**Energy Efficient Thermal Management for Natural
Gas Engine Aftertreatment via Active Flow Control**

Final Report

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Abstract

The project is focused on the development of an energy efficient aftertreatment system capable of reducing NO_x and methane by 90% from lean-burn natural gas engines by applying active exhaust flow control. Compared to conventional passive flow-through reactors, the proposed scheme cuts supplemental energy by 50%-70%. The system consists of a Lean NO_x Trap (LNT) system and an oxidation catalyst. Through alternating flow control, a major amount of engine exhaust flows through a large portion of the LNT system in the absorption mode, while a small amount of exhaust goes through a small portion of the LNT system in the regeneration or desulfurization mode. By periodically reversing the exhaust gas flow through the oxidation catalyst, a higher temperature profile is maintained in the catalyst bed resulting in greater efficiency of the oxidation catalyst at lower exhaust temperatures. The project involves conceptual design, theoretical analysis, computer simulation, prototype fabrication, and empirical studies.

This report details the progress during the first twelve months of the project. The primary activities have been to develop the bench flow reactor system, develop the computer simulation and modeling of the reverse-flow oxidation catalyst, install the engine into the test cell, and begin design of the LNT system.

Table of Contents

Disclaimer	ii
Abstract	iii
Table of Contents	iv
Table of Figures.....	v
Table of Tables.....	ix
Table of Tables.....	ix
Introduction	10
Overview	11
Bench Flow Reactor Design and Modeling Review.....	11
Bench-Flow Reactor System	11
Reverse-Flow Oxidation Catalyst Reactor	11
Lean NO _x Trap Catalyst Reactor	11
Data Acquisition System	11
Mathematical Modeling of Reverse Flow Oxidation Catalyst.....	12
Bench Flow Reactor Design and Modeling Modifications.....	12
Bench-Flow Reactor System Modifications.....	12
Reverse-Flow Oxidation Reactor Modifications	15
Lean NO _x Trap Catalyst Reactor Modifications	18
Data Acquisition Modifications.....	19
Reverse Flow Reactor Model Modifications	19
Bench Flow Reactor Design and Modeling 2004 Progress	23
Reverse-Flow Oxidation Catalyst Reactor Progress.....	23
Bench Flow Reactor Design and Modeling Conclusion.....	32
Bench-Flow Reactor System	32
Reverse-Flow Oxidation Catalyst Reactor	33
Lean NO _x Trap Catalyst Reactor	61
Conceptual Design of a Partial Flow LNT Regeneration and Gas Divider System Review	89
System Concept.....	89
Four-Way Single Diversion Valve Conceptual Schematic and Operation	91
Conceptual Design of a Partial Flow LNT Regeneration and Gas Divider System Progress.....	96
Estimation of the Main Dimensions of the Periodical Reverse Flow Catalyst Mechanism.....	96
Four-Way Single Diversion Valve Design	102
Lean Burn Natural Gas Engine Testing and NO _x Reduction Strategy Review	111
Test Bed Development	111
Initial Engine Baseline.....	112
Development of LNT Regeneration Strategy	112
Lean Burn Natural Gas Engine Testing and NO _x Reduction Strategy Progress.....	113
Exhaust Aftertreatment System	113
Complete Baseline Testing.....	116
LNT Capacity Estimation.....	124
Development of Regeneration Parameters	126
Lean NO _x Trap Evaluation.....	132
Nomenclature	148
Bibliography	149

Table of Figures

Figure 1 Instrument Cabinet Modifications.....	13
Figure 2 Peristaltic Pump	13
Figure 3 Three-Way Branching Valves.....	14
Figure 4 Catalyst Thermocouple Orientations.....	15
Figure 5 No Water Addition, Unidirectional Flow, Methane 3000ppm Space Velocity - 40,000hr-1	16
Figure 6 Reverse Flow Oxidation Catalyst Reactor	17
Figure 7 Reactor End Fitting	18
Figure 8 The Components of Fuel Injection System	19
Figure 9 Temperature Profile along the Length of Catalyst as a Function of Time	22
Figure 10 Conversion of Different Species as a Function of Time	23
Figure 11 RFOCR Temperature Profile and Conversion Percentage	25
Figure 12 RFOCR Temperature Profile and Conversion Percentage	25
Figure 13 RFOCR Temperature Profile and Conversion Percentage	26
Figure 14 RFOCR Temperature Profile and Conversion Percentage	27
Figure 15 RFOCR Temperature Profile and Conversion Percentage	27
Figure 16 RFOCR Temperature Profile and Conversion Percentage	28
Figure 17 RFOCR Temperature Profile and Conversion Percentage	28
Figure 18 RFOCR Temperature Profile and Conversion Percentage	29
Figure 19 RFOCR Temperature Profile and Conversion Percentage	30
Figure 20 RFOCR Temperature Profile and Conversion Percentage	30
Figure 21 RFOCR Temperature Profile and Conversion Percentage	31
Figure 22 Schematic of Bench Flow Reactor System	32
Figure 23 Bench-Flow Reactor System.....	33
Figure 24 Reverse Flow Oxidation Catalyst Reactor	34
Figure 25 Reverse Flow Oxidation Catalyst Reactor (Top View).....	35
Figure 27 Power Supplies with Solid State Relays.....	36
Figure 28. Pneumatic Valve Operation	37
Figure 29. Physical Parameters and Characteristics of Catalyst.....	37
Figure 30 Methane Conversion at a Reactor Furnace Temperature of 450°C, GHSV of 40,000 hr-1, and a ST of 10s	39
Figure 31 Temperature Profiles Across the Catalyst Length at Various Times at a Reactor Furnace Temperature of 450°C, GHSV of 40,000 hr-1, and a ST of 10s.....	39
Figure 32 Temperature Profiles Across the Catalyst Length at a Reactor Furnace Temperature of 450°C and a GHSV of 40,000 hr-1 with Unidirectional Flow	40
Figure 33 Baseline Unidirectional Temperature Profiles for 10 and 45s ST Experimental Runs at a Reactor Furnace Temperature of 400oC, a GHSV of 20,000 hr-1.....	45
Figure 34 Illustration of Dead Volume Associated with a RFR.....	46
Figure 35 Carbon Monoxide Concentration at a Reactor Furnace Temperature of 450oC, a GHSV of 40,000 hr-1, and a ST of 10s	47
Figure 36 Effects of Switching Time on CH4 Conversion with GHSV as a Parameter at a Temperature of 400oC	49
Figure 37 Temperature Profile Across the Catalyst at a Reactor Furnace Temperature of 400oC, a GHSV of 20,000 hr-1, and a ST of 10s at Various Experimental Run Times	49
Figure 38 Temperature Profiles Across the Catalyst at Various Times During an Experimental Run at a Reactor Furnace Temperature of 400oC, GHSV of 20,000 hr-1, and a ST of 30s	50
Figure 39 Effects of Switching Time on CH4 Conversion with GHSV as a Parameter at a Temperature of 450oC	50
Figure 40 Representations of Various Regimes on an Arrhenius Plot. Reprinted from Hayes and Kolaczowski [9].....	51
Figure 41 Temperature Profile at a Reactor Furnace Temperature of 450oC, GHSV of 40,000 hr-1, and a ST of 45s at Various Experimental Run Times	52
Figure 42 Effects of Switching Time on CH4 Conversion with GHSV as a Parameter at Temperature of 550oC	53
Figure 43 Effects of Temperature on CH4 Conversion with Temperature as a Parameter at a GHSV of 80,000 hr-1 and a ST of 10s	54

Figure 44 Effects of Temperature on CH ₄ Conversion with GHSV as a Parameter at a ST of 10s	55
Figure 45 Methane Conversion during Unidirectional Flow Operations with 25 10-Second Pulses of SFI, a Reactor Furnace Temperature of 350oC, and a GHSV of 20,000 hr-1	57
Figure 46 Temperature Profile across the Catalyst during Unidirectional Flow Operations at Various Instances of Time with 25 10-Second Pulses of SFI, a Reactor Furnace Temperature of 350oC and a GHSV of 20,000 hr-1	57
Figure 47 Methane Conversion with 25 10-Second Pulses of SFI, a Reactor Furnace Temperature of 350oC, a GHSV of 20,000 hr-1, and a ST of 20s	58
Figure 48 Temperature Profile across the Catalyst at Various Instances of Time with 25 10-Second Pulses of SFI, a Reactor Furnace Temperature of 350oC and a GHSV of 20,000 hr-1	59
Figure 49 Temperature Profile across the Catalyst at Various Instances of Time with 25 10-Second Pulses of SFI, a Reactor Furnace Temperature of 350oC and a GHSV of 20,000 hr-1	60
Figure 50 Instrument Panel (Front)	61
Figure 51 Steam Generator	63
Figure 52 Front Panel of Horiba Exhaust Gas Analyzer	64
Figure 53 Components of Fuel Injection System	65
Figure 54 Schematic of Bench-Flow Reactor System - Including Three-Way Branching Valve	66
Figure 55 XRD Spectra of Fresh EmeraChem LNT	68
Figure 56 TEM Image of Pt particles in Fresh EmeraChem LNT with Magnification of 100,000 X	69
Figure 57 EPMA maps of (a) back scatter, (b) Pt, (c) Ba, (d) K and (e) Ce for fresh EmeraChem LNT	69
Figure 58 EPMA line scan for K, Ba, Pt, Ce, Al, and Si for fresh EmeraChem LNT	70
Figure 59 NO _x concentration versus time at a temperature of 350 °C and a	71
Figure 60 NO _x concentration versus time at various temperature and	72
Figure 61 NO _x concentration versus time at various temperature and	72
Figure 62 NO _x concentration versus time at various temperature and 500 ppm of inlet NO _x concentration at SV=75,000h-1	73
Figure 63 Temperature and NO _x concentration histories during regeneration phase of absorption isotherm performed at 400 °C and GHSV of 25,000 hr-1	74
Figure 64 Area of NO _x storage obtained from the plot of NO _x outlet concentration versus time	75
Figure 65 NO _x storage capacity as a function of temperature and GHSV	76
Figure 66 Breakthrough time as a function of temperature and gas hourly space-velocity	78
Figure 67 Ratio of NO ₂ to NO outlet concentration during absorption isotherm experiments performed at a GHSV of 75,000 hr-1 and equilibrium ratio	79
Figure 68 Desorption experiment performed at T = 350C and GHSV = 25,000 hr-1	80
Figure 69 Desorption experiment performed at T = 500 °C and GHSV = 25,000 hr-1	80
Figure 70 NO _x Conversion versus time with 500ppm of NO _x inlet concentration (50s lean and 10s rich, CO=4%, H ₂ =1.33%, T=350C, SV=50K)	81
Figure 71 NO _x Conversion versus time with 500ppm of NO _x inlet concentration (50s lean and 5s rich, CO=4%, H ₂ =1.33%, T=350C, SV=50K)	82
Figure 72 NO _x Conversion versus time with 500ppm of NO _x inlet concentration (100s lean and 5s rich, CO=4%, H ₂ =1.33%, T=350C, SV=50K)	82
Figure 73 NO _x Conversion versus time with 500ppm of NO _x inlet concentration (100s lean and 5s rich, CO=2%, H ₂ =0.67%, T=350C, SV=50K)	83
Figure 74 NO _x Conversion versus time with 500ppm of NO _x inlet concentration (100s lean and 5s rich, CO = 4%, T=350C, SV=50K)	84
Figure 75 NO _x Conversion versus time with 500ppm of NO _x inlet concentration (100s lean and 5s rich, H ₂ = 4%, T=350C, SV=50K)	84
Figure 76 NO _x Conversion versus time for various CO injections using DFI in the absence of O ₂ with 500ppm of NO _x inlet concentration (100s lean and 5s rich, T=350C, GHSV=50,000 hr-1)	86
Figure 77 NO _x Conversion versus time for various H ₂ injections using DFI with 500ppm of NO _x inlet concentration (100s lean and 5s rich without oxygen, T=350C, SV=50K)	87
Figure 78 NO _x Conversion versus time for various CO injections using DFI with 500ppm of NO _x inlet concentration (100s lean and 5s rich with oxygen, T=350C, and SV=50K)	87
Figure 79 NO _x Conversion versus time for various H ₂ injections using DFI with 500ppm of NO _x inlet concentration (100s lean and 5s rich with oxygen, T=350C, SV=50K)	88
Figure 80 Schematic of rotating gas divider	89

