{red}, \text{in}} - \dot{m}_{\text{red}, O_2} - \dot{m}_{\text{red}, \text{NO}_x} \quad (132) \]
\[ \dot{m}_{O_2,\text{out}} = \dot{m}_{O_2,\text{in}} - \dot{m}_{\text{ads},O_2} \]  

(133)

Where:

- \( m_{O_2} \) = mass of stored oxygen (state variable)
- \( B_1 \) = stoichiometric constant for reductant to stored oxygen
- \( \dot{m}_{\text{red},O_2} \) = mass flow rate of reductant used for \( O_2 \) reduction
- \( B_3 \) = stoichiometric constant for free oxygen to stored oxygen
- \( \dot{m}_{\text{ads},O_2} \) = mass flow rate of free oxygen used of \( O_2 \) readsorption
- \( m_{NO_x} \) = mass of stored \( NO_x \) (state variable)
- \( B_2 \) = stoichiometric constant for reductant to stored \( NO_x \)
- \( \dot{m}_{\text{red},NO_x} \) = mass flow rate of reductant used for stored \( NO_x \) depletion
- \( T \) = temperature of catalyst element (state variable)
- \( C_1 \) = temperature rise coefficient for stored oxygen reduction
- \( C_2 \) = temperature rise coefficient for oxygen readsorption
- \( C_3 \) = temperature rise coefficient for \( NO_x \) reduction
- \( \dot{m}_{\text{red},\text{in}} \) = mass flow rate of equivalent reductant into the catalyst
- \( \dot{m}_{O_2,\text{in}} \) = mass flow rate of gaseous oxygen into the catalyst
- \( A_1(T) \) = reductant limit constant for \( O_2 \) reduction,
- \( A_2(T) \) = reductant limit constant for \( NO_x \) reduction
- \( A_3(T) \) = oxygen limit constant for \( O_2 \) adsorption
Equations (122) through (125) are the state equations for the model. These two equations model the desorption of stored oxygen during rich conditions and the adsorption of oxygen during lean conditions. As indicated by the switching conditions, only one of these two state equations is active at a time. Equation (124) is the state equation for the mass of stored $\text{NO}_x$. For a regeneration event, the mass of stored $\text{NO}_x$ will only decrease, since no new $\text{NO}_x$ is entering the catalyst during regeneration. The values of $\dot{m}_{\text{red}, \text{O}_2}$, $\dot{m}_{\text{ads}, \text{O}_2}$, and $\dot{m}_{\text{red}, \text{NO}_x}$ are determined by the equations listed in (126) through (131). The structure of these equations is such that it places limits on the maximum rate that reductant or oxygen can be used by the oxygen and $\text{NO}_x$ storage states. In the case of reductant, it also enforces the preference of the reductant going first to oxygen storage and then to $\text{NO}_x$ storage. The $A$ parameters in the model are functions of temperature, which is a state. This is one source of non-linearity in the model. As shown in the equations, the maximum use of reductant is dependent on the amount of stored oxidizer. In the case of oxygen readesorption, it is proportional to the deficiency from the saturated state of oxygen storage. The temperature state equation given by Equation (125), is straightforward. The rate of temperature rise is related to the rate that oxygen is desorbed, the rate that $\text{NO}_x$ is desorbed, and the rate that oxygen is adsorbed. These rates are multiplied by a constant that is related to the heat release for the reaction as well as the thermal and mass properties of the catalyst.

For a number or reasons cited above, the model is non-linear. Under certain conditions, the model can be represented reasonably well by a linearized system. For instance, the dependence of temperature on the $A$ coefficients is relative low for small changes of temperature, therefore, a nominal constant value could be used with only small losses in accuracy. For the sake of simulation, non-linearities are not a problem. For development of control algorithms, however, this simplification will be called upon in later chapters. The reader will notice that a great deal of similarity between the temperature state equations and the theoretical explanation of exotherm analysis provided in Chapter 3.
6.3 Model Calibration

The fact that the regeneration model presented above requires internal knowledge of the catalyst during regeneration might be a point of concern. Typically, it is not possible to measure such things as chemical reaction rates inside a catalyst. It is clearly possible to measure the input and output gas concentrations, but correlating that to what is happening spatially inside the catalyst would prove difficult using conventional testing methods employed in the automotive industry. By bringing exotherm analysis to bear on the problem, a tool is available for doing just what is required: To see reaction rates inside the catalyst both temporally and spatially resolved. Although it likely does not appear to be true, the equation set that makes up the regeneration model is formulated with the specific purpose of allowing easy calibration of the model through exotherm analysis. In the following sections, a description of the calibration process and resulting parameter value and functions will be detailed.

6.3.1 Cell Oxygen Storage Initialization

As discussed above, it is necessary to initialize the catalyst oxygen storage state when the regeneration model becomes active. The most straightforward method of determining the oxygen storage of the catalyst is to integrate the oxygen entering and exiting the catalyst using the signals from the pre and post catalyst UEGO sensors in conjunction with the air flow rate that is entering the catalyst. Immediately after a full regeneration, the oxygen storage is in a depleted state. By delivering air to the catalyst at this time, it is possible to get an absolute measurement of oxygen storage. Figure 112 shows the experimental data and the curve fit used to represent the oxygen storage. The use of a static function for oxygen storage rather than including it as a state in the storage model is based on the following reasoning, all of which ensure that the catalyst oxygen storage is saturated for a NOx storage of typical length:

1. The storage phase is typically very long ( > 1 minute)

2. Diesel engines have high levels of excess oxygen
3. The uptake of oxygen is rapid (< 5 seconds)

In the vehicle implementation, this function of oxygen storage is adapted online to account for changes in oxygen storage over the life of the vehicle.

![LNT Oxygen Storage](image)

Figure 112: LNT Maximum Oxygen Storage Function

6.3.2 Reductant Stoichiometric Factors

The parameters $B_1$ and $B_2$ relate a mass of reductant to the mass of oxygen or NO$_x$ that it can remove from storage. These are essentially mass based stoichiometric factors for the entire reaction sequence in the reduction of these stored oxidizers. These factors are best determined using experimental data rather than calculating them outright, since there are some uncertainties in the reaction mechanisms involved in the
process. Determination of both of the factors arise from the same types of tests. At a fixed engine operating point, the LNT is allowed to store for various lengths of time before a complete regeneration is conducted. By using different time intervals, a varying amount of NOx is stored during each storage phase. From this data set, it is possible to calculate the mass of NOx stored during the storage phase as well as the amount of reductant needed for the complete regeneration. The result of 14 or these storage cycles conducted at an engine speed of 2000 rpm and a load of 90 ft-lb are shown in Figure 113. The points, regardless of operating conditions, lie on a nearly straight line with an offset. The slope of this line has units of grams of CO per gram of NOx. The inverse of this slope is the coefficient, $B_2$, that is used in the regeneration model. The coefficient used in the model is the weighted average of the slopes of several operating points, all which have very similar slopes. The $B_1$ parameter is also available from Figure 113, in the offset of the curve fit. In the absence of oxygen storage, one would expect the offset of this plot to pass through the origin. However, the oxygen storage is there consuming reductant even at near zero NOx storage, which results in the offset. By comparing the offset term of the curve fit with the oxygen storage measurement at the operating condition, it is possible to arrive at a constant value for $B_1$. The final stoichiometric factor, $B_3$, is equal to unity, since it is simply a mass integral of oxygen without the need for a stoichiometric factor.
The temperature state coefficients, $C_1$, $C_2$, and $C_3$, used in equation (125) relate the mass of NO$_x$ and oxygen reduced or adsorbed to a corresponding temperature rise. These factors are, once again, fairly easy to determine using data from the same set of experiments used to identify the $B$ parameters. Figure 114 shows results from this same data set with the average temperature rise of a catalyst cell on the $y$-axis instead of the reductant usage. The slope of the curve fit in the figure has units of degrees C per gram of NO$_x$. The slope of this line is the parameter $C_2$, which relates the mass of NO$_x$ reduced to a temperature rise that it generates when reduced. Just as before, the $y$-intercept of the plot is due to the oxygen storage
of the catalyst. Using these intercepts in conjunction with the oxygen storage measurement for the operating point, it is possible to directly compute the value of $C_1$.

![Figure 114: NOx Stored versus Temperature Rise](image)

The $C_3$ term relates the mass of oxygen adsorbed during the lean phase to the corresponding temperature rise. As with the previous parameters, by plotting the oxygen storage versus the associated temperature rise, a trend line can be fit and the slope of this line is the parameter value. Figure 115 shows this plot for a data set. Unlike the previous cases, there is not a linear trend between the two values as was originally expected. It is not clear what the exact cause of this non-linearity is, but one suggestion is that there are different oxygen storage mechanisms involved. It is known that, in addition to ceria, oxygen can be stored
on alumina, the precious metal sites, and event on the NO\textsubscript{x} storage sites. Since the stored oxygen mass depends on temperature, it is possible that these different oxygen storage mechanisms are active in different degrees at varying oxygen storage levels. Since these storage mechanisms could all have different heat release characteristics, it would explain the non-linearity. Regardless of not knowing the mechanism behind the non-linearity, it still is a simple matter of using the slope of this curve for the $C_3$ parameter. The only difference is that this parameter is not a simple constant, but a function of oxygen storage.

![Figure 115: Oxygen Stored Versus Lean Temperature Rise](image)

6.3.4 Maximum Reductant Usage Functions

The only remaining parameters in the regeneration model are $A_1$, $A_2$, and $A_3$. These parameters, as defined in the equation set, place a limit on the maximum rate that reductant can be used to reduce oxygen
and NOₓ and the maximum rate that O₂ can be adsorbed by the catalyst. Since this process of limiting the reductant varies with the amount of stored reductant, which in turn varies with time, it is necessary to calibrate these parameters using time-domain data rather than the static methods used for the previous parameters. The approach used to calibrate the rich coefficients, \( A₁ \) and \( A₂ \), is to force the catalyst into a state where it reveals the dynamics that are being sought. In this case, the appropriate test is to supply the catalyst with an extremely high flow rate of reductant, such that the catalyst is utilizing the reductant at as high of a rate the chemical kinetics will allow. In practice this is relatively easy to accomplish, one simply turns up the reductant flow rate to an appropriate level and acquires the necessary measurements. In this case, the required measurements are the substrate temperature measurements. As demonstrated earlier, these measurements can be correlated directly to the reduction of stored oxygen and NOₓ in the region of the measurement. If one normalized the temperature measurement such that it varies from 0 to 1, and then subtracts this value from one, the resulting time trace is a non-dimensional analog to the amount of oxidizer stored on the catalyst in the region of the measurement. The results of the above approach is illustrated in and Figure 117. The figures shows four sets of normalized and inverted temperature traces from a regeneration event in which the trap filled to capacity and was provided an excess of reductants. As indicated in the figure, the plots of the four exotherms are virtually identical, indicating that the goal of flooding the catalyst with more reductant than it could utilize was achieved. shows a fit of the data with a first order decaying response, which is the solution of differential equation form suggested in Equations (126) through (131) for the rate limit. This does a reasonable job at matching the data, however, the persistent low slope tail that persist out to 25 seconds is not captured by the model. The form of the fitting equation is provided as Equation (134).
Figure 116: Parameter Identification of Rich Reaction Rate - First Order
Figure 117: Parameter Identification of Rich Reaction Rate - Second Order

A better fit to the data is shown in the Figure 117, which uses the natural response of an over-damped second order system. The functional form of the second order response is restricted slightly based on the nature of the data to form shown as Equation (135). By reducing the number of free parameters to three, the function is constrained to equal 1 at a time value of 0, which is a required. The second order fit, as shown in, matches the data very well. The need for, essentially, two time constants is hypothesized to lie in the mechanism of stored oxidizer reduction. It has been suggested that, in addition to surface storage, the bulk storage is also present in the LNT. This bulk storage would manifest itself in a prolonged but low rate depletion of oxidizer, which is just what is indicated by the results. For this particular case, the value of $a$ is 0.65, the value of $\tau_1 = 1.4$ seconds, and the value of $\tau_2 = 6.5$ seconds.
First Order Fit:

\[ y = \exp \left( -\frac{t}{\tau} \right) \]  \hspace{1cm} (134)

Second Order Fit:

\[ y = a \cdot \exp \left( -\frac{t}{\tau_1} \right) + \left( 1 - a \right) \cdot \exp \left( -\frac{t}{\tau_2} \right) \]  \hspace{1cm} (135)

Figure 118: Maximum Rate of Reductant Usage

For the first order reductant usage function, the impact of temperature can be represented simply by having the single parameter of the model depend on temperature. Experimental data showing this parameter as well as the resulting curve fit are shown in Figure 119. Note that, at low temperatures, this parameter is
significantly higher than at the higher temperatures. Since this parameter is essentially a time constant, it is clear at low regeneration temperatures that the duration of the regeneration will be much longer than at higher temperatures. The particular shape and magnitude of this time constant parameter is dependent on the catalyst formulation. For the other type of catalyst used in the testing, there was evidence that the time constant at low temperatures was roughly half of what is shown in the figure. Unfortunately, a full evaluate of this catalyst could not be conducted due to damage of the catalysts. Any decrease in this time constant would be beneficial to the system.

Figure 119: Reductant Limit Constant versus Temperature
6.3.5 Simulink Block Implementation

The building blocks of the regeneration model described are used to construct a Simulink model of a single storage element. The equation set itself proved fairly simple to implement. Managing the initialization and hand off of states between the regeneration and storage model proved to be somewhat complicated, but an effective solution was found using Simulink's triggered subsystem functions and integral state ports to prevent algebraic loops.

6.4 Pre-LNT DOC Model

The pre-LNT DOC model consisted of a thermal model and a reductant equilibration model. The thermal model is identical to the LNT thermal model, except that it only has three states since the catalyst is half of the size of the LNT. It also modeled the effect of eliminating and free oxygen in the regeneration gas stream and removing the corresponding amount of reductant that would be oxidized. It was assumed that the activity of this catalyst was high enough to promote complete removal of oxygen at all temperatures.

6.5 Equivalent Reductant Concept

The concept of equivalent reductant is a convenient method of simplifying the regeneration model. The reductant mix that is provided for the regeneration is translated into an equivalent mass flow rate of reductant in grams of carbon monoxide per second. This translation is accomplished using the stoichiometric factors for the reduction of NO₂ with the reductant. This convenient approach has proven to provide acceptable results and has been used elsewhere in the literature [33].

6.6 Reductant Slip Model

Since all of the reductants are converted into a single mass flow rate of equivalent reductant, it is necessary to reconstitute the equivalent reductant back into mass flow rates of the H₂, CO, and THC. To accomplish
this, the experimental observation that hydrocarbon slip occurs before CO slip was used to establish a priority of reductant slip. As equivalent reductant begins to slip from the catalyst, it is assumed to be entirely hydrocarbons, up to the level of the LNT inlet hydrocarbons. Once the outlet hydrocarbons equal the inlet hydrocarbons the remaining reductant is assumed to be carbon monoxide. It would be possible to further extend this to hydrogen, however, this was not deemed necessary. Since hydrogen and carbon monoxide are both almost completely oxidized a cleanup catalyst, thus there is no need to distinguish between the two.

