THESIS

SELECTIVE CATALYTIC REDUCTION: TESTING, NUMERIC MODELING, AND CONTROL STRATEGIES

Submitted by

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In partial fulfillment of the requirements

For the Degree of Master of Science

Colorado State University

Fort Collins, Colorado

Spring 2010

COLORADO STATE UNIVERSITY

March 4, 2010

WE HEREBY RECOMMEND THAT THIS THESIS PREPARED UNDER OUR SUPERVISION BY JOSHUA C. SCHMITT ENTITLED SELECTIVE CATALYTIC REDUCTION: TESTING, NUMERIC MODELING, AND CONTROL STRATEGIES BE ACCEPTED AS FULFILLING IN PART REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE.

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ABSTRACT OF THESIS

SELECTIVE CATALYTIC REDUCTION: TESTING, NUMERIC MODELING, AND CONTROL STRATEGIES

Selective Catalytic Reduction (SCR) catalysts respond slowly to transient inputs, which is troublesome when designing ammonia feed controllers. An experimental SCR test apparatus was installed on a Cooper Bessemer GMV-4 natural gas engine. Transient data was taken of commercially available SCR Catalysts. These transient tests are used to quantify SCR catalyst response. Space velocity, catalyst temperature, inlet NOx concentration, and ammonia to NOx molar feed ratio were varied. A Simulink numeric model was created to examine the SCR transient phenomena. The Simulink numeric model showed in-catalyst ammonia and NOx concentration as a function of length in the direction of exhaust flow. This helped explain the SCR transient results. Transient testing showed a fifteen minute delayed response in NOx reduction from ammonia transitions. Ammonia slip succeeded ammonia transitions by thirty minutes. Simulink modeling revealed that these delays are caused by large quantities of ammonia stored in the catalyst. Due to ammonia storage, ammonia waves propagate through the catalyst, front to back. Emission of these constituents through the catalyst is delayed because the wave takes time to propagate through the entire catalyst length.

Ammonia feed rate control testing was done on the experimental setup to improve ammonia and NOx emissions from the catalyst. Three control algorithms were used: feed forward control, using a pre ammonia injection ceramic NOx sensor; a feed forward plus feedback control, using a pre ammonia injection ceramic NOx sensor and post catalyst ceramic NOx sensor to generate feed signals; and a feed forward plus feedback algorithm that used a pre ammonia injection ceramic NOx sensor and a mid catalyst ceramic NOx sensor to generate feed forward and feedback signals. The feed forward controller used molar ratio as the control variable, and the feedback system used a technique that minimized the post catalyst ceramic NOx sensor signal. Ammonia to NOx molar ratio was stepped every five or fifteen minutes, and the algorithm made decisions, based on the catalyst response to the step. The decisions were made to minimize the post catalyst ceramic NOx sensor. Feed forward testing revealed that the lack of pressure compensation on ceramic NOx sensors causes errors in feed forward NOx readings, and sub optimal ammonia feed. Feedback testing revealed that a minimization technique can be used successfully with a feedback step rate of one step per fifteen minutes, and a step size of 5% ammonia to NOx molar ratio. The feedback algorithm, with the feedback ceramic NOx sensor located one third the way through the catalyst length, worked poorly. The technique approached a lean ammonia to NOx molar ratio, and stabilized slower than the post catalyst feedback ceramic NOx sensor technique. These phenomena are explained with the Simulink numeric model.

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1 INTRODUCTION

1.1 Background

1.1.1 Engines and Emissions

Reciprocating internal combustion engines play a key role in mechanizing society. Combustion engines convert chemical energy into usable mechanical and electrical energy, which replaces energy intensive human labor, improving quality of life. Since there are no known, immediately viable alternative to internal combustion engines as a source of energy, internal combustion engines will remain institutional in human lives for the foreseeable future.

The chemical energy that drives internal combustion engines is realeased through a chemical process called combustion. When air and fuel combust, chemical reactions occur that result in small traces of undesirable molecules. These chemicals can be environmentally detrimental and hazardous to human health. Primary restricted chemicals include: oxides of nitrogen (NOx); carbon monoxide (CO); hydrocarbons (HC or THC), or unburnt/partially burnt fuel; and particulate matter, small pieces of solid hydrocarbon that are suspended in exhaust gas.

1.1.2 EPA Restrictions

Due to the negative side effects of certain components in engine exhaust, government institutions create laws to restrict emission of harmful chemicals. In the United States, the institution responsible for creating these rules is the Environmental Protection Agency (EPA). The EPA perpetually tightens these emissions restrictions to progressively lower levels to continually reduce harmful impact on humans and the environment. To meet future EPA restrictions, engine manufacturers develop new technology to abate these harmful emissions. The EPA has tightened restrictions particularly on NOx emission. For more information on EPA restrictions, visit www.epa.gov.

1.1.3 Emissions Reduction Techniques

Today, there are several methods of reducing harmful emissions. First, for rich burn engines that operate close to stoichiometric air-fuel ratio, a three-way catalyst is used. A threeway catalyst is a technology which reduces NOx, CO, and THC. This technology has been used since 1981 on automobile engines [1]. Three-way catalysts are not used on diesel, two stroke, or other lean burn engines because they require near stoichiometric air fuel ratios. Exhaust gas recirculation (EGR) is a technology used on diesel engines and gasoline engines for NOx reduction. EGR technology circulates exhaust back into the engine's intake. By doing this, overall exhaust flow rate is reduced because part of the exhaust flow is diverted into the engine intake, reducing emission flow rate. The compromise in EGR is destabilized combustion, resulting in increased CO and THC emissions [2]. Diesel particulate filters (DPFs) are used to reduce diesel particulate emissions. This technology uses a ceramic filter element to trap and chemically oxidize particulate matter. Finally, selective catalytic reduction (SCR) is another catalytic technology used to reduce engine exhaust NOx, and can be applied in lean burn engines. The primary use of SCR is in stationary power plants and automotive diesel engines. In SCR, a reagent is injected into the engine exhaust and passed through a catalyst. The reagent reacts with exhaust NOx, breaking down into chemically benign diatomic nitrogen and water, reducing overall NOx emissions.

1.2 Literature Review

A literature review was necessary to aid numerical modeling and controls. It was quintessential to determine current controls practices, and understand governing chemical kinetic mechanisms.

1.2.1 Chemical Kinetics

SCR chemical kinetics includes three kinetic pathways. Two of these pathways are called Standard SCR and Fast SCR, and are shown in Equations 1.1 and 1.2, respectively. Fast SCR is dominant when the NO/NO₂ ratio is near one, and Standard SCR is dominant otherwise [3]. Equation 1.2 plays a "minor role in the process", when NO₂ concentration is less than 5% of total NOx [4]. Equation 1.3 is the global reaction that is predominant when NO₂ is the primary NOx constituent. Ammonia oxidation, is shown in Equation 1.4. Note that stoichiometry between ammonia and NOx remains one to one through the standard and fast SCR reaction pathways, as long as ammonia oxidation is small.

$$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O \tag{1.1}$$

$$2NH_3 + NO + NO_2 \rightarrow 2N_2 + 3H_2O \tag{1.2}$$

$$6NO_2 + 8NH_3 \rightarrow 7N_2 + 12H_2O \tag{1.3}$$

$$4NH_3 + O_2 \rightarrow 2N_2 + 6H_2O \tag{1.4}$$

The SCR chemical kinetic mechanism is an Eley-Rideal mechanism, where the catalyst surface adsorbs ammonia, and NOx reacts from a gaseous state. This Eley-Rideal mechanism can accurately predict catalytic response [6], [7]. Vanadia-titania catalyst chemical reactions begin with Equation 1.5, in which ammonia is adsorbed onto the active catalyst site, V_2O_5H [6]. NO is destroyed in Equation 1.6, in which NO and adsorbed ammonia react [6]. The catalyst inactive

site is re-oxidized, shown in Equation 1.7, during which the dormant site, $V_2O_5H_2$, is re-activated to V_2O_5H [6].

$$NH_3 + V_2O_5H \rightarrow V_2O_5NH_4 \tag{1.5}$$

$$V_2 O_5 N H_4 + N O \rightarrow V_2 O_5 H_2 + N_2 + H_2 O$$
 (1.6)

$$4V_2O_5H_2 + O_2 \to 4V_2O_5H + 2H_2O \tag{1.7}$$

NO destruction proceeds much slower than ammonia adsorption and catalyst site reactivation [6]. Two assumptions are made. First, ammonia is constantly in equilibrium with its adsorbed state. Second, O_2 , N_2 , and H_2O concentration is much higher than that of ammonia or NO. Therefore, O_2 , N2, and H_2O concentration changes are negligible. V_2O_5H can be represented simply as S, or an active catalyst site, and $V_2O_5NH_4$ can be simplified to NH_3^* , or ammonia in its adsorbed state. Through the above assumptions, Equation 1.5, 1.6, and 1.7 can be reduced to Equation 1.8 and 1.9.

$$S + NH_3 \leftrightarrow NH_3^*$$
 (1.8)

$$NH_3^{\circ} + NO \rightarrow S$$
 (1.9)

A variable, θ , is introduced to represent the coverage of NH₃^{*} with respect to the maximum NH₃^{*} coverage, NH_{3,max}^{*}. Equation 1.10 is used to calculate θ . Maximum ammonia coverage is the same as catalyst site density.

$$\theta = \frac{NH_3^*}{NH_{3,max}^*} \tag{1.10}$$

Equations 1.11 and 1.12 govern θ and NO reduction rate, respectively:

$$\theta = \frac{K_{NH_3}C_{NH_3}}{1 + K_{NH_3}C_{NH_3}} \tag{1.11}$$

$$R_{NO} = K_{NO}C_{NO}\theta \tag{1.12}$$

where K_{NH3} is defined in Equation 1.13; C_{NH3} is the concentration of ammonia in mol/m³; R_{NO} is the rate at which NO is reduced in mol/s-m²; K_{NO} is defined in Equation 1.14; and C_{NO} is the concentration of NO in mol/m³;

$$K_{_{NH_3}} = K_0 e^{\frac{-\Delta H}{R_T}}$$
(1.13)

$$K_{NO} = K_1 e^{\frac{-E_a}{RT}}$$
(1.14)

where K_0 , the pre-exponent term, is .863 m^3/mol [8]; ΔH , the enthalpy of ammonia adsorption, is -3.867E4 J/mol [8]; R is the universal gas constant 8.314 J/mol-k; and T is the catalyst operating temperature in Kelvin; K_1 is 5.046 m/s [8]; and E_a is the activation energy, 1.614E4 J/mol [8].

When ammonia adsorption and desorption rates are calculated, as done in work by Forzatti, et al [5], ammonia adsorption equations change. Instead of calculating θ directly using Equation 1.11, Equation 1.15 is used to calculate rate of ammonia adsorption,

$$R_{NH_3} = K_{ads}C_{NH_3}(1-\theta) - K_{des}\theta$$
(1.15)

where R_{NH3} is ammonia adsorption rate in mol/sec-m². Calculation of K_{ads} and K_{des} is done experimentally. Note that $K_{ads}/K_{des}=K_{NH3}$ if R_{NH3} is set to zero in Equation 1.15. This fact is discussed later in this thesis in the numerical model section.

1.3 Control Techniques

Reagent feed rate is very important to NOx reduction efficiency and ammonia slip. Control techniques have been studied to improve SCR performance. In the case of mobile applications, the high level of transience requires fast feedback response. In the case of stationary engine applications where operation is steadier and slower, more stable feedback response is needed. Two techniques will be discussed: one for fast response in mobile applications; and the other for slower, stationary applications. The technique for slow, stationary applications is developed in this thesis. In both applications, feedforward algorithms were used to follow basic system transitions. Feedback algorithms were used to compensate for feedforward errors, such as sensor drift and ammonia injector nozzle clogging.

Although the feedback portion of the control technique by Schär, Onder, and Geering [10] is most innovative, their feedforward algorithm as well as their testing technique is also important to analyze. In their tests, they implemented four feedforward techniques. All four algorithms worked well, with the fourth responding best to sudden transients [10]. All four algorithms were tested in a manner that required much faster response than tests described in this paper. Consequently, these feedforward algorithms were not studied in as much detail as their feedback algorithms.

Schär, Onder, and Geering [10] used a feedback signal generated with a ceramic NOx sensor. Ammonia interferes with ceramic NOx sensors. Ceramic NOx sensors respond approximately as is shown in Equation 1.16 [10],

$$R_{CNS} = C_{NOX} + .65C_{NH_2}$$
(1.16)

where R_{CNS} is the ceramic NOx sensor reading.

This is important in SCR feedback applications because both ammonia and NOx are present post catalyst. As a result, it is difficult to determine whether the sensor is responding to NOx or ammonia. Schär, Onder, and Geering [10] created a method of differentiating between ammonia and NOx. The method feeds a quickly oscillating signal into the catalyst. A feedback signal is generated from analyzing this oscillating signal. The ammonia feed signal is supplemented with a high frequency sine wave, or excitation. A Fourier transform is performed on the post catalyst ceramic NOx sensor signal, and the excitation frequency is isolated. The amplitude of the excitation frequency is used to determine whether the signal is primarily NOx or ammonia. As θ goes up, the catalyst dampens the propagation of the excitation signal by adsorbing and desorbing ammonia. The catalyst cannot adsorb or desorb ammonia at low ammonia feed rates due to lack of ammonia. Therefore, the excitation signal propagates through the catalyst if the adsorbed fraction of ammonia is low. If the excitation signal amplitude, as read by the post catalyst ceramic NOx sensor, is lower than a threshold value, ammonia concentration is assumed much higher than NOx. Otherwise, post catalyst NOx concentration is assumed to be much higher than ammonia. If the post catalyst exhaust consists of primarily ammonia, the feedback signal is the negated post catalyst ceramic NOx sensor reading, and if the exhaust consists of primarily NOx, the sensor reading is proportional to the post catalyst ceramic NOx sensor reading. Through this method, a feedback error signal is generated. The error signal is fed into a proportion plus integral controller, and multiplied by the feedforward signal to generate an ammonia flow control set point.