Figure 81 The heat trap effect for reverse flow catalytic converter (a, b – forward mode; c, d – reverse mode, e - temperature profile at the quasi-steady-state	90
Figure 82 Four-way single valve system: (a) - forward mode; (b) reverse mode.....	91
Figure 83 Exploded View of the Stator and Rotor Assembly	92
Figure 84 Four-Way Single Diversion Valve Conceptual Schematic with Unidirectional Rotation.....	93
Figure 85 Flow Rate/Rotation Diagram for Four-Way Single Diversion Valve with Unidirectional Rotation	94
Figure 86 Four-Way Single Diversion Valve Conceptual Schematic with Multidirectional Rotation.....	95
Figure 87 Flow Rate/Rotation Diagram for Four-Way Single Diversion Valve with Multi-directional Rotation	96
Figure 88 Four-Way Single Diversion Valve – (1)Outer cylinder; (2) Inner cylinder; (3) Partition Plate; (4) Top cap; (5) Top flange.....	102
Figure 89 Outer Cylinder/Stator – (1) Elliptical hole; (2) Flange seating; (3) Labyrinth sealing; (4) Sleeve seating.....	103
Figure 90 Flange – (1) Flange Seating; (2) Assembly Bolt Holes; (3) Gasket Groove	104
Figure 91 Inner Cylinder – (1)Elliptical opening; (2) Perforated in elliptical opening; (3) Labyrinth sealing; (4) Lower Base plate with groove for partition plate; (5) Projection to maintain gap.....	105
Figure 92 Top Plate - (1) Labyrinth sealing; (2) Slot for partition plate; (3) Shaft Hole.....	105
Figure 93 Top Cap - (1) Hole for Rotation Shaft; (2) Labyrinth Sealing	106
Figure 94 Valve Assembly - (1) Outer Cylinder; (2) Inner Cylinder; (3) Top Plate; (4) Top Cap; (5) Assembly Bolt Holes; (6) Copper Gasket; (7) Steel Washer	107
Figure 95 Pipe Connector	108
Figure 96 Schematic Diagram of the Motion Control Mechanism.....	109
Figure 97 (A) Shaft; (B) Coupler; (C) Steel arm	109
Figure 98 Schematic of Assembled Motion Control Arm	110
Figure 99 Dual leg Catalyst System Schematic.....	112
Figure 100 NOx Rating	113
Figure 101 Exhaust Aftertreatment System Photograph	114
Figure 102 Natural Gas Injectors.....	115
Figure 103 Flow Control Valves	115
Figure 104 Engine CO Map	119
Figure 105 Engine NOx Map	119
Figure 106 Engine NO Map	120
Figure 107 Engine THC Map	120
Figure 108 Engine Methane map.....	121
Figure 109 Engine CO2 Map	121
Figure 110 Engine O2 Map	122
Figure 111 Experimental Schematic for Slip Flow Estimations.....	127
Figure 112 Control Volume for Slip Flow Analysis.....	127
Figure 113 Exhaust Flow Rates During Adsorption and Regeneration.....	129
Figure 114 Sample Positions for Methane Oxidation Study	131
Figure 115 Methane Oxidation vs. Catalyst Temperatures	132
Figure 116 Typical NOx Profiles	133
Figure 117 Fuel Flow and Exhaust Stoichiometry	133
Figure 118 Catalyst Temperatures.....	134
Figure 119 50% Load NOx Trapping Efficiencies.....	136
Figure 120 50% Load NOx Ratings and Fuel Penalties	136
Figure 121 50% Load NOx Profiles for Optimal Regen	137
Figure 122 25% Load NOx Trapping Efficiencies.....	138
Figure 123 25% Load NOx Ratings and Fuel Penalties	138
Figure 124 25% Load NOx Profiles for Optimal Regen	139
Figure 125 10% Load NOx Trapping Efficiencies.....	140
Figure 126 10% Load NOx Ratings and Fuel Penalties	140
Figure 127 10% Load NOx Profiles for Optimal Regen	141
Figure 128 10% Load NOx Trapping Efficiencies with Full Slip Flow	142
Figure 129 10% Load NOx Ratings with Full Slip Flow	142

Figure 130 10% Load Fuel Penalties with Full Slip Flow	143
Figure 131 LNT Storage Capacity vs. Temperature.....	144
Figure 132 NOx Ratings with Fixed Temperature Adsorption.....	145
Figure 133 50% Load CO Production and Consumption	146
Figure 134 25% Load CO Production and Consumption	147

Table of Tables

Table 1 Different Species Concentration for the Differential Mode	20
Table 2 Typical Exhaust Gas Mixture	24
Table 3 Average Methane Conversion for the Unidirectional and Flow Reversal Regimes at Reactor Furnace Temperatures of 400, 450, 500, and 600oC, STs of 10, 15, 20, 30, and 45s, and a GHSV of 20,000 hr-1	41
Table 4 Average Methane Conversion for the Unidirectional and Flow Reversal Regimes at Reactor Furnace Temperatures of 400, 450, 500, and 600oC, STs of 10, 15, 20, 30, and 45s, and a GHSV of 40,000 hr-1	42
Table 5 Average Methane Conversion for the Unidirectional and Flow Reversal Regimes at Reactor Furnace Temperatures of 400, 450, 500, and 600oC, STs of 10, 15, 20, 30, and 45s, and a GHSV of 60,000 hr-1	43
Table 6 Average Methane Conversion for the Unidirectional and Flow Reversal Regimes at Reactor Furnace Temperatures of 400, 450, 500, and 600oC, STs of 10, 15, 20, 30, and 45s, and a GHSV of 80,000 hr-1	44
Table 7 Effects of Switching Time on CO Concentration Bypassing the Catalyst at a Reactor Furnace Temperature of 450oC, a GHSV of 40,000hr-1, and a ST of 10,15, 20, 30, and 45s.....	47
Table 8 RFOCR Residence Times for the Total Exhaust Mixture at all Reactor Inlet Temperatures and GHSVs.....	51
Table 9 Average CH ₄ Conversion With and Without SFI for Unidirectional Flow and Flow Reversal at a Reactor Furnace Temperature of 350oC, a GHSV of 20,000 hr-1, and a ST of 20s for Flow Reversal Operations	60
Table 10 Gas Composition Used in Isothermal Absorption and Regeneration Experiments	71
Table 11 NO _x Storage Capacities at 25,000hr-1	75
Table 12 NO _x Storage Capacities at 50,000hr-1	76
Table 13 NO _x Storage Capacities at 75,000hr-1	76
Table 14. Breakthrough Time at 25,000hr-1	77
Table 15. Breakthrough Time at 50,000hr-1	77
Table 16. Breakthrough Time at 75,000hr-1	78
Table 17 Result of Cycling 100sec lean and 5sec rich experiment with T=350 C and SV=50,000hr-1.....	83
Table 18 Results from Direct Fuel Injection Without O ₂ (100s lean /5s rich cycle at T=350C & SV=50K)	85
Table 19 Result from Direct Fuel Injection With O ₂ (5s rich & 100s lean at T=350C & SV=50K)	86
Table 20 Natural Gas Engine Exhaust Parameters	97
Table 21 Cummins Engine Specifications.....	111
Table 22 Baseline Test Matrix.....	117
Table 23 Baseline Power Map.....	122
Table 24 Baseline Boost Pressure Map	122
Table 25 Baseline Inlet Air Flow Map	122
Table 26 Baseline Fuel Flow Map.....	123
Table 27 Baseline Exhaust Flow Map	123
Table 28 Baseline BSFC Map	123
Table 29 Baseline BMEP Map	123
Table 30 Baseline Exhaust Back Pressure Map.....	123
Table 31 Baseline NO _x Rating Map.....	124
Table 32 Baseline Air to Fuel Ratio Map	124
Table 33 Baseline Turbo Out Temperature Map	124
Table 34 Weighting Factors	124
Table 35 Conditions for Bench Flow Study	125
Table 36 Results from Bench Flow Study	125
Table 37 LNT Capacity Estimations	125
Table 38 Exhaust Flow Rates During Adsorption and Regeneration	128
Table 39 Exhaust Composition Control	130
Table 40 Methane Oxidation Results	131

Introduction

Lean burn natural gas engines have high thermal efficiency and durability. However, lean burn engine exhaust has a wide temperature span and is rich in oxygen, which makes aftertreatment difficult. Lean burn NO_x levels can be much lower than stoichiometric burn levels, but are still too high to meet the 0.1 g/hp-hr target and a de- NO_x scheme has to be applied. The leading de- NO_x contenders for lean burn engines are Lean NO_x Catalyst (LNC), Selective Catalytic Reduction (SCR), and Lean NO_x Trap (LNT) [1].

A Lean NO_x Trap, or NO_x adsorber, is a flow-through catalyst-bed that temporarily stores exhaust NO_x during typical lean burn operations. Before the NO_x adsorbent becomes fully saturated, the exhaust gas composition must be adjusted to produce a fuel-rich exhaust. This adjustment may be accomplished by either by modifying engine fueling strategy or by introducing fuel into the exhaust stream. Under fuel rich conditions, the stored NO_x is released from the adsorbent and subsequently reduced to N_2 over precious metal sites. A desulfurization process must be conducted at high temperature and fuel rich conditions [3-8]. Such Lean NO_x Traps have demonstrated high NO_x conversion efficiencies; approaching 95%, for lean burn gasoline engines and diesel engines [4-8].

The LNT is the focus of this research. It should be pointed out that the LNT approach has to overcome the dilemma that while the oxidation of methane requires high temperatures, the NO_x absorption requires much lower temperatures. Significantly, de- NO_x systems normally involve hydrocarbon slip. In the case of compressed natural gas (CNG) fuel, the predominant hydrocarbon is methane, which is difficult to destroy in downstream catalytic treatment of the exhaust. Presently, LNT research has not been as successful for CNG applications as when applied to lean burn gasoline engines or diesel engines [4-11]. Energy efficient breakthroughs are needed for LNT regeneration, desulfurization, and methane oxidation. The objective of this project is to develop a system capable of improving the effectiveness of LNTs applied to CNG-fueled lean-burn engines.

This project is focused on the development of an energy efficient aftertreatment system capable of reducing NO_x and methane by 90% from lean-burn natural gas engines by applying active exhaust flow control. The system consists of a Lean NO_x Trap (LNT) system and an oxidation catalyst. Through alternating flow control, a major amount of engine exhaust flows through a large portion of the LNT system in the absorption mode, while a small amount of exhaust goes through a small portion of the LNT system in the regeneration or desulfurization mode. The restricted partial flow has a very low space velocity that reduces the requirement for secondary fuel. By periodically reversing the exhaust gas flow through the oxidation catalyst, a higher temperature profile is maintained in the catalyst bed resulting in greater efficiency of the oxidation catalyst at lower exhaust temperatures. The project involves conceptual design, theoretical analysis, computer simulation, prototype fabrication, and empirical studies.

An integrated LNT -oxidation embedment is being developed which will have no negative impacts on engine operation in terms of output, efficiency, durability, and maintenance. The flow reversal system is being designed with zero slip during switching. The results of this research will help to attain the long-term NO_x emission target of 0.1 g/hp-hr, energy efficiency of 50%, and cost reduction of 10%.