6.7 Clean-Up Catalyst Model

One possible system configuration of a bypass-regeneration system is to include a clean-up oxidation catalyst after the point that the regeneration gasses mix with the lean exhaust. In this configuration, any reductant slip that happens during a regeneration can be treated by the catalyst, since the bypassed exhaust stream has excess oxygen that can promote the reduction of carbon monoxide, hydrogen, and hydrocarbons. In this application, the concentration and the speciation of the hydrocarbons is different than those in the normal Diesel exhaust. Typically, the hydrocarbons exiting the catalyst will be more difficult to oxidize. To address this issue, the flame reformer output was directed into the exhaust upstream of the clean-up oxidation catalyst. The ability of the catalyst to oxidize this stream of hydrocarbons and carbon monoxide is shown in Figure 120. The catalyst under consideration was a conventional Diesel oxidation catalyst with a 1.25L volume. The DOC used in the testing proved not to have as good as performance of what is currently possible. It is expected that, with an improved formulation, that the efficiency of hydrocarbon removal could be greatly improved.
6.8 Model Validation

Validation of the model was conducted using both carbon monoxide only regenerations as well as flame-reformer data. In each case, the only difference in the model that was necessary to get good agreement was changing the transport delays of between regeneration elements. This is simply a result of the flame reformer delivering a more dilute stream of reductants, which had the effect of reducing the transport delay. Data comparing experimental results for a CO only regeneration is provided in Figure 121 and Figure 122. The first figure shows the case for a saturation storage, and the second for the regeneration of a partially filled trap, which is more typical of normal operation. Figure 123 shows the results for a partial storage regeneration using the flame reformer. In all of the cases, the magnitude agreement is very good, which is a result of the fact that exotherms correlate well to the mass of NO\textsubscript{x} stored. The trajectories and timing of
the temperatures rises agree reasonably well with the experimental results. Since this model is used for control strategy development and verification, it is deemed to represent the catalyst enough to provide meaningful results.

Figure 121: Comparison of Model Output with Simulated Output at Full Storage
Figure 122: Comparison of Model Output with Simulated Output at Partial Storage
Figure 123: Simulated Catalyst Exotherms for the Flame Reformer
In addition to predicting the temperature rises of the catalyst, the second goal of the model was to predict the timing and magnitude of the reductant slip. Figure 124 shows a validation case of the flame reformer reductant slip timing. The timing of the slip agrees very well with the measurement if one considers the response time of the hydrocarbon measurement device. In the simulation case, the reductant command continues past 35 seconds, which explains why it continues to remain at a high level without dropping.

6.9 Conclusions

In the proceeding sections, a complete regeneration model was articulated and a rigorous method of calibration was presented on the measurements of catalyst bed temperatures. The goal of the model, which is to accurately represent the physical catalyst for control strategy verification was met, as demonstrated in
the sample validation data. The model structure is believed to be intuitive based in the context of exotherm analysis. It does, however, have a number of non-linearities which must be addressed in later chapters for the development of a regeneration control algorithm. Figure 125 shows the all of components of the regeneration model and the interconnections between them.

Figure 125: Diagram of Regeneration Model Components
CHAPTER 7

AN ADAPTIVE, EXOTHERM-BASED, LNT MANAGEMENT ALGORITHM

7.1 Motivation

The goal of the LNT management algorithm is to demonstrate a successful algorithm in which the main control inputs are the catalyst bed temperature measurements. There are a number of reasons behind the selection of the catalyst bed temperature measurements as the main sensor set. One of the prime motivations of the choice of a temperature measurement based sensor set is cost. The current control methods that are applied to LNT management require the use of at least two oxygen sensors, typically the more expensive wide range type. NOx sensors, which also serve as wide-range oxygen sensors, are often applied to the control of LNT catalysts.

Another motivation behind the use of temperature measurements as the primary feedback signal is that they offer a chance for superior performance. As has been demonstrated, the catalyst bed temperature measurements allow gathering information from inside the catalyst. The regeneration gasses can be detected by the control algorithm and provide a real-time feedback signal. With exhaust gas sensors, it is only possible to sense the gas stream after it exits the catalyst, which could be too late to take proper action.

The last major motivation, is once again, cost. The required calibration effort for an engine-based regeneration algorithm is substantial. If one just considers the engine, the there are four distinct operating modes that must be present: normal lean mode, DPF regeneration mode, SO2 regeneration mode, and NOx regeneration mode. Developing each of these calibrations is time consuming and expensive. The proposed
system and algorithm eliminate three of these calibrations, and because of the nature of the system, is replaces it with a much simpler calibration process with very high reuse from platform to platform.

As final reason, although minor, is because it is a completely novel concept. There exists no reference to such direct control of a LNT based on axially distributed temperature measurements. Because of this, it is a unique opportunity to explore a method that has, until now, been overlooked. The theoretical and mathematical foundation for a algorithm based entirely on catalyst temperature measurements is laid out in the following chapter. Theory and math are good up to a certain point, but it is always necessary to back them up with experimental evidence. To this end, two of the most critical sub-algorithms are experimentally investigated to ensure that they are possible to implement in practice.

The first algorithm that is tested experimentally is the regeneration control algorithm. If the catalyst is regenerated improperly, there are two unfavorable outcomes that will result. If the catalyst is under-regenerated, the back parts of the catalyst will not be purged of their stored NOx. On the subsequent regeneration, the NOx conversion efficiency will suffer since the rear of the catalyst is not trapping with the effectiveness that it should. The second outcome of an improper regeneration is an over-regeneration. From a NOx standpoint, this situation is good because it ensures that all of the NOx has been removed from the catalyst. However, an over-regeneration leads to reductant slip. Given the stringent hydrocarbon emissions, one cannot afford to have more than trace amount of reductant slip on a regeneration, or the hydrocarbon standard will be violated. Obviously, it is not possible in practice to get a "perfect" regeneration, in which there is no reductant slip and the NOx is completely depleted. In general, it seems more prudent to err on the side of under-regeneration, since a small loss in NOx efficiency can be made up in other ways. An algorithm to ensure acceptable regenerations is developed and validated.

The second sub-algorithm that is critical to the operation of the catalyst is a learning algorithm for the LNT storage model. This model is the heart of the regeneration scheduling algorithm; thus, inaccuracies with this model will lead to unwanted deviations in tailpipe-out NOx. The main thing that this learning algorithm must deal with is the ever present effect of sulfur poisoning. As the catalyst accumulates sulfur,
the efficiency becomes significantly lower than the non-poisoned catalyst. As demonstrated in an earlier chapter, the effect of sulfur poisoning can be detected via the distribution of NO\textsubscript{x} in the catalyst. The algorithm presented in the previous chapter outlines a method that the catalyst model can be adapted online to account for this reduction in efficiency. In this way, the regeneration scheduling algorithm has an accurate estimate of catalyst out NO\textsubscript{x} on which to schedule the regenerations. If this algorithm is not capable of operating in practice, then the entire control system begins to unravel.

### 7.2 Regeneration Scheduling

Regeneration scheduling is the process of determining when to conduct a NO\textsubscript{x} regeneration on an LNT. The LNT is a unique aftertreatment device in that it allows the control strategy to have wide authority over the level of NO\textsubscript{x} conversion. By scheduling the frequency of the regenerations, it is possible to vary the NO\textsubscript{x} efficiency from very low conversions, to over 95%. Because of this, it requires a specific control algorithm to manage the regeneration timing. The context of this discussion is of a dual-catalyst system only, as the single trap bypass system requires some special considerations that will not be touched on in this work. The goal of the emissions control system is to control the cumulative emissions of the vehicle over a trip to be less than the relevant emissions standards. The trips of relevance in this case are the Tier 2 emissions testing cycles, which, for the purpose of this work, consists of the UDDS, the HWFET, and the US06.

The simplest regeneration scheduling method would be a simple time-based regeneration schedule. One stores NO\textsubscript{x} for a set duration of time, regenerates, and then resumes trapping. This trapping time can be scheduled based on engine operating points, or it can be a fixed time. This method is trivial to apply, but obviously has a number of limitations. The biggest limitation is that it has no direct concept either the efficiency of the catalyst or the engine-out NO\textsubscript{x}. These factors would be considered in the calibration process of the trap time, but the algorithm itself does not sense and react to these factors. Despite these drawbacks, it is still discussed in the literature as a control method for regeneration scheduling.
A second more viable option is to schedule regenerations based on the trapping efficiency of the LNT. Once the trapping efficiency drops below a threshold level, a regeneration event is conducted to regain the efficiency. This method, unlike the previous method, has awareness of the trapping efficiency of the catalyst and thus is a step closer to a workable regeneration scheduling algorithm. It would require an engine-out NO\textsubscript{x} measurement or estimate as well as a catalyst-out measurement or estimate. It is easy to imagine that one could determine this threshold efficiency from testing or simulation, and, after applying a safety factor, be confident that the vehicle would meet the emissions standards. The downfall of this method is that it has no perception of the mass of NO\textsubscript{x} being emitted. The most straightforward case of this would be the impact of the LNT operating at 90% efficiency with an inlet NO\textsubscript{x} flow rate of 0.005 g/s versus 0.05 g/s. In the first case, a mere 0.0005 g/s of NO\textsubscript{x} is leaving the catalyst. The latter case, however, is emitting ten times more NO\textsubscript{x} even though the trapping efficiency is identical. These cases are realistic of actual engine operating cases. It is clear from this simple exercise that this strategy, though workable, is lacking a necessary component as well. Because of the lack of awareness of the mass of NO\textsubscript{x} emitted, calibration would be required to ensure that this method works for all of the required driving conditions.

The evolution of the previous strategy would be to integrate the engine-out NO\textsubscript{x} as well as the tailpipe or catalyst NO\textsubscript{x} from the start of a storage event. From these values, a cumulative NO\textsubscript{x} storage efficiency for the current storage event can be calculated. With this method, the mass of NO\textsubscript{x} is accounted for because of the integral of the mass flow rates. This approach, at last, is a workable approach for regeneration scheduling. It would be possible to set the desired cumulative efficiency of the LNT, and this algorithm would deliver that efficiency per storage cycle. It still requires some calibration effort in order to determine what the desired cumulative efficiency should be, but it is much improved over the other methods.

The previous method is still lacking a crucial element for regeneration scheduling, which is the speed of the vehicle. Speed, of course, relates to the distance that the vehicle has traveled. Emissions standards are articulated in terms of mass per unit distance. It is therefore necessary to include distance in the formulation of the algorithm. A basic example of the impact that vehicle speed has is shown in Figure 126. Using a vehicle simulator, the steady-state NO\textsubscript{x} emissions at speeds ranging from 10 to 70 miles per hour
were determined. With these values, it was possible to determine the engine-out $\text{NO}_x$ emissions per mile at each speed. These values were then used to determine the required average $\text{NO}_x$ efficiency to meet a 0.05 g/mile $\text{NO}_x$ standard. As indicated in the figure, the values range from 72% to 85%, which is a considerable difference. The reason for this is that $\text{NO}_x$ does not increase linearly with vehicle speed, thus at certain speeds the $\text{NO}_x$ per mile is lower than others.

The impact of this behavior on the previous regeneration scheduling is that, for a constant cumulative regeneration efficiency that it will be regenerating to frequently or not frequently enough. For a driving cycle of mixed speeds, like the EPA tests, this effect would be averaged out somewhat. However, on a high speed test, like the HWFET, it would be fairly pronounced since there is not as high of a fluctuation in speed. This will cause either too frequent or infrequent regenerations which will effect g/mile $\text{NO}_x$ emissions as well as fuel economy. Note that the characteristic shown in Figure 126 is not general, and would vary from vehicle platform to vehicle platform.
From the above evolution, a final working control strategy has emerged. It must consider tailpipe-out NOx, vehicle speed, and time. At the start of each trapping event, the distance traveled and cumulative tailpipe-out emissions are reset. The distance traveled during the NOx storage is integrated based on vehicle speed and time. Simultaneously, the estimated or measured tailpipe-out emissions are integrated into a cumulative mass of NOx emitted. These two calculated values are divided to create a cumulative grams/mile estimate for the current trapping cycle. When the LNT has low amounts of stored NOx, the cumulative distance weighted mass of NOx stays at a low value. As the trapping efficiency begins to decrease, the cumulative distance weighted mass of NOx emitted begins to increase more rapidly. Eventually, it will pass a threshold value which is based on applicable emissions standard with some safety factor. Once this threshold is passed, the trap is regenerated and the process starts again.
There are a limited number of augmentations to the above method that must be made to make the above algorithm into a working control. The first is that a special condition exists when a regeneration event ends while the vehicle is at rest. Under these conditions, the cumulative tailpipe NO\textsubscript{x} is reset to zero and the distance traveled is set to zero. The first and most obvious problem is a division by zero, which of course, is not a good thing to have in a control algorithm. But the meaning of this division by zero is important. Under this circumstance, the distance traveled as long as the vehicle remains at rest is zero, while the tailpipe NO\textsubscript{x} emissions continue to accumulate, giving an infinite value of grams of NO\textsubscript{x} per mile. The simplest way to side step this problem is to simply handle this condition as an exception to the algorithm. If this condition is detected, the mass of NO\textsubscript{x} at idle is integrated and the normal mass per distance calculation is suspended. Once the vehicle has traveled a short distance the calculation is resumed. In the event of a prolonged idle, such as a traffic stoppage, it would be necessary to resort to the previous method based on a cumulative mass efficiency. The exact requirements of this mode of operation would need to be determined from the applicable emissions regulations.

The second modification to the basic algorithm is a low-pass filter on the vehicle speed. The goal of the algorithm is to regenerate the LNT when the cumulative emissions over the storage phase divided by the distance traveled pass a threshold. Because of the sometimes sharp changes in speed and NO\textsubscript{x} mass flow rate, the cumulative estimate of the distance weighted mass of emitted NO\textsubscript{x} has fluctuations. For low target values of engine-out NO\textsubscript{x}, which is what is required by the upcoming emissions standards, this fluctuation can be enough to trigger a regeneration at an earlier time than necessary. To overcome this, the vehicle speed signal is low-pass filtered with a relatively long time constant first-order filter. In doing this, it is possible to smooth out the fluctuations that can lead to early regeneration triggering.

The above algorithm is a good working method, however, it is not proven to be optimal in the control sense. However, short of incorporating predictions of the speed and NO\textsubscript{x} emissions of the vehicle this algorithm should hold up well against other algorithms. Although not proven in any rigorous sense, it would seem that the type of prediction that would be possible, which is on the order of a few seconds, would simply not provide any useful impact on the control since the trapping durations are on the order of
several seconds to minutes. In simulation studies, the algorithm performs as intended, as the cumulative tailpipe emissions approach the desired value asymptotically.