The second feedback control design responds slower than the first design. In the second design, a feedback loop minimizes the post catalyst ceramic NOx sensor signal. This is similar to the feedback technique used in [11]. If the ceramic NOx sensor responds proportionally to the sum of ammonia and NOx, minimizing this signal would minimize the sum of ammonia and post-catalyst NOx. To initiate the process, a small transition in NH₃/NOx molar ratio is made. In

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response, catalytic reduction either improves or diminishes, and the ceramic NOx sensor signal either increases or decreases. There are four possibilities:

- 1. The system is operating lean (too little ammonia) and the feedback system steps ammonia down.
- 2. The system is lean and the feedback system steps ammonia up.
- 3. The catalyst is rich when the feedback system steps ammonia up.
- 4. The catalyst is rich (too much ammonia) when the feedback system steps ammonia down.

The second and fourth operations improve SCR performance, while the first and third operations reduce catalytic performance. Since the goal is to minimize the ceramic NOx sensor signal, if the transition decreased the signal, another step is taken in the same direction. If the transition increased the signal, the next step is taken in the opposite direction. Eventually, the algorithm will cross the feedback ceramic NOx sensor minimum, and reverse direction, oscillating back and fourth across the optimum molar feed ratio. Through this method, the ceramic NOx sensor signal is minimized, and the system approaches an optimum.

1.4 Thesis Overview

This thesis has two main parts: (1) experimental evaluation of a commercial SCR catalyst and (2) SCR modeling in Simulink. The experimental setup is discussed in Chapter Two. The Simulink numeric model is presented in Chapter Three. Topics are: software selection, determination of catalyst site density, model setup and validation, and model results. Transient testing of the catalyst is described in Chapter Four. The transient test plan was designed to represent engine load changes, in which temperature and space velocity transition simultaneously. Chapter Five covers controls development for SCR applications. This chapter outlines three control mechanisms, including feedforward control, feedback control using a ceramic NOx sensor signal minimization technique, and feedback control using the minimization technique with the ceramic NOx sensor located mid way through the catalyst material length.

2 Experimental Setup

This chapter describes the hardware assembly used to test SCR transient response and control algorithms. The catalyst slipstream and engine are specified. Data acquisition and slipstream control instrumentation is described, and NOx sensor calibration is documented.

Figure 1 shows the exhaust flow schematic. Shown is each component in the slipstream that will be discussed in order of its respective position on the slipstream. The gas flow in Figure 1 starts at the engine, flows as indicated by the arrows, and ends where exhaust is emitted into the atmosphere. The four engine cylinders are shown. These four cylinders are connected to four exhaust elbows that connect to the main exhaust stream, through which most exhaust flows. The SCR slipstream removes a small portion of exhaust from each of the four exhaust elbows, conditions it, directs it through the SCR catalyst, then reconnects with the main exhaust. Exhaust conditioning is done through temperature control, exhaust flow control, and reagent concentration control. Conditioned exhaust flows into the catalyst material where NOx and ammonia are catalytically reduced. After passing through the catalyst and through a flow measurement orifice, the slipstream gas is recombined with the main exhaust stream, and released.



Figure 1 Exhaust flow schematic.

2.1 Engine

The test engine is a Cooper Bessemer GMV-4TF, four cylinder, two stroke, natural gas, internal combustion engine, rated at 440 bhp (330 kW). Engine torque is controlled by a water brake dyno that dissipates the engine's energy through a heat exchanger into ambient air. This engine has pre-combustion chambers, and intake and exhaust pressure control, which allow intake boost to be adjusted from 3.5 "Hg (11.8 kPa), to 23 "Hg (77.9 kPa) gauge. Exhaust backpressure was always set 2.5 "Hg (8.46 kPa) less than intake pressure, and controlled by a butterfly valve in the main exhaust stream. Engine out NOx was controlled by varying boost. During testing, intake pressure was usually set between 12 and 16 "Hg (40.6 and 54.2 kPa) gauge, which resulted in backpressure between 9.5 and 13.5 "Hg (32.2 and 45.7 kPa) gauge. Figure 2 is a photo of the test engine. Further description of the test engine is in [12] and [13].



Figure 2 Photo of the Cooper Bessemer GMV-4TF engine used in SCR catalyst testing.

2.2 Slipstream

Figure 3 is a photo of the SCR slipstream. Labeled are: engine main exhaust pipe, slipstream inlet flow, temperature control heat exchanger, space velocity control valve, catalyst housings, outlet flow, and railing.



Figure 3 Photo of the SCR slipstream.

The slipstream was designed to receive exhaust gas from the four exhaust elbows, each of which corresponds to one of the engine cylinders. Each elbow connected the exhaust port of the cylinder to the main exhaust manifold. Four two-inch NPT ports extracted sample exhaust from the elbow surface, and directed it to a mixing box. The mixing box connected the four upstream, two inch lines, to a four inch line feeding the slipstream. The mixing box was designed to generate turbulence, and ensure sufficient mixing of the four streams.

A heat exchanger controlled temperature of the exhaust gas, and the operating temperature of the catalyst. The heat exchanger was a cross flow type, in which air at ambient temperature flowed across a finned tube bank. Exhaust gas rejected heat into the cross flowing air, through the finned tube bank. Cool air, to which exhaust heat was rejected, was compressed air, stored at approximately 150 psi in large tanks. Temperature of downstream exhaust gas was controlled by varying flow rate of compressed air through the heat exchanger. The heat exchanger had a temperature control range of 450 to 600 °F (505 to 589 K).

A butterfly valve was used to control exhaust flow rate through the slipstream. The butterfly valve was located inside the slipstream pipe and positioned by a Belimo AF24-SR actuator. The actuator turned the butterfly valve inside the slipstream tube, varying the flow area and the exhaust flow rate through the slipstream.

During testing, two different ammonia injectors were used. One injector was used for anhydrous ammonia injection, and the other for aqueous ammonia injection. The anhydrous ammonia injector was constructed of 3/8" stainless steel tubing that was welded shut at the end, and had a 3/16" hole drilled in the side. The 3/8" stainless steel tube was inserted perpendicularly into the slip stream tube such that the drilled hole was in the exhaust flow stream center, facing the same direction as the flowing exhaust. The anhydrous ammonia injector is shown in Figure 4.

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Figure 4 Anhydrous ammonia injector.

The aqueous ammonia injector was an air assisted type, supplied by CPI International. The design used two Swagelok tubes, one 1/8" diameter, and the other 1/16" diameter. The smaller tube was inside the 1/8" tube, and a calibrated crimp was on its end. Air flowed through the smaller tube, and aqueous ammonia flowed in between the large and small tube. Aqueous ammonia was atomized by air blowing rapidly by the calibrated crimp. The smallest diameter in this atomizer was 1/16", so the air assisted design was not prone to clogging.



Figure 5 Aqueous ammonia injector.

The aqueous ammonia air assisted atomizer was mounted to an elbow in the flow stream so that the atomizer could spray in the same direction as the exhaust flow, without modifying or bending the atomizer. The atomizer was inserted into a box mounted to a 90° bend, aligned with exhaust as it exited the bend.

A vane mixer was used to ensure gaseous homogeneity. It caused swirl about the axis of the slipstream pipe. The mixer was placed between the ammonia injector and the catalyst. It had two flat plates that were cut in half circles and welded at 90° from each other on adjacent sides of the slipstream pipe, as shown in Figure 6. Experimental and CFD analyses were done by Ivaturi [14] to quantify reagent mixing.



Figure 6 Exhaust/reagent mixer.

2.3 Catalyst Housing and Modules

A commercial company provided the catalyst modules. The cylindrical modules were 9" diameter by 5" long. The cylinders had 1/16" square cross hatching, which extended the catalyst length, creating channels or monoliths, which are discussed in the numeric model section of this thesis. A vanadia-titania mixture coated the surface of the catalyst, which catalyzed the chemical reactions between NOx and ammonia. Figure 7 shows the catalyst modules.



Figure 7 Catalyst modules.

The catalyst housing was built out of ¼" stainless steel plate, which was rolled to 9 ¼" inside diameter. Ends were fabricated to connect to the 4" stainless steel pipe inlet and outlet. The single exhaust stream was broken into two shorter, parallel streams, with three modules in each stream. Splitting the slipstream flow into two parallel streams reduced the pressure drop across the catalyst modules. Compared to a single stream, two parallel streams had increased catalyst frontal area, and reduced monolith path length. Figure 8 shows the catalyst housing used.



Figure 8 Catalyst housing.

2.4 Emissions Measurement System

An exhaust sample probe fabricated according to EPA Method 1 [15], and installed on the slipstream. The sample probe was a 3/8" stainless steel tube with four holes drilled into the side, and the end welded shut. The probe was mounted such that the four drilled holes face toward exhaust flow. Sampled exhaust flowed through the sample probe, and into a heated sample line. The heated sample line, temperature controlled to 230 °F (383 K), directed the sample into a Continuous Emissions Measurement System (CEMS) and a Fourier Transform Infra-Red (FTIR) spectrometer.

Carbon dioxide (CO₂), CO, oxygen (O₂), THC, and NOx, were measured using five dedicated measurement modules in the CEMS. The CEMS incorporates a chiller that condensed water out of the sample, so all measurements made by the CEMS analyzer were dry. To calibrate the analyzers, zero and span calibrations were done to create a linear interpolation function between known zero and span species concentration values. Calibration zero and span gasses were certified master class. Bias checks were done to ensure leaks of ambient air into sample exhaust did not create measurement inaccuracies. Zero and span calibrations were done once an hour, and bias checks were done at least twice per test day. The bias checks were done at the beginning and the end of the test day.

An FTIR spectrometer was used to measure ammonia, water, and hydrogen cyanide. The FTIR spectrometer sampled wet exhaust gas, which means FTIR spectrometer measurements were converted to dry. For more details on the emissions measurement equipment, see [16].

2.5 Flow and Temperature Measurements

To measure slipstream exhaust flow, a 1.75" diameter orifice, with a pressure measurement before and after, was used. Differential pressure across the orifice, static pressure at the orifice, and temperature at the orifice were measured to calculate exhaust flow.

Ammonia flow control is important for proper SCR operation, and ammonia flow was varied during many test maps. Two flow controllers were used. Anhydrous ammonia flow was controlled with a FloCat GFC-017 flow controller, with a span of 0 to 1000 ml/min. A manual, mechanical, variable area flow meter, with a needle valve, was used in parallel with the electronic FloCat flow controller to enable high total ammonia flow rates, with the controllability associated with the electronic FloCat.

Aqueous ammonia flow was controlled by an Eldex Optos Series 1HM positive displacement, single cylinder piston pump. Flow pulsations, caused by piston surges of the positive displacement pump, were eliminated by a flow restrictor and a length of pipe. The flow restrictor acted like a resistor and the length of pipe acted like a capacitor, creating a low pass filter. The resistor was a needle valve, turned down slightly to create backpressure. This aqueous ammonia flow control setup was poor for testing applications because when the control algorithm called for a rapid ammonia flow increase, pressure drop across the pinch valve increased rapidly, often damaging pressure gauges and other equipment upstream of the valve.

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This test skid used 1/8" Omega K-type thermocouples for temperature measurements that were attached to the slipstream with a weld-o-let fitting and a Swagelok bored-through fitting. Swagelok compression fittings sealed exhaust gas from atmosphere, and held the thermocouples in place. Thermocouples were located at every point of interest along the catalyst slipstream, including directly before and after the catalyst modules, and at the flow measurement orifice.

2.6 Data Acquisition and Control

Measurements in these experiments were made electronically, using National Instruments data acquisition systems and LabVIEW software. The National Instruments hardware consisted of a compact field point, cFP 2100 unit with: TC 120, AI 110, AO 200, and DIO 550 input/output modules. The modules were used for thermocouple inputs, analog inputs, analog outputs, and digital inputs and outputs.

A program written in LabVIEW is known as a VI, or Virtual Instrument. A VI controlled basic functionality of the slipstream system, including catalyst temperature, sample line temperature, space velocity, and ammonia to NOx molar ratio. The LabVIEW program also read and recorded basic system parameters, e.g., temperatures and pressures, during data points. The recorded data could be read and processed in Excel. Temperature and space velocity controls were proportion plus integral plus derivative (PID) type. Ammonia to NOx molar ratio control was performed using the approaches discussed in the controls section of Chapter One, and is a major topic of discussion in this thesis. Appendix B shows the Labview VI in full detail.

2.7 Ceramic NOx Sensor

During the controls portion of catalyst testing, ECM ceramic NOx sensors, part number 06-01, were used to create feedforward and feedback loops to control ammonia flow. The sensors were mounted to an O_2 bung, which was welded directly to the side of slip stream pipe.

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NOx sensors were connected to an ECM CANopen NOx/O_2 Module, which communicated via ModBus to an ECM NOx 5210 module. The 5210 module communicated with two NOx sensors at a time, and relayed the signal, via 0-5 V analog, to a National Instruments compact field point unit. The sensors detected NOx, O_2 , and air fuel ratio.