Overview

The goals of the project will be achieved through a union of modeling, bench testing, conceptual design, fabrication, and experimental testing. To reach these goals, the following tasks were outlined and presented in the Annual Technical Progress Report dated April 2005.

- I. Bench Flow Reactor Design and Modeling
 - II. Conceptual Design of a Partial Flow LNT Regeneration and Gas Divider System
 - III. Lean Burn Natural Gas Engine Testing and NO_x Reduction Strategy Development
- Each of these tasks be updated with the program's conclusion.

Bench Flow Reactor Design and Modeling Review

Bench-Flow Reactor System

The bench-flow reactor (BFR) was built to supply necessary kinetic data and system optimization information for the ARES natural gas (NG) stationary power-generating engine. The data collected provided the ARES program with vital information pertaining to nitric oxides (NO_x) and total hydrocarbon (THC) conversion efficiency. Both NO_x and THC conversion are functions of the catalyst type and loading, space velocity, temperature, and exhaust gas mixture. Each of these parameters were controlled and examined to obtain the needed data in a laboratory setting. A full design of the reactor can be reviewed in the Annual Report from April of 2004.

Reverse-Flow Oxidation Catalyst Reactor

At elevated temperatures, the total hydrocarbon (THC) catalytic chemical reaction is exothermic and the reverse-flow configuration of the reactor has the capacity to take advantage of this increased temperature event. The switching of the inlet and outlet exhaust direction "traps" the temperature inside the reactor, thus increasing the overall temperature of the exhaust gas through the catalyst. THC reduction was investigated as a function of the direction and duration of the exhaust gases through the catalyst, space velocity, exhaust gas mixture concentration, and temperature. The catalyst used in the reactor was a palladium oxidation catalyst provided by EmeraChem.

Lean NO_x Trap Catalyst Reactor

The objective of the lean NO_x trap catalyst reactor (LNT) was to study the reduction of NO_x in the simulated natural gas exhaust flow. At varying temperatures and space velocities, the following parameters were investigated; NO_x breakthrough time, NO_x capacity storage, catalyst saturation, maximizing the storage by shifting between the lean phase mode and the rich phase mode, maximizing the storage by direct fuel injection, and identifying the best reductant (CO or H₂) in the rich phase.

Data Acquisition System

The data acquisition system (DAC) consists of hardware and software components purchased commercially from National Instruments. The purpose of the DAC, besides simply data logging, is to be a flexible system that can adapt with the BFR system as the experiments change. The system was designed with the capability for multiple component interfaces to be logged at a user defined sampling rate.

Mathematical Modeling of Reverse Flow Oxidation Catalyst

The most important objective of modeling the BFR was to simulate the forward-flow and reverse-flow of the exhaust gas through the RFOCR. With the help of a one-dimensional model, a mathematical code was developed in FORTRAN. To keep the modeling code compact and uncomplicated, the complex energy and mass balance equations, which are non-linear partial differential equations, were simplified into algebraic equations by using the backward difference method.

The main objective of the RFOCR is to increase the temperature profile over the catalyst surface and hence to increase the THC conversion efficiency. To gain an understanding how this was optimized, it was important to predict the effect of the following parameters on the temperature profile and methane (CH₄) conversion:

1. exhaust gas flow rate
2. exhaust gas temperature
3. switching time

The model required the kinetics of the global reaction over palladium. By operating the BFR in a differential mode with a 1/2" palladium based catalyst, the kinetics of the global reaction can be extracted.

Bench Flow Reactor Design and Modeling Modifications

Bench-Flow Reactor System Modifications

A number of revisions have been made to the BFR systems instrument cabinet in order to accomplish goals set for the system. In order to have the capability to switch from lean and rich banks, described in the LNT reactor section of 2004 Annual report, additional mass flow controllers (MFC), solenoids, and a solid-state relay were added to the instrument cabinet. Modifications of the previous and present set-up of the cabinet can be compared in Figure 1 below and Figure 10 of the 2004 Annual Report.

The importance of water to the BFR system was discussed in the 2004 report and to properly simulate an actual engine exhaust mixture it is necessary for water vapor to be incorporated into the feed stream. A syringe pump, made by Harvard, was initially utilized for water injection into the system. Due to the relatively small reservoir of the syringe pump, it proved impractical to use for experimental runs with longer durations. Subsequently, the syringe pump was replaced by a peristaltic pump manufactured by Masterflex and was incorporated for use on the longer duration runs. The peristaltic pump, shown in Figure 2, allows for continuous water injection due to the pump's inlet being placed into a large water reservoir

Figure 1 Instrument Cabinet Modifications

Figure 2 Peristaltic Pump

Figure 3 Three-Way Branching Valves

The BFR consists of two reactors, the RFOCR and the LNT reactor. Both reactors use the same components upstream of the reactor branching valves, shown in Figure 3. The major upstream components consist of the instrument cabinet, peristaltic pump, and steam-generating furnace. Because each particular reactor experiment must be run independently, a valve system was devised to stop the gas flow to the reactor that is not being utilized. This system of valves replaces the pneumatic valve that directed the exhaust mixture to the RFOCR or the LNT reactor.

Reverse-Flow Oxidation Reactor Modifications

Figure 4 Catalyst Thermocouple Orientations

A number of revisions to the RFOCR have been made to improve the data collected for the ARES program. These modifications to this reactor include temperature stabilization of the system, oxidation catalyst replacement, and the modification of the reactor end fittings. Furthermore, two additional thermocouples were added to the RFOCR and placed to record the inlet and outlet temperature of the reactor furnace. Figure 4 shows the thermocouple orientation in relation to the catalyst sample inside the RFOCR.

The earlier version of the RFOCR obtained adiabatic conditions by an insulating jacket and a heating tape assembly. The heating tape was coiled around the reactor for temperature regulation while the insulating jacket was used to prevent heat loss. As seen in Figure 5, this temperature-regulating set-up resulted with the reactor temperature being unable to reach a steady-state temperature. As discussed in the 2004 annual report, the heating tape is controlled via LabVIEW, in conjunction with a steady-state relay and a thermocouple. The LabVIEW temperature-control program works similar to a home thermostat. A temperature set point is set and if the actual reactor temperature is greater than the set point, the voltage to the heat tape is shut off. Likewise if the temperature inside the reactor is less than the set point, a voltage is applied to the heat tape controller to raise the temperature. Because the heating time response of the heating tape was slow, oscillations occurred in the experiment. This resulted in severe temperature over and undershoots from the temperature set point. Moreover, due to the method of coiling the heat tape around the reactor, non-uniform temperature heating resulted in RFOCR. This produced a non-

Figure 5 No Water Addition, Unidirectional Flow, Methane 3000ppm Space Velocity - 40,000hr-1

uniform temperature distribution throughout the reactor during experimental runs. The inability for accurate and uniform temperature control resulted in data that does not appear useful for real-world engine applications and were thought to have consequences to Total Hydrocarbon (THC) conversion

To alleviate the problem of temperature oscillations, a new approach was developed to control the RFOCR temperature. The early version was replaced with a tubular furnace, similar the set-up for the LNT reactor. Because of the different physical dimensions of the two setups, modifications to the tubing for the simulated exhaust and the pneumatic high-temperature switching valves (HTSV) were altered.

Initially EmeraChem donated several oxidation catalyst samples to the project with various loadings ranging from 25, 50, 75, and 100 g-Pd / ft³. In the first RFOCR system set-up, the oxidation catalyst sample used had a precious metal loading of 100 g-Pd / ft³. This catalyst sample was three inches long, 7/8 of an inch thick and had a cell density of 300 cells / in² (cps).

Figure 6 Reverse Flow Oxidation Catalyst Reactor

Unfortunately, the initial catalyst sample used was damaged in the process of completing the modifications the RFOCR system. For continuity, a fresh 100 g-Pd / ft³ catalyst sample was used again to compare the experimental data between the initial and present RFOCR system set-ups. A picture of the experimental set-up with the fresh catalyst in place can be seen in Figure 6. The catalyst, as described in the 2004 Project Annual Report, is placed at the mid-point of the reactor and is wrapped with FiberFrax to prevent the simulated exhaust gas from “slipping” around the catalyst sample. Five thermocouples are installed into the RFOCR to determine both end temperatures of the sample and the temperature at 1/4, 1/2, and 3/4 the length of the catalyst.

The final modification to the RFOCR system was the reactor end fittings. The fittings, seen in Figure 7, were modified to prevent the exhaust mixture from escaping at the reactor end fitting. The previous set-up was very similar to the present set-up shown in Figure 7 with the exception of the graphite ferrule. Due to the high temperatures that the system attained the O-rings would fatigue and fail. The failure would cause leaks at the reactor end fittings and as a result of the mixture leak, the emission data collected was inaccurate.

This component failure was resolved by replacing the reactor end fitting completely. While the basic design is very similar, using a graphite ferrule to seal the reactor allows the RFOCR system to obtain high temperatures without sacrificing the reactor end fittings integrity. The reactor end fittings may also be carefully removed from the reactor tube without damaging or destroying the graphite ferrule. This advantage allows the service of damaged thermocouples or the replacement the catalyst sample inside the reactor tube without having to replace the end fitting.

Figure 7 Reactor End Fitting

Lean NO_x Trap Catalyst Reactor Modifications

Several modifications were made from the original LNT design. A fuel injection system (FIS) was added to evaluate the performance of regeneration using direct fuel injection. As shown in Figure 8, the FIS has four major components: a pressure regulator and pressure gage, an amplifier, a piezoelectric valve, and a rotameter. The pressure of fuel is precisely regulated since the fuel flow rate through the piezoelectric valve is strongly dependent on the pressure. A small change of pressure during the experiment induces a large change in the amount of fuel injected. The amplifier increases the voltage of input signal from the LabView control program to control the piezoelectric valve. The voltage range of the input signal from LabView is 0 to 5V, whereas the amplified voltage of output signal to the piezoelectric valve is 0 to 100V. The output signal is linearly proportional to the input signal. The Maxtek MV-112 piezoelectric valve regulates the precise amount of fuel to be injected into the reactor. The response time of the piezoelectric valve is 2 milliseconds and is fast enough to neglect time lag within FIS. Flow range of the valve is 0 to 500 cc/m at standard pressure, but it can be increased to a higher pressure condition (max 50psi). To measure the fuel flow rate from the piezoelectric valve, A Dwyer rotameter was used. The rotameter has a range between 0 and 4717 cc/m.

In the original configuration, the LNT catalyst sample was placed at the mid point of the quartz tube. Glass beads were filled in the inlet to maintain a uniform temperature profile. Using K-type thermocouples it was found that a temperature was approximately 20° lower at the inlet than that at the outlet. As a result, the catalyst sample was repositioned towards the exit side of the reactor and more glass beads were added. In this manner, the simulated exhaust gases would have adequate time to be heated up to the desired temperature. Heavy insulation was also added to the lines to minimize the heat lose to the surroundings.

Figure 8 The Components of Fuel Injection System

Data Acquisition Modifications

Although no major hardware changes or additions have been made to the data acquisition system since last year's report, a modest amount of modifications have been made to incorporate the BFR system modifications with additions in the LabVIEW controlling program. Switching between the rich and lean bank and fuel injection pulsing were implemented into LabVIEW program giving the BFR system greater capability and flexibility when compared with the previous version.

In the new LabVIEW program, the BFR operator is now able to switch between a fuel-rich or fuel-lean mixture. The program allows for variable switching times between one bank to the other during the experiment, which is similar to the program designed for varying the forward- and reverse-flow durations in the RFOCR. Additionally, this particular program function is used in regenerating the LNT catalyst. In this part of the program, the operator can open or close the valve for fuel injection into the LNT reactor, the duration of the pulse, and the number of cycles during the experiment. One cycle consists of the fuel injection valve opening, closing, and opening again.