7.3 LNT NO\textsubscript{x} Storage Balancing

The above regeneration scheduling algorithm is applied to each catalyst in the dual-catalyst system. However, with the dual-catalyst system, it can be shown that the best efficiency can be obtained if the regenerations are staggered. Since the entire flow rate of exhaust is bypassed to the second catalyst during regeneration, the trapping efficiency of the catalyst during this time is doubly important. If one assumes that the average NO\textsubscript{x} flow into the catalyst is constant, it is possible to demonstrate that the optimal overall trapping efficiency occurs when the time interval between regenerations of the traps is equal. This is demonstrated in Figure 127. In this example, the inlet NO\textsubscript{x} is constant and the LNTs have a 100 second storage phase with a 10 second regeneration duration. The phase shift between the regenerations is varied from 10 seconds, which is one regenerating right after the other, to 55 seconds, which is alternating at equal time intervals, to 110 seconds, which is back to being one after another. As shown in the figure, the NO\textsubscript{x} that is emitted during the regeneration is lowest when the regenerations are perfectly out of phase. The trend in total emitted NO\textsubscript{x} is identical, although not as dramatic since this focuses on the time window when the difference is greatest. In terms of total mass emitted, the difference between the worst phasing and best phasing is on the order of 10%, so it is certainly worth accounting for.
Even if the catalysts are initially established at this optimal phasing, they will slowly drift away from this point due to differing amount of NO\textsubscript{x} entering the catalysts during regeneration as well as the difference in trapping efficiency when they are both exposed to the same feedgas NO\textsubscript{x}. When the regeneration scheduling algorithm decides it is necessary to regenerate an LNT, it will regenerate the trap which has the highest amount of stored NO\textsubscript{x}. To overcome this, it is necessary to balance the control the regeneration phasing of catalysts. If proportional control of the bypass flow of the exhaust to each catalyst were possible, it would provide an effective method of slowly balancing the phasing of the traps. However, this would require a proportional actuator and position sensor, which is a considerable added cost compared to the sensor-less, on-off actuation of a solenoid. Although not evaluated rigorously, it is expected that the gains from this additional level of control are not warranted. Because of this, the method of balancing the traps is based on binary valve actuation.
Before addressing the algorithm, it is necessary to come up with a proxy for the use storage time in the algorithm. The use of time in the algorithm is problematic, because from one trapping event to the next the time can vary substantially due to the different levels of NOx output. Balancing the trap times in the face of this would prove difficult and inaccurate. As a proxy for time, the cumulative g/mile values of the traps are used. Provided that the trapping efficiencies of the LNT are maintained at high levels, which indeed they must be, the increase in stored NOx in the catalysts offers a convenient signal for balancing the regeneration phasing. When a trap is required to be regenerated, the second trap should have approximately half of the NOx stored as the first. This can be achieved in practice, by holding the just regenerated trap offline until the second trap "catches up" in terms of the NOx level.

### 7.4 Optimal Regeneration Control

Regeneration control refers to the low-level control of the regeneration process. The regeneration scheduling algorithm determines when to do the regeneration, the regeneration control algorithm determines how long to regenerate and how to control the actuators during the regeneration. For this work, an optimal regeneration is one that takes the least amount of time, has the lowest reductant slip, and totally reduces all of the stored oxidizer in the LNT. This last constraint, as discussed later, will be relaxed for practical reasons, but will be included for now.

The system that is being controlled is the LNT and reductant delivery system, which has a single input which is reductant flow rate request and one output of current interest, which is reductant slip. Provided that the catalyst is at a reasonable operating temperature; it is possible, in practice, to achieve nearly total depletion of stored oxidizer while having negligible reductant slip. If, over the entire course of a regeneration, the catalyst is supplied with the maximum amount of reductant that it can consume, the objectives of the optimal control are meant. If reductant is supplied at this maximum rate, the duration of the regeneration is minimized. If no reductant slip occurs, then this is also the best possible case. Finally, it is also guaranteed that the catalyst will be depleted of stored oxidizer since the maximum rate of reductant consumption is zero if and only if the mass of stored oxidizer is zero. Based on this, the optimal
control problem is to maximize the input to the system, which is reductant flow rate, while minimizing the relevant output of the system, which is reductant slip. This control problem is the exact opposite of a typical optimal control problem, in which the goal is to minimize the control energy required to achieve a desired output. In this case, it is required to maximize the control input while maintaining exactly zero output.

For this derivation, stored NO$_x$ and O$_2$ are lumped together as a stored mass of oxidizer. The mass of stored oxidizer in a catalyst element $i$ is represented by the state variable $x_i$. Since it is assumed that we are operating at the maximum rate of reductant consumption, the non-linearities arising from the reductant usage vanish, and it results in the state equation in Equation (136). The reductant consumed by the catalyst element is related to the rate of oxidizer depletion by a stoichiometric factor, $B$, as shown in Equation (137). Lastly, the temperature state equation of the catalyst cell is also related to the rate of oxidizer depletion by another factor related to the heat of reaction and specific heat of the catalyst element, which is shown in Equation (138).

\[ \dot{x}_i = -A(T_i)x_i \]  
\[ r_i = A(T)Bx_i \]  
\[ \dot{T}_i = A(T)Cx_i \]

The only non-linearity included in the above equation set is the dependence of the factor $A$ on temperature, which is a state. Since the temperature rise of the catalyst element is relatively small and the dependence on temperature under normal operating conditions is relatively low, it will be assumed that $A$ is a constant.

\[ \dot{x}_i = Ax_i \]

Equations (136) through (138) can be solved as the homogenous response of a first order system and basic calculus, where subscript $i$ indicates the initial value.
From these results, it is possible to derive an expression for the maximum rate of reductant that the catalyst can consume, which is the goal of this derivation. As shown above, this is related to the decay of the stored oxidizer from its initial condition by the constants $A$ and $B$. If one sums up the maximum reductant consumption of all of the elements in the catalyst, here six, an expression for the maximum reductant consumption is obtained in Equation (143). Any reductant above this amount would result in reductant slip, thus, this is the optimal reductant rate expression for the system. As a simplification, the summation and constants are lumped into a single value, $r_{\text{max}}$, which is the peak rate of reductant consumption.

$$r_{\text{max}} = AB\left(\sum_{i=1}^{6} x_{i,0}\right) e^{-\frac{t}{A}}$$  \hspace{1cm} (143)

$$r_{\text{opt}} = r_{\text{max}} e^{-\frac{t}{A}}$$  \hspace{1cm} (145)

The above expression for optimal reductant flow rate could be used by itself. In practice, this requires an accurate knowledge of the factors in $r_{\text{max}}$ as well as the assumptions made earlier regarding the non-linearities to be entirely correct. The factors in $r_{\text{max}}$ involve estimates of the initial states of the amounts of stored oxidizer, as well as what amounts to the rate constants or reductant consumption. All of these parameters are not available as measurements by the control system, moreover the catalyst properties are in
constant change due to sulfur poisoning and aging. Because of the above uncertainties, it is necessary and preferable to rely on a feedback signal. The source of this feedback signal is a temperature measurement from the catalyst. Equation (141) can be rewritten as shown in Equation (146). This form is convenient, as the temperature of the catalyst element can be measured at the beginning of purge and stored. Any temperature rise from this point can be calculated by subtracting from this initial temperature.

\[ \Delta T_i = x_{i,o} C \left( 1 - e^{-\gamma/A} \right) \]  

(146)

Rearrangement of (146) leads to Equation (147). Substituting this equation into (145) yields the expression listed as Equation (148). This expression relates the optimal reductant flow rate to the maximum reductant flow rate, the change in temperature of a catalyst element, and the initial condition of the element multiplied by the constant C. A further simplification of the expression comes when it is noted that \( x_{i,o} C \) is the maximum temperature rise or the catalyst element. This final substitution yields an equation for the optimal reductant flow rate that can be reduced to practice for closed-loop control of the reductant flow rate.

\[ e^{-\gamma/A} = 1 - \frac{\Delta T_i}{x_{i,o} C} \]  

(147)

\[ r_{opt} = r_{max} \left( 1 - \frac{\Delta T_i}{x_{i,o} C} \right) \]  

(148)

\[ r_{opt} = r_{max} \left( 1 - \frac{\Delta T_i}{\Delta T_{i,max}} \right) \]  

(149)
There are a few practical issues that must be addressed to implement Equation (149). The first is the determination of which catalyst temperature to use as feedback. In theory, any of the temperature, or any combination of them, can be used with identical results. In practice, use of the most rearward temperature measurement is the logical choice. Since there are a number of uncertainties that are present, it is best to keep as many of these uncertainties "upstream" of the feedback location. In this way, deviations in the behavior of the plant will be sensed and accounted for through the feedback path. A second issue is the calculation of the maximum reductant flow rate. Based on (149), it is clear that the initial reductant command will be the value of $r_{\text{max}}$. This maximum reductant can be estimated based on the amount of NO$_x$ and oxygen stored in the catalyst as well as the $A$ factors, all of which can be estimated with reasonable accuracy. If the estimate is too high, the initial reductant flow rate will exceed the catalysts maximum rate of usage and reductant slip will occur. It will then take the feedback control system a small amount of time to compensate and bring the reductant slip to zero. Because of this, it is practical to set the maximum reductant flow rate to a value somewhat lower than the prediction. A lower value will result in a longer regeneration time, but this is not as unfavorable as reductant slip.

An issue related to the maximum reductant flow rate is the saturation of the regeneration gas actuator. In this case, the flame reformer is providing the rich gasses for regeneration of the LNT. Regardless of the design of the device, it will have some maximum flow rate of reductant that it can deliver. It is likely that, under certain conditions, that the optimal maximum flow rate will be higher than that achievable in practice. In this case, it is possible to use the true value of $r_{\text{max}}$, and allow saturation of the reductant output to occur. The closed-loop control will compensate accordingly to account for the lower than expected reductant delivery.

Another value that must be determined at the start of each regeneration is the value of the maximum temperature rise of the feedback temperature measurement. Provided that an accurate estimate of the stored oxygen and NO$_x$, this value is relatively easy to calculate. The penalty for overestimating the temperature rise, however, is substantial. If the temperature rise is set higher than the actual temperature the plant actually undergoes, then the reductant flow rate command will not go to zero and regeneration gas
flow will continue even though the catalyst is depleted of oxidizers. This would continue indefinitely unless additional measures were taken. Because of this reason, it is necessary to select a value of the max temperature rise of the element slightly lower than the estimated value. If the feedback temperature is at the rear of the catalyst, which is preferred, this approach will result in the rear of the catalyst not being fully depleted of oxidizers during a regeneration. This results in NO\textsubscript{x} building up at the rear of the catalyst. This results in slightly lowered NO\textsubscript{x} efficiency for the catalyst. It also builds up an buffer of stored oxidizers at the rear of the catalyst which can be beneficial in preventing reductant slip.

Another factor that needs discussed in this implementation is the effect of the temperature variation on the parameter $A$. For moderate to high temperatures, $A$ has a moderate dependence on temperature. At low temperatures, however, $A$ can decrease substantially over the 10ºC to 50ºC temperature rise that the catalyst will see during regeneration. Since a decrease in $A$ results in the catalyst being capable of consuming reductant at a higher rate, it results in a the reductant flow rate lower than optimal as the catalyst heats up during regeneration. This effect can be compensated for by applying a correction factor based on temperature during the regeneration. However, neglecting this effect results in only slightly longer regeneration times than the minimum, and thus is negligible.

Another factor that is neglected in the derivation of the optimal control is the effect of transport delay on the control. This must first be addressed at the system level, by reducing the volume between the reductant injection point and the catalyst, however, there will always be some dead volume present. The effect of this volume is to store reductant that is injected, such that when the temperature change is sensed, it is not possible to shut off the flow of reductant instantaneously. The reductant in the dead volume will eventually reach the catalyst, and possibly lead to reductant slip if it is not considered accordingly. It is felt that with proper system design and calibration, that this is not a great concern for the regeneration control.

This result leads to a closed-loop control with the structure shown in Figure 128.
7.5 Catalyst Regeneration Control Experimental Validation

Because of the importance of the regeneration control algorithm, it was tested experimentally over a range of operating conditions. For the tests, the reductant used was carbon monoxide diluted with carbon dioxide to mimic the approximate ratio of reductant to inert gas that would be typical of the flame reformer output. Carbon monoxide gas was used for this series of tests because of the simple controls for the flame reformer prototype would not permit dynamic operation. The flow of carbon monoxide gas to the catalyst was controlled via a PC running National Instruments Labview software. The actuator for the CO control was a continuously proportional valve.

7.5.1 Control Implementation

The regeneration control was implemented using on a PC using Labview's graphical programming language. The control loop rate was set at 10 Hz, which is quite slow considering the rates required for closed-loop control of air-to-fuel ratio in gasoline engines and Diesel engines during LNT regeneration.
The temperature measurement used for feedback control at each iteration was the average of the measurements acquired since the last control action. The sampling frequency was 1000 Hz, thus this accounted for 100 samples per average. This large number of samples is not required, provided that attention is given to noise reduction for the thermocouple signal. This control system was a slave to the main test cell data acquisition and control system, which coordinated the actuation of the valves and the logging of all data.

### 7.5.2 Experimental Results

As discussed in an earlier chapter, there were a number of simplifying assumptions made to derive the regeneration control algorithm. Of these assumptions, the one that caused the most trouble in extending the method to the physical system was neglecting transport delay. In the catalyst test rig, there is a considerable dead space in front of the LNT system which creates a transport delay from the regeneration actuator to the LNT. If the system were redesigned, this dead space could be reduced substantially; however, for the this initial trial it was necessary to cope with the current configuration. The effect of this transport delay is that a significant mass of reductant is already on its way to the before its effect can be sensed by the exotherms. If this effect is uncompensated for, it leads to reductant slip. The method of compensation for this effect was to use the next-to-last thermocouple measurement rather than the last thermocouple measurement as the feedback for the control. By setting the expected temperature rise slightly less than the actual temperature rise, it was possible to leave enough stored oxidizer in the rear of the catalyst to consume the reductant that would have slipped if this method were not employed.

Figure 129 shows the catalyst exotherms as well as the control signal to the proportional valve for a regeneration at 2000 rpm and 90 ft-lb of torque. The proportional command jumps immediately to the selected saturation value, in this case approximately 50%. The command remains at 50% until the fifth thermocouple begins to increase, and then it tapers off with the mirror image of this temperature rise. The sixth thermocouple shows a small temperature rise as it catches some of the reductant that is not used by
the upstream parts of the catalyst. For this case, negligible reductant slip occurred. This is indicated by both the post-catalyst CO measurement and the post-catalyst AFR measurement.