2.7.1 Ammonia Interference

Figure 9 shows trends of ceramic NOx sensor readings plotted against Chemi-Luminescence Detector (CLD) readings of the same exhaust gas. The first series plots the readings absent of ammonia, while the second series plot is in the presence of .85 ammonia/NOx molar ratio. The ceramic NOx sensors have a predictable, positive reaction to ammonia.



Figure 9 Ceramic NOx sensor signal vs. CEMS NOx in the presence of ammonia and the absence of ammonia.

Ceramic NOx sensors have cross sensitivity to ammonia, and when tested, sensitivity was .65 that of NOx [10]. This means that for every 100ppm of ammonia, the ceramic NOx sensor returned a 65ppm higher reading than NOx concentration. The formula to calculate ceramic NOx sensor Reading is shown in, Equation 2.1.

$$Ceramic_Sensor_Reading = NOx_Concentration + X (Ammonia_Concentration)$$
(2.1)

where X represents the ceramic NOx sensor sensitivity to ammonia. In literature, X was .65 [10], and in this text, X is 1.

In application, sensitivity to ammonia does not affect feedforward control, but is troublesome in feedback control. While the feedforward ceramic NOx sensor can be placed upstream of ammonia injection, the feedback sensor is always immersed in both ammonia and NOx. Therefore, neither post catalyst NOx concentration nor post catalyst ammonia concentration can be derived using a ceramic NOx sensor.

2.7.2 Signal Filtering

Filtering the NOx sensor signal is necessary because the sensor noise band is often greater than the slipstream NOx concentration. The noise band, shown in Figure 16, is 30ppm, and post catalyst NOx concentrations approached 5ppm. The filter implemented a least squares linear fit to the previous one minute of data. A moving one minute frame was used, a least squares linear fit was calculated, and the linear fit was solved for the current time. Figure 10 is a simulated graphical representation of the filter. The line represents a sixty second linear fit, and the end point is the filtered value. Figure 11 shows simulated data that represents a 30 second ramp from 30 ppm to 50 ppm. In the figure, the simulated data shows pre-filter NOx concentration, NOx concentration as read by the ceramic NOx sensor, and filtered NOx concentration. The thirty second ramp time is used to demonstrate filter performance, because a thirty second transition is the fastest transition a stationary SCR system will likely encounter.



Figure 10 Graphical representation of the ceramic NOx sensor filter.



Figure 11 Result of ceramic NOx sensor filter.

2.7.3 Calibration

Calibration of the NOx sensor was performed using exhaust gas. Ammonia was first purged from the slipstream. The engine was operated at 100% load and low boost (low air-fuel ratio), which yields higher NOx emissions. CLD and sensor readings were allowed to stabilize, and a five minute average data point was taken. The engine was then operated at 100% load and high boost (lower NOx level), and a five minute average was taken with the two analyzers of the stable system. A linear fit was applied to the ceramic NOx sensor to force the two five minute averages of the sensor to match that of the CLD. Figure 12 is a flow diagram showing calibration procedures.



Figure 12 Flow of the Ceramic NOx sensor calibration.

Calibration span values are important to ceramic NOx sensor reading accuracy because NOx concentrations vary for different applications (10-2000 ppm). The heuristic rule followed in this work is: the high span NOx concentration should be no larger than twice the highest expected operational NOx concentration, and the low span value should be low enough that the range includes all operating NOx concentrations. In the case of the SCR catalyst used in our testing, the upper and lower span concentrations of the pre-catalyst sensor were 314ppm and 52.8ppm. These span values corresponded to 3.15V and 1.85V, respectively. The post-catalyst NOx sensor was spanned between 11.6ppm and 52.8ppm, corresponding to 1.85V and 2.83V, respectively. Pre catalyst and post catalyst ceramic NOx sensor calibration results can be seen in Figure 13 and Figure 14, respectively. In the graphs, the linear fits are plotted against factory calibrations.



Figure 13 Pre catalyst ceramic NOx sensor calibration results.



Figure 14 Post catalyst ceramic NOx sensor calibration results.

Post-catalyst NOx sensor 0-5V analog communication to National Instruments equipment was set up to include negative NOx concentrations. This was done because when 0V corresponds to 0ppm NOx, and the actual NOx concentration is 5ppm, noise fluctuations causes much data to be lost through the 0-5V analog signal. The analog signal cannot communicate negative voltage, so any part of the NOx sensor noise that is less than zero results in a zero reading, which is incorrect. Instead, 0V was set to correspond to -50ppm, so no data was lost in analog communication at low NOx concentrations. Figure 15 shows NOx concentration as read by the computer, through 0-5V analog communication to the ceramic NOx sensor when 0ppm corresponds to 0V. A truncation occurs at 0ppm, and data is lost because negative datapoints are defaulted to zero. Figure 16 shows NOx concentration as read from the NOx sensor through the 0-5V signal after corrections were made such that 0V corresponds with -50ppm NOx concentration.



Figure 15 Shows loss of data that is caused by truncation of ceramic NOx sensor readings.



Figure 16 Shows communicated data, including negative values.

3 SCR NUMERICAL MODELING

3.1 Software Selection

Several software packages are available that are capable of modeling SCR catalyst reaction. Fluent is a computational fluid dynamics solver with chemical kinetic capabilities and surface reaction options. Chemkin is a chemical kinetic differential equation solver with plug flow proficiency. Simulink is an ODE solver with a graphical user interface, commonly used for controls development.

SCR modeling was broken into two parts. First, a numeric model of an SCR catalyst was created, which included ammonia adsorption, NO destruction, and species diffusion across the catalyst width. Control of the numeric catalyst was the second part of the model, in which the modeled catalyst inputs and outputs were used to control the modeled catalyst, so observations could be made of the controller efficacy. These two model requirements lend themselves to different software packages. Software with built in computational fluid dynamics chemical kinetic equation solvers did not have built in controls software, such as simple differentiators and integrators. In order to implement any control system in the computational fluid dynamics or chemical kinetics software package, the control software would have to be built in an archaic c-based language, or an interface to Matlab would need to be built; these requirements are outside the knowledge of this author. Simulink was chosen because it appeared more direct to create an SCR model in Simulink, than create a controls program in Fluent or Chemkin. This is because extensive SCR research had already been done, expediting the model building process. Overall, using Simulink to model the entire SCR catalyst system, including chemical reactions and

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controls strategies, was a direct and simple solution, and more elegant solutions may have existed. An additional benefit to the Simulink model is transparency; if Fluent or Chemkin were used to model SCR chemistry, many solver details would be unknown, whereas Simulink allows knowledge of, and control over, every aspect of the model.

3.2 Site Density Calculation

A key constant in SCR numeric modeling is site density. Site density is the density of active catalytic sites per unit area on the catalyst surface. Units for site density are mol/m². Active catalytic sites are sites which cause chemical reactions. In SCR, one catalyst site first adsorbs one ammonia molecule. Then, one NOx molecule reacts with one adsorbed ammonia molecule to form nitrogen and water. Then, oxygen re-activates the catalyst site. Catalyst site density affects ammonia storage, NOx reaction rate, and transient response.

The total reactive area is calculated using the catalyst characteristic length. Characteristic length is calculated by isolating one square catalyst monolith, and dividing the channel cross sectional area, by the channel wall length. Pictorial descriptions of the channel cross sectional area and wall length are shown in Figure 17. The figure is a front view of a single square of the catalyst. Width and height of the catalyst channel are 1/16", and ceramic material area is assumed to consume 30% of the total area. Table 1 shows calculations. Characteristic length for the modeled catalyst is 0.0332 cm. Catalyst volume divided by characteristic length is the total catalyst area.


Figure 17 Zoomed in, frontal view of one catalyst channel.

Variable	Value	Units
Total Channel Area	0.0252	cm ²
Ceramic Material Area	0.0076	cm ²
Channel Flow Area	0.018	cm ²
Channel Perimeter Length	0.53	cm
Catalyst Characteristic Length	0.05	cm
Total Catalyst Volume	31275	cm ³
Total Catalyst Area	659314	cm ²
Flow Characteristic Length	0.033	cm

Table 1 Characteristic length calculations.

To calculate the amount of absorbed ammonia in moles, a transient data point was taken with the experimental setup at operating temperature. The catalyst was fed reagent at a molar ratio of 1 until the catalyst stabilized. Ammonia flow rate was reduced to zero and post-catalyst NOx vs. time was recorded. The integral with respect to time of NOx reduced plus ammonia slip, from ammonia shutoff time to system stabilization time, is the total adsorbed ammonia. The integral of NOx reduced corresponds directly to ammonia stored because the two compounds react at a molecular ratio of one. One to one molecular ratio is consistent for temperatures below 750° F (672 K). Once ammonia flow is turned off, NOx reacts with ammonia stored in the catalyst. A heuristic integration time offset of 30 seconds was used to account for sample delays. Figure 18 shows the area of integration. The area under the curve is multiplied by inlet NOx molar flowrate to obtain 0.368 mol of ammonia stored in the catalyst. The number of moles is divided by total catalyst area resulting is 5.578e-7 gmol/cm².



Figure 18 Integrated area for site density calculation.

3.3 Model Setup

Simulink is an ordinary differential equation (ODE) solver, and the SCR equations are partial differential equations (PDE). The PDE must be divided spatially into several nodes and approximated as a group of ODE's. Node spacing is constant throughout the catalyst length. The model was simplified by excluding all but a single catalyst monolith, and simplified as a two dimensional flat plate. The model was broken into 12 nodes lengthwise by one node widthwise. The two dimensional channel was modeled with its width equivalent to the catalyst flow characteristic length of .0332 cm. Figure 19 shows the modeled channel nodes, not to scale. Labeled are: exhaust flow direction, species diffusion direction, catalyst wall material, and nodes 1 through 12. Exhaust flow and species diffusion directions are referred to as the axial direction and the tangential direction, respectively.



Figure 19 Breakdown of modeled nodes.

Each node is a lumped model, in which perfect axial mixing is assumed. Figure 20 shows an expanded single node. Exhaust is shown entering the node, diffusing into and out of the catalyst wall, chemically reacting on the catalyst surface, and flowing out of the node.



Figure 20 Breakdown of individual nodes in the numerical model.

Exhaust flow rate, space velocity, species molar flow rate, and catalyst volume are related by Equation 3.1,

$$\frac{Standard_Space_Velocity}{Standard_Molar_Volume} = \frac{Molar_Flow_Rate}{Catalyst_Volume}$$
(3.1)

where standard molar volume is 4.46×10^{-5} m³/mol and catalyst volume is 4.99×10^{-3} m³. Relative molar concentration is measured in ppm or %. Relative molar concentrations differ at inlet and outlet conditions because of catalytic reactions.

Inlet concentration for the first node is the catalyst inlet concentration, prescribed by the user. Inlet concentrations for subsequent nodes are the preceding node's outlet concentration, as shown in Equation 3.2, and outlet concentration in a given node is the bulk concentration in that node, shown in Equation 3.3.

$$Inlet_Concentration_{i,c} = Bulk_Concentration_{i-1,c}$$
(3.2)

$$Outlet_Concentration_{i,c} = Bulk_Concentration_{i,c}$$
(3.3)

Bulk concentration of a species, c, at a given node, i, is the species concentration throughout the node volume. For example, inlet NO concentration for node four would be the bulk NO concentration in node three. Net flow in is defined in Equation 3.4.

 $\frac{Net_Flow_In_{i,c}}{Molar_Flow_Rate_{i,c}} = Inlet_Concentration_{i,c} - Outlet_Concentration_{i,c}$ (3.4)

Diffusion in the tangential direction is calculated using Equation 3.5,

$$\frac{Diffusion_Rate_{i,c}}{D_c 2} = \frac{Bulk_Concentration_{i,c} - Wall_Concentration_{i,c}}{Flow_Characteristic_Length}$$
(3.5)

where wall concentration is species concentration at the catalytic surface and diffusion rate is the rate at which species diffuse tangentially across the channel in a given node. Units of diffusion are mol/m^2 -sec. The calculation for binary diffusion coefficient is shown in Equation 3.6,

$$D = D_0 \left(\frac{T}{T_0}\right)^{\frac{3}{2}} \left(\frac{P}{P_0}\right)^{-1}$$
(3.6)

where T, P, T₀ and P₀ are temperature, pressure, 273K and 101.3kPa, respectively, and D₀ is 2.056×10^{-5} and 2.8×10^{-5} for NO and NH3, respectively. Units of D₀ are m²/sec.

Constants from Bai and Chwu [8] were used in the calculation of NO destruction rate. The Bai and Chwu numerical model assumed infinitely fast ammonia adsorption, which was not done in this numerical model. Ammonia adsorption rate calculations were made to improve numerical stability. A constant, K_r , was introduced to limit ammonia adsorption and desorption rate under extreme circumstances, such as step inputs. Equation 3.7 and 3.8 relate K_{ads} and K_{des} , to K_{NH3} and K_r ,

$$K_{ads} = K_r K_{NH_3} \tag{3.7}$$

$$K_{des} = K_r \tag{3.8}$$

where K_r was set high enough by the user that it did not limit ammonia adsorption rate. K_r only changed catalyst operation during extreme transience that would otherwise cause numeric instability. K_r was set to 1 for all catalyst modeling. By varying K_r from .5 to 10, and observing modeled catalyst performance, it was insured that K_r had negligible affect on modeled catalyst performance. Equation 3.9 defines R_{NH3} using K_r and K_{NH3} .

$$\frac{R_{NH_3}}{K_r} = \left[K_{NH_3} C_{NH_3} (1-\theta) - \theta \right]$$
(3.9)

Node volume capacitance is represented in Equation 3.10. Net Reaction Rate is defined in Equation 3.11.

$$\frac{d}{dt} \left(Bulk_Concentration_{i,c} \right) = \frac{Net_Flow_In_{i,c} - Net_Reaction_Rate_{i,c}}{Node_Volume}$$
(3.10)

$$Net_Reaction_Rate_{ic} = AreaR_{ic}$$
(3.11)

In Equation 3.11, area is the reactive area of the catalyst node, $.0318m^2$, and $R_{i,c}$ is R_{NH3} or R_{NO} for node i and constituent c. Screen prints of the Simulink model are in Appendix A.