Reverse Flow Reactor Model Modifications

Reaction Kinetics

To develop the code for the reverse flow oxidation, considering the surface reaction between methane and oxygen over palladium, it is necessary to know the reaction kinetics. It is important to have the correct values of the decisive parameters like the activation energy, the specific rate constants, and the pre-exponential term. Furthermore when the oxidation of methane over palladium in the presence of CO₂ and water vapor is considered, it is necessary to find the effects of all these constituent gases on the reaction as well as finding the reaction order. And finally it is

important to find the heat energy involved in the reaction to determine the reaction rate and predict the correct reaction mechanism that would represent the actual reaction.

A detailed review of related literature gave the activation energy for the oxidation of methane over palladium but does not tell anything about the specific rate constants involved with the reaction. In order to supply the input values for the model code and to conduct experiments using the BFR, it was necessary to know the specific rate. To do so the reactor is run in a differential mode. This method employs both a global and a detailed chemical kinetic approach to the heterogeneous and homogeneous oxidation mechanisms. Some of the main factors that are considered in this mode are the length of the catalyst, the catalyst loading, the reactor temperature, the composition of the gases, the methane conversion, and the space velocity. A preview of each of these parameters is explained below.

While the temperature is one of the basic parameter that defines the kinetics and the reaction rates, the length of the catalyst is very important as well. To minimize the effects of temperature variation, it is necessary to maintain a uniform temperature through out the length of the catalyst. This is made easier by using a small length of catalyst. A longer catalyst will have a definite temperature variation along the length of sample. One more reason for having a smaller catalyst length is to keep the conversion down. Because the conversion process is exothermic in nature, keeping the conversion as low as 10% helps to minimize the effect of any temperature rise. It is necessary to maintain a constant temperature as the reaction rates are exponentially dependent in the temperature. The literature review revealed that experiments are done at temperatures varying from 300°C to 600°C. It has been found that conducting experiments with a wide temperature range results in more accurate kinetics

One of the other important criteria is the space velocity. While the space velocity determines the residence time of the gases in the catalyst; it becomes necessary to have a proper control of it As mentioned earlier, it is necessary to have a low conversion to minimize the effect of temperature. What's more, to low of a space velocity has an increased residence time which allows the reaction a longer time to occur resulting in increased conversion. The increased conversion results in a larger temperature difference thus resulting in the uncertainty of the accuracy of the determined kinetics. So the space velocity is kept high to minimize the residence time and to lower the conversion. Due to convection increasing the flow rate also has an affect on the temperature. But keeping the catalyst sample short and preheated close to the temperature of the reactor that effect can be minimized.

To study the effect of catalyst loading, samples loaded to 100, 150 and 200g/ cubic feet per foot palladium can be used. Using helium as an inert gas , the effect of constituent gases in the feed stream can be studied using methane, oxygen, carbon dioxide and water vapor. A generalized concentration of these gases is shown in Table 1. below. The gas species concentrations are varied one at a time so that the effect of that particular gas can be found.

Table 1 Different Species Concentration for the Differential Mode

Species (%)	CH ₄	O ₂	CO ₂	H ₂ O	He
CH ₄	0.3 – 5.7	5	0	0	Balance
O ₂	1	0.5 - 8	0	0	Balance
CO ₂	1	5	0.3 – 1.7	0	Balance
H ₂ O	1	5	0	0.3 – 3.5	Balance

By utilizing the method of excess, it is possible to determine the relationship between reaction rate and the concentration of the species. The reaction mechanism shown in the 2004 Annual report to find the global reaction rate is considered again. Initially just methane and oxygen are flowed through the catalyst with the above concentrations along with helium or another inert gas. We know that

$$-r_{CH_4} = kC_{CH_4}^{\alpha}C_{O_2}^{\beta} \quad (1)$$

Where both α and β are unknown, the reaction could be first run in an excess of O_2 so that C_{O_2} remains essentially unchanged during the course of the reaction and

$$-r_{CH_4} = k'C_{CH_4}^{\alpha} \quad (2)$$

Where

$$k' = kC_{O_2}^{\beta} \approx kC_{O_2,0}^{\beta} \quad (3)$$

So after determining α , the reaction is carried out in the excess of A, for which the rate law is approximated as

$$-r_{CH_4} = k''C_{O_2}^{\beta} \quad (4)$$

This can be used to find the value of β . Then a similar run with carbon dioxide and water vapor can be run to find the reaction order of those species. The order is found by plotting the change in concentration with time along the y axis and the concentration along the x axis. The slope of this graph gives the order of the reaction with respect to that species. A similar plot can be done for all the species to find the order.

To find the above it is necessary to know the reaction rate. This is found out using the formula given below

$$-r_{CH_4} = \frac{F_{CH_4,0}X}{W} \quad (5)$$

Where $F_{CH_4,0}$ is the volumetric flow rate of the methane, X is the conversion percentage and W is the mass of the catalyst which is known from the catalyst loading.

FORTRAN Compiler

The previous report had a brief introduction about the need for a compiler and about the Compaq Visual FORTRAN Compiler. The code that was previously used had lots of subroutines which required more linking and so a visual compiler was more suitable. It was easy to traverse between subroutines and simpler to debug. There were some problems with the numerical handling of the compiler. It repeatedly gave errors or wrong results due to the high math involved within the code and the poor number handling capacity. The current code has one main program and a solver for ordinary differential equation. So the Intel FORTRAN compiler for Linux was used. This compiler is used along with the VI editor.

The current code works perfectly for the forward flow. Test runs conducted with the kinetics of propylene over platinum corresponded well to the literature. Once the kinetics for oxidation of methane over palladium was obtained, it was incorporated into the code to obtain the results for the forward flow. With an input file that has all the required parameters, the program has the option of running it either in unidirectional flow or with reverse flow. This option is setup in the input file. This can also be used to determine the temperature and conversion with the kinetics of methane over palladium. The input file also has parameters like temperature at which the simulation is to be done, the flow rate, the composition, and all the other required input parameters.

Figure 9 shows the temperature profile along the length of the catalyst at varying time. It is seen from the graph that the temperature starts increasing from the tail end of the catalyst and the peak moves towards the entrance as time proceeds. This is the trend of curve that has been observed in literature. Figure 10 shows the conversion of all the gases. As said before these are for propylene over platinum and it is just to show how the results are obtained from the code.

Figure 9 Temperature Profile along the Length of Catalyst as a Function of Time

Figure 10 Conversion of Different Species as a Function of Time

The current code for the reverse flow has to be debugged. There is a convergence error with the Newton iteration method. This method is used to predict the temperature and concentration at each node and has to converge to the specified tolerance level. When the flow is reversed after a particular time, the inlet temperature, when reversed, is too high compared to the forward flow. Since the temperature difference is so high, the initial guess that is required to solve the Newton method is way off from what it has to be and so the value does not converge to a preset tolerance. Varying the tolerance to suit this problem is not a good method to debug the problem as it affects the accuracy of the results obtained. Several different methods were tried to rectify this convergence problem. One such method is called the global Newton method. This method has a subroutine which checks each iteration. Once the iteration does not converge to the set tolerance and diverges, that particular iteration is omitted and the entire iteration is started with a different initial guess. By doing this we see through that we always converge. Unfortunately this method could not be used at this time due to code incompatibility.

One of the other methods considered was the bisection method. In this method, the extreme values are considered and the range is made closer and closer until it reaches the required value. This is a very reliable method but it is a very time consuming process. Considering the number of nodes and the number of iterations required this method would slow down the program too much and as the tolerance limit set smaller, it further increases the time required to complete. So this method was not incorporated either. Some of the other methods like the Broydens method and the secant method are currently being reviewed for the feasibility of incorporating one into this code.

Bench Flow Reactor Design and Modeling 2004 Progress

Reverse-Flow Oxidation Catalyst Reactor Progress

As previously stated, the objective of the RFOCR is to prove that the reverse-flow configuration increases THC conversion and to optimize the system for maximum THC conversion. Below are several representative plots of experimental data to date. Further experimental data can be found

in the Appendix section of this report. The RFOCR results are categorized into three major groups: the effects of varying switching time, exhaust gas mixture space velocity (flowrate), and temperature. The exhaust gas mixture concentrations for the RFOCR experiments remain constant and are shown in Table 2.

Table 2 Typical Exhaust Gas Mixture

Gas Concentrations	Concentration
H ₂ O Vapor (%)	10
O ₂ (%)	6
CO ₂ (%)	6
CO (%)	0.5
NO _x (ppm)	0
CH ₄ (ppm)	2000
H ₂ (%)	0

Varying Switching Time

The switching time increments are defined as the amount of time the exhaust mixture is allowed to flow in one direction. For example, a switching time of 15 seconds implies that the gas stream flows in the forward-flow direction for 15 seconds and then the gas flow direction is switched to the reverse-flow direction for 15 seconds. To date all experiments were performed with symmetric switching time duration.

In Figures 11 to 13 below, the temperature, concentration, and space velocity all remain constant. The RFOCR furnace temperature is 500°C, methane concentration is 2000ppm, and the space velocity is 20,000 hr⁻¹. It is immediately apparent that the reversing the flow through the catalyst does have a significant impact on the THC conversion. As seen in these figures it appears there is little affect on THC conversion between having a 15 or 20 second switching time duration. Both appear to have an approximate THC conversion of 90% at a space velocity of 20,000 hr⁻¹. A switching time duration of thirty seconds appeared to lower THC conversion to an approximate value of 87%. Through simple comparisons as these it is believed possible to determine a more suitable time duration scheme for maximum THC conversion. At the present time, shorter switching time durations are being further investigated in order to maximize THC conversion efficiency.

Figure 11 RFOCR Temperature Profile and Conversion Percentage

Figure 12 RFOCR Temperature Profile and Conversion Percentage

Figure 13 RFOCR Temperature Profile and Conversion Percentage

In Figures 14 to 16 the temperature, switching time, and exhaust concentration are the same as the previous plots above. However, the space velocity is increased to $40,000 \text{ hr}^{-1}$. When THC conversion is compared with the plots of $20,000$ and $40,000 \text{ hr}^{-1}$ it is clear that increasing the simulated exhaust gas flowrate THC conversion decreases. At a space velocity of $40,000 \text{ hr}^{-1}$ an average THC conversion of 70% is obtained. This conversion is approximately 20% lower than the same experiment with a space velocity of $20,000 \text{ hr}^{-1}$. As in the first set of $20,000 \text{ hr}^{-1}$ plots, the set of $40,000 \text{ hr}^{-1}$ plots show a slight advantage in the shorter duration switching time in THC conversion.

Figure 14 RFOCR Temperature Profile and Conversion Percentage

Figure 15 RFOCR Temperature Profile and Conversion Percentage

Figure 16 RFOCR Temperature Profile and Conversion Percentage

Figure 17 RFOCR Temperature Profile and Conversion Percentage

Figure 17 shows the results at a furnace temperature of 500°C, a switching time of 30 seconds, and a space velocity of 60,000 hr⁻¹. It can be seen the dramatic affect that space velocity has on THC conversion in this plot. The 20,000, 40,000, and 60,000 hr⁻¹ space velocity plots, at a

switching duration of thirty seconds, have a THC conversion of 87%, 68%, and 35%, respectively. Comparison of these results shows that in order to achieve a maximum THC conversion a RFOCR configuration should be at shorter switching time durations and lower space velocities

Varying Temperature

In Figures 18 to 21 the effects of temperature on THC conversion is plotted. Space velocity, switching time duration, and mixture concentration are all held constant for this set of plots. Here the RFOCR furnace is varied from 400-550°C in 50°C increments. Figure 20 shows that at a relatively low temperature that reversing the flow through the catalyst reactor has little or no effect on THC conversion. THC conversion for a furnace temperature of 400, 450, 500, and 550°C is approximately 5%, 20%, 55%, and 85%, respectively.