Figure 129: Experimental Results for Regeneration Control at 60 ft-lb, 2000 rpm

The following three figures, Figure 130 through Figure 132, show the impact of varying the maximum reductant command for three identical NOx storage levels at 2000 rpm, 60 ft-lb. In each plot, the pre and post-catalyst AFR is shown as well as the command issued to the reductant flow control valve. As the maximum reductant flow is varied from 100% to 84% to 75%, the amount of reductant slip approaches zero. In Figure 130, there is a clear dip in the post-catalyst AFR below stoichiometric, which is an indication of reductant slip. Similarly, in Figure 131, there is a much smaller dip in post-catalyst AFR. Finally, in Figure 132, there is no perceivable dip in the post-catalyst AFR. Thus, in reducing the
maximum flow rate, it is possible to arrive at an algorithm which achieves good regeneration with negligible reductant slip.

Figure 130: Experimental Results for Regeneration Control at 60 ft-lb, 2000 rpm
Figure 131: Experimental Results for Regeneration Control Strategy at 60 ft-lb, 2000 rpm
Figure 132: Experimental Results for Regeneration Control at 60 ft-lb, 2000 rpm
Figure 133: Experimental Results for Regeneration Control at 30 ft-lb, 2000 rpm
Figure 134: Experimental Results for Regeneration Control at 30 ft-lb, 2000 rpm
Figure 135: Post-Catalyst CO Emissions for Good and Bad Regenerations at 30 ft-lb, 2000 rpm

Figure 135 demonstrates the importance of minimizing reductant slip. The upper figure shows the post-catalyst carbon monoxide emissions for a case where the AFR signal indicates no reductant slip. The peak value of carbon monoxide is around 400 ppm. The lower plot in the same figure shows the results when the post-catalyst AFR drops 1.5 units below stoichiometric. Under this seemingly minor AFR drop, the post-catalyst carbon monoxide reaches a peak value of nearly 6%, a full two orders of magnitude greater than the "good" regeneration. CO emissions are not generally a problem since they are readily oxidized in the post LNT system clean-up catalyst. If the flame reformer were being used to provide the reductants, there would be a substantial amount of hydrocarbon emissions accompanying the CO slip. Hydrocarbon slip is particularly bad, since it is not controlled by the clean-up catalyst as nearly as well as carbon monoxide.
7.6 Flame Reformer Operating Point Determination

The optimal control strategy developed above is just one piece of a regeneration control algorithm; the second is the determination of the operating point of the flame reformer. The closed-loop control generates only a flow rate request for equivalent reductant, the flame reformer can provide this flow rate with multiple combinations of fuel and air. Each of these combinations would give a different pair of hydrocarbon emissions and efficiency. There is a clear tradeoff between these two factors, as shown in Figure 136. The hydrocarbons are lowest at low values of equivalence ratio; however, efficiency is poor at low equivalence ratios. Furthermore, efficiency peaks at a mid-range equivalence ratio while hydrocarbon emissions continue to increase.

Figure 136: Flame Reformer Efficiency and THC Emissions versus Fuel-Air Equivalence Ratio
First an investigation into just the flame reformer will be undertaken, without considering the potential effect the catalyst conditions may have on choosing an operating point. Using a simple optimization method, the hydrocarbon emissions at each equivalence ratio is normalized to fall between zero and one. The efficiency of the flame reformer is inverted, since low efficiency should be penalized, and then normalized in the same fashion. A penalty factor is then applied to the hydrocarbon emissions and efficiency at each equivalence ratio, such that the sum of the penalty factor is one. The minimum of this optimization function is an optimum for the particular penalty factors. The resulting equivalence ratio from this simple optimization for various penalty functions on hydrocarbons is shown in Figure 137. For a high THC penalty, the optimal equivalence ratio is unity, where hydrocarbons are lowest. As the THC penalty is reduced and more emphasis is placed on efficiency, the optimum equivalence ratio rapidly rises. It then gradually approaches the equivalence ratio where the peak efficiency occurs, at approximately 1.55.

![Figure 137: Optimal Flame Reformer Equivalence Ratio versus THC Penalty Factor](image-url)
The above exercise illustrates the basic tradeoff with the flame reformer operating point, however, this does not include the effect of the catalyst. When the catalyst is a relatively high temperature, it is capable of utilizing a high percentage of the hydrocarbons that the flame reformer generates. Under this situation, the hydrocarbons that are able to be consumed should be not be penalized as hydrocarbon slip, since they are consumed as reductant. Furthermore, since this quantity of hydrocarbons is going to serve the desired purpose, it should go towards raising the flame reformer efficiency. At low catalyst temperatures, in which a low portion of the hydrocarbons are used for reduction of stored oxidizer, the situation approaches the problem articulated above. Therefore it is clear that temperature needs to be included as a second dimension to the optimization problem.

The fraction of hydrocarbons used by the catalyst was presented earlier as Figure 97. By applying this information to the flame reformer output, it is possible to recalculate the efficiency and unused hydrocarbon emissions as a function of fuel-air equivalence ratio and catalyst temperature. This new representation of the previously presented maps are provided as Figure 138 and Figure 139. Note that, at high catalyst temperatures, virtually all hydrocarbons emitted from the burner can be used by the catalyst. This also has the benefit of increasing the efficiency dramatically, up to the nearly 50% theoretical efficiency that would be expected at a fuel to air equivalence ratio of 2.
This new dimension to the optimization problem does not alter the method of analysis from before. These new maps are weighted in the same manner; however, they are now functions of temperature and equivalence ratio. Figure 140 shows the resulting value of the optimization function value for several values of hydrocarbon penalty. Note that the optimization function values have been inverted for clarity, so that the maximum value is the optimal value. For each value of catalyst temperature, it is desirable to determine the peak value of the optimization function, which then gives the optimal value of phi for each THC weighting factor. These values have been evaluated, and are shown as the black lines on the surface of the optimization function in Figure 140. This series of plots and optimal traces are intuitive. At a low THC penalty, the optimum favors highest efficiency, which starts at around a phi of 1.55. As the catalyst warms up and begins to be able to process hydrocarbons as reductant, it rapidly moves to phi of 2.0 and stays there.
Figure 139: Flame Reformer Efficiency with Catalyst Temperature Effect
Figure 140: Flame Reformer Optimization Surfaces and Optimal Path
The optimal paths from the optimization can be plotted in two dimensions to show the optimal value of phi for a given temperature for each hydrocarbon weighting factor. Figure 141 shows the optimal equivalence ratio for hydrocarbon penalties of 0 to 1 in increments of 0.1. Note that at temperatures above around 375°C, all of the curves collapse to phi of 2, except for the one that places a penalty of 1.0 on hydrocarbon emissions. At temperatures above 375°C, it is clear that a phi of 2.0 is the obvious choice. At temperatures below 375°C, the THC penalty factor has a more dominant role in the optimization. Clearly, this is a tradeoff that must be decided using other factors. In practice, one would select the curve based on the emissions performance of the vehicle. If the vehicle was borderline on the THC standard, it would be necessary to use one of the paths at a higher weight. However, if THC emissions from the vehicle were low, then it would be possible to sacrifice some additional THC emissions in order to gain efficiency. Based on simulation results, it is clear that the dominant factor is indeed THC emissions. Because of the low fuel penalty (<2%) associated with the bypass-regeneration, gaining 10% efficiency on the flame reformer efficiency has a minimal impact on the overall fuel economy of the vehicle. Therefore, a reasonable selection of a path would be the dashed line in the figure, which corresponds to a THC penalty of 0.7.
Because the regeneration control strategy is formulated to operate in terms of equivalent reductant, it is necessary to covert this request into a flame reformer air and fuel command. The fuel-air equivalence ratio is determined as shown above, but this leaves one of the inputs to the flame reformer to be specified. Fuel was selected over air, since there is a more intuitive connection between reductant production and fuel input. Since the desired fuel-air equivalence ratio is known, the selection of the fuel command amount to a 2 dimensional look-up table with fuel-air equivalence ratio as one index and average catalyst temperature as the second index. The table values are the equivalent reductant that is generated by the flame reformer per gram of fuel input. Figure 142 shows the surface of the resulting table. This figure is virtually identical in shape to the efficiency plots shown above, which is simply a result of the fact that the heating value of the reformer products correlates directly to its ability to oxidize stored NOx and oxygen. By dividing the desired equivalent reductant by the lookup value of fuel mass normalized equivalence reductant, the
required fuel command is determined. The air command then follows directly from the fuel command based on the desired value of fuel-air equivalence ratio.

Figure 142: Flame Reformer Equivalent Reductant Output

7.7 Adaptive Algorithms

There are two pieces of information that must be acquired during the regeneration. The first is the magnitude of the rich exotherm at all available measurement locations. As demonstrated, the magnitude of this temperature rise can be correlated with acceptable accuracy to the amount of stored NOx regenerated from the catalyst. The critical point to realize with this, however, is that in order to arrive at the NOx estimate it is imperative to also know what the temperature rise due to oxygen storage was for the rich
exotherm. This is necessary because there is no way to distinguish between the NO\textsubscript{x} temperature rise and the oxygen temperature rise because they happen at the same time.

### 7.8 Oxygen Storage Measurement Algorithm

There are three features of the physical process that allow the adoption of an algorithm that learns that oxygen storage as it changes over time. For normal storage cycle durations, it is accurate to assume that the catalyst has achieved saturation of its oxygen stores at the time of regeneration. Because of this, it can be assumed that, at each regeneration, the full amount of oxygen is stored in each section. Additionally, the degradation of oxygen storage is a relatively slow process and is much more resistant to poisoning than the NO\textsubscript{x} storage of the catalyst. Lastly, if the catalyst is subjected to a controlled lean phase after the rich regeneration, it is possible to accurately measure the lean exotherm, which is correlated directly to the oxygen storage. Because of these reasons, it is possible to construct an algorithm that achieves the desired goal of tracking oxygen storage over the life of the catalyst.

The oxygen storage algorithm would need to be initialized with an initial map of oxygen storage. The first time the vehicle was started, this map would have to be a default map which would allow the control algorithm to work without having a chance to adapt. As the vehicle accumulated more regenerations, and thus more O\textsubscript{2} storage data, this map would evolve into an accurate depiction of the catalyst's oxygen storage. This updated map would be stored at key-off and then be reloaded upon key-on, so that the system starts with an accurate map of the catalyst.

The most dominant factor influencing the oxygen storage of the catalyst is the temperature of the catalyst substrate. Other factors, besides temperature, could be used as indices in this map if relevant, but temperature is the most dominant. At every regeneration event, oxygen storage information is available, provided that a controlled lean exotherm is generated, which is at the discretion of the control algorithm. The generation of a lean exotherm is not necessary for the operation of the LNT and increases the time that the LNT is removed from trapping. Depending on how much data is required to track the oxygen storage,
it is highly likely that data is not needed on each regeneration. If this were the case, then there is no need to generate a lean exotherm, and the time required for regeneration could be shortened. This would be prudent on aggressive driving conditions, where the duration of the regeneration is critical.

An important distinction must be made in discussing the temperature effect on oxygen storage. The temperature of relevance for the rich regeneration is the temperature at the end of the storage phase. In this statement, it is assumed that the catalyst is saturated with oxygen at the time it last has access to oxygen, which is just before the start rich regeneration. Therefore, the most meaningful temperature relating the mass of oxygen reduced during the rich regeneration this initial temperature. During the lean exotherm, the same assumption must be made but with the opposite result. In this process, the temperature at the end of the lean exotherm is the temperature of interest. During the lean exotherm, the temperature of the catalyst increases, thus, its oxygen storage ability changes. Under most conditions, the catalyst oxygen storage increases with temperature. As the catalyst temperature increases, its oxygen storage capacity will increase, allowing it to adsorb more oxygen. Therefore, the most accurate temperature to correlate the oxygen storage to is the final temperature of the catalyst.

For every regeneration that a lean exotherm is generated, the algorithm acquires one oxygen storage "measurement" per temperature measurement that corresponds to the temperature at the end of the lean exotherm. This value can be compared to the stored map of oxygen storage versus temperature and used to modify the map based to better reflect the current state of the catalyst. Because the number of regenerations is high compared to the rate of oxygen storage degradation, this method should provide an accurate characterization of the oxygen storage of the catalyst at all times. There may be some initial errors during at the beginning of the vehicles life, but these should not cause major disruptions in the control algorithm provided that the fresh catalyst agrees with the oxygen storage model that is the default into the engine controller.

By necessity, the above algorithm must be extended to compensate for axial differences in catalyst. Oxygen of a fresh catalyst is generally the same throughout the catalyst, however, as the catalyst ages this
is not the case. Oxygen storage degradation is a slow process, but tends to affect the front of the catalyst more severely than the rear. Because of this, it would be necessary to have an oxygen storage map for each temperature measurement location or to compensate based on the difference at each location based on a single map. The last thing to note is that, in general, the catalyst sections will start at different temperatures during the regeneration. Because of the rapid fluctuations in inlet temperature during most driving cycles and slow temperature dynamics of the catalyst, the catalyst temperature varies considerably along the catalyst.  A description of this process of acquiring a measurement and adapting the model is the following:

\[
\begin{align*}
\text{At } t = 0, & \quad T_{i,C} = T_i \\
\text{At } t = t_{\text{lean,end}}, & \quad T_{i,D} = T_i \\
\Delta T_{i,\text{lean, total}} & = T_{i,D} - T_{i,C} \\
M_{i,O2} & = \frac{\Delta T_{i,\text{lean, total}}}{C_{O2}} \text{ at } T = T_{i,D} \\
\text{Adjust } f_{O2}(T) \text{ with new data at } T_{i,D}, M_{i,O2}
\end{align*}
\]

Where:

t = time after start of lean exotherm

i = catalyst temperature measurement location number

t_{\text{lean,end}} = time at end of the rich exotherm

T_i = catalyst temperature measurement

T_{i,C} = temperature at the start of lean exotherm

T_{i,D} = temperature at end of lean exotherm
\[ \Delta T_{\text{total}} = \text{total change in temperature for the lean exotherm} \]

\[ C_{\text{O2}} = \text{constant relating temperature rise to mass of stored oxygen} \]

\[ M_{\text{i,NOx}} = \text{mass of NOx regenerated from the catalyst at location i} \]

\[ f_{\text{O2}}(T) = \text{oxygen storage model} \]

### 7.9 NOx Storage Measurement Algorithm

After each regeneration event, there is an estimate available for the amount of NOx that was regenerated from the catalyst. If the regeneration approaches being a total regeneration, then this estimate approaches the amount of NOx that was stored in the previous storage phase. Based on practical limitations, it is generally not possible to completely regenerate the trap, however, the front and middle regions of the catalyst are reliably regenerated under all conditions. Since, at high cumulative trapping efficiencies, the majority of the stored NOx is trapped in these regions, this does not create a major problem in arriving at an estimate of the NOx accumulated during the previous storage cycle.