3.4 Model Discussion

The model created in Simulink included two reactions: NH_3 adsorption and NO destruction. A two-reaction model does not model the SCR system completely. It excludes all oxides of nitrogen except NO, which can cause differences in NOx destruction rate and stoichiometric ammonia/NOx ratio. Calculation of catalyst site density was inaccurate because, after running the numerical model at stoichiometric ammonia to NOx molar ratio, the catalyst is not entirely saturated. Therefore, the method under predicted catalyst site density, resulting in the model predicting shorter delay times than seen in real life, as seen in Figure 22.

3.5 Model Validation

The SCR Simulink numeric model is validated in this section. "Knowledge Validation becomes a process of building confidence in its usefulness with respect to a purpose.", Pederson et al [17], which implies that a purpose must first be defined, i.e. the model's use must be assigned. The purpose of this numeric model is to predict general transient phenomena inside the SCR catalyst. "Numerical algorithm verification and SQA activities consist of accumulating evidence substantiating that the code does not have any apparent algorithmic or programming errors and that the code functions properly on the chosen hardware and system software," Oberkampf et al [20]. By this, a model is validated by showing the model is error-free, and support evidence is the basis of validation. The model must be validated both qualitatively, and quantitatively [17]. Qualitative validation verifies the model's building blocks, structure, and example problems logically [17]. Validating a model qualitatively justifies each individual piece of the model. In our case, each node and their sub-nodes and functions are validated [17]. Qualitative validation confirms the assembly, or the connections between nodes and sub-nodes [17]. Comparative tests are run on the computer model and the test system, and qualitative validation justifies these comparative tests, i.e. the test run on the model must be adequate and reproducible [17]. Quantitative validation involves running comparative tests (that are qualified), quantifying the model response, showing that the model operated as intended in the tests, and showing the model will operate as well in other examples [17]. These can be broken into six steps, or the "Validation Square" [17]. The six steps are listed below.

- 1) Validate Individual Model Nodes
- 2) Validate Connection Between Nodes
- 3) Qualify Comparative Test Between Computer Model and Real SCR System
- 4) Quantify Accuracy of Model in Comparative Test
- 5) Show Model to Experimental Correlation Is Due to Model's Design
- 6) Argue Model will Operate as Accurately in Other Examples

The comparison between the SCR system and the Simulink model is done using two comparative tests: ammonia turn on, and ammonia turn off. In the ammonia turn on comparison, the SCR system and Simulink model were allowed to stabilize before ammonia was turned on. Ammonia and NOx concentrations were recorded. In the ammonia turn off example, similar procedures were followed. The SCR system and Simulink model stabilized at standard operating conditions and stoichiometric ammonia/NOx feed rate. Ammonia feed was shut off, and data was recorded that showed the transient catalyst response.

Step one and two, validation of individual model nodes, as well as their assembly, was done in the description of the model. This description included a breakdown of the nodes, their purpose, and a description of, and justification for, their assembly.

Step three, qualification of performed comparative tests is done by arguing that the tests are relevant, and sufficiently analyzing the model's ability to follow experimental SCR results. The comparative tests are relevant because they show the model operating in transience, which is the purpose of the model. The comparisons assess catalyst performance sufficiently because the tests show catalyst performance in a wide range of operation, from zero to stoichiometric ammonia/NOx molar ratio. The systems undergo rapid transitions that show inaccuracies readily. The first comparison, in which ammonia is turned on, shows differences in catalyst operation as the catalyst stabilizes. The second comparison, in which ammonia is shut off, provides another transient response scenario, and improves model confidence.

Step four addresses the correlation between the Simulink model and the experimental SCR test system that are qualified in the preceeding paragraph. Figure 21 shows the transient response of the SCR system and the Simulink model, following ammonia turn-on. At time zero, reagent flow is turned on to stoichiometric ammonia/NOx ratio. NOx reduction in both series begins at zero, and rises. Initial NOx reduction on the experimental test is delayed, which can be attributed to sample system delays. The experimental system NOx reduction, rapidly increases, surpassing the Simulink model, and stabilizes around 98%. This test shows that the Simulink model slightly under predicts SCR catalyst performance. Figure 22 shows the SCR system and the model, following ammonia shutoff. Reagent feed is shut off at time zero, and NOx reduction

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is presented. This graph displays the Simulink model NOx reduction decreasing and stabilizing in about ten minutes, and the experimental SCR reduction diminishing in about fifteen minutes. This test shows a loose correlation between the two series. The difference between the Simulink model and the experimental setup is of NOx reduction drop off delay. The model predicts NOx reduction to fall off ten minutes, whereas the experimental SCR test skid showed ammonia drop off in fifteen minutes. Differences between the experimental SCR catalyst test and the Simulink model prediction can be attributed to three causes: (1) the constants, K_{NH3} and K_{N0} were obtained from literature, and could differ substantially from the correct values; (2) catalyst site density was under-predicted; (3) false, numeric diffusion, in which averaging of the numerical nodes overpredicts diffusion in the axial direction. These comparative tests show the Simulink model matches experimental trends, but under predicts catalytic delay time. This is acceptable because the model's purpose is to display general trends, rather than make accurate, quantitative predictions.



Figure 21 Comparison between modeled and experimental NOx reduction following reagent feed turn-on.



Figure 22 Comparison between modeled and experimental NOx reduction following reagent feed turn-off.

Step five is an argument that the model operated as intended during the test, and that the correlation between the experimental data and the model's prediction was due to the model's design, rather than a coincidence. According to Pederson et al [17], this is done by analyzing the results of the individual nodes inside the model. This is done in chapter 3.3.

Step six, or showing the model will operate correctly under conditions other than those tested is a "leap of faith" [17]. The accumulation of evidence during steps one through five facilitates the leap of faith, and allows us to "claim generality" [17]. Wthout loss of generality, since all evidence shows the Simulink model works as intended at all five levels of analysis defined by Pederson et al [17], and is error free, then, for its purpose, the model is validated.

3.6 Step Input Results

3.6.1 Rapid Molar Ratio Transitions

Transient and controls testing described in Chapter Four will quantify the slow SCR catalyst responses. The Simulink numeric model gives insight into the mechanism for the slow response. An ammonia/NOx molar ratio step input is modeled in this section to explore the mechanism of slow catalytic response.

The computer model was run at 500°F [533 K] and 10,000 1/hr space velocity, with 150 ppm NOx inlet. The catalyst was fed .8 stoichiometric ammonia/NOx ratio (lean) and allowed to stabilize. A transition was made to 1.2 times stoichiometric ammonia/NOx ratio in a step. The system's time response was observed following the transient. Figure 23 shows ammonia concentration as a function of catalyst length at t=0, t=50, 100, 250, 500, 1000, and 2000 sec. Figure 23 shows an NH₃ wave propagating lengthwise through the catalyst. This wave occurs because NH₃ adsorbs onto the catalyst much faster than NOx is reduced. Rapid ammonia adsorption has been assumed in previous texts [8]. Due to this, large quantities of NH₃ can be

adsorbed in a short catalyst length. The catalyst is initially starved of ammonia and chemical reactions are ammonia limited; reagent is depleted before NOx can be reduced. When the transition is made to higher reagent feed, ammonia begins adsorbing at the front of the catalyst first. When the front catalyst sites become saturated and cannot further adsorb ammonia, ammonia, then, flows through saturated catalyst sections, until it reaches unsaturated catalyst material, and is rapidly adsorbed. In this way, the wave of ammonia propagates through the catalyst front to back. This explains long catalyst delays, because substantial ammonia can be fed into the catalyst before the ammonia wave reaches the back of the catalyst. In other words, the ammonia wave has to propagate through the whole catalyst length before excess ammonia can be detected post catalyst.

Figure 24 shows ammonia slip following the ammonia feed ratio step transient. This figure shows ammonia slip staying stagnant and rising after a delay of about 500 s. This matches general observations of on-engine SCR tests.



Figure 23 In-catalyst ammonia concentration following step input of ammonia/NOx feed ratio from .8 to 1.2.



Figure 24 Ammonia emission following ammonia/NOx feed ratio transition from .8 to 1.2.

In the validation section, it was discovered that the real catalyst responds with slightly longer delays, with steeper transitions. This means the on-engine catalyst would have more accentuated, slower propagating waves than predicted by this model.

3.6.2 Rapid Temperature Transitions

Prior work has shown NOx and ammonia spikes resulting from rapid temperature changes [18], [19], [20], [21], [22]. This phenomenon was investigated with the Simulink model. Catalyst temperature was stepped up to represent a rapid temperature change from 500°F [533 K] to 550°F [561 K]. The model was fed stoichiometric ammonia to NOx ratio and 150 ppm NOx. Temperature transitioned after 4000 seconds of stabilization. Data was recorded for another 4000 seconds.

Figure 25, 26, and 27 show time plots of the 8,000 second simulation. Each plot contains multiple curves corresponding to different locations along the catalyst length in the direction of flow. NOx concentrations, NH3 concentrations, and relative NH₃ concentration $(\theta = NH_3^*/NH_{3,max}^*)$ are higher toward the beginning of the catalyst, and lower toward the end. Figure 25 shows NH₃ concentration as a function of time during the simulation. At time zero, NH_3 concentration is zero, by default. For the first 4,000 seconds, the SCR catalyst emissions stabilize at 500°F [533 K]. Each series in the graph represents a distance down the catalyst length. Shorter distances stabilize faster because there is less preceding catalyst material to adsorb and release NH₃, which must first stabilize. The temperature transient is at 4,000 seconds. Shorter distances show quick spikes in NH₃ concentration, caused by temperature induced ammonia desorption; ammonia adsorption decreases as temperature increases. Longer distances show the same quick spike, caused by ammonia release, followed by a long transient, during which ammonia that has released from the prior catalyst portions, propagate into downstream catalyst portions. This long transient decreases in amplitude and increases in duration as it moves through the catalyst, into downstream catalyst portions. Figure 26 shows θ as a function of time during the same transient. θ stabilizes in the first 4,000 seconds, starting at zero by default. Short distances release adsorbed ammonia quickly, caused by increasing temperature. As the distances get longer, the reaction changes because ammonia released from upstream catalyst sites pass through the catalyst, causing an increase in adsorbed ammonia. This adsorbed ammonia slowly releases, eventually stabilizing at a lower value. Figure 27 shows NOx as a function of time for the same transient. NOx stabilizes over the first 4,000 seconds. At 4,000 seconds, when the temperature transient occurs, NOx concentration has a two mode transition. First, there is a short increase in NOx that lasts about 0.02 seconds. This peak is caused by the way the numeric solver solves for NOx concentration, and is unimportant. After an initial increase, NOx drops off. The NOx drop off can be attributed to high θ due to low preceding temperatures, and high R_{NO} caused by high temperature. The catalyst maintains high ammonia adsorption for some time after the

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temperature is increased, and R_{NO} is high due to high temperature, causing a surge in catalytic activity. The NOx depression propagates through the catalyst, becoming less intense and longer in duration as catalyst length increases.



Figure 25 In-catalyst ammonia concentration following rapid temperature transient from 500° F [533 K] to 550° F [561 K].



Figure 26 In-catalyst θ following a rapid temperature transient from 500° F [533 K] to 550° F [561 K].



Figure 27 In-catalyst NOx concentration following a rapid temperature transient from 500° F [533 K] to 550° F [561 K].

 θ tends to decrease with temperature, while R_{NO} increases with temperature. These two inversely trending variables cause an interesting catalyst response. Overall catalyst effectiveness depends very little on temperature at stable conditions. Stable NOx and ammonia slip are almost independent of temperature. NOx slip decreases from 5.7 ppm to 5.6 ppm, from t=3,999 s to t=7,999 s. θ increase almost entirely negates R_{NO} decrease at low temperatures. Internal operation of the catalyst varies greatly at different temperatures. At high temperatures, R_{NO} increases and θ decreases. R_{NO} increasing expedites NOx destruction, and low θ reduces available ammonia. These two effects oppose each other on steady state chemical reduction. When temperature transients are introduced, the catalyst adsorbs and releases significant amounts of NH₃ to re-stabilize, causing NH₃ and NOx waves to propagate through the catalyst, a two mode θ response, and a single mode NH₃ and NOx response.

Figure 28 was created to show θ as a function of catalyst length at multiple time series. This figure represents the same data as Figure 26. θ starts at a stable operating condition at time zero. When temperature steps up, θ begins to decrease, starting at the front of the catalyst. As θ decreases, NH₃ is released into the channel, allowed to flow downstream, and adsorbed by downstream catalyst material. This is why the temperature step shows an initial increase in ammonia emission, due to the catalyst material releasing ammonia, then a slight decrease, due to increased chemical kinetic rates.