Figure 18 RFOCR Temperature Profile and Conversion Percentage

Figure 19 RFOCR Temperature Profile and Conversion Percentage

Figure 20 RFOCR Temperature Profile and Conversion Percentage

Figure 21 RFOCR Temperature Profile and Conversion Percentage

Bench Flow Reactor Design and Modeling Conclusion

Bench-Flow Reactor System

A final schematic and a photograph of the bench-flow (BFR) are shown in Figures 22 and 23, respectively. Simulated natural gas exhaust emissions are introduced into the bench-flow reactor system by means of mass flow controllers. The simulated exhaust gases consist of CO_2 , H_2 , NO_x , CH_4 , Air, N_2 , and CO . An updated example of a typical exhaust gas mixture is shown in Table 3. Water vapor is introduced into the system via the steam generator. Downstream of the steam generator the system is divided into two separate reactor systems, the Lean NO_x Trap Catalyst Reactor (LNT) or the Reverse-Flow Oxidation Catalyst Reactor (RFOCR). The exhaust gas is then sent to the Horiba analyzer bench. Experimental data is acquired through a Nation Instruments LabVIEW data acquisition system.

Figure 22 Schematic of Bench Flow Reactor System

Figure 23 Bench-Flow Reactor System

Table 3 Typical Simulated Exhaust Gas Composition

NO _x	1000 ppm
H ₂	750 ppm
CO	0.5%
CH ₄	1500 ppm
CO ₂	8%
H ₂ O	10%
O ₂	10%
N ₂	Balance

Reverse-Flow Oxidation Catalyst Reactor

The present and previous versions of the reverse-flow oxidation catalyst reactor (RFOCR) configuration are shown in Figure 24 and 25, respectively. Modifications of the RFOCR are discussed in the BFR system modifications and additions section of this report. The RFOCR system consists of stainless steel tubing, several valves, thermocouples, heating tape, insulation, a pressure transducer, and an oxidation catalyst. The purpose of these components is to obtain specified operating conditions for the bench-flow reactor.

The RFOCR consists of, as the entire BFR system, ¼” stainless steel tubing manufactured by Swagelok. This is used to contain and direct the simulated natural gas exhaust gas. As seen in Figure 25, the tubing is arranged in a manner to minimize the dead volume in the RFOCR system.

The RF oxidation reactor system consists of four high temperature pneumatically-operated valves produced by Swagelok, and dubbed as “switching valves”, as seen in Figure 28. The operating air pressure of these valves is 60 psi. Shown in Figure 27, two Peter Paul 24 VDC three-way solenoid valves are used to pneumatically actuate the four switching valves. Alwitco Solenoid mufflers are added to each solenoid valve to minimize noise during operation. A power supply in conjunction with solid-state relays controls the three-way solenoid valves via LabVIEW. LabVIEW is used to control the solenoid valves, and in turn the switching valves, giving the operator the ability for precise control of the RFOCR. Switching valves one and four and switching valves two and three, shown in Figure 26, can be manipulated in such way allowing the exhaust gas stream to flow in the forward direction or in the reverse direction through the oxidation reactor.

Figure 24 Reverse Flow Oxidation Catalyst Reactor

Figure 25 Reverse Flow Oxidation Catalyst Reactor (Top View)

Figure 26 Reverse Flow Schematic and Temperature Profile

Figure 27 Power Supplies with Solid State Relays

Adiabatic conditions are maintained in the RFOCR by a system of heating tapes, insulation, thermocouples, solid-state relay switches, and LabVIEW. To avoid condensation and to maintain a constant gas temperature throughout the RF oxidation system, high temperature heating tape produced by Omega Engineering and insulation, manufactured by Zetex, are wrapped around the stainless steel tubing. Omega Engineering Type-K thermocouples are located between the preheater furnace and RFOCR, before switching valves 1 and 2, and five thermocouples are located in the RF oxidation catalyst reactor. The heating tapes are wired to relay switches enabling the gas temperature to be controlled via LabVIEW. High temperature Zetex insulation is wrapped around the outside of the heating tapes and tubing for adiabatic conditions as well as for safety purposes.

Extensive examination of several technical papers concerning natural gas (NG) exhaust catalytic combustion concluded that noble metal-based catalysts (palladium, platinum, and rhodium) generally have higher activity and resistance to sulfur poisoning than metal/transition oxide-based catalysts. Results show that CH_4 conversion efficiency varies by the following: palladium>platinum>rhodium, all on alumina substrate. Based on these findings, a palladium catalyst was selected for the oxidation of CH_4 in the BFR system. All catalysts were obtained from Emerchem. Specifications of the two reactor catalysts, the LNT reactor and RFOCR, are shown in Figure 22. The catalyst sample is placed inside a 12" long quartz tube with an OD of 1". To ensure that leakage around the catalyst once placed in the reactor was kept to a minimal, FiberFrax was wound around the catalyst before inserting the sample into the quartz tube.

Figure 28. Pneumatic Valve Operation

Figure 29. Physical Parameters and Characteristics of Catalyst

Reverse-Flow Oxidation Catalyst Reactor Without Supplemental Fuel Injection

All experimental runs for the RFOCR study with flow reversal are divided into three sections, with the total length of the run lasting 1200 seconds in duration. The first 300 seconds consists of

an experimental baseline with unidirectional flow, followed by 600 seconds of exhaust flow reversal, and concludes with 300 seconds of unidirectional flow.

Experimental results show that CH_4 conversion is significantly improved with periodic exhaust gas flow reversal when compared with unidirectional flow. Figures 30 and 31 illustrate methane conversion and the temperature profile across the catalyst for a typical experimental run at a constant reactor furnace temperature of 450°C , a gas hourly space velocity (GHSV) of $40,000 \text{ hr}^{-1}$, and a switching time (ST) of 10 seconds. Figure 30 shows methane conversion increases more than 47% during flow reversal when compared to unidirectional CH_4 conversion. This increase in CH_4 conversion is attributed to the trapping of heat from the combustion of methane across the length of the catalyst due to flow reversal. The temperature profile across the catalyst is examined at several instances of time in the unidirectional flow regime and the flow reversal regime of the experimental run. From Figure 31 the unidirectional temperature profiles ($t = 210$ and 1155 seconds) continually increase due to the exothermic chemical reaction of CH_4 as it travels across the catalyst. The temperature profiles across the catalyst length before and after flow reversal ($t = 210$ and 1155 seconds) are noted as not having repeatable steady-state temperature profiles, however given time the difference in steady-state CH_4 conversion for both unidirectional regime (pre and post flow reversal) does decrease. Additionally, at an experimental run time of $t = 300$ seconds to $t = 900$ seconds the flow direction through the catalyst reactor is then periodically reversed, at a switching time of 10 seconds. During periodic flow reversal the elevated temperature at the exit of the catalyst reactor is used to preheat the feed stream, increasing the reaction rate. After a sufficient amount of periodic flow reversal a considerable amount of heat is trapped across the length of the catalyst, i.e., the heat trap effect. Figure 31 illustrates the development of the heat trap effect from the flow reversal temperature profiles ($300 < t < 900$ seconds) across the catalyst. From the figure it is shown that periodically reversing the exhaust mixture increases the average temperature ($^\circ\text{C}$) across the catalyst reactor by 6% when comparing the fully developed flow reversal temperature profile at $t = 840$ seconds to the unidirectional temperature profile at $t = 210$ seconds.

Figure 32 illustrates the temperature profiles across the catalyst with both a combustible gas composition and an inert gas composition. Both experimental runs are conducted at a reactor furnace temperature of 450°C and a GHSV of $40,000 \text{ hr}^{-1}$. The inert exhaust gas composition consists of a mixture of 6% O_2 , 10% H_2O , and a N_2 balance. Due to the composition of the inert gas mixture no exothermic chemical reaction is taking place on the surface of the catalyst. The temperature at inlet of the catalyst reactor is lower than the outlet of the catalyst due to convective heat transport of the inert gas composition. The combustible gas composition consists of a mixture of 2000ppm CH_4 , 0.5% CO , 6% CO_2 , 6% O_2 , 10% H_2O , and a N_2 balance. From the figure the temperature across the catalyst is increased when oxidation occurs at the surface of the catalyst.

A significant temperature increase occurs after the first 2-centimeters of the catalyst. This temperature increase is due to CH_4 diffusing and reacting at the surface of the catalyst resulting in an exothermic reaction. Additionally, a list of all average methane conversions for the unidirectional flow regime and the flow reversal regime for all experimental runs are shown in Tables 3 through 6.

Figure 30 Methane Conversion at a Reactor Furnace Temperature of 450°C, GHSV of 40,000 hr⁻¹, and a ST of 10s

Figure 31 Temperature Profiles Across the Catalyst Length at Various Times at a Reactor Furnace Temperature of 450°C, GHSV of 40,000 hr⁻¹, and a ST of 10s

Figure 32 Temperature Profiles Across the Catalyst Length at a Reactor Furnace Temperature of 450°C and a GHSV of 40,000 hr⁻¹ with Unidirectional Flow

From the Tables 3 through 6 it is noted that the average unidirectional CH₄ conversion baselines are not consistent at a particular GHSV and reactor furnace temperature. This is due to each of the switching time experiments being run in sequence of one another at a particular GHSV and reactor furnace temperature, which initially resulted in a gradual catalyst warming trend. To attempt to create a repeatable unidirectional CH₄ conversion baseline for each experimental run at a particular GHSV and reactor furnace temperature a unidirectional “cool down time” of 11 minutes was allowed between flow reversal operations. As a result, the cool down time between flow reversal operation proved to insufficient to obtain repeatable unidirectional baseline conversion prior to flow reversal operations, however direct comparison of the average flow reversal CH₄ conversions at a particular GHSV and furnace temperature may still be preformed. The rationale to directly compare flow reversal CH₄ conversion with dissimilar unidirectional baselines is illustrated in Figure 33. Figure 33 illustrates the temperature profiles of two different experimental runs. The reactor furnace temperature and GHSV for both runs are 400°C and 20,000 hr⁻¹, respectively. The switching times for the experimental runs are 10 seconds and 45 seconds. From Table 4.1 the unidirectional average CH₄ conversion is 8.1% at a reactor furnace temperature of 400°C, a GHSV of 20,000 hr⁻¹, and a ST of 10 seconds, which corresponds to the temperature profile in Figure 33 at a experimental run time of $t = 210$ seconds. The average unidirectional CH₄ conversion is 17.8% at a reactor furnace temperature of 400°C, a GHSV of 20,000 hr⁻¹, and a ST of 45 seconds, which corresponds to the temperature profile at experimental run time of $t = 318$ seconds. From the figure the temperature profile of the experimental run at a ST of 10 seconds is initially lower than the temperature profile of the experimental run at a ST of 45, hence the difference in the baseline conversion. However, from the figure the temperature profiles are nearly identical through the center portion of the catalyst at an experimental run time of approximately 319 seconds.