The data shown in previous chapters showing the correlation between catalyst temperature rise and NOx were conducted at steady-state conditions, thus the catalyst was at a uniform temperature. In a vehicle application, the catalyst will more than likely not be at a uniform temperature due to the transient changes in exhaust temperature. If the temperatures are considerably different, then the level of oxygen storage at the different temperature measurement locations will be different. This has an important impact on the analysis of the rich exotherms, since the temperature rise due to oxygen storage will be different depending on the state of the catalyst. As described in the previous section, it will be necessary to adaptively learn the oxygen storage at each of the measurement locations, thus it is a simple matter to correct for the effect of varying temperatures. The following describes the steps in this algorithm:
At \( t = 0 \), \( T_{i,A} = T_i \)  

\( \Delta T_{\text{rich, total}} = T_{i,B} - T_{i,A} \)  

\( \Delta T_{i,O2} = f_{i,O2}(T_{i,B}) C_{O2} \)  

\( \Delta T_{i,NOx} = \Delta T_{\text{rich, total}} - \Delta T_{i,O2} \)  

\( M_{i,NOx} = \Delta T_{i,NOx} C_{NOx} \)  

Where:

\( t \) = time after start of rich exotherm  

\( i \) = catalyst temperature measurement location number  

\( t_{\text{rich, end}} \) = time at end of rich exotherm  

\( T_i \) = catalyst temperature measurement  

\( T_{i,A} \) = temperature at the start of rich exotherm  

\( T_{i,B} \) = temperature at end of rich exotherm  

\( \Delta T_{\text{rich, total}} \) = total change in temperature for rich exotherm  

\( \Delta T_{i,O2} \) = change in temperature due to stored oxygen  

\( f_{i,O2} \) = learned oxygen storage capacity function  

\( C_{O2} \) = constant relating temperature rise to mass of stored oxygen
\[ \Delta T_{i,\text{NO}_x} = \text{temperature rise due only to stored NO}_x \]

\[ M_{i,\text{NO}_x} = \text{mass of NO}_x \text{ regenerated from the catalyst at location i} \]

\[ C_{\text{NO}_x} = \text{constant relating mass of stored NO}_x \text{ to temperature rise} \]

During a regeneration, the amount of NO\textsubscript{x} that is stored in the catalyst can be estimated. In the context of this algorithm, this is considered a measurement. If one considers the process of measuring something, it must be noted that there are very few measurements that actually measure the true parameter being measured. For instance, automotive mass air flow sensors sense the heat loss from a thin heated body and correlate this to air flow. Similarly, the temperature rise in the catalyst can be correlated to the amount of stored NO\textsubscript{x} and oxygen in the catalyst.

### 7.10 Adaptation of the Engine-Out NO\textsubscript{x} Model and the LNT Storage Model

For the control algorithm under discussion, it is necessary to have an engine-out NO\textsubscript{x} estimator as well as an LNT storage model that serves as a catalyst-out NO\textsubscript{x} estimator. This is necessary to make up for the lack of direct measurements of engine-out and tailpipe NO\textsubscript{x} emissions. Due to uncertainties in the models, plant parameter changes, and part-to-part variation it is certain that any model will not be accurate over the life of the vehicle. The only measurement that is available is the NO\textsubscript{x} storage measurement, which is available after each regeneration. During the operation of the aftertreatment system, there are three situations that can arise:

1. The NO\textsubscript{x} storage estimate is higher than the NO\textsubscript{x} storage measurement

2. The NO\textsubscript{x} storage estimate is lower than the NO\textsubscript{x} storage measurement

3. The NO\textsubscript{x} storage estimate is about the same as the NO\textsubscript{x} storage measurement
There are two places that these disagreements in the measurement and the estimate can be attributed to: the engine-out NO\textsubscript{x} model and/or the catalyst storage model. In general, it can be assumed that the catalyst changes slowly over time due to aging effects. It is, of course, possible that the catalyst undergoes a sudden change in characteristics, as in the case of thermal damage. These effects are not considered, since they would not occur in normal operation. On the other hand, the engine-out NO\textsubscript{x} model could have errors which change on a short time scale. Something as innocuous as a rain storm, which increases relative humidity, would be enough to cause a small, but significant, change in engine-out NO\textsubscript{x} emissions. Since humidity sensors are not in the normal engine sensor set, the engine-out NO\textsubscript{x} estimate is not aware of this.

A difficulty arises in determining the source of the disagreement between the measured NO\textsubscript{x} and the estimated NO\textsubscript{x}. If the NO\textsubscript{x} storage estimate is higher than the measurement, this could be due to the catalyst model predicting more NO\textsubscript{x} is trapped than actually was. Alternatively, it could be due to the engine-out NO\textsubscript{x} estimator overestimating the NO\textsubscript{x} output of the engine. If the NO\textsubscript{x} storage estimate is lower than the measurement, then the opposite situation would occur. In order to separate these similar effects, it is necessary to develop two model adaptation algorithms, each which utilize a different relationship between the NO\textsubscript{x} storage measurement and the NO\textsubscript{x} storage estimate.

The first relationship that will be exploited by the control algorithm is that the NO\textsubscript{x} storage estimate distribution must agree with the NO\textsubscript{x} storage measurement. Since the effect of sulfur poisoning is to cause differences in the distribution of NO\textsubscript{x} storage, this relationship will be used for the adaptation of the NO\textsubscript{x} storage model. The second relationship that will be used is that the estimate of total NO\textsubscript{x} stored in the trap must agree with the measured total mass of NO\textsubscript{x} stored. This may seem like use of the same information twice, but there is an important and subtle difference.

For illustration, consider that there is a 20% underestimation of the engine-out NO\textsubscript{x} by the engine-out NO\textsubscript{x} model. This would result in the storage model underestimating the amount of NO\textsubscript{x} stored in the trap when compared to the measurement. If the engine-out adaptation was disabled, the catalyst storage adaptive estimator would modify the parameters of the catalyst in an effort to make the model match the measured
distribution of NO\textsubscript{x} by raising the storage efficiency. Because of the physics of the process, the adaptive algorithm adjusts the parameters from the front of the catalyst back. Over several trapping cycles, the parameters will be adjusted and NO\textsubscript{x} will get moved towards the front of the catalyst in an effort to match the measurement. A situation that arises is that, in moving NO\textsubscript{x} towards the front of the catalyst, the middle and rear sections of the catalyst begin to show deficiencies in stored NO\textsubscript{x}. If left unchecked, the catalyst adaptation algorithm will continue raising the efficiency of the catalyst elements at the rear of the catalyst, with no resulting increase in NO\textsubscript{x} storage. This is due to the fact that there is simply not enough "virtual" NO\textsubscript{x} \textit{(i.e., the output of the engine-out NO\textsubscript{x} estimator)} to match the actual amount in the LNT. Because an LNT operates at approximately 90% efficiency, most of the NO\textsubscript{x} leaving the engine is trapped by the catalyst. An underestimation in NO\textsubscript{x} leaves less NO\textsubscript{x} in storage model, thus it can not adjust the efficiency parameters high enough to get the NO\textsubscript{x} storage to match the measurements. Because of the high trapping efficiencies required of the LNT system, it is possible to use the mass of NO\textsubscript{x} stored condition to adapt the engine-out NO\textsubscript{x} model. There are, of course, some limits to the engine-out NO\textsubscript{x} error that can be corrected for.

7.11 Catalyst Model Adaptation for Degradation

The catalyst adaptation algorithm is formulated on the assumption that the engine-out NO\textsubscript{x} estimator error is negligible. This does not mean that the estimate is perfect, just that the errors are of a sufficiently high frequency and have a zero mean value, such that they do not impact the cumulative NO\textsubscript{x} over a storage cycle. Specifics on how to deal with other types of errors in the engine-out NO\textsubscript{x} model will be discussed in the following sections.

The catalyst model that is imbedded in the control algorithm is identical to the storage model previously presented. The model is a distributed lump model with six identical sections, which correspond to the measurement locations of the catalyst thermocouples. Each element has one state, which has parameters which vary with the measured temperature of the catalyst. Based on the sulfur poisoning results discussed previously, sulfur poisoning can have an impact on two factors in the model. The first factor is the
maximum NO\textsubscript{x} storage capacity function, which is simply the maximum amount of NO\textsubscript{x} that can be store in the catalyst for a given temperature. Due to the distributed nature of sulfur poisoning, it will impact the maximum storage capacity most aggressively at the front of the catalyst. The second parameter that is affected is the shape of the efficiency curve, which in the model structure has a dependence on temperature. The dependant variable of the efficiency curve is the NO\textsubscript{x} fill ratio, which is the mass of NO\textsubscript{x} in the catalyst element divided by the maximum capacity of the trap for the current temperature. Because of this relationship, the shape of the efficiency curve, in terms of mass of NO\textsubscript{x} is affected by the trap capacity.

For the proposed algorithm, it was decided to let only one parameter be adapted. For this, the parameter that controls the shape of the efficiency curve was selected for the following reasons:

1. NO\textsubscript{x} storage capacity can be, if needed, measured on-board the vehicle through an intrusive test.

2. The shape of the efficiency curve can not be measured in-vehicle without the use of exhaust gas NO\textsubscript{x} sensors.

3. The sulfur poisoning tests indicated that the change in the efficiency curve shape had a more dominant effect then the total trap capacity.

4. Over the region of the trap used to achieve high efficiency, the shape of the efficiency curve can approximate the effect of a loss in trap capacity.

The first three reasons above are acceptable, but the last one is perhaps the most concrete. Consider Figure 143, which illustrates this point. The series of solid lines show the change in the shape of the efficiency curve function as the constant in the function varies from -1 to -6, with the assumption that the trap capacity remains constant at 0.5 grams of NO\textsubscript{x}. This is typical for what would occur in practice for sulfur poisoning. The region that the LNT is operated in is limited to the high efficiency area of y-axis, in the range of 80% and above. In this region, the efficiency functions are very nearly straight lines. Now note the dark dashed line in the figure, which represents changing the capacity of the trap from 0.5 to 0.35 grams while leaving the efficiency curve shape constant at -1. Over the high efficiency region of interest, this
curve lines up almost exactly with the case where the shape constant equals -2. It is possible that either one of the methods of degradation can be accounted for by varying just one of the parameters over the region of interest. The shape constant is the best choice for the adaptation parameter, given the additional reasons listed above.

Figure 143: Changes in Storage Efficiency Curve Shape

Now that the method of adapting the model to account for sulfur poisoning is identified, it is necessary to describe how the adaptation occurs. To perform the adaptation, there are two pieces of information available. The first is the measurement of NOx from the catalyst temperature measurements. The second is the estimate of the NOx stored in the same locations, as predicted by the catalyst model. Assuming that the engine-out NOx estimate is correct, the error between the measurements and the predictions is due to errors in the catalyst model parameters. It is this error that is used to drive the adaptation of the storage model. If
one were performing the calculation offline, it would be possible to store the entire sequence of engine-out NO\textsubscript{x} flow rates and catalyst temperatures and then perform a non-linear optimization to adjust the six storage shape parameters to get minimum error in the NO\textsubscript{x} predictions. The required computing power and memory are simply not present in an automotive powertrain controller; therefore, a more computationally efficient method is used.

If the shape parameter for one of the catalyst cells in the storage model is varied over a representative storage cycle, it is observed that NO\textsubscript{x} storage changes almost linearly. As shown in Figure 144, the resulting curve is reasonably linear over a wide range of values. The slope of this curve can be used as the basis for a feedforward gain to adjust the model parameters. The region of interest of this curve is the region about the origin, since the expected errors in the stored NO\textsubscript{x} should be small from one storage event to the other. The slope of this curve in this region is 21.3. The value of this number is that, when multiplied by the error in the NO\textsubscript{x} estimate, it yields a correction that can be used to adjust the erroneous shape parameter. In practice, this adjustment will not yield the exact value of the parameter. However, an error measurement is available after each storage cycle. Thus, the effect of the parameter change will be measured on subsequent storage cycles and can be further adapted as necessary. This method is essentially a closed-loop control which acts on the model parameters to bring the errors between the model and the plant to zero.
The basic method of adaptation is described above, however, it requires a few more components to be useful in practice. In the catalyst model, any time the efficiency shape parameter is changed, it has an effect on all of the downstream NOx storage elements. If the efficiency of the first storage element is reduced, then there is more NOx available downstream, and the result is slightly increased NOx storage in these cells. If one ignores this downstream effect, and adjusts the downstream values of the shape parameters after making an upstream change, it will result in the updated parameters being slightly off. For a typical case, a shape parameter change which causes a certain predicted reduction in the mass storage of an element will have the effect of increasing the NOx storage of all downstream elements by 10 to 15% of the NOx change of the element. Because of this, it is necessary to work from the front to the back of the catalyst when adjusting the shape parameters and to adjust the NOx estimates by the factor so that they are not needlessly adjusted.
The last component of the storage model parameter adaptation algorithm is necessary to reduce the effect of noise in the NOx measurements. It is inevitable that there will be inaccuracies in the NOx measurements. If not addressed, the noise will cause unnecessary changes in the parameters of the model. To combat this, the updated parameters that are used to modify the storage model are low-passed filtered using a first-order, digital low pass filter. In this algorithm, the filter is updated every regeneration event, which is effectively the sample clock for the filter. The time constant of the filter needs to be selected such that it allows the parameters to adapt fast enough to track the expected changes in the catalyst due to oxygen storage, but not so low that it allows noise to cause unwanted parameter changes. In the algorithm experimental validation presented shortly, this time constant was set to two events. This is much lower than it would be in practice, since the validation was done on the accelerated sulfur poisoning data presented earlier. A time constant on the order of 10-20 events would probably be used in a vehicle application, however, this would need to be determined from experimental data.