Figure 28 θ vs Catalyst Length at various times after temperature transition from 500° F [533 K] to 550° F [561 K].

3.6.3 Rapid Space Velocity Transitions

The Simulink model was set up to run for 4,000 seconds, and then a 5,000 1/hr to 20,000 1/hr space velocity change was imparted. The model was run for another 4,000 seconds after the transition.

Figure 29, 30, and 31 show ammonia, θ , and NOx, respectively, as a function of catalyst length through the simulation duration. The system was allowed to stabilize for 4,000 seconds. At 4,000 seconds, the space velocity step executed. Figure 29 shows several series of NH₃ as a function of catalyst length, where each series is of constant time following the space velocity step. In Figure 29, ammonia concentration drops as a function of length for all time series. In this figure, there are two stable points, at time zero, and at 4,000 seconds. The zero time series is the stable catalyst operating condition at 5,000 1/hr space velocity, and 4,000 seconds is the stable operating condition at 20,000 1/hr space velocity. These two stable conditions are operating bounds for all other time series in Figure 29. At time zero, ammonia concentration follows, approximately, a logarithmic curve. After space velocity is stepped up, ammonia immediately (within 10 seconds) increases at the front of the catalyst, while at the back of the catalyst, ammonia concentration is unaffected. Ammonia concentrations propagate as a wave from front to back, starting at the 5,000 1/hr space velocity stable series, and ending at 20,000 1/hr space velocity stable series. The wave slows down, decreases in magnitude, and spreads out toward the back of the catalyst. Whereas the wave is well defined at the front of the catalyst, it is long and drawn out at the back of the catalyst, taking an additional 450 seconds to propagate through the last half of the catalyst.

Figure 30 shows θ , which displays a single mode transition following the space velocity change. In this graph, the lowest series is time zero, and the highest series is 4,000 seconds. These two series are the bounds of operation, and increased rapidly in the front, and slowly in the back, creating a wave propagating front to back through the catalyst. θ increased substantially over the length of the catalyst. As ammonia slip through the catalyst increases, adsorbed ammonia increases. This it explains why space velocity appeared to have little affect on NOx reduction over most of the standard catalyst operating range. As space velocity goes up, so does adsorbed ammonia. Adsorbed ammonia increases NOx reduction rate, and partially offsets the reduced residence time of higher space velocity.

Figure 31 shows NOx through the simulation. In Figure 31, the "t=0" series is the lowest series, and is substantially different than the other series. Immediately after the transition, NOx increased to its maximum point, and then decreased slowly. NOx showed a two mode response. This two mode response is because, when space velocity was initially increased, θ was very low. This caused NOx to initially increase because there was insufficient adsorbed ammonia to react

with the NOx. As ammonia adsorbed onto the catalyst, θ increased, improving NOx reduction. This reduced outlet NOx. This effect proceeded quickly at the short catalyst lengths, and propagated slowly through the catalyst, having its greatest impact on the latter portions of the catalyst.

The space velocity transition simulations show the resultant NOx reduction has a two mode response. NOx reduction decreases immediately, and then increases slowly.



Figure 29 In catalyst ammonia concentration for various times after space velocity transition from 5,000 to 20,000 1/hr.



Figure 30 In-catalyst adsorbed fraction for various times space velocity transition from 5,000 to 20,000 1/hr.



Figure 31 In-catalyst NOx concentration for various times following space velocity transition from 5,000 to 20,000 1/hr.

3.7 Sensitivity Analysis

A sensitivity analysis was done to show the model's sensitivity to varying input constants. The constants used in simulations presented above came directly from literature, or had been calculated from experimental, transient data. In this section, simulations were run with varying constants to determine the model sensitivity to the constants. The four constants analyzed were: number of nodes in the model; K_{NH3} , or the rate constant for ammonia adsorption in equation 1.13; K_1 , or the pre-exponential rate constant for NO destruction in equation 1.14; and catalyst active site density, or the density of active catalyst sites on the catalyst surface. In the simulations, space velocity was set at 10,000 1/hr, catalyst temperature was set at 500°F [533 K], and ammonia to NOx ratio was stepped up from 0 to 1 at time zero, and back down to zero at time 4,000 sec. Through these simulations, ammonia turn on and ammonia turn off were analyzed. In all simulations, the constants that were not varied were set at the values described in chapter 1.

Four values of K_{NH3} were simulated: .25, .5, 1, 2, and 4. Figure 32 shows NOx concentration following ammonia turn-on. In Figure 32, NOx emission drops slightly more rapidly for the low K_{NH3} values. Figure 33 shows the NOx emission from the catalyst, following ammonia turn-off. In the figure, NOx emission increases for all series. NOx emission increases immediately in instances of lower K_{NH3} . The series representing higher K_{NH3} values tend to maintain low NOx emissions longer. The experimental curve is shown in both figures. The experimental post catalyst NOx concentration drops off faster than all four simulated curves in Figure 32, and is delayed much longer than all four simulated curves in Figure 33.



Figure 32 Showing NOx emission from catalyst, following ammonia turn-on, with varied K_{NH3} values.



Figure 33 Shows simulated post-catalyst NOx concentration following ammonia turn-off, with varied $$\rm K_{\rm NH3}$$ values.

As K_{NH3} increases, the adsorbed fraction tends to increase. Because of this, high K_{NH3} tends to cause a front loading of ammonia inside the catalyst. Therefore, high K_{NH3} values are associated with higher adsorbed fractions in the front of the catalyst. This high adsorbed fraction in the catalyst increases delay times following ammonia turn off.

Four values of K_1 were explored: 0.5, 1, 2, and 4. K_1 controls the rate of NO destruction. Figure 34 shows post-catalyst NO concentration following ammonia turn on. All four curves show NO emission drop off, with the higher K_1 values having faster drop off and lower K_1 values having slower drop off. Figure 35 shows post-catalyst NO concentration following ammonia turn off. This plot shows NOx increase, as the simulated catalyst is purged of ammonia. The curves with high K_1 values tend to hold low NO values for longer than those with low K_1 values, as seen in the first 100 seconds following the transition. The curves with high K_1 values have a very sharp increase in NO emission, whereas those with low K_1 values have long, drawn out increase. The experimental curve is labeled, and falls off somewhere between the $K_1 = 1$ curve and the $K_1 = 4$ curve.



Figure 34 Shows post-catalyst NOx concentration following ammonia turn-on, with varied K_1 values.



Figure 35 Shows post-catalyst NOx concentration following ammonia turn-off, with varied K1 values.

Figure 34 shows NO decreasing over 1,000 seconds following ammonia turn on. In the figure, trendlines with low K_1 values show more rapid NO drop off, whereas those with high K_1 values show slow NO drop off. During ammonia turn on, NO destruction rate is limited by the adsorbed fraction (θ) on the catalyst surface. High K_1 values result in faster NO destruction, which requires less adsorbed ammonia for an equivalent NO destruction rate. Therefore, the catalyst adsorbs less ammonia and stabilizes faster. Figure 35 shows post-catalyst NO concentration following ammonia turn off. In this figure, trendlines with low K_1 values initially show increased NO emission, because NO destruction along the catalyst length is lower, and less NO is destroyed. Immediately after the transition, trendlines with high K_1 values hold a stable, low, NO emission, for a period, before beginning their NO concentration ascent. This is because the higher K_1 value allows the catalyst to use its adsorbed ammonia more efficiently, and hold

high NO reduction for a period of time. When the stored ammonia is depleted, the NO concentration rises more rapidly in the high K₁ trendlines. This is because a high K₁ tends to approach binary NO destruction. If K₁ were infinity, the catalyst would reduce 100% of NO if there were a trace of ammonia adsorbed in the catalyst. If K₁ were infinity and ammonia feed was shut off, NO emission would remain at 0 ppm until the catalyst was completely depleted of ammonia, at which point post catalyst NO concentration would increase immediately to that of pre-catalyst NO concentration; the emission would be either 0 ppm or pre catalyst NO concentration. It would never be in the middle. As K₁ increases, transient NO emission approaches this behavior. The experimental trendline followed the simulated trendlines very closely in Figure 34. In Figure 35, the experimental trendline deviated significantly from the simulated trendlines. This could be due to several factors. There were many immeasurable transients during the experimental test. The amount of ammonia that was adsorbed in the catalyst at the time of ammonia shut off was unknown. Ammonia can adsorb on surfaces such as sample transfer tubing walls, which can affect response times. The specific reason for the difference between the simulated and experimental results is unclear.

Figure 36 shows the simulation of the post catalyst NO concentration, following ammonia turn on. In this simulation, seven node counts were simulated: 1, 2, 4, 8, 16, 32, and 64. The experimental result is also plotted. The figure shows decreasing NO concentration, as time progresses. This is because, as ammonia adsorbs onto the catalyst, NO reduction improves, and post catalyst NO concentration decreases. Increasing node count predicts faster drop off in post catalyst NO concentration, and lower stable NO emission. The experimental curve is below all the simulated curves. The 64 node count simulation is closest to the experimental curve in this figure.

Figure 37 shows simulated post catalyst ammonia concentration following an ammonia turn off transient. Post catalyst NO concentration increases with increasing time in all

simulations. NO concentration is initially low because the catalyst is stable at one to one ammonia to NO molar ratio. When ammonia is turned off, the chemical reactions consume adsorbed ammonia, so NO concentration increases as adsorbed ammonia is consumed. The higher node count trendlines predict a longer delay and sharper NO concentration increase than lower node count series.



Figure 36 Shows post catalyst NO emissions following ammonia turn on, with varying node count in model.



Figure 37 Shows the Simulink model dependence on node count following ammonia shutoff transient.

Figure 36 shows simulated NO concentration following ammonia turn on. The higher node count simulations predict faster post catalyst NO drop off. This is because, with a higher number of discretizations, ammonia and NOx dropoff in the front of the catalyst are better modeled. The low node simulations have an error associated with the bulk assumptions within the node. This error results in a false diffusion that causes predicted NO and ammonia concentrations to falsely smear down the catalyst length. This smearing effect causes higher predicted ammonia and NO emissions. This smearing effect also does not allow the simulation to adsorb ammonia on the front of the catalyst, which causes the predicted post catalyst NO concentration following ammonia turn off. As with the ammonia turn on example, the low node count simulations have lower predicted catalyst performance, and slower, more drawn out curves. This is due to the smearing effect of the false diffusion that is due to the bulk assumptions inside the individual nodes. Since bulk assumptions are made inside each node, NO concentration through

the length of the node is constant, so any NO inside the first node propagates immediately into the second node, which immediately propagates into the third node, et cetera. This effect causes simulated NO and ammonia to short circuit through the catalyst, and causes high predicted NO and ammonia emissions. This also causes the simulated catalyst to have smeared NO transience, as shown in Figure 37.

Figure 38 shows simulated post catalyst NO concentration following ammonia turn on. Four site density values were used: .0025, .005, .01, and .02. Units of site density are mol/m³. In the figure, post catalyst NO concentration drops off as time increases. This is because, after ammonia is turned on, the catalyst adsorbs ammonia and allows NO to be reduced, decreasing post catalyst NO concentration. In the figure, trendlines representing high site density simulations stabilized slower. Those representing low site density simulations showed faster NO dropoff and faster stabilization. Figure 39 shows post catalyst NO concentration following ammonia turn on. In the figure, post catalyst NO concentration increases because ammonia flow is turned of and ammonia that was adsorbed on the catalyst is consumed in the NO destruction reaction. As the ammonia is consumed, the NO destruction reaction proceeds slower, and less NO is destroyed in the catalyst. As less NO is destroyed in the catalyst, NO emission increases. The trendlines representing high site densities showed slower, delayed response. The experimental results are plotted in both figures. In Figure 38, the experimental curve is between the .0025 and .005 site density simulated curves. In Figure 39, the experimental curve is closest to the .02 site density simulated curve. In Figure 39, the experimental result had a sharper post catalyst NO increase than the .02 site density simulated curve.



Figure 38 Shows post catalyst NO concentration following ammonia turn on for various catalyst active site density values.



Figure 39 Shows post catalyst NO concentration following ammonia turn off for various catalyst active site densities.

Figure 38 shows that increasing site density affects the post catalyst transient response by slowing down the catalyst response, following ammonia turn on. Figure 39 shows that increasing active site density affects catalyst operation similar to in the ammonia turn on case, by slowing down the response. In general, increased catalyst active site density will increase the time the catalyst requires to stabilize. This is because, for a given NO destruction rate, as the active site density increases, more ammonia needs to be adsorbed onto the catalyst surface. Since more ammonia must be adsorbed, it takes longer to feed the required amount of ammonia into the catalyst, to reduce NO sufficiently.

4 Transient Testing

Steady state SCR catalyst tests were done to characterize post catalyst emissions, post catalyst emission tradeoffs between NOx and ammonia, and the influence of temperature and space velocity on catalyst operation. Post catalyst ammonia emission (ammonia slip) was fixed and NOx emission was recorded at various temperatures and space velocities. This method of SCR testing was time intensive because the catalyst responded slowly to varying ammonia inputs. Slow catalyst response caused long delay times between test points and inaccuracies due to a constantly transitioning system. To better characterize SCR catalysts, transient data was taken.

4.1 Transient Procedures and Test Map

During the transient tests, space velocity, catalyst temperature, and ammonia to NOx molar ratio were varied. Figure 40 is a graph of space velocity, catalyst temperature, and NH₃/NOx molar ratio variation through the transient test.