Table 3 Average Methane Conversion for the Unidirectional and Flow Reversal Regimes at Reactor Furnace Temperatures of 400, 450, 500, and 600oC, STs of 10, 15, 20, 30, and 45s, and a GHSV of 20,000 hr⁻¹

20,000 hr ⁻¹ GHSV			
Temperature (°C)	Switching Time (s)	Unidirectional Flow	Flow Reversal
400	10	8%	14%
	15	11%	18%
	20	13%	22%
	30	15%	26%
	45	18%	29%
450	10	76%	82%
	15	76%	86%
	20	75%	85%
	30	71%	83%
	45	68%	81%
500	10	N/A	N/A
	15	N/A	N/A
	20	N/A	N/A
	30	N/A	N/A
	45	N/A	N/A
550	10	N/A	N/A
	15	N/A	N/A
	20	N/A	N/A
	30	N/A	N/A
	45	N/A	N/A
600	10	N/A	N/A
	15	N/A	N/A
	20	N/A	N/A
	30	N/A	N/A
	45	N/A	N/A

Table 4 Average Methane Conversion for the Unidirectional and Flow Reversal Regimes at Reactor Furnace Temperatures of 400, 450, 500, and 600oC, STs of 10, 15, 20, 30, and 45s, and a GHSV of 40,000 hr⁻¹

40,000 hr ⁻¹ GHSV			
Temperature (°C)	Switching Time (s)	Unidirectional Flow	Flow Reversal
400	10	7%	12%
	15	11%	17%
	20	14%	18%
	30	14%	16%
	45	13%	14%
450	10	41%	60%
	15	34%	52%
	20	30%	45%
	30	27%	39%
	45	25%	34%
500	10	56%	77%
	15	52%	73%
	20	47%	68%
	30	44%	63%
	45	41%	57%
550	10	68%	87%
	15	70%	86%
	20	67%	84%
	30	64%	81%
	45	61%	78%
600	10	N/A	N/A
	15	N/A	N/A
	20	N/A	N/A
	30	N/A	N/A
	45	N/A	N/A

Table 5 Average Methane Conversion for the Unidirectional and Flow Reversal Regimes at Reactor Furnace Temperatures of 400, 450, 500, and 600oC, STs of 10, 15, 20, 30, and 45s, and a GHSV of 60,000 hr⁻¹

60,000 hr ⁻¹ GHSV			
Temperature (°C)	Switching Time (s)	Unidirectional Flow	Flow Reversal
400	10	3%	8%
	15	4%	12%
	20	6%	15%
	30	6%	14%
	45	6%	12%
450	10	30%	55%
	15	28%	49%
	20	26%	43%
	30	24%	37%
	45	21%	31%
500	10	54%	73%
	15	53%	69%
	20	50%	65%
	30	38%	56%
	45	43%	53%
550	10	64%	81%
	15	62%	78%
	20	59%	75%
	30	56%	71%
	45	54%	66%
600	10	N/A	N/A
	15	N/A	N/A
	20	N/A	N/A
	30	N/A	N/A
	45	N/A	N/A

Table 6 Average Methane Conversion for the Unidirectional and Flow Reversal Regimes at Reactor Furnace Temperatures of 400, 450, 500, and 600oC, STs of 10, 15, 20, 30, and 45s, and a GHSV of 80,000 hr⁻¹

80,000 hr ⁻¹ GHSV			
Temperature (°C)	Switching Time (s)	Unidirectional Flow	Flow Reversal
400	10	N/A	N/A
	15	N/A	N/A
	20	N/A	N/A
	30	N/A	N/A
	45	N/A	N/A
450	10	8%	20%
	15	8%	19%
	20	6%	13%
	30	4%	8%
	45	3%	6%
500	10	9%	27%
	15	7%	20%
	20	6%	16%
	30	5%	14%
	45	5%	12%
550	10	14%	54%
	15	19%	48%
	20	17%	43%
	30	16%	38%
	45	15%	34%
600	10	25%	69%
	15	30%	65%
	20	28%	60%
	30	27%	55%
	45	26%	51%

Figure 33 Baseline Unidirectional Temperature Profiles for 10 and 45s ST Experimental Runs at a Reactor Furnace Temperature of 400oC, a GHSV of 20,000 hr-1

Based on the results presented the initial warming trend of the first experiment to the last experimental run in a particular data set does influence the initial unidirectional average conversion, however the variation in the temperature profile is quickly recovered during the initial flow reversals. Due to this fact it is proper to compare average flow reversal CH_4 conversions at a particular GHSV and reactor furnace temperatures though the unidirectional CH_4 conversions are not constant.

Exhaust Mixture Bypassing the Catalyst Due to Flow Reversal

Periodic flow reversal causes a finite amount of the exhaust mixture to bypass the catalyst reactor due to the dead volume associated with a reverse-flow reactor (RFR). The dead volume is expressed as a volume of space in the flow system, where a dead-end passageway or cavity retains a portion of the exhaust gas mixture. During flow reversal operations a portion of the exhaust mixture is pushed out of the catalyst reactor on the subsequent flow reversal, bypassing the combustion process. Figure 34 illustrates an example of how the exhaust mixture bypasses the catalyst reactor during flow reversal. As the exhaust gases flow into the catalyst reactor in the forward flow direction (Figure 34(a)), a portion of the exhaust mixture is trapped between the switching valve (switching valve 1) and the catalyst reactor upon the subsequent flow reversal (Figure 34(b)) and is pushed out of the RFOCR.

As a result of the dead volume associated with a RFR higher concentrations of constituents of the exhaust mixture are found during flow reversal operations. This is best illustrated by carbon

monoxide concentrations in the exhaust mixture during experimental runs with flow reversal. During the unidirectional regime of the experimental runs the entire amount of CO in the exhaust mixture is oxidized to CO₂. An example of this CO oxidation is illustrated in Figure 4.5 and the chemical reaction is shown in Equation 6.

Figure 34 Illustration of Dead Volume Associated with a RFR.

Figure 35 illustrates CO concentration for an experimental run at a reactor furnace temperature of 450°C, a GHSV of 40,000 hr⁻¹, and a ST of 10 seconds. From the figure it is clearly seen that flow reversal allows a finite amount of exhaust gases to bypass the catalyst reactor permitting a portion of the exhaust mixture to escape the combustion process. Table 7 displays the average CO concentration during flow reversal for experimental runs at a reactor furnace temperature of 450°C, a GHSV of 40,000 hr⁻¹, and STs of 10, 15, 20, 30, and 45 seconds. From the table it is seen that the frequency of flow reversal corresponds to the amount of average CO concentration bypassing the catalyst reactor. The correlation between the frequency of flow reversal and catalyst bypass is explained by the lower the frequency of the flow reversal the closer the flow operations are to unidirectional flow, which do not suffer from reactor bypass associated with the dead volume of a reverse-flow reactor.

Figure 35 Carbon Monoxide Concentration at a Reactor Furnace Temperature of 450oC, a GHSV of 40,000 hr⁻¹, and a ST of 10s

Table 7 Effects of Switching Time on CO Concentration Bypassing the Catalyst at a Reactor Furnace Temperature of 450oC, a GHSV of 40,000hr⁻¹, and a ST of 10,15, 20, 30, and 45s

Switching Time (s)	Average CO (ppm)
10	106
15	68
20	50
30	31
45	20

Effects of Switching Time and Gas Hourly Space Velocity on CH₄ Conversion

Experimental results confirm that periodically reversing the exhaust mixture through a catalyst reactor CH₄ conversion can be significantly improved when compared with unidirectional flow conversion. Results also indicate that the effects of switching time on CH₄ conversion vary significantly with GHSV and temperature. In the course of examining the experimental data several trends emerged for CH₄ conversion with respect to switching time. Experiments with flow reversal indicate that at a GHSV of 20,000 hr⁻¹ and reactor furnace temperature of 400°C a maximum methane conversion is obtained at lower frequency switching times (30 and 45 seconds). This trend is illustrated in Figure 36 at a reactor furnace temperature of 400°C and a GHSV of 20,000 hr⁻¹. Methane conversion at a GHSV of 20,000 hr⁻¹ is at a minimum at high frequency switching times (10-20 seconds) due to premature flow reversal, which results in a failure to trap large portion of heat across the catalyst. The development of a premature flow reversal temperature profile is shown in Figure 37 at a reactor furnace temperature of 400°C, a GHSV of 20,000 hr⁻¹, and a switching time of 10 seconds. Premature flow reversal is attributed to the preheated reactor inlet temperature not being given ample time to travel across the catalyst before flow reversal. This premature flow reversal results in the elevated temperature being pushed outside the length of the catalyst, which lowers the overall reactor temperature and decreases CH₄ conversion. From Figure 37 the fully developed temperature profile associated with a RFR (see Figure 2.7(e)) at experimental run time $t = 840$ seconds is shifted away from the center of the catalyst length. As described before the loss of trapped heat across the catalyst directly correlates to a reduction in CH₄ conversion. Figure 38 is at a reactor furnace temperature of 400°C, a GHSV of 20,000 hr⁻¹, and a switching time of 30 seconds. Figure 38 illustrates that correctly timing the switching duration leads to a maximum temperature profile across the length of the catalyst. Comparison of the fully developed temperature profiles associated with a RFR in Figures 37 and 38 demonstrates the importance of selecting the proper switching time at a specific gas hourly space velocity and feed temperature.

Experimental results at a reactor furnace temperature of 450°C and a GHSV of 20,000 hr⁻¹ do not follow the trend of increasing CH₄ conversion as switching time increase. Figure 39 illustrates that CH₄ conversion is relative consistent across the entire range of switching times. This phenomenon is attributed to the chemical reaction for the dissociation of CH₄ falling into the diffusion limited regime of an Arrhenius plot, shown in Figure 40. The figure is an Arrhenius plot with the natural log of the apparent rate constant of the chemical reaction plotted against the inverse of temperature. The figure shows that once in the diffusion limited regime the chemical reaction approaches an asymptote where no amount of temperature increase will improve the chemical reaction rate constant. Figure 40 shows that varying switching time does not enhance CH₄ conversion due to the fact that all STs presented at a GHSV of 20,000 hr⁻¹ and a reactor furnace temperature of 450°C are limited to the time the chemical species has to diffuse to the surface of the catalyst and, therefore, CH₄ conversion is relatively constant across all STs presented. The time a chemical species has to diffuse to the surface of the catalyst is expressed as the residence time or the contact time. Table 8 lists all residence times for the RFOCR system at particular reactor furnace temperatures and gas

Figure 36 Effects of Switching Time on CH₄ Conversion with GHSV as a Parameter at a Temperature of 400°C

Figure 37 Temperature Profile Across the Catalyst at a Reactor Furnace Temperature of 400°C, a GHSV of 20,000 hr⁻¹, and a ST of 10s at Various Experimental Run Times

Figure 38 Temperature Profiles Across the Catalyst at Various Times During an Experimental Run at a Reactor Furnace Temperature of 400oC, GHSV of 20,000 hr-1, and a ST of 30s

Figure 39 Effects of Switching Time on CH₄ Conversion with GHSV as a Parameter at a Temperature of 450oC

Figure 40 Representations of Various Regimes on an Arrhenius Plot. Reprinted from Hayes and Kolaczowski [9]

Table 8 RFOCR Residence Times for the Total Exhaust Mixture at all Reactor Inlet Temperatures and GHSVs

Furnace Temperature	GHSV 20,000 hr ⁻¹	GHSV 40,000 hr ⁻¹	GHSV 60,000 hr ⁻¹	GHSV 80,000 hr ⁻¹
400°C	185 ms	93 ms	62 ms	46 ms
450°C	174 ms	86 ms	57 ms	43 ms
500°C	N/A	81 ms	54 ms	40 ms
550°C	N/A	76 ms	50 ms	38 ms
600°C	N/A	N/A	N/A	36 ms

Experimental results also confirm that maximum CH₄ conversion occurs at higher frequency switching times (10-20 seconds) for experiments at a GHSV of 40,000 hr⁻¹, with the exception of the experimental run at a reactor furnace temperature of 550°C. This trend of greater CH₄ conversions at switching times of 15 and 20 seconds at a GHSV of 40,000 hr⁻¹ can be seen in Figure 39. The loss in CH₄ conversion at lower frequency switching times (30 and 45 seconds) is attributed to a delayed switching. Similar to the preheated exhaust temperature being pushed out of the reactor due to premature flow reversal (as is the case for a ST of 10 seconds, a GHSV of 40,000 hr⁻¹, and a reactor furnace temperature of 400°C), the STs of 30 and 45 seconds at a GHSV of 40,000 hr⁻¹ experience an inability to trap elevated temperatures across the catalyst reactor due to delayed flow reversal. If the flow reversal is too low in frequency the elevated temperature is allowed to travel from one end of the catalyst to the other during flow reversal cycles without trapping a large amount of elevated temperature across the center of the catalyst. As a result of the delayed flow reversal a portion of the fully developed temperature profile

associated with a RFR is pushed outside the length of the catalyst. The development of the delayed flow reversal temperature profile at a reactor furnace temperature of 450°C, a GHSV of 40,000 hr⁻¹, and a ST of 45 seconds is illustrated in Figure 41. The figure shows an inability to trap the elevated temperature across the length of the catalyst resulting in a pseudo-unidirectional temperature profile during flow reversal, thereby reducing the overall temperature across the catalyst and lowering CH₄ conversion.