Figure 145: Catalyst Model Adaptation Scheme

Figure 145 shows a block diagram of the proposed NOx model adaptation scheme. The input to the algorithm is the measured NOx at each temperature measurement location. The estimated NOx stored from the catalyst model is used to generate an error vector. The error vector is acted upon by a gain matrix to produce an output vector. This output vector is an incremental change to the current catalyst model.
parameters, which should drive the error closer to zero. This incremental change of parameters is added to
the last iterations parameters to generate parameter values. These parameters values are then low-pass
filtered to control noise in the NO\textsubscript{x} measurements. Since the catalyst degradation is quite slow, it is
possible to have an aggressive low pass filter such that the parameter adaptation process proceeds slowly.
The following matrix equations show the error terms, as well as the gain matrix formulation which is
suggested by the physics of the process. In simulation, only two gain values are used: one for the diagonal
elements and one for all of the other non-zero gains.

\[
\begin{bmatrix}
E_1 \\
E_2 \\
E_3 \\
E_4 \\
E_5 \\
E_6
\end{bmatrix}
= \begin{bmatrix}
NO_{x,1} \\
NO_{x,2} \\
NO_{x,3} \\
NO_{x,4} \\
NO_{x,5} \\
NO_{x,6}
\end{bmatrix} - \begin{bmatrix}
NO_{e,1} \\
NO_{e,2} \\
NO_{e,3} \\
NO_{e,4} \\
NO_{e,5} \\
NO_{e,6}
\end{bmatrix}
\]

(161)

\[
\begin{bmatrix}
P_1 \\
P_2 \\
P_3 \\
P_4 \\
P_5 \\
P_6
\end{bmatrix}
= \begin{bmatrix}
K_{1,1} & 0 & 0 & 0 & 0 & 0 \\
K_{2,1} & K_{2,2} & 0 & 0 & 0 & 0 \\
K_{3,1} & K_{3,2} & K_{3,3} & 0 & 0 & 0 \\
K_{4,1} & K_{4,2} & K_{4,3} & K_{4,4} & 0 & 0 \\
K_{5,1} & K_{5,2} & K_{5,3} & K_{5,4} & K_{5,5} & 0 \\
K_{6,1} & K_{6,2} & K_{6,3} & K_{6,4} & K_{6,5} & K_{6,6}
\end{bmatrix}
\begin{bmatrix}
E_1 \\
E_2 \\
E_3 \\
E_4 \\
E_5 \\
E_6
\end{bmatrix}
\]

(162)

7.12 Catalyst Degradation Adaptation Experimental Validation

As described in the previous section, it is possible to adapt the catalyst model via the information provided
by the catalyst temperature measurements to account for the effect of catalyst degradation. To validate this
method, the sulfur poisoning data that was collected was used as an input to the catalyst model and adaptive
component. The results, although conducted offline, were conducted in a manner such that they would
behave exactly the same as if conducted at the time of the experiments.
7.12.1 Initialization of the Algorithm

Because this is just a validation run and the data set is limited, only the necessary components of the algorithm were implemented. For this set of experiments, the catalysts were nearly a steady-state temperature, thus the oxygen storage capacity of the catalyst was assumed not to vary with temperature. The six element storage model was initially calibrated using a data set that had the fresh LNT trapping to saturation. The model parameters for the storage efficiency functions were used as the initial starting point for the algorithm. The values of maximum NO\textsubscript{x} storage and the DeNO\textsubscript{x} efficiency were the average values over the entire data set. In reality, these parameters could be changed, or in the case of NO\textsubscript{x} storage, measured online. However, since the variation was reasonably small, they were left at average values, since the learning algorithm can account for slight errors in these parameters. The value of the constant relating mass of NO\textsubscript{x} stored to temperature rise was taken from data from a different catalyst with the same formulation. The value relating the lean exotherm temperature rise of due to oxygen storage to the contribution of stored oxygen to rich exotherm temperature rise was calculated from as an average of the non-poisoned catalyst over ten two minute trapping cycles.

7.12.2 Algorithm Simulation Methodology

From the sulfur poisoning experiments, nine sets of ten two minute NO\textsubscript{x} storage cycles are used as the input to the storage model. During all but the first and second cycle, the catalyst is being exposed to an elevated level of sulfur that is about ten times the normal inlet mass; thus, the cumulative efficiency of the trap degrades rapidly. The measured feedgas from the data set is fed to the catalyst model, which estimates the amount of NO\textsubscript{x} stored in each of the six elements. At the time of regeneration, the adaptive algorithm converts the temperature rises into an estimate of NO\textsubscript{x} stored in each of the six elements. Based on the difference between the estimate from the model and the measurement calculated from the exotherms, it adjusts the storage efficiency functions appropriately. These new values are then used on the next storage cycle and the process continues through the 90 storage sequences. Since the model predicts catalyst-out
NO\textsubscript{x} and catalyst-out NO\textsubscript{x} was measured, it is possible to compare the actual experimental results to the adaptive model.

### 7.12.3 Experimental Results of Catalyst Degradation Learning Algorithm

Based on the above conditions, the offline experiment was run and the performance of the algorithm evaluated. As shown in Figure 146, the agreement of the cumulative NO\textsubscript{x} stored during the two minute trapping cycles agrees within +/- 4% over the entire data set. Due to the sulfur poisoning, the amount of NO\textsubscript{x} trapped drops from 2.7 grams to 2.3 grams. In general, the estimate is approximately 2% low of the measured value. The cumulative trapping efficiency over the two minute trapping cycles had a much greater variation over the 90 cycles used in the offline experiment. Over the 90 cycles, the cumulative efficiency varied from 95% to 78%. Figure 147 shows the experimental results compared to the estimate as well as a plot of the percent difference between the measured and estimate value. Once again, the estimator generally underestimates the actual value by about 2%, but the estimate stays within a +/- 4% error band. To stress the effectiveness of the learning algorithm, without the learning feature, the algorithm would have had greater than 20% error by the end of the 90 cycles.

Figure 148 shows how the parameters changed over the course of the 90 storage cycles. They steadily move lower and lower, which modifies the storage efficiency curves so that they store less NO\textsubscript{x}. Because of the limited number of measurements over such a steep decline in NO\textsubscript{x} efficiency, that there is considerable noise in the parameters. In the field, there would be many more measurements which would allow for greater filtering of the parameters and better accuracy of the method. This gives a large number of samples over a slowly varying sulfur poisoning level. By having a large number of samples, the noise in the NO\textsubscript{x} measurements from the catalyst temperatures will be diminished. Considering this, the above test was actually quite extreme. In reality, the number of measurements over a similar level of degradation would be over an order of magnitude greater.
Figure 146: Catalyst Degradation Model Cumulative NOx Storage Estimate Results
Figure 147: Catalyst Degradation Model Cumulative Storage Efficiency Estimate Results
of measurements over a similar level of degradation would be over an order of magnitude greater.

7.12.4 Engine-Out NO\textsubscript{x} Estimator Adaptation

In the adaptive algorithm for the storage model, it is assumed that the estimate of engine-out NO\textsubscript{x} has no error. This, of course, is not going to be the case, and it is necessary to adapt the engine-out NO\textsubscript{x} estimator to account for these errors. In order to properly formulate an adaptive algorithm to compensate for engine-out NO\textsubscript{x} estimate errors, some assumption will be made regarding the nature of the errors that it will make. Unfortunately, no references were found that address the issue of engine-out NO\textsubscript{x} estimator errors in the depth required. Since designing and validating an engine-out NO\textsubscript{x} estimator was out of the scope of this work, the following algorithm is designed to be as realistic and general as possible with regard to the errors.
The best case scenario for the errors would be an error that has a mean of zero and occurs at a high frequency with respect to the time scale of a NOx storage event. Under these circumstances, the error would not affect the control algorithm in the slightest, since it is based on integral values of NOx rather than instantaneous values of NOx. Based on the literature, it is guaranteed that such high frequency errors will be made, but the criteria for having a zero mean does not have any basis. Based on the sensor set, there is simply no way of detecting these transient errors, other than by the effect that they have on the mean NOx emissions. This is a result of only having a sample of cumulative NOx on the order of tens of seconds. With this poor of time resolution, there is no method of reliably back-tracking to find specifically where the NOx estimation error occurred.

This leads to the two types of errors that can be detected by the sensor set. The first, as mentioned above, is a fast, transient error with a non-zero mean. The second type of error would be a systematic error that persists for a long period of time with respect to the length of the storage phase. This type of error could be due to part-to-part variation of engine components or degradation of engine components which influences the NOx emissions, such that they vary from the estimator prediction. An example would be the stack-up of tolerances in the injection system (common-rail pump, rail-pressure sensor, injectors, injector drivers, etc…) causing deviations in the mass and timing of the fuel injection. In the context of this algorithm, the source or the error does not matter, only its cumulative effect on the engine-out NOx emissions over the duration of the storage cycle.

Assuming that the algorithm is not compensating for engine-out NOx errors, the catalyst model would sense these errors and adapt the catalyst model in an attempt to account for the difference in measured and estimated stored NOx. To the catalyst learning algorithm, an error in the engine-out NOx estimate looks like an error in the catalyst storage efficiency parameters. It will then proceed to adjust the catalyst storage model parameters based on the flawed NOx estimate to drive the error between the measured and the flamed estimated of NOx stored to zero. This will eliminate the error, but lead to problems in the regeneration scheduling since it is only masking the engine-out NOx estimate error. If the NOx error occurs
for only a few storage cycles, then the filtering of the adaptive parameters will minimize the impact of the error. But for systematic error over several storage cycles, this would not be the case.

The most direct effect of this erroneous adaptation is on the regeneration scheduling algorithm. If the engine-out NO\textsubscript{x} estimator is over predicting NO\textsubscript{x}, the catalyst learning algorithm will see more estimated NO\textsubscript{x} in the catalyst than the NO\textsubscript{x} measurements indicate. This will cause the catalyst adaptive algorithm to decrease the storage efficiency of catalyst model. This, in turn, will lead to the cumulative NO\textsubscript{x} emissions estimate growing faster than it the actual cumulative emissions, triggering more frequent regenerations. This leads to increased fuel consumption and lower NO\textsubscript{x} emissions than necessary to meet regulations. The opposite of the above is if the engine-out estimator is underestimating NO\textsubscript{x} emissions. In this case, the catalyst model adaptive algorithm will predict less NO\textsubscript{x} in the LNT then the measurements indicate. The adaptive algorithm will proceed to increase the storage efficiency of the catalyst in order to drive the error between the estimate and the measurement to zero. This will have the effect of underestimating the amount of NO\textsubscript{x} exiting the catalyst, which will result in longer storage periods than desired. This, in turn, leads to increased NO\textsubscript{x} emissions.

For a number of reasons, it is possible to safely assume that the NO\textsubscript{x} estimator does not overestimate the engine-out NO\textsubscript{x} emissions. As shown below, this is a necessary condition for the developed algorithm to function. This assumption is based on the following:

1. Diesel Calibrations Optimize for Minimum NO\textsubscript{x} - The engine is calibrated to operate, in general, with the lowest NO\textsubscript{x} emissions possible. Because of this, it is unlikely that some type of parameter change would lead to lower NO\textsubscript{x} than anticipated. If such a parameter change does occur, it is unlikely that it will be very large of an overestimation.

2. Engine-Out Overestimation Results in Better NO\textsubscript{x} Emissions - An overestimation of engine-out NO\textsubscript{x} leads to a lower cumulative NO\textsubscript{x} emissions because of the more frequent regenerations. Because of this, it is not as great of a problem as an underestimation error.
3. Engine-Out NO\textsubscript{x} can be Bounded - Provided that the engine-out adaptation algorithm functions, it is possible to initialize the engine-out NO\textsubscript{x} estimator with a "best case" NO\textsubscript{x} model. Based on experimental results, it would be easy to develop a NO\textsubscript{x} estimator that was guaranteed to be lower than the engine-out levels that would be seen in the field. The adaptation algorithm would then increase this minimum NO\textsubscript{x} map to match the plant.

A typical cumulative operating efficiency of the LNT system is 90%, thus, 90% of the engine-out NO\textsubscript{x} is stored in the catalyst. If 10 units of NO\textsubscript{x} are emitted, 9 units are stored in the catalyst. If the engine-out NO\textsubscript{x} is being underestimated by 20%, the catalyst model will indicate only about 7.2 units of NO\textsubscript{x} stored in. As the catalyst adaptive algorithm adapts the efficiency parameters, it tries to move the 7.2 units of "virtual NO\textsubscript{x}" around in order to match the 9 units indicated by the measurement. The algorithm places priority on matching the NO\textsubscript{x} in the front of the catalyst, since that is how the NO\textsubscript{x} is stored in the physical process. Typically, it can adjust the efficiency parameters to match the NO\textsubscript{x} in the first three or four catalyst elements, but after that it runs out of NO\textsubscript{x} to eliminate the error at the back of the catalyst. The indicator of this is that it continues to increase the efficiency of the rear catalyst elements in an effort to get them to store more NO\textsubscript{x}. However, since the front of the catalyst is storing most of the NO\textsubscript{x}, the rear efficiency parameters keeps increasing each iteration with little effect on the amount of NO\textsubscript{x} stored in that location. This phenomenon provides a signal to close a loop around the engine-out NO\textsubscript{x} estimator. This effect is shown in Figure 149 through simulated results. The catalyst model was initialized with correct efficiency parameters for the state of the virtual catalyst plant. Only the first five efficiency parameters are permitted to adapt, and the first two parameters adapt a small amount in the direction of higher efficiency. The third and fourth parameters adapt a little more, and the fifth is adapted so far that it surpasses the efficiency of the fresh catalyst, which is the zero line on the y-axis.
The effect of this mis-adaptation was investigated using the previous validation of the catalyst adaptive model. In this exercise, the same conditions were used, except the engine-out NOx value that was fed to the catalyst model was multiplied by an error factor. This error factored varied from 0.8 to 1.2, which encompasses the likely range of engine-out NOx estimate errors. The resulting error in the catalyst model is quite severe, as shown in Figure 150 through Figure 154. A NOx estimate error factor of 0.8 results in an average error of 10% in the estimation of two-minute trapping efficiency. This can lead to problems in the regeneration scheduling algorithm. This topic is addressed more in the following chapter through simulation studies, but for now it is clear that it is desirable to compensate for the engine-out NOx error.

There are three proposed methods of tackling the problem of NOx estimator error:
1. Ignore it - If one can identify the maximum error that the NOₓ estimator would have, then it would be possible to add a safety margin into the desired NOₓ reduction. This would, of course, not be the ideal case since it would lead to reduced performance. However, if the NOₓ estimator error is small this would be a viable option.

2. Add an engine-out NOₓ sensor - One way to eliminate the uncertainty in the engine-out NOₓ estimate is to simply measure it. This eliminates the uncertainty in modeling the NOₓ, but contributes the added cost of a sensor.

3. Implement an adaptive algorithm - If such an algorithm can be developed, then it would be the most desirable approach. Developing a potential algorithm is the focus of the remainder of this section.

Because of the cumulative nature of the NOₓ measurements, there is only the possibility of adapting the engine-out NOₓ model for long-term changes in NOₓ. The method of adaptation used in this work is a simple scalar factor applied to the engine-out NOₓ estimator. This scalar value could also be applied as an additive factor; however, based on the types of errors that one would expect to cause a shift in NOₓ emissions, the correction is made as a multiplicative factor.
Figure 150: Catalyst Model Adaptation to NOx Error Factor of 0.8
Figure 151: Catalyst Model Adaptation to NOx Error Factor of 0.9
Figure 152: Catalyst Model Adaptation to NOx Error Factor of 1.0
Figure 153: Catalyst Model Adaptation to NOx Error Factor of 1.1
The structure of the algorithm used for the engine-out NOx model adaptation is very similar to the previous algorithm presented for the storage model. The algorithm is shown in Figure 155. The only substantial difference in the method is in the selection of the gain matrix and in the selection of the low-pass filter gains. Because only a scalar parameter is produced by the adaptive algorithm, the gain matrix is a 1x6 matrix, such that the product with the 6x1 error vector generates the require scalar. The error calculation as well as the gain matrix is shown in Equations (163) and (164).
A detailed look at sulfur regeneration was out of the scope of this research. However, based on the literature and some of the experimental results, it is possible to briefly discuss this topic.