Figure 40 Graph of the input variables during the transient test map.

The five hour map was split into five one hour data points, and five transitions were defined. Each transition was designed to represent a rapid engine load change. The experimental setup was initially allowed to stabilize at 7,728 1/hr space velocity, 500°F [533 K] catalyst temperature, and zero ammonia flow. A pre-catalyst steady state data point was taken to determine engine out NOx concentration. This NOx concentration was used to calculate NH₃/ NOx molar ratio during the rest of the transient data point. The emissions analyzers were calibrated at the beginning of each five hour set of transient data points. Bias checks were done at the beginning and end of each five hour set of transient data points, and zero and span checks were done every hour. At time zero, ammonia was turned on to 0.85 NH₃/NOx molar ratio. The first transition occurred at hour one, during which space velocity and catalyst temperature were increased to 11,040 1/hr and 550°F [561 K], respectively. Space velocity increased very rapidly. Temperature increased slower due to the system thermal capacity. The second transition occurred at hour two, during which space velocity and temperature were increased to 12,144 1/hr and 600°F [589 K], respectively. The third transition was at hour three, during which space velocity

and temperature were reduced to 7,728 1/hr and 500°F [533 K], respectively. At three hours, twenty five minutes, NH_3/NOx molar ratio was changed from 0.85 to 0.6 for five minutes, and at three hours thirty five minutes, molar ratio was changed from 0.85 to 1.1 for five minutes. These last molar ratio transitions in the third hour were designed to duplicate a faulty NOx measurement, ammonia injection nozzle fouling, or anything that would cause ammonia to NOx ratio to suddenly change. Figure 41 is a step by step list of the procedure taken during the test point.

1.	. Stabilize engine		
	a. At 140ppm NOx at 15% O2		
	b. SCR 500°F, 7,728 space velocity, no ammonia		
2.	. Take 5 minute averaged pre catalyst data point		
3.	. Switch to post		
	a. Allow analyzers to stabilize		
4.	RECORD 1 hour		
	a. Record for 3 min, then introduce ammonia at .85		
	ammonia/NOx molar ratio		
	i. When temperature & space velocity are stable,		
	record pressure drop across catalyst		
	b. When finished, publish data		
5.	RECORD 1 hour		
	a. Record for 3 min, then increase temperature to 550°F, 11,040		
	space velocity		
	i. When temperature & space velocity are stable,		
	record pressure drop		
	b. Ensure ammonia flow compensates for change		
	c. When finished, publish data		
6.	RECORD 1 hour		
	a. Record for 3 min, then increase to 600°F, 12,144		
	space velocity		
	b. When temperature & space velocity are stable,		
	record pressure drop		
	c. Ensure ammonia flow compensates for change		
	d. When finished, publish data		
7.	RECORD 1 hour		
	a. Record for 3 min, then decrease to 500°F, 7,728 space velocity		
	i. When temperature & space velocity are stable,		
	record pressure drop		
	b. Ensure ammonia flow compensates for change		
	c. When finished, publish data		
8.	. RECORD 1 hour		
	a. Record for 3 min, then turn ammonia off via solenoid		
	b. When finished, publish data		
9.	. Switch sampeling system to pre catalyst		
1	a. Allow analyzers to stabilize		
	b. Take 5 minute averaged pre catalyst data point		
	c. Investigate post data from last 1 hour point		

Figure 41 Procedure for performing transient test.

4.2 Transient Results and Discussion

Figure 42 shows results from the transient test. From the beginning, NOx reduction

started at zero and climbed rapidly. At 30 minutes, NOx reduction stabilized at 97.5%.

Ammonia slip rose very slowly through the first hour, peaking around 4.5 ppm at one hour.

Through this time, space velocity and temperature held very steady. At one hour, the first

transition was made. Space velocity rose rapidly, and in one minute, space velocity stabilized at

10,000 1/hr. Temperature rose very slowly, requiring a half hour to stabilize at 550°F [561 K]. NOx reduction decreased to 97%. At hour three, space velocity and temperature were increased again. At this point, the pressure across the orifice exceeded the maximum differential pressure the sensor could read. This resulted in low space velocity measurement, low NH₃/NOx feed ratio, and low NOx reduction. This anomaly was beneficial because it subjected the catalyst to an additional, realistic transition. After the sensor calibration was corrected, NOx reduction returned to 98%. At hour three, the third transition was made. NOx reduction remained stable and ammonia slip increased slightly. The molar ratio changes in the third hour had almost no affect on catalyst performance. When reagent feed was shut off, a small delay (~15 min) was followed by a rapid drop off in NOx reduction and slow (~1 hr half life) drop off in ammonia slip.



Figure 42 Transient test results.
The results of this test revealed two things. First, NOx reduction potential depended very little on space velocity. As space velocity increased, NOx reduction decreased very little. This effect is explained in the numeric model section, by asserting that, as space velocity increases, so does the adsorbed fraction of ammonia (θ), increasing catalytic activity throughout the whole catalyst length, partially offsetting the reduced residence time caused by higher space velocity. NOx reduction and ammonia slip depended very little on temperature, as shown by the numeric model, because decreasing NOx destruction rate (R_{NO}) is almost entirely offset by increased catalyst ammonia affinity, and increased adsorbed fraction (θ). Second, ammonia slip responds more slowly than NOx reduction. When ammonia was turned on, NOx reduction increased very rapidly and stabilized within 30 minutes, whereas ammonia slip took an hour to stabilize. Ideal temperature for SCR systems is 700°F [644 K], whereas this engine has lower exhaust gas temperatures, around 500 to 550°F [533-561 K]. Increased θ and higher adsorption capacity is a result, which explains slow response times. More detail about this is in the numeric model chapter.

Figure 43, 44, and 45 show the transient test startup, anomaly, and shutdown, respectively. In Figure 43, ammonia flow was turned on. Ammonia flow stabilized around 450 ml/min, and NOx reduction rose quickly. Ammonia slip rose to around 4 ppm in one half hour. Figure 44 shows the anomaly in the transient test point, when the space velocity exceeded the sensor measurement range. During this anomaly, between 2.1 and 2.25 hours, NOx reduction dropped off dramatically, to 55% at its minimum. During this time, ammonia slip reduced from 4.5 ppm, to just under 4 ppm. This shows ammonia slip responding slowly, even under extreme transience. This is because the ammonia wave did not propagate through the whole catalyst length before ammonia feed returned. Figure 45 shows ammonia flow shutoff. Ammonia flow stopped after three minutes. NOx emissions dropped off fifteen minutes following ammonia flow

shutoff. Ammonia slip remained high through the entire hour, reducing from 4 ppm to 1.5 ppm throughout the hour.



Figure 43 First hour of transient test. Ammonia injection rate, ammonia slip, and NOx reduction are plotted during initial ammonia turn on.



Figure 44 Anomaly in transient test data point. Ammonia injection rate, NOx reduction, and ammonia slip are plotted during the data point error.



Figure 45 Ammonia shutoff in transient test. Plotted are ammonia injection rate, NOx reduction, and ammonia slip, following ammonia shut off.

Considerable time is required to determine the emissions of an engine equipped with an SCR catalyst. It takes an SCR catalyst about an hour to adsorb ammonia and stabilize under the conditions tested. Ammonia surge (when in-catalyst ammonia builds up for a period of time, and is released slowly) takes roughly an hour to dissipate and re-stabilize. To fully describe the average emission of a natural gas engine similar to the GMV, equipped with SCR, a minimum of two hours of data is needed.

4.3 Hydrogen Cyanide Formation

During transient testing, hydrogen cyanide became an indicator of ammonia slip. When ammonia was overfed into the catalyst, hydrogen cyanide emissions increase just before ammonia emissions. Figure 46 shows a plot of ammonia and hydrogen cyanide during ammonia overfeed transience. In Figure 46, hydrogen cyanide and ammonia start at about .5 ppm and 4 ppm, respectively. At five minutes, hydrogen cyanide increases to.8 ppm. Between 10 minutes and 35 minutes, ammonia ramps up to 15 ppm.



Figure 46 Demonstration of hydrogen cyanide preceding ammonia slip.

Figure 46 shows that the hydrogen cyanide increase leads ammonia slip by about seven minutes. Seven minutes before ammonia slip begins to rise, hydrogen cyanide increases very quickly, like a step function. It is interesting that hydrogen cyanide increases so quickly, and stabilizes so quickly. The numeric model shows that ammonia concentration produces a wave that propagates forward through the catalyst, and as the wave reaches the end of the catalyst, exits the catalyst. Based on this, a hydrogen cyanide (or a hydrogen cyanide forming radical) wave, is located in a very specific portion of the catalyst, extending from the catalyst beginning, to just past the end of the ammonia wave. This could be very useful in designing control algorithms because the most difficult part of designing SCR control algorithms is time delay, and reducing that delay by seven minutes would enable faster, more robust controls.

5 Controls Development

Steady state and transient testing showed that catalyst performance depends highly on reagent feed control, so ammonia feed control algorithms were tested on the experimental SCR system. The first algorithm was an open loop, feedforward algorithm that maintained a constant NH₃/NOx molar feed ratio, and used a ceramic NOx sensor to supply NOx concentration. The second algorithm was a feedback, plus feedforward control technique that used ceramic NOx sensors for feedforward and feedback signals.

5.1 Feedforward and Feedback Control

The control algorithms used in these tests are described, starting with the feedforward algorithm. The feedforward algorithm used a simple, constant molar ratio calculation. This calculation is done in Equation 5.1,

$$\frac{Ammonia_Flow_Rate}{Exhaust_Flow_Rate} = (NOx_Concentration) (Molar_Ratio)$$
(5.1)

Ammonia_Flow_Rate is the rate at which ammonia is injected into the exhaust stream, Exhaust_Flow_Rate is the exhaust flow rate through the catalyst, NOx_Concentration is the relative concentration of NOx in the pre catalyst exhaust, and Molar_Ratio is the NH₃/ NOx molar ratio. Units of Ammonia_Flow_Rate and Exhaust_Flow_Rate is mol/sec. Units of ppm must be normalized, by dividing by one million. Molar_Ratio must also be normal. Figure 47 shows the feedback control algorithm loop. The feedback algorithm used feedforward calculations to create ammonia flow rate. The feedback algorithm provided NH_3 /NOx molar ratio to the feedforward algorithm.



Figure 47 Flow diagram of the feedback algorithm.

5.2 Feedforward Testing

In these tests, a constant molar ratio feedforward algorithm was tested. A pre catalyst, pre ammonia injection, ceramic NOx sensor was used to generate the NOx concentration signal. Exhaust flow was measured with an orifice, static pressure gauge, and differential pressure gauge, as described in the Chapter 2. Molar ratio was user input, and was stoichiometric, or about .85 NH₃/NOx molar ratio.

5.2.1 Feedforward Test Map

Figure 48 shows the feedforward test map. There were three transitions: first, occurring at one hour is a step transition in which space velocity, pre catalyst NOx, and catalyst temperature were increased from 7,000 1/hr, 50 ppm, and 500°F [533 K] to 10,000 1/hr, 150 ppm, and 525°F [547 K], respectively; second, at one and a half hours, a step transition of space velocity, pre-

catalyst NOx, and catalyst temperature from 10,000 1/hr, 150 ppm, and 525°F [547 K], to 13,000 1/hr, 200 ppm, and 550°F [561 K], respectively; and the third transition was a slow transition, starting at hour two, in which space velocity, pre-catalyst NOx, and catalyst temperature were reduced from 13,000 1/hr, 200 ppm, and 550°F [561 K], to 7,000 1/hr, 50 ppm, and 500°F [533 K], linearly over the duration of two hours. This test map was designed to represent loading and unloading of an industrial, natural gas engine.

The test map in Figure 48 is the objective. Figure 49 shows actual space velocity, temperature, and pre-catalyst NOx variables throughout the point. Space velocity followed the two step inputs and the ramp down closely throughout the point. This was because space velocity was controlled by the slipstream, independent of engine exhaust flow. Catalyst temperature did not reach the Figure 48 objective due to slow heat exchanger response and varying engine exhaust temperature from NOx control adjustments. Temperature oscillated on the ramp down, and did not stabilize at 500°F [533 K] at the end of the data point. NOx varied significantly from the Figure 48 objective. NOx was adjusted manually by changing engine boost, which changed trapped air-fuel ratio. Slow engine response made it difficult to replicate the Figure 48 curve. However, the actual transitions in Figure 49 are good representations of in-field catalyst operation.



Figure 48 Feedforward control evaluation test map.



Figure 49 Experimental feedforward parameters.

Figure 50 shows the result of the feedforward control test. Figure 49 shows the inputs, and Figure 50 shows the outputs. Inputs of the ammonia flow control system are space velocity, temperature, and NOx concentration. Outputs of the ammonia flow control system are NOx reduction and ammonia slip. First, ammonia feed was turned on, NOx reduction approached 60%, and ammonia slip approached 2-3 ppm. This is because ammonia feed rate was too low. Low ammonia feed rate is an error that can be explained by ceramic NOx sensor pressure compensation. Ceramic NOx sensors are sensitive to pressure changes, but the sensors used in this application were not pressure compensated. The sensors were calibrated at 10,000 1/hr space velocity, and initial startup was 7,000 1/hr space velocity. Since the exhaust flow control valve was upstream of the feedforward NOx sensor, reduced space velocity caused reduced exhaust flow. Reduced exhaust flow resulted in reduced pressure drop across the catalyst, resulting in reduced feedforward ceramic NOx sensor reading. This caused a lean condition, in which not enough ammonia was injected. NOx reduction was less than optimal, and ammonia slip was low.