Methane conversion at a GHSV of 40,000 hr⁻¹ follows the general trend of producing the greatest CH₄ conversion at more frequent STs with the exception of the experiments at a reactor furnace temperature of 550°C (Figure 42). Experimental variations in the switching time had little effect on CH₄ conversion for experiments at a GHSV of 40,000 hr⁻¹ and reactor furnace temperature of 550°C. Figure 42 illustrates that the increase in CH₄ conversion is reasonably flat across the switching times of 10 to 45 seconds. As discussed before, this phenomenon is also attributed to the chemical reaction for the dissociation of CH₄ falling into the diffusion limited regime of an Arrhenius plot.

Figure 41 Temperature Profile at a Reactor Furnace Temperature of 450°C, GHSV of 40,000 hr⁻¹, and a ST of 45s at Various Experimental Run Times

Figure 42 Effects of Switching Time on CH₄ Conversion with GHSV as a Parameter at Temperature of 550°C

Methane conversion for experiments with flow reversal for GHSVs of 60,000 and 80,000 hr⁻¹ is similar to the trends presented for GHSVs of 40,000 hr⁻¹. Generally, higher frequency STs produced higher CH₄ conversions than that of the lower frequency STs for GHSVs of 60,000 and 80,000 hr⁻¹. GHSV of 60,000 hr⁻¹ shows a maximum CH₄ conversion at a ST of 20 seconds. As previously discussed, the lesser CH₄ conversions in the figure are attributed to either premature or delayed flow reversal, both of which lead to a decrease in the overall catalyst temperature and a reduction in CH₄ conversion. As in the case for a GHSV of 40,000 hr⁻¹ CH₄ conversion begins to become more constant across the range of switching times at a reactor furnace temperature of 550°C. This constant CH₄ conversion at a GHSV of 60,000 hr⁻¹ is attribute to the chemical reaction for the dissociation of CH₄ falling into the diffusion limited regime of an Arrhenius plot. Experiments with flow reversal at GHSVs of 80,000 hr⁻¹ consistently demonstrate that the greatest improvement in CH₄ conversion is at a switching time of 10 seconds. The decline in CH₄ conversion at lower frequency switching times is attributed to a delay in flow reversal resulting in a failure to trap a majority of the elevated temperature across the catalyst reactor.

Effect of Temperature and Gas Hourly Space Velocity on CH₄ Conversion

Experimental results indicate that CH₄ conversion continually improves with or without flow reversal as the reactor furnace temperature increases and as GHSV decreases. Figure 43 illustrates CH₄ conversions plotted against time with temperature as a parameter at a constant GHSV of 80,000 hr⁻¹ and at a switching time of 10 seconds. As previously discussed both figures are divided into three separate regimes: the unidirectional regime, the flow reversal regime, and the concluding unidirectional regime. Figure 43 shows CH₄ conversion increases in all regimes as temperature increases. This increase is due to the exponential effect of temperature on the dissociation of methane and may be seen in the Arrhenius rate law shown in Equation 7. The equation illustrates that as temperature increases the rate constant increase, which corresponds to an increase in CH₄ conversion.

Figure 43 Effects of Temperature on CH₄ Conversion with Temperature as a Parameter at a GHSV of 80,000 hr⁻¹ and a ST of 10s

$$k(T) = A \exp (-E_A/R_u T) \quad (7)$$

where, k = rate constant

A = pre-exponential factor

E_A = activation energy

R_u = universal gas constant

T = temperature

Furthermore, at relatively low reactor furnace temperatures CH₄ conversion only benefits modestly with flow reversal. This is attributed to a relatively low CH₄ conversion temperature across the catalyst, which produces a small amount of heat to be trapped, resulting in only slight improvements in CH₄ conversion due to flow reversal. This can be seen in Figure 43 at reactor furnace temperatures of 450°C. Conversely, the effect flow reversal has on enhancing CH₄ conversion diminishes as the temperature increases at relatively high reactor furnace temperatures. As previously discussed this is attributed to the chemical reaction of the dissociation of CH₄ falling into the diffusion limiting regime. In the diffusion limited regime the chemical reaction becomes dependent on the gas-phase diffusivity, which is only a weak function of temperature. An example of the diminishing effect on the increase of temperature with respect to flow reversal is shown in Figure 44.

Experimental results establish that GHSV can have a significant effect on CH₄ conversion. Figure 44 illustrates the effects of GHSV at a ST of 10 seconds with GHSV as a parameter across a reactor furnace temperature range. Figure 44 illustrates that as GHSV

increases CH₄ conversion decreases. This is due to residence time, or length of time a molecule spends in the catalyst reactor. As the GHSV is increased the amount of time a molecule spends in the catalyst reactor decreases. This decrease in residence time results in a lower CH₄ conversion due to the limited time the molecule has to diffuse to the surface of the catalyst.

Figure 44 Effects of Temperature on CH₄ Conversion with GHSV as a Parameter at a ST of 10s

Reverse-Flow Oxidation Catalyst Reactor With Supplemental Fuel Injection

Supplemental fuel is introduced into the RFOCR system to simulate fuel injection from a partial oxidation catalyst reactor at low engine load conditions. The supplemental fuel consists of a carbon monoxide and hydrogen mixture at a 3:1 ratio, respectively. This ratio is derived from the partial oxidation of methane and is described in Equation 8. Equation 9 describes the water-gas shift reaction, but due to equilibrium, Equation 4.4 does not proceed to completion. Furthermore, at typical exhaust temperatures (approximately 400°C) CO concentrations are three times that of H₂ concentrations for partial oxidation reactors; hence the 3:1 ratio of carbon-to-hydrogen used for supplemental fuel injection.

Two separate experimental runs with supplemental fuel injection were conducted to evaluate the effects of SFI on CH₄ conversion both with and without flow reversal at low engine load conditions. First, an experimental run was conducted solely with unidirectional flow operations to serve as a supplemental fuel injection baseline, with the total length of the run lasting 1200 seconds in duration. The second experimental run with SFI was conducted with flow reversal with a switching time of 20 seconds. This run with flow reversal is divided into three sections,

with the total length of the run also lasting 1200 seconds in duration. The first 300 seconds of the experimental run is conducted with unidirectional flow, followed by 600 seconds of exhaust mixture flow reversal, and concludes with 300 seconds of unidirectional flow. Both experimental runs introduce supplemental fuel into the exhaust mixture prior to the reactor catalyst at experimental run times of $t = 300$ seconds to $t = 800$ seconds. The total volumetric flowrate of the supplemental fuel introduced into the exhaust mixture is 350 cc/min at STP, which corresponds to an exhaust gas mixture concentration of 0.96% of carbon monoxide and 0.32% of hydrogen.

Effects of Supplemental Fuel Injection on CH₄ Conversion

Experimental results confirm introducing supplemental fuel into the RFOCR improves CH₄ conversion by elevating the temperature across the catalyst reactor through the combustion of carbon monoxide and hydrogen and is described by the chemical reactions in Equations 10 and 10.

Figure 45 illustrates CH₄ conversion during unidirectional flow operations with 25 10-second pulses of supplemental fuel injection, with a 10 second intermission between pulses at a reactor furnace temperature of 350°C and a GHSV of 20,000 hr⁻¹. From the figure CH₄ conversion is extremely low without supplemental fuel injection (1%), while the average CH₄ conversion increases considerably (10%) with supplemental fuel injection. This increase in CH₄ conversion is attributed to the increase in temperature due to the combustion of the supplemental fuel. This increase in catalyst temperature is illustrated in Figure 46. The temperature profile across the catalyst reactor is shown at various instance of time for the unidirectional flow experimental run. As previously discussed supplemental fuel was injected from an experimental run time of $t = 300$ seconds to $t = 800$ seconds, and it is clearly demonstrated from Figure 46 that the combustion of supplemental fuel corresponds to the increase in the temperature profile across the catalyst, thereby increasing CH₄ conversion.

The second experimental run with SFI incorporated flow reversal into the experimental run. The purpose of this experimental run is to investigate the effects of flow reversal on CH₄ conversion while introducing supplemental fuel into the catalyst reactor. In addition, supplemental fuel injection was introduced into the exhaust mixture from an experimental run time of $t = 310$ seconds to 810 seconds, while flow reversal continued for an additional 90 seconds after SFI was terminated. The purpose of continuing flow reversal is to examine the possibility of continuing prolonged durations of enhanced CH₄ conversion after terminating supplemental fuel injection.

Figure 45 Methane Conversion during Unidirectional Flow Operations with 25 10-Second Pulses of SFI, a Reactor Furnace Temperature of 350oC, and a GHSV of 20,000 hr-1

Figure 46 Temperature Profile across the Catalyst during Unidirectional Flow Operations at Various Instances of Time with 25 10-Second Pulses of SFI, a Reactor Furnace Temperature of 350oC and a GHSV of 20,000 hr-1

Experimental results demonstrate that CH_4 conversion is significantly enhanced with SFI and flow reversal. Figure 47 illustrates an experimental run conducted with flow reversal with 25 10-second pulses of supplemental fuel injection, with a 10 second intermission between fuel pulses at a reactor furnace temperature of 350°C , a GHSV of $20,000 \text{ hr}^{-1}$, and a ST of 20 seconds. From the figure CH_4 conversion without SFI or flow reversal is extremely low (2%), while the average CH_4 conversion is significantly increased with SFI and flow reversal (15%). This dramatic increase in CH_4 conversion is attributed to the increase in temperature across the catalyst due to the combustion of supplemental fuel and the trapping of heat across the catalyst due to flow reversal. Figure 48 illustrates the increase in the temperature profile across the length of the catalyst due to SFI and flow reversal at various times during the course of the experimental run. From Figure 48 the increase in CH_4 conversion during SFI and flow reversal is clearly attributed to the increase in temperature across the length of the catalyst. Furthermore, the temperature profile associated with reverse flow operations develops at an experimental run time of $t > 419$ seconds, but due to improperly timed flow reversal only a portion of the heat is trapped across the catalyst. As previously discussed, premature or delayed flow reversal causes a portion of the temperature profile associated with a reverse-flow reactor to be pushed outside the length of the catalyst. As a result of this premature or delayed flow reversal the temperature across the catalyst is lowered and CH_4 conversion suffers. Based on the results obtained for the RFOCR without supplemental fuel injection, properly timing flow reversal durations could increase CH_4 conversion, however the optimization of CH_4 conversion with respect to switching time with SFI is out of the scope of this study.

Figure 47 Methane Conversion with 25 10-Second Pulses of SFI, a Reactor Furnace Temperature of 350°C , a GHSV of $20,000 \text{ hr}^{-1}$, and a ST of 20s

Figure 48 Temperature Profile across the Catalyst at Various Instances of Time with 25 10-Second Pulses of SFI, a Reactor Furnace Temperature of 350oC and a GHSV of 20,000 hr-1

In addition to the examination of the effects of SFI with flow reversal on CH₄ conversion the possibility of continuing prolonged durations of enhanced CH₄ conversion after terminating supplemental fuel injection was investigated. Experimental results indicate that extended durations of increased CH₄ conversion due to flow reversal is not possible after the SFI pulses have concluded and this is shown in Figure 47. Figure 47 illustrates that CH₄ conversion substantially decreases after less than 20 seconds subsequent to SFI being terminated. This decrease in CH₄ conversion is attributed to a reduction in temperature across the reactor. Figure 49 demonstrates the decline in temperature across the catalyst during flow reversal after SFI is terminated. The high rate of reduction of temperature across the catalyst is attributed to an improperly timed switching duration, which pushes the trapped heat out of the length of the catalyst. As described before this reduction in temperature directly correlates to a reduction in CH₄ conversion. From the results obtained for the RFOCR without SFI CH₄ conversion could be maintained for longer durations after SFI is terminated if the switching time is properly. A table demonstrating the average CH₄ conversion for the SFI experimental runs both with and without flow reversal is shown in Table 9.