In scheduling of sulfur regenerations, the following factors must be considered:
1. Increase in fuel penalty due to more frequent regenerations of a poisoned catalyst - As the catalyst loses the ability to effectively store NO\textsubscript{x}, it requires more frequent NO\textsubscript{x} regenerations to maintain the desired tailpipe efficiency.

2. Loss of NO\textsubscript{x} efficiency due to the sulfur regeneration - Although sulfur regeneration leads to a recovery in NO\textsubscript{x} storage ability, the efficiency does not typically recover completely. This leads to a gradual decline in NO\textsubscript{x} storage efficiency over time.

3. Fuel required to perform sulfur regeneration - Performing sulfur regeneration requires fuel to provide the prolonged rich conditions necessary for sulfur regeneration.

4. Increase in NO\textsubscript{x} emissions when one LNT is taken off-line for desulphation - Because the catalyst undergoing regeneration is removed from service, there will be some additional NO\textsubscript{x} emissions since the remaining trap will be treating the entire exhaust.

Since the proposed control and adaptation method estimates parameters such as sulfur degradation and cumulative NO\textsubscript{x} efficiency, there is a clear path towards developing a rigorous approach to sulfur regeneration scheduling. With a better knowledge of the exact tradeoffs in fuel economy and NO\textsubscript{x} emissions from the factors above, it would be possible to develop the algorithm. This would be a necessary component in implementing this system, but is left for future work.

7.14 Conclusions

The control algorithm is summarized in block diagram form in Figure 156. One advantage of the algorithm and the aftertreatment system described in the previous chapter should come with reduced calibration time. Because the aftertreatment system and control algorithm is independent of the engine, the same aftertreatment system and control algorithm should be able to be used on a number of vehicle platforms with only minor modifications. If one takes, for example, the engine-based LNT management method typically described. For a vehicle platform, it requires a calibration for normal operation, a calibration for
LNT regeneration, a calibration for sulfur regeneration, and a calibration for DPF regeneration. On top of these calibrations, it is required to calibrate the control strategies required for the management of the LNT regeneration, sulfur regeneration, and DPF regeneration. Now consider that, for a given vehicle, there may be several combinations of Diesel engine and transmission. For example, a base engine with manual transmission, a base engine with automatic transmission, a sport engine with manual transmission, and a sport engine with an automotive transmission. Each of these different platforms will require modifications to the calibrations, some would likely be quite extensive.

The proposed aftertreatment system and control algorithm alleviates much of the calibration effort. It eliminates the need for three of the engine calibration sets, since it requires only the normal lean Diesel mode. Furthermore, the task of calibrating the LNT management for the system needs to be done only once. The advantage of the system is that once the bypass valve closes, the system consists of only the LNT and the flame reformer with no influence from any external factors. Provided that the initial status of the LNT can be ascertained accurately, which it can, then there is very high reuse of the control algorithm.
Oxygen Storage Model, NOx Storage Model, and Engine-Out NOx Model

Regeneration Closed-Loop Control

Regeneration Scheduling

Figure 156: Complete LNT Management Algorithm
CHAPTER 8

CONTROL ALGORITHM SIMULATION RESULTS

8.1 Introduction

Simulations were conducted using the LNT model over the UDDS, HWFET, and US06 driving cycles. The regeneration control algorithm, the regeneration scheduling algorithm, the adaptive catalyst model, and the adaptive engine-out NOx estimator were all implemented. The goal of these simulations was to assess the ability of the system to meet Tier 2 standards and to evaluate the ability of the control algorithms and adaptive models to perform their respective function. The following sections detail some of the typical model outputs, as well as a number of batch simulations exploring the sensitivity of various errors and system parameters.

8.2 Vehicle Simulation Input Files

The simulations were conducted using simulation data from three difference cycles, the UDDS cycle, the HWFET cycle, and the US06 cycle. These cycles are the primary cycles of interest for Tier 2 Federal emissions standards; and they represent an urban cycle, a highway cycle, and an aggressive high speed driving cycle respectively. The velocity and acceleration profiles are shown in Figure 157, Figure 158, and Figure 159. The vehicle used in the simulator was selected to approximate one reported on in a series of papers in the literature, which was discussed in Chapter 6. An identically sized engine was used for the simulation, however, the engine in the simulator had much higher NOx emissions over the cycles then the
engine reported on in the literature. This is because the engine in the simulator was a EURO III calibration, which is no longer state of the art. To overcome this, the NO\textsubscript{x} emissions were scaled by a constant factor to bring them into agreement with the published results. Since the LNT is essentially an integrator, making the cumulative NO\textsubscript{x} emissions of the simulator agree with the published results is a reasonable approximation.

![Vehicle Speed for UDDS Cycle](image1)

![Vehicle Acceleration for UDDS Cycle](image2)

Figure 157: UDDS Cycle Velocity and Acceleration Profiles
Figure 158: HWFET Cycle Velocity and Acceleration Profiles
All of the driving cycles are also run under hot-start conditions. This was done for the following reasons:

1. The majority of the models were not validated under cold start conditions.

2. The literature reports that light-off times of LNTs using engine-management techniques can be under thirty seconds.

3. The flame reformer offers a number of synergies that improve the cold start performance of the system.

The physical aftertreatment system, of course, has no notion of vehicle speed. However, the demands placed on the vehicle to meet the each particular driving cycle create a unique profile of exhaust conditions for the aftertreatment system. In particular, rapid accelerations create high load conditions which can
create extremely high levels of NO\textsubscript{x} emissions. The average speed of the cycle has a major influence on the catalyst temperature, as does the amount of time spent idling. To indicate some of the important effects that arise based on the drive cycle, Figure 157 through Figure 159 are provided which shows the engine-out temperature profile and engine-out NO\textsubscript{x} profile for the three cycles used for the simulations.

The UDDS poses a particular challenge in that it has significant idle time, resulting in cool engine-out temperatures which bring down the catalyst temperature. Compounding this effect, the average speed and accelerations are quite mild. The HWFET is the most favorable of the three cycles for LNT operation, since it has reasonably high temperatures and the NO\textsubscript{x} emissions are generally fairly mild. The worst of the three cycles is by far the US06. Because of the high engine speeds and high rates of acceleration, the NO\textsubscript{x} emissions for this cycle are significantly higher than the others. The only positive feature of the US06 is that it has a high average temperature, which improves regeneration performance.
Figure 160: Drive Cycle Exhaust and NOx Histograms
8.3 Emissions Standards and Targets

The most popular target for a Diesel vehicle in the Tier 2 emissions standards is the bin 5 standard. There are many subtleties to the emissions regulations, but Table 7 summarizes the basic requirements of the Tier 2, bin 5 certification. As indicated in the table, for the FTP and the HWFET cycles, there are two different standards, depending on the mileage of the vehicle. The first being the "Intermediate Useful Life", which is 50,000 miles, and the second being the "Full Useful Life", which can be either 120,000 miles or 150,000 miles, depending how the vehicle is aged. For the sake of this work, the more stringent Intermediate Useful Life will be taken as the target, since it is the more aggressive standard. In practice, it is likely that the Full Useful Life standards will be the more difficult for an LNT system, since LNTs age poorly. Note that the particulate matter standard is blank for the intermediate useful life. This indicates that no measurable particulates are permitted, using the gravimetric method used by the EPA for PM measurement. In general, this is achievable with a modern, high-efficiency particulate trap and a good engine calibration.

<table>
<thead>
<tr>
<th></th>
<th>FTP 50k / &gt;120k [g/mile]</th>
<th>HWFET 50k / &gt;120k [g/mile]</th>
<th>US06 4k [g/mile]</th>
</tr>
</thead>
<tbody>
<tr>
<td>NOx</td>
<td>0.05 / 0.07</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>NMOG</td>
<td>0.075 / 0.09</td>
<td>1.33 x FTP</td>
<td>n/a</td>
</tr>
<tr>
<td>CO</td>
<td>3.4 / 4.2</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>PM</td>
<td>- / 0.01</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>HCHO</td>
<td>0.015 / 0.018</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>NMHC + NOx</td>
<td>n/a</td>
<td>n/a</td>
<td>0.14</td>
</tr>
</tbody>
</table>

Table 7: Tier 2, Bin 5 Standards for Light-Duty Vehicles

Because of the low confidence in the THC and CO data from the vehicle simulator, the values for THC and CO presented in this work will be expressed as only the net increase in CO and THC at the tailpipe as contributed by the LNT regeneration process. The CO value is so low as to be negligible, and thus is typically not reported.
8.4 Simulation Results in Depth

To illustrate what is happening with the control during a typical drive cycle, a representative simulation case will be presented in depth. The case selected for this in-depth look is two consecutive UDDS cycles. The UDDS was selected because it is the more difficult of the two standard cycles in terms of NOx due to the lower temperatures. Two cycles were ran back to back such that it provided several NOx regenerations and to provide long enough of a sample to show the effect of the regeneration scheduling algorithm.

8.4.1 Catalyst Temperatures

The temperature of the catalysts is the most important feedback signal to the proposed control algorithm. Figure 161 and Figure 162 shows the temperatures of the six temperature measurements for each of the LNT catalyst. Despite very rapidly fluctuating temperature of the inlet exhaust, the temperatures of the catalyst elements are smooth due to the high thermal inertia of the catalysts. Also noted on the two figures are the five regenerations that occurred over the trip, labeled regenerations 1-A, 1-B, 1-C, 2-A, and 2-B. As indicated in the figures, the temperature rise during regeneration is very rapid when compared to that of the catalyst during the storage phase. A close-up of regeneration 1-B is provided as Figure 163. The exotherms are clearly visible as they proceed from the front of the catalyst to the rear of the catalyst. During the regeneration process, the next to last exotherm is monitored for use as the feedback signal for the regeneration control.
Figure 161: Catalyst Temperatures of LNT 1 during a Double UDDS Cycle
Figure 162: Catalyst Temperatures of LNT 2 during a Double UDDS Cycle
Figure 163: Close-Up of Catalyst Temperatures during NOx Regeneration

**8.4.2 Regeneration Control Algorithm**

The goal of the regeneration control algorithm is to regenerate the catalyst quickly with minimal reductant slip. To accomplish this goal, there are a number of things that take place in the algorithm. At the moment that the regeneration control algorithm receives the regeneration command from the regeneration scheduler, it assesses the current conditions of the catalyst. Before issuing a regeneration command, the estimates of NOx and oxygen storage are used to predict the temperature rise of the feedback temperature sensor, which is the next to last sensor in the catalyst. This value is used in the feedforward portion of the regeneration control. The other parameter that must be estimated is the maximum reductant usage ability of the catalyst, which is based on the temperature and the amount of stored oxidizer in the catalyst. Both of these parameters are passed to the regeneration controller at the start of the regeneration and are used to calculate
the equivalent reductant command during the regeneration. Because of the strong temperature dependence
on the maximum reductant usage rate, regenerations at higher temperatures can handle higher reductant
flow rates.

The equivalent reductant command is translated into a fuel command using the flame reformer optimization
maps that were presented in an earlier table. A value of phi is first selected based on the average
temperature of the catalyst, which is then used with the requested equivalent reductant, to generate the fuel
and air command based on the flame reformer maps. Figure 164 shows both the fuel command to the
flame reformer as well as the optimal value of fuel-air equivalence ratio. If one refers back to Figure 161,
the dependence of the desired fuel-air equivalence ratio on temperature is clear. At high temperatures, the
value is saturated at 2.0, at intermediate temperatures is drifts up and down with temperature.

![Graph](image)

Figure 164: Equivalent Reductant Request from Regeneration Controller 1
Figure 165 shows a close-up of the fuel command and feedback temperature during regeneration 1-B. The fuel command starts out at its initially high value, which is based on the temperature of the catalyst as well as the stored oxidizer. It then tapers off to zero as the feedback temperature increases to the target temperature rise value. In this particular case, the target temperature was set to be 90% of the expected temperature rise. The resulting hydrocarbon slip from this regeneration is shown in Figure 166. This plot represents the net contribution to the tailpipe hydrocarbons by the regeneration, and does not include any of the engine-out hydrocarbons. This is typical for a regeneration, in which the hydrocarbon slip has a steep initial rise, and then a gradual taper as the fuel command is reduced. In this particular case, as indicated by the arrow, the regeneration was not quite ideal, as there is a small increase in hydrocarbons towards the end of the regeneration. This is due primarily to the transport delays in the system as well as the dynamics of the flame reformer, which is modeled as a first-order low-pass filter. The small amount of hydrocarbon slip
is considered acceptable when compared to the unavoidable slip that occurred from 1540 seconds to 1565 seconds.

Figure 166: Hydrocarbon Slip during Regeneration of LNT 1

8.4.3 Regeneration Scheduling Algorithm

The regeneration scheduling algorithm is illustrated in Figure 167. The upper figure shows the cumulative catalyst out NO\textsubscript{x} in grams per mile for both LNTs in the system. They both start initially empty, and therefore, the traces overlap for the most of the first 500 seconds of the cycle. At this point, the first trap crosses the dark dashed horizontal line, which is 40% of the desired tailpipe NO\textsubscript{x} target of 0.035 g/mile. This triggers a regeneration event for the first trap, so that the regenerations are forced out of phase. After the first trap is regenerated, it immediately begins trapping. The second trap continues to increase until it
hits the dotted dark line, which is the NO\textsubscript{x} target of 0.035 g/mile. Crossing this threshold triggers a regeneration of the second trap. Note that the second trap remains at zero cumulative NO\textsubscript{x} for over 100 seconds. During this time, as indicated in the lower plot, the regeneration controller has issued a hold command for the second catalyst. This hold command is maintained until the first catalyst crosses the 40\% target line, upon which the second trap begins storing. This hold feature is required to keep the NO\textsubscript{x} traps balanced in the desired out of phase condition. This process continues and the catalysts remain, for the most part, out of phase.

Figure 168 shows the cumulative tailpipe NO\textsubscript{x} if grams per mile over the entire trip. The goal of the regeneration scheduling algorithm is to just meet the target cumulative NO\textsubscript{x} emissions, which in this case is 0.035 grams per mile. Over the two UDDS cycles, it is approaching this value, but the cumulative emissions are significantly lower than the target value. This is mainly a result of the catalyst starting in an empty condition, which is possible with the flame reformer by doing key-off NO\textsubscript{x} regeneration. In theory, it would be possible to let the traps store for longer earlier in the cycle, which would raise the cumulative NO\textsubscript{x} up to the target value. However, one never knows how long a cycle will be or exactly what the velocity and NO\textsubscript{x} profile will be in the near future. Based on this, it seems prudent to aim for the target cumulative NO\textsubscript{x} for each storage cycle and accept that it may have higher than required NO\textsubscript{x} reductions on certain driving schedules.
Figure 167: Regeneration Scheduler Cumulative NOx and Hold Commands
8.4.4 Hydrocarbon Emissions

As demonstrated above, the NO\textsubscript{x} emissions for over the simulated cycle stayed below the target value, which is considerably less than the Tier 2, bin 5 target. But as shown in Figure 166, there is a small but significant amount of hydrocarbon slip during each regeneration event. The top plot in Figure 169 shows the cumulative mass emissions of THC that the LNT system contributes to the tailpipe. At each regeneration, there is a small amount slipped that nudges the cumulative mass higher. When one looks at these results in terms of mass weighted by distance traveled, as shown in the bottom plot, the contribution to the cycle THC emissions is less than 0.01 grams per mile. The applicable standard for this cycle would be 0.075 g/mile. Therefore, the hydrocarbon emissions are significant relative to the standard, but it is not expected that this added amount of hydrocarbons would be enough to raise the vehicle over the standard.
Data reported in the literature indicates that Diesel engines can achieve 0.025 g/mile of THC emissions, which allows considerable room for the hydrocarbon emissions from the LNT regeneration in the Tier 2 bin 5 standard.