At hour one, space velocity, temperature, and NOx were stepped up. NOx reduction increased to 80% after an upward, then downward NOx reduction peak. The upward peak is explained in the SCR numeric model section, and is due to increased the rate of NOx destruction, R_{NO} . The downward peak was caused by slow ammonia injector response, in which the ammonia to NOx ratio decreased, because of slow ammonia injection response. 80% NOx reduction and low ammonia slip is representative of a slightly lean condition.

When the second transition was made at hour two, space velocity, temperature, and NOx inlet concentration increased. After this transition, NOx reduction increased to around 97%, followed by an ammonia slip spike about thirty minutes later. This ammonia slip spike is due to ceramic NOx sensor pressure compensation. When space velocity was increased to 13,000 1/hr, exhaust flow and pressure were higher than that at which the sensor was calibrated, causing a

high NOx reading, and ammonia overfeed. Thirty minutes later, an ammonia surge occurred. This is because ammonia had been overfed for a half hour, during which the catalyst became oversaturated with ammonia, excess adsorbed ammonia eventually released, and ammonia slip remained high for about one hour, before slowly decreasing.

Space velocity, temperature, and NOx decreased slowly and linearly during the third transition. At the start of the downward ramp, ammonia was just starting to spike from the ammonia overfeed, so NOx reduction was high throughout the ramp. Ammonia slip slowly decreased from the overfeed incidence, and at about three hours, fifty minutes, the catalyst approached a lean condition. NOx reduction and ammonia slip decreased, approaching NOx reduction and ammonia slip of 80% and 2-3 ppm, respectively.



Figure 50 Result of feedforward test map.

5.2.2 Feedforward Control Discussion

Purely open loop, feedforward control is poor if ceramic NOx sensors are used without pressure compensation. When using purely open loop control, catalyst performance is only as good as the accuracy of the feedforward sensors. In this case, without pressure compensation, the NOx sensor is accurate within about 40%, and the ceramic NOx sensor is the limiting factor in emissions reduction.

Adsorbed ammonia can build up, and when released, can cause high ammonia slip for an hour or more. Ammonia adsorption is extensive at these temperatures, as shown in the Simulink model, and the catalyst adsorbs ammonia in the form of a wave propagating from the front of the catalyst material, ending at the back of the catalyst material. Because of this, ammonia slip does not increase until the entire catalyst is saturated. Once excessive ammonia begins to slip, ammonia continues to slip until the catalyst is no longer saturated. Ammonia desorption propagates through the catalyst front to back, and the ammonia desorption wave must propagate through the entire catalyst before ammonia slip stabilizes.

When adequate ammonia is in the catalyst, the catalyst doesn't transmit high frequency inputs. As stated by Schär, Onder , and Geering [10], the SCR catalyst can act like a low frequency pass filter when proper ammonia is adsorbed in the catalyst. Inadequate ammonia flow is indicated by high frequency NOx concentration variation (peaks and valleys), and low ammonia slip, which can be seen in the first hour of catalyst operation, in Figure 50. NOx reduction increases and decreases rapidly during the first two hours of testing, and when the catalyst had adsorbed sufficient ammonia, NOx reduction stabilized and high frequency peaks and valleys disappeared. This transient test confirms the work by Schär, Onder , and Geering [10].

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5.3 Feedback Control

5.3.1 Feedback Control Test Map

Feedback algorithms, or closed loop control techniques, are effective at compensating for long term calibration errors. In the case of this SCR system, long term error can be caused by inaccurate initial NOx sensor calibration or sensor drift (a sensor's tendency to drift away from correct calibration through time). The ceramic NOx sensor signal feedback algorithm was designed to correct these calibration errors. Fast transient effects caused by engine load transitions, space velocity transitions, NOx concentration variation, and temperature changes, are handled by the feedforward system. Most of these errors progress slowly over hours or days, so the stabilization timeframe of the feedback system should be able to compensate for these errors, over a few hours. Feedback testing was done at steady state, and stabilization time was the focus. The closed loop control algorithm is described in the introduction.

The first test was performed with a fifteen minute decision time and 5% step increment, and the second test was done with a five minute decision time and 2.5% step increment. A step increment is a step in ammonia to NOx molar ratio. The size of the step increment is relative to stoichiometric molar ratio. Decision time is the time between steps. The fifteen minute test was started at 0.5 NH₃/ NOx molar ratio, and the five minute test was started at 0.8 NH₃/NOx molar ratio. The test was done to see if the algorithm approached an appropriate molar ratio, and how long the algorithm took to stabilize.

5.3.2 Feedback Results and Discussion

Figure 51 shows the result of the first feedback control test. Ammonia was turned on at time zero. Molar ratio was the controlled parameter in the feedback system. NOx reduction increased to about 50%, which is expected since NH_3 / NOx molar ratio was around 0.5. At about

fifteen minutes, when NOx reduction dropped off momentarily, the ammonia feed pump malfunctioned. After this, the algorithm increased the molar ratio appropriately. At about one hour, forty five minutes, when NOx reduction dropped off again, there was another pump malfunction. At this point, the algorithm made one incorrect step, but corrected, and the system took about four hours to stabilize.

Figure 52 shows the inputs and outputs during the test. In the figure, the input and output is shown. The input is ammonia to NOx molar ratio, and the output is the post catalyst ceramic NOx sensor signal. In the figure, molar ratio begins low, and the signal is resultantly high. As the feedback loop increases the molar ratio, the catalyst approaches stoichiometric operation, ammonia and NOx slip decrease, and the ceramic NOx sensor signal decreases. At one hour, thirty minutes, the feedback algorithm makde an incorrect decision and decreased NH₃/ NOx feed ratio. At this point, NOx increased, increasing the ceramic NOx sensor signal. The algorithm reversed its direction, and continued to an appropriate molar ratio.



Figure 51 Fifteen minute decision time feedback control results.



Figure 52 Input and output of feedback control during fifteen minute decision time test. Input is post catalyst ceramic NOx sensor signal, and output is molar ratio.

Overall, this minimization algorithm proved very effective and robust with a 15 minute decision time and a 5% increment. The system approached an appropriate molar ratio, despite equipment malfunctions. The equipment malfunctions, although unplanned, displayed control algorithm robustness.

Figure 53 shows the result of the second feedback control test. In Figure 53, ammonia was turned on and NOx reduction increased to about 90%. The algorithm, at this point, made incorrect decisions, decreasing molar ratio to .7, until NOx reduction decreased to 85%, and the controller began making correct decisions. Over the course of the next hour and a half, the system increased molar ratio to somewhere between .8 and .85, stabilizing.

Figure 54 shows the inputs and outputs of the feedback algorithm during the test. In the beginning, the post catalyst ceramic NOx sensor surged. This is because NOx reduction was low at the beginning of this data point. As ammonia feed was turned on, NOx reduction dropped quickly. As the algorithm initially made incorrect decisions, the post catalyst ceramic NOx signal increased. Around one half hour, the algorithm began making correct decisions. The post catalyst ceramic NOx sensor signal began decreasing. At about 1.25 hours, the system stabilized. The post catalyst ceramic NOx signal leveled, and the molar ratio control signal displayed random step directions.



Figure 53 Five minute decision time feedback control.



Figure 54 Ammonia to NOx molar ratio feed and post catalyst ceramic NOx sensor signal during five minute decision time test.

Overall, with a five minute decision time and 2.5% step size, the system made incorrect decisions, but stabilized much faster than the fifteen minute decision time algorithm. When the system was turned on, NOx reduction increased, decreasing the feedback signal from the ceramic NOx sensor. The algorithm reduced molar ratio for several steps, which was incorrect. Although the five minute decision time is significantly faster than the fifteen minute decision time feedback system, the fifteen minute system is fast enough to correct for sensor drift, and more robust than the five minute system. The fifteen minute decision time system made very few incorrect decisions during stabilization, whereas the five minute decision time system made many incorrect decisions. The feedback system should ensure that long term sensor drift does not significantly affect engine emissions. Since sensor drift occurs in the timeframe of hours and days, both the five minute and fifteen minute systems should be sufficiently fast to account for this.

NOx reduction was around 98% on both systems at the stabilization point, while maintaining ammonia slip under 5 ppm. This shows that the control technique is very effective at ensuring the catalyst is operating properly.

These tests described the algorithm's response given constant space velocity, temperature, and NOx concentration. The tests did not test the feedback algorithm's sensitivity to varying inputs. If NOx, were to increase rapidly, causing rapid ammonia slip or NOx reduction transition, the feedback algorithm might respond to the varying input, as if the transition was initiated by a feedback step. Because of the uncertainty of other variables, this feedback signal minimization algorithm may need to be slowed down further for actual applications.

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5.4 Feedback Control Using Minimization Technique and Mid-Catalyst NOx Sensor

5.4.1 Justification For Mid-Catalyst Feedback Sensor Location

Numeric modeling in Simulink showed two things. First, SCR catalyst transients propagate from front to back in waves. Second, neither NOx nor ammonia reduction are linear as a function of catalyst length. Both NOx and ammonia reduce quickly in the front most catalyst sections, and slowly in the back sections. As seen in the t=0 series of Figure 31, 60% of NOx and ammonia are reduced in the first one third of catalyst length. Chapter Three shows how ammonia and NOx propagate lengthwise through the catalyst. These two factors are why the feedback ceramic NOx sensor was moved forward, one third the way through the catalyst length. Most NOx and ammonia reduction occurs in the first third of the catalyst material, which means steady state NOx and ammonia concentrations midway through the catalyst are similar to that at the exhaust of the catalyst. Since waves propagate front to back through the catalyst because the ceramic NOx sensor will see any ammonia or NOx waves propagating through the catalyst before they are exhausted, and corrections can be made sooner. Also, as ammonia and NOx waves propagate through the catalyst, they reduce in amplitude, so if the NOx sensor is moved forward, any excess ammonia or NOx will be more extreme, and can be detected more easily.

Figure 55 shows the feedback ceramic NOx sensor location, as tested in this section. This is a cross section looking down onto the catalyst modules. The exhaust flow is split into two streams, as seen in the upper and lower portions of the figure. The ceramic NOx sensor measured only one of the streams. Assuming sufficient exhaust homogeneity, the two streams should have similar NOx and ammonia concentration. Labeled are the catalyst modules, exhaust flow inlet and outlet, and the ceramic NOx sensor.



Figure 55 Shows the mid catalyst feedback ceramic NOx sensor location relative to catalyst modules. This location was used in mid catalyst feedback ceramic NOx sensor control testing.

5.4.2 Mid Catalyst NOx Sensor Control Technique Test Map

The feedback algorithm in this section is the same as in Chapter 5.3. The mid catalyst sensor setup was compared to the post catalyst sensor setup by doing similar tests. The engine and SCR slipstream system were set at a constant operating condition, 10,000 1/hr space velocity, 500°F [533 K] catalyst temperature, and about 150 ppm inlet NOx. The molar ratio was set to approximately 0.3, and the algorithm was allowed to stabilize.

5.4.3 Mid Catalyst NOx Sensor Feedback Control Results and Discussion

By moving the sensor forward, faster feedback response was expected, so the first decision time evaluated was 2.5 minutes, and a step size of 2.5% molar ratio. The results of the 2.5 min decision time test are shown in Figure 56. The test started with an initial NH₃/NOx molar ratio of 0.325. Random fluctuations were seen during the first ten minutes, and then molar ratio increased until it oscillated between .4 and .425. The random fluctuations meant the data point had stabilized, and the data point was ended.

Figure 57 shows the input and output of the feedback control. The input was ammonia to NOx molar ratio, and the output was the mid catalyst ceramic NOx sensor signal. This figure shows the feedback signal responded very little to changes in input, which made the technique ineffective. This lack of output response is due to the flat minimum of the feedback ceramic NOx sensor at this location, and the fact that the datapoint was started at a molar ratio near the sensor signal minimum. This is explained later in this section by the numeric model.



Figure 56 Mid catalyst feedback NOx sensor location control, shows that NOx reduction is poor due to lean catalyst operation.



Figure 57 Input and outputs of 2.5 min decision time, with 2.5% molar ratio increments. This figure shows that the technique was ineffective, because the feedback signal didn't respond to ammonia to NOx molar ratio input changes.

Since the 2.5 minute decision time and 2.5% step size showed randomness, the time step was increased to 5 minute, and the step size was increased to 5%. Figure 58 shows the result. In this test, the controlled molar ratio started at 0.3 and began increasing. At about 50 minutes, molar ratio stabilized around 0.6. Both these points showed less than 1 ppm ammonia slip throughout. This makes sense because the catalyst was operating lean, at less than stoichiometric ammonia to NOx ratio, which is indicated by low NOx reduction and low ammonia slip.

Figure 59 shows the input and output of the control technique with 5 min decision time and 5% step size. Similar to the 2.5 min decision time example, the input and output show little correlation. This caused the control system to operate poorly. The minimum of the feedback sensor signal is broad. The data point was started near the sensor signal minimum. These two factors caused a low correlation between the ceramic NOx sensor signal and the NH₃/ NOx molar ratio. This is explained later in this section by the numeric model.



Figure 58 Second mid-catalyst feedback NOx sensor control test, shows similar results as 2.5 min decision time test.



Figure 59 Input and output of 5 minute decision time, mid catalyst feedback ceramic NOx sensor results. Shows lack of correlation between control input and output.