![Cumulative Tailpipe THC from LNTs](image1)

![Cumulative Tailpipe THC Per Mile from LNTs](image2)

Figure 169: Cumulative THC Slip from the LNT System

### 8.4.5 Fuel Economy Penalty

The fuel economy penalty over the cycle due to the LNT regenerations was 0.9%, which is quite good. The fuel reformer required 11.5 grams of Diesel fuel while the engine consumed 1321 grams of Diesel fuel. For this cycle, the average fuel cost per regeneration was 2.3 grams per regeneration. The cumulative fuel consumption of the flame reformer is shown in Figure 170. As shown in the figure, this cost per reasonably constant, but varies slightly with the amount of stored NOx in the trap, the stored oxygen in the trap, and the
operating efficiency of the flame reformer. In general, the lower the target efficiency of the system is, the cheaper the regeneration becomes because the frequency of the regeneration is lower, which leads to less fuel being used for oxygen storage. Since a certain amount of fuel is required to deplete the oxygen storage, frequent regenerations with low amount of NOx stored result in higher costs in fuel penalties.

![Cumulative Flame Reformer Fuel Consumption](image)

Figure 170: Cumulative Flame Reformer Fuel Consumption

8.5 Effect of Engine-Out NOx Estimator Error

The need for an adaptive engine-out NOx estimator was cited in the previous chapter. The goal of the adaptive estimator is to adjust the engine-out NOx estimator to minimize the error between the actual engine-out NOx and the estimated engine-out NOx. To determine the effect of an uncompensated error, a set of simulations was conducted to determine how sensitive the control strategy is to such an error. Different levels of error were introduced as a multiplier to the output of the engine-out NOx estimator.
Values of 0.7, 0.8, 0.9, 1.0, 1.1, 1.2, and 1.3 were simulated on a UDDS, HWET, and a US06 driving cycle. For all of these tests the adaptive catalyst model was disabled.

The results in terms of engine-out NO\textsubscript{x} and fuel economy are shown in Figure 171, Figure 172, and Figure 173. In each of the cases, the target emissions level was 0.035 g/miles, which is indicated by the dashed line in the plot. For all of the cases, an underestimation in NO\textsubscript{x} resulted in an increase in NO\textsubscript{x} emissions while an overestimation resulted in less NO\textsubscript{x} emissions. An underestimation error leads to the catalyst model to fill up more rapidly than the actual catalyst. This results in more frequent regeneration than actually necessary to meet the desired standard. An underestimate is the more critical of the two errors, since it has the opposite effect, which leads to higher tailpipe NO\textsubscript{x} emissions. In all cases, the higher fuel economy penalty is associated with an overestimation, since it results in more frequent regenerations. Because of this, overestimations are also undesirable since they will tend to increase fuel consumption slightly. If the NO\textsubscript{x} estimator errors are compensated for correctly, than the emissions and fuel economy turn out to be exactly what the figures indicated for a NO\textsubscript{x} error factor of 1.0. Overall, it is clear that it makes sense to err on the side of overestimating NO\textsubscript{x} rather than underestimating NO\textsubscript{x}, since emissions compliance is more important than a small percent decrease in fuel economy.
Figure 171: Effect of Uncompensated Engine-Out NOx Estimator Error - UDDS
Figure 172: Effect of Uncompensated Engine-Out NOx Estimator Error - HWFET
8.6 Effect of Catalyst Model Errors

As presented in the previous chapter, an adaptive catalyst model is required for a number of reasons, with the main one being the effect of sulfur poisoning. To determine the effect that sulfur degradation has, a simulation study was conducted on the UDDS and HWFET cycle for five different levels of sulfur poisoning. The degree of sulfur poisoning is represented as a "SO₂ Poisoning Level", where 1 indicates a non-poisoned LNT and 5 indicates an LNT that is equivalent to the state of the LNT at the end of the SO₂ poisoning experiments reported on earlier. Additionally, the simulations were run for two conditions, one in which the sulfur poisoning effect was not accounted for in the LNT model and one in which it was compensated for by the catalyst model through the parameter adaptation. The state of the uncompensated catalyst model is that of the fresh catalyst.
The results of this study are shown in Figure 174 through Figure 177. In all of the trials, the target NO$_x$ emissions was 0.35 g/mile. In each of the uncompensated cases, the NO$_x$ emissions increase substantially with increasing sulfur poisoning. The magnitude of the increase is more than a factor of three for the UDDS and HWFET, which shows the importance of this effect. For all cases, there is a slight decrease in the fuel economy penalty with increasing sulfur poisoning, which is due to less NO$_x$ is stored in the catalyst with greater sulfur poisoning. Less stored NO$_x$ results in less fuel required for regenerations.

Figure 175 and Figure 177 show the results if the sulfur poisoning of the plant is accurately depicted by the catalyst model. This would be the ideal case for the adaptive catalyst model was working perfectly. For the UDDS and the HWFET, the NO$_x$ increase is relatively low with increasing sulfur poisoning. These two cycles, however, show a dramatic increase in fuel economy penalty with increasing sulfur poisoning. For a highly poisoned catalyst, a lesser amount of NO$_x$ can be stored when compared to a fresh catalyst. This results in more frequent regeneration with less stored NO$_x$. The oxygen storage level of the catalyst remains virtually unchanged with increasing sulfur poisoning. Because of this, the fraction of fuel required for the regeneration that goes towards NO$_x$ reduction is lower in the case of the poisoned catalyst. Figure 178 shows a bar chart of the fraction of fuel used for NO$_x$ reduction over the UDDS cycle for the compensated cases. Note that there is a substantial difference between the fresh catalyst and the aged catalyst, from 38% down to 13%.
Figure 174: Effect of an Uncompensated Catalyst Model Errors - UDDS
Figure 175: Effect of a Compensated Catalyst Model Errors - UDDS
Figure 176: Effect of an Uncompensated Catalyst Model Errors - HWFET
Figure 177: Effect of a Compensated Catalyst Model Errors - HWFET
8.7 Effect of Catalyst NO\textsubscript{x} Storage Capacity

The simulator was used to evaluate the effect of varying the maximum storage capacity of the catalyst as well as the target cumulative NO\textsubscript{x} emissions. This exercise was undertaken to evaluate the sensitivity of the control algorithm to the NO\textsubscript{x} storage capacity of the catalyst as well as the ability for it to meet the target cumulative emissions set point. For this simulation set, the control strategy was assumed to have no faults of any kind. The NO\textsubscript{x} storage of the catalyst was set at 100\%, 75\%, and 50\% of the nominal value of the model. The target NO\textsubscript{x} emissions was set at 0.07, 0.05, and 0.03 grams per mile. This gives a total of
nine different cases for each of the three driving cycles. The data is provided in Table 8, Table 9, and Table 10.

The regeneration scheduling controller has the largest effect on the cumulative NO$_x$ emissions, since it schedules when the regenerations occur for each of the LNTs. As indicated by the data, the target NO$_x$ is met or exceeded for all of the UDDS and HWFET cases. For the less aggressive reductions with the full catalyst NO$_x$ storage capacity, the cumulative NO$_x$ emissions are considerably less than the target. This is a result of the fact that the catalyst capacity is large enough that the traps are only regenerated one or two times over the cycle. For one of the HWFET cases, the LNTs did not require a single regeneration to meet the 0.07 g/mile target. Given that the regeneration scheduling algorithm is capable of meeting the tightest cumulative NO$_x$ target on the UDDS and HWFET, even with a 50% reduction, is encouraging for the method.

The US06, however, is a different situation entirely. Not a single one of the trials were capable of meeting their target emissions standard. This is a result of the aggressive nature of the driving cycle which generates high levels of NO$_x$. Fortunately, the emissions standards allow a relaxed standard for the US06 cycle for Tier 2 emissions. For the class of vehicle simulated, this standard is 0.14 g/mile of NO$_x$, which is double the Tier 2, bin 5 that is the target of Diesel vehicles. All of the simulations came in under this standard, with the exception of two. In these particular cases, the regenerations are being conducted as frequently as possible for the catalysts, which have reduced NO$_x$ storage. This demonstrates that NO$_x$ capacity seems to have more of an impact on the more aggressive cycle. If the catalyst were capable of being regenerated faster (i.e. a higher maximum reductant usage rate), this would also improve the situation by allowing the catalyst to be offline for less time for regeneration. This property depends entirely on catalyst formulation, and therefore would be improved with a more recent catalyst formulation than the ones modeled for the simulator.
<table>
<thead>
<tr>
<th>NOx Storage Factor</th>
<th>Target NOx Emissions [g/mile]</th>
<th>NOx Emissions [g/mile]</th>
<th>ΔTHC Emissions [g/mile]</th>
<th>Fuel Penalty [%]</th>
<th>Number of Regen's</th>
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Table 8: Effect of Catalyst NOx Storage Capacity on UDDS Cycle Performance

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<th>NOx Storage Factor</th>
<th>Target NOx Emissions [g/mile]</th>
<th>NOx Emissions [g/mile]</th>
<th>ΔTHC Emissions [g/mile]</th>
<th>Fuel Penalty [%]</th>
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</tr>
</thead>
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Table 9: Effect of Catalyst NOx Storage Capacity on HWFET Cycle Performance

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<th>Target NOx Emissions [g/mile]</th>
<th>NOx Emissions [g/mile]</th>
<th>ΔTHC Emissions [g/mile]</th>
<th>Fuel Penalty [%]</th>
<th>Number of Regen's</th>
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Table 10: Effect of Catalyst NOx Storage Capacity on US06 Cycle Performance
8.8 Conclusions

Though the simulation results provided in this chapter, the operation of the various elements of the control strategy were demonstrated and discussed. Moreover, the need for the adaptive catalyst model and engine-out NO\textsubscript{x} estimator was demonstrated through batch simulations of various compensated errors in the agreement between the models and the virtual physical system. Provided that the errors were compensated for, which is the goal of the adaptive estimators, the NO\textsubscript{x} performance of the algorithm remained near the target value. Lastly, the algorithm proved insensitive to variations in the NO\textsubscript{x} storage of the system, which is a proxy for the size of the catalyst. Furthermore, it demonstrates that the algorithm should hold up well to the inevitable aging of the catalyst over time. The results presented in this chapter demonstrate that the LNT management algorithm developed in the previous chapter works successfully on the simulated system. This, of course, is not the same as it working well on the physical system, but is the step towards demonstrating the strategy in the vehicle.
CHAPTER 9

CONCLUSIONS AND RECOMMENDATIONS

9.1 Summary

All of the results from this body of work strongly indicate that a bypass-regeneration system has the ability to meet Tier 2 emissions standards at a very low fuel economy penalty. There is, of course, an increase in the initial cost of the system hardware when compared to engine-based regeneration techniques that must be offset. Due to the many advantages and synergies of the bypass-regeneration system, a strong case can be made that this increase in cost can be made up with number of cost reductions elsewhere. These results, although backed up by experimental and simulation work, are not conclusive. With further vehicle-based investigations, it is expected that this assessment of the bypass system, as articulated in this document, will agree well with the predicted results.

Referring back to the first chapter, the work presented in this dissertation set out to contribute to the areas in the following list. In each of these areas, it is felt that a significant contribution as been made to the research community through the completion of this research. The summary of the work is as follows:

1. Total Flow Bypass-Regeneration - A model structure was developed that accurately captures the process of total flow bypass-regeneration. This structure was used to model the behavior of one particular catalyst formulation with good success. In conjunction with this model, a storage model of similar structure to that in the literature was adapted in to a multi-element model to provide the required spatial resolution. Both of these models were validated with experimental results.
2. Model-Based Control Methods for Bypass-Regeneration - Using the regeneration and storage models, a complete LNT management algorithm was articulated and evaluated both experimentally and through simulation. The method of control utilizes the principles of model-based control to improve control performance and reduce calibration effort. As part of this control development, a number of adaptive estimators were developed as well as an optimal regeneration control for a slightly simplified system. These adaptive estimators allowed the control system to automatically compensate for sulfur poisoning in-vehicle.

3. Catalyst Temperature Measurements Analysis - Methods were developed in this document for the use of catalyst temperature measurements for measuring a host of catalyst parameters. These techniques have wide applicability in the lab as well as a very key role in the control methods developed in this work.

4. Flame Reforming for LNT Management - A prototype device for generating reductants for LNT regeneration was experimentally tested and proved to be a very effective method. The device overcomes many of the shortcomings of the methods currently reported in the literature while doing so at a cost that is expected to be dramatically lower.

9.2 Future Work

Very few research endeavors are pursued to their very end, and this is certainly not one of them. Although many research questions were answered in this work, the following list contains some direction for future work in this area:

1. Light-Duty Vehicle Testing - The control algorithm showed good performance with the simulator, but this is just the first stage of validating the algorithm. To fully evaluate the algorithm, it would be of value to conduct vehicle-based testing. This testing would need to evaluate the ability of the system to perform in the less controlled environment of the vehicle as well as the ability to deal with sulfur poisoning and catalyst aging.
2. Extension of Model-Based Control Methods to Gas Sensors - The algorithm developed in this work relied exclusively on catalyst temperature measurements. Because this is a new concept, it will be met with resistance in industry until it has been proven (or disproved) to be able to meet cost and durability requirements. Regardless of the outcome of this evaluation, it would be of value to extend the control-based methods to that of an EGO or UEGO sensor. Considerable work has been done on this topic for engine-based regeneration, but nothing comprehensive on bypass-regeneration.

3. Experimental Validation of Desulphation with the Flame Reformer - The flame reformer offers a number of benefits; however, improving sulfur regeneration is perhaps the most critical. An experimental validation of this aspect of the flame reformer, as well as a control strategy, would be of interest to the research community.

4. Up-Scaling of the Methods to Heavy-Duty Engines - This work looked exclusively at the LNT management problem for a light-duty application. As discussed in the introduction, the light-duty Diesel vehicle market in the US is not very strong, but in the heavy-duty market the Diesel is the dominant engine type. Extending these techniques to heavy-duty engines would allow the work to have a greater impact, in the event that it turns out to be a practical path for addressing the challenge of LNT management.