The results of this these tests are disappointing. First, the feedback system stayed at a very lean operating point. Second, the system did not make decisions faster than the post catalyst NOx sensor setup.

Figure 60 is used to show why the mid catalyst feedback ceramic NOx sensor control technique resulted in a lean NH_3 / NOx molar ratio. Figure 60 shows a graph of the sum of ammonia and NOx as a function of molar ratio. In Figure 60, NOx concentration is fixed at 150 ppm. The upper series in Figure 60 represents the ceramic NOx sensor signal, pre catalyst, post ammonia injection. The series increases linearly, and starts at 150 ppm at zero molar ratio. The upper series starts at 150 ppm because there is 150 ppm of NOx and 0 ppm of ammonia at zero NH₃/NOx molar ratio. As molar ratio increases, the NOx portion of the signal remains constant, while the ammonia portion of the signal increases linearly. The lower series in Figure 60 is the sum of ammonia and NOx, or the post catalyst ceramic NOx sensor signal, if the catalyst were infinitely long. This series represents a complete reaction between ammonia and NOx. Starting at zero NH_3/NOx molar ratio, the series is at 150 ppm. The series is 150 ppm because there is no ammonia to destroy the NOx. As NH₃/NOx molar ratio increases, there is increasingly more ammonia to destroy the NOx. Since the reaction is assumed complete, the reaction destroys all the ammonia, leaving only the excess NOx. At NH₃/NOx molar ratios less than stoichiometric, the reaction is ammonia limited, and the NOx sensor signal represents NOx only. At NH₃/NOx molar ratios greater than one, the reaction destroys all the NOx, leaving only excess ammonia. In this region, the sensor signal represents ammonia only.



Figure 60 Ceramic NOx sensor signal vs. molar ratio at zero catalyst length and infinite catalyst length.

Figure 61 is a graph of simulated sensor signal versus molar ratio, at various catalyst lengths. X axis units are normalized molar ratio. The very lowest line is labeled Inf, for infinity, and represents perfect reduction of ammonia and NOx. The data was generated by the numeric model, at a catalyst temperature of 500° F [533 K] and 10,000 1/hr space velocity. All series, particularly those of long catalyst lengths, follow the Inf series very closely. As molar ratio increases, all series depart from the Inf series. This occurs because the reduction is partially limited by residence time, and is not perfect. The shorter catalyst length series depart first, with longer, more obtuse curves. The longer catalyst lengths depart with shorter, sharper curves. As catalyst length goes up, series stay closer to the Inf series longer, have a sharper bottom, and stay closer to the Inf series as NH₃/NOx ratio increases. Short catalyst distance series have a broad, sweeping minimum. Long catalyst distance series have a sharp minimum. Also of particular importance is the molar ratio at which the sensor signal is minimized. At catalyst length 3.18 cm, the signal is minimum at 0.35 molar ratio; at catalyst length 6.35 cm, the signal is minimized at 0.55 normalized molar ratio; at catalyst length 9.53 cm, the signal is minimized at 0.7 normalized molar ratio; at catalyst length 12.7 cm, the signal is minimized at about 0.75 normalized molar ratio; and so on. As catalyst length approaches infinity, the signal minimum occurs at stoichiometric NH₃/NOx molar ratio. This is why the system approached a lean NH₃/NOx molar ratio. The sensor signal minimum occurs at lean conditions always, gets leaner as catalyst length decreases, and approaches stoichiometric as catalyst length approaches infinity. In this test, catalyst length was five inches (12.7 cm), so this numeric model predicts the system would approach a normalized molar ratio of about 0.75, which is close to the stable normalized molar ratio in the experimental test. The mid catalyst sensor setup does not operate faster than the post catalyst feedback sensor setup because the derivative of the short catalyst length series change slowly. This causes difficult decision making near the sensor minimum. Because the differential changes very slowly near the minimum of the curve, molar ratio changes make very little difference in the feedback signal. The signal is comparatively flat over much of the catalyst operating range. For example, the 12.7 cm curve has a slope near zero for a wide molar ratio interval when compared to the 38.1 cm curve, and the infinity curve has no interval where the curve has near zero slope. This means that, at 12.7 cm, more molar ratio error is required to correctly decide the signal's slope, than at 38.1 cm.

The numeric model may have over predicted mid location catalyst performance because in the model, perfect mixing was assumed at the catalyst inlet. We know this is not the case in the experimental catalyst because perfect mixing would require infinite mixing time. Behind the first catalyst module, any non homogeneity at the catalyst inlet is constant throughout the module, because inter-channel mixing cannot occur within a module. Separation between modules allows reagent and exhaust to further mix in the distance between the modules, allowing better overall mixing and better performance; so reagent mixing is more critical for ammonia slip and NOx reduction at a mid catalyst location, than a post catalyst location.

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Although this test failed with the feedback sensor located at a 12.7 cm catalyst length, or one third of the way through the catalyst material, it would be worthwhile to test the system with the feedback ceramic NOx sensor located at 25.4 cm, or two thirds of the way through the catalyst material. This would negate much of the adverse effect from moving the feedback sensor forward, while allowing the advantages of faster response time and the ability to sense ammonia and NOx emissions before they occur. In Figure 61, the 25.4 cm series is very close to the 38.1 cm series, and very far from the 12.7 cm series, and might be a compromise that has advantages of both systems.



Figure 61 Ceramic NOx sensor signal at various catalyst lengths and molar ratios; series are of constant catalyst length.

6 Conclusion

An experimental device was used to perform SCR testing. This setup included the ability to control catalyst temperature, exhaust flow rate, NH_3 / NOx molar ratio, and pre-catalyst NOx concentration. The setup included a sample system with the ability to measure exhaust NOx and ammonia, and ceramic NOx sensors that were used to measure NOx and implement controls.

A numeric model was used to describe transient SCR phenomena, and initiate an understanding of SCR transient responses and their underlying causes by exploring the lengthwise catalyst activity, ammonia adsorption and desorption, and NOx destruction. The numeric model was used to study ammonia absorption and surface reaction kinetics of the SCR catalyst. This numeric model was then used to show transient response to three step inputs: temperature, space velocity, and molar ratio. These step input transients resulted in ammonia and NOx waves that generally propagated from the front of the catalyst, to the back of the catalyst. Step increases in NH₃/ NOx molar ratio results in an ammonia wave that adsorbs onto the catalyst, propagating front to back. Step increases in space velocity result in an initial surge in NOx emissions. This NOx emission surge is caused by a combination of the low levels of adsorbed ammonia in the catalyst and high space velocity. This NOx surge eventually reduces to a NOx emission slightly greater than that of pre space velocity step. Step increases in temperature causes an initial desorption of ammonia from the catalyst wall, particularly toward the front of the catalyst. This desorbed ammonia flows through the catalyst, and is adsorbed onto back portions of the catalyst. This results in a surge in ammonia at the exhaust of the catalyst. Step increases in temperature cause an initial drop in NOx emissions, caused by raised ammonia

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in the catalyst and increased rate of NOx destruction (R_{NO}). This initial NOx emission decrease is temporary. NOx emissions eventually increase back to approximately pre step emissions levels.

Transient testing was done to quantify the transient response of SCR catalysts on two stroke, natural gas, stationary, legacy, slow speed engines. These tests were done because the catalyst responded slowly during prior, steady state testing. Transient tests quantified the delay times between ammonia flow input and NOx reduction output. Transient tests asserted that hydrogen cyanide is formed inside the catalyst, and hydrogen cyanide precedes ammonia slip surges by seven minutes.

Control systems were developed for SCR systems to control ammonia injection flow rate. Three algorithms were experimentally tested: first was a feedforward control algorithm that used a ceramic NOx sensor to detect pre catalyst NOx; second was a feedforward plus feedback algorithm which used a pre and post catalyst ceramic NOx sensor to generate feedforward and feedback signals, respectively; and third, a feedforward plus feedback algorithm that used a pre and mid catalyst ceramic NOx sensor to generate feedforward and feedback signals, respectively. The feedforward control algorithm had difficulty following space velocity transients, because the ceramic NOx sensor was not pressure compensated, which lead to overfeeding of ammonia at high space velocities and underfeeding of ammonia at low space velocities. The feedforward plus feedback algorithm used an algorithm that minimized the post catalyst ceramic NOx sensor signal. This feedback technique controlled the molar ratio, which is a parameter of the feedforward algorithm. Two decision times were tested: a fifteen minute decision time and a five minute decision time. The fifteen minute decision time algorithm was able to approach appropriate ammonia feed, a 40% correction, in about four hours, at steady state feedforward conditions. The fifteen minute decision time algorithm was robust and operated fast enough to account for sensor drift in stationary engine applications. The five minute decision time algorithm stabilized much faster, in about one and a half hours, but was less robust. The

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feedforward plus feedback algorithm that used pre and mid catalyst ceramic NOx sensors, worked poorly. The algorithm approached a very lean condition, and was no faster than the post catalyst feedback ceramic NOx sensor location. The Simulink numerical model was used to determine the reason for these problems. It was concluded that the ceramic NOx sensor minimum occurs at lean conditions at mid catalyst positions. Incorrect decisions were caused by a broad minimum of the ceramic NOx sensor signal, which made the algorithm less responsive to ammonia flow rate changes. These tests demonstrated that a post catalyst ceramic NOx sensor minimization technique can successfully control ammonia feed rate.

This thesis discusses SCR catalyst operation, testing, modeling, and controls development. Knowledge of SCR catalyst operation has the potential to improve catalyst performance by improving ammonia feed controls. In addition, NOx emissions from engines can be reduced and ammonia slip minimized. This reduction in NOx emissions allows internal combustion engines to meet the ever-tightening emissions standards of the EPA, and reduces their impact on the environment. This allows engines to be used further into the future. The use of internal combustion engines will continue to enrich human lives, as they have in the past century.

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Appendix A Simulink Numeric Model

The Simulink model consists of several pieces that were assembled to create the system model. To start, Figure 62 is a screen print of the total catalyst model. In Figure 62, the inputs feed into the first node, whose outputs are the inputs of the second node, whose outputs are the inputs of the final node. Figure 62 contains three subsystems shown in Figure 63. The primary outputs of the whole system are NH3, NOx, and θ for the twelve nodes in the system.



Figure 62 Simulink model.


Figure 63 Simulink model, one of three nodes from Figure 62.

Figure 64 shows the contents of Figure 63, which is four sub nodes, each of which represents one node. In Figure 64, the inputs and outputs are the same as those in Figure 63. The two tiered subsystem setup was used so no one system would get too large, and be difficult to fit on one screen. Figure 65 shows one of the nodes in Figure 64; all the nodes are the same.



Figure 64 Four nodes inside three overlying nodes, contents of Figure 63.



Figure 65 Individual nodes. Four contained in Figure 64.

Figure 66 shows the vitals of Figure 65. Figure 66 shows several subsystems that represent key equations solved. The figures that follow show the subsystems of Figure 66; they are: Figure 67, basic unit conversions from ppm and % to relative concentration; Figure 68, space velocity, molar flow rate, and volumetric flow rate are solved; Figure 69, binary diffusion coefficients are solved as a function of temperature; Figure 70, chemical kinetic Arrhenius rates are calculated; Figure 71, the volumetric capacitance integral is performed to determine bulk concentration in the node; Figure 72, the site density is calculated; Figure 73 is used to adjust binary diffusion coefficients for temperature and pressure; Figure 74, θ calculation and NH₃ adsorption rate calculation; Figure 75, calculation of NO destruction rate; and Figure 76 calculations of species diffusion across the width of the channel.



Figure 66 Internals of individual nodes, contents of Figure 65.



Figure 67 Unit conversion subsystem of Figure 66.



Figure 68 Basic density, volume, and concentration subsystem of Figure 66.



Figure 69 Binary diffusion coefficients subsystem of Figure 66.



Figure 70 Arrhenius Rates Subsystem of Figure 66



Figure 71 Volume capacitance subsystem of Figure 66.



Figure 72 Site density subsystem of Figure 66.



Figure 73 Binary diffusion coefficient subsystem of Figure 69



Figure 74 Ammonia adsorption subsystem of Figure 66.







Figure 76 Diffusion across channel width subsystem of Figure 66.

Appendix B LabVIEW Code

The LabVIEW virtual instrument used in these tests is briefly described in this appendix section. Only the key parts of the virtual instrument will be discussed: the main front panel and the feedback control step function. Figure 77, Figure 78, and Figure 79 are the main front panel tabs.



Figure 77 SCR front panel controls tab.

In the main SCR front panel "Logger" tab, Figure 78, is the data logger control. The data logger control allows variable data point length, mid-point stop ability, and sample rate selection.



Figure 78 SCR front panel logger tab.

Figure 78 is the "Gasses" tab in SCR main program front panel. The VI allowed recording NOx, CO_2 , CO, O_2 , and THC emissions.



Figure 79 SCR front panel gasses tab

Figure 80 and Figure 81 show the step function for the minimization feedback control technique. This subVI is designed to be put into a for-loop, with Sensor 1 NOx, Sensor 2 NOx, and Filtered as its outputs. In this subVI, molar ratio is the processed feedback control NH₃/ NOx molar ratio that should be multiplied by feedforward NOx flow rate to obtain the ammonia flow signal. Raw signal is the average signal the subVI compares to the previous average signal that determines which way the subVI will take its next step. Filtered is the feedforward output, after it has gone through the low pass filter. The 3000 constant that feeds into the remainder-quotient node is the number of iterations between each decision.



Figure 80 Feedback step function true condition.



Figure 81 Feedback step function false condition.