Comparing the two SFI experimental runs it is clear that flow reversal enhances CH₄ conversion when compared to the purely unidirectional flow experimental run. As previously described this increase in CH₄ conversion is attributed to the trapping of heat across the catalyst during flow reversal operations.

Figure 49 Temperature Profile across the Catalyst at Various Instances of Time with 25 10-Second Pulses of SFI, a Reactor Furnace Temperature of 350oC and a GHSV of 20,000 hr-1

Table 9 Average CH₄ Conversion With and Without SFI for Unidirectional Flow and Flow Reversal at a Reactor Furnace Temperature of 350oC, a GHSV of 20,000 hr-1, and a ST of 20s for Flow Reversal Operations

	Unidirectional Flow	Flow Reversal
Average CH ₄ conversion without SFI	1%	10%
Average CH ₄ conversion with SFI	2%	15%

Lean NO_x Trap Catalyst Reactor

The Lean NO_x Trap System (LNT) consists mainly of three components namely; Peristaltic Pump, Steam Generator System and the LNT Reactor. As mentioned earlier, the outputs from the MFC's have two paths, one through the steam generator to the LNT inlet manifold and the other directly to the LNT manifold. All components are connected by quarter inch stainless steel tubing and are insulated.

Ten monolith catalysts for the LNT were obtained from Emerachem. The catalyst has a cordierite substrate and alumina washcoat with Barium Oxide. The cell density of the catalyst is 300 cells/inch² and has 100g/ft³ of platinum. The catalyst is 3" long and 7/8" diameter. The catalyst was placed in a quartz tube which had a 1" OD and 7/8" ID. The catalyst is wrapped with glass wool to prevent the gas from flowing through the edges of the catalyst. The inlet side of the tube is fixed with 5mm beads, made of Pyrex, to maintain a uniform temperature through the catalyst. Temperature probes are placed at the inlet, the middle, and the exit of the catalyst to identify the temperature change across the catalyst. Two probes are fixed as close as 0.2" from the catalyst edges and are made sure that the probes do not touch the catalyst surface. One probe is fixed inside catalyst to measure the surface temperature at the middle. The tube furnace, manufactured by Lindberg, Model TF55035A-1, can reach a maximum temperature of 1100oC. The tubing from exit is wrapped with silicone rubber heating tape, produced by Omegalux, and insulated to insure through that the water vapor does not condense before reaching the analyzer.

The instrument panel, shown in Figure 50, houses three major components of the Bench Flow Reactor System. Mass flow controllers (MFC) control the exhaust gas mixture that is introduced to the BFR. The data acquisition system (DAC) interfaces the analyzer output signal with LabVIEW. The instrument panel also houses a number of displays. These displays represent the temperature and pressure of the exhaust gas at specific points across the BFR system. The data is also displayed in LabVIEW for easy data storage.

Figure 50 Instrument Panel (Front)

The Mass Flow Controllers (MFC) are used to control the flow of all the components of the simulated exhaust gases through the bench flow reactor. A MFC is used for each of the gas species used, which include Carbon Monoxide (CO), Oxides of Nitrogen (NO_x), Methane (CH₄), Hydrogen (H₂), Air, Nitrogen (N₂), and Carbon Dioxide (CO₂). MFC's require a 15 V DC power supply and are controlled by the LabVIEW software. Varying input voltages controls the MFC's flowrate output.

There are several different ranges for the MFC. The operating range for CO is 0 – 1 L/min. The operating range for NO_x, CH₄ and H₂ is 0 – 5 L/min and N₂ and CO₂ is 0 – 10 L/min. The operating range for air is the maximum in the BFR system, which is 0 – 20 L/min. All the Mass Flow Controllers are in a linear correspondence with a voltage range of 0 – 5 V. All the MFC's are calibrated by the manufacturer in terms of N₂ and so it is necessary to have a correction factor, called the K-factor, for the other gas species flowing through them. The concentrations of different gases that need to flow through the MFC are calculated keeping in mind the K-factor correction.

The MFC has a feedback system, which measures the difference between the user input and the actual output. The output from the MFC's for H₂, CH₄, NO_x, CO and air are combined into one flow manifold, which is controlled by a solenoid valve connected to LabVIEW. The output from the solenoid valve is sent either to the inlet of the BFR or directly to the exhaust gas analyzer (BFR system bypass). N₂ and CO₂ are combined into another manifold and is controlled by another solenoid valve. These two gases are then sent to the steam generator to sweep out water vapor or to the BFR system bypass line, directly to the gas analyzer.

The system includes 4 Cole Parmer pressure transducers, Model 68072 – 06, and 14 type-K Omega temperature thermocouples. These are connected to four pressure displays, Cole Parmer, Model 94785 – 00, and nine temperature displays, Omega, Model DP 18-KC1, that are housed in the cabinet. The other five temperature output can be displayed using a Omega, Model MDP – 18 single temperature scanner. The analog output from the pressure transducer is 4 to 20 mA and this is in linear correspondence with a pressure range of 0 to 50 psi. The temperature displays have a range of 0 – 1250oC. The three pressure transducers are placed at the following positions in the system:

- i. Inlet of the steam generator
- ii. Outlet of the oxidation catalyst
- iii. Outlet of the LNT

Out of 14 thermocouples for measuring the temperature, the Reverse-Flow Oxidation Catalyst System is using seven thermocouples. The remaining 7 are positioned as described below:

- i. Inlet of the steam generating furnace
- ii. Inlet of the steam generating furnace bypass
- iii. Inlet manifold of the LNT reactor
- iv. Near the entrance of the catalyst inside the LNT furnace

- v. Near the exit of the catalyst, inside the LNT furnace
- vi. Inlet of the preheater furnace
- vii. Outlet of the preheater furnace

There are two heating tape controllers (Model – XT16) mounted on the front side of the cabinet. This is used to control the two heating tapes, manufactured by Omega heavily insulated Samox, that are wrapped around the LNT furnace inlet manifold. The purpose of the heating tape is to maintain the temperature from dropping due to heat loss to the environment from the stainless steel tubing. The heating tape has a maximum range of 760°C.

There are three manual switches in the front of the cabinet to control the following:

- i. Analyzer bypass
- ii. Heating tape between steam generator and three-way valve
- iii. Heating tape between three-way valve and LNT inlet manifold

After the peristaltic pump injects the required amount of water into the BFR system, it is forced into the steam generator and is swept out by N₂ and CO₂. Both the inlet and outlet of the steam generator are sealed with copper gasket and stainless steel flange (1.75" ID and 2 3/16" OD). The flanges are assembled using a torque wrench to ensure there are no leaks in the steam generator portion of the BFR system. The steam generator has a wick strip inside to help the water from pooling in the tube. The stainless steel tubing can be heated up to 1010°C using a Lindberg heavy-duty tube furnace. A photograph of the steam generator is shown in Figure 51.

Figure 51 Steam Generator

Because of the high “light-off” temperature of methane (CH₄), the simulated NG exhaust gas is heated to a specified temperature and uniformly maintained in the preheater furnace manufactured by Inberg. Pyrex beads (5mm diameter), held in place by stainless steel mesh disks, and are placed inside a 22” long stainless steel pipe with a 1” ID. Due to the high temperature (~500°C) of the preheater, Pyrex was selected for its specific physical properties and working temperature of the glass beads. The purpose of the Pyrex beads is to assist in a uniform temperature increase of the exhaust gas.

Three pressure transducers are positioned in the BFR system to ensure there is no pressure loss or backpressure in the system. Cole Parmer pressure transducers are exclusively used in the BFR system. Pressure transducers are mounted at the steam generator bypass line and downstream of the NO_x absorbing and RF oxidation catalyst reactors. The purpose of positioning a pressure transducer inline of the steam generator bypass line is to assure that there is not a large pressure difference between the outlet of the steam generator and the steam generator bypass line. A pressure difference between the exhaust gases flowing through the steam generator and the steam generator bypass line runs the possibility of one of the exhaust gas lines to cease to flow. Pressure transducers located downstream of the two reactors are positioned to allow a pressure loss to be detected through the respective catalyst reactors.

Exhaust emission conversion efficiency is of primary concern for the BFR system, namely methane (CH₄) and nitric oxide (NO_x) conversion. In order to maximize conversion efficiency the exhaust gas must be analyzed for the species mixture concentration. This is accomplished via the Horiba analyzer bench. This bench, shown in Figure 52, consists of four analyzers, CO (Low)/CO₂ and CO (High) (AIA-220), Hydrocarbon (FIA-210), and NO_x (CLA-220). All analyzers are calibrated and utilized at standard range settings. Calibration and spanning procedures for each analyzer is strictly followed per protocol of Horiba Instruments.

Figure 52 Front Panel of Horiba Exhaust Gas Analyzer

Prior to each experimental run of the BFR, each analyzer is spanned for accuracy. Both the span gas and the inert gas (N₂) are fed through the gas divider and to the analyzer at various percentages of the span gas concentration. Full calibration of the analyzers is performed monthly, as per Horiba instruction.

Diesel Fuel Injection System

Direct Fuel Injection (DFI) system is added to the LNT system to compare the performance of the LNT regeneration with cycling lean and rich conditions in the main stream. As shown in Figure 53, the DFI system has four major components: a pressure regulator with pressure gage, piezoelectric valve, amplifier, and rotameter. The pressure of fuel was precisely regulated since the flow rate of fuel through the piezoelectric valve was strongly depending on the pressure. A small change of pressure during the experiment induces a large change in the amount of fuel injected. The amplifier was used to step up the voltage of the output signal from LabVIEW program to control the piezoelectric valve. The voltage range of the output signal from LabView is 0 to 5V, whereas the amplified voltage of output signal to the piezoelectric valve is 0 to 100V. The output signal is linearly proportional to the input signal. The Maxtek MV-112 piezoelectric valve is the main component of the DFI system; it regulates the precise amount of fuel to be injected into the LNT reactor. The response time of the piezoelectric valve is 2 milliseconds, which is fast enough to neglect time lag within the DFI system. Flow range of the valve is 0 to 0.5 L/min (LPM) at standard pressure, but it can be increased by operating at high pressure condition (max 3.447 bar or 50psi). To measure the fuel flow rate from the piezoelectric valve, a Dwyer rotameter was installed in the DFI system. The range of the rotameter is between 0 and 4.717 LPM.

Figure 53 Components of Fuel Injection System

Reactor Branching Valves

The BFR consists of three reactors, the LNT reactor, the LNT thermal aging reactor, and the Reverse-Flow Oxidation Catalyst Reactor (RFOCR). All reactors share the same components such as the instrument cabinet, peristaltic pump, and steam generator, which are located in the upstream of the reactor branching valves, as shown in Figure 3.2. Each particular reactor experiment must be run independently, and a valve system is devised to direct the gas flow only to the reactor that is being in operation. Due to the high operating temperature range ($140^{\circ}\text{C} \sim 350^{\circ}\text{C}$) of the simulated exhaust gases in the upstream of the reactors, three Swagelok high temperature bellow valves (SS-4BW) are employed for branching the flow, as shown in Figure 54. The maximum operational temperature of the valves is around 450°C .

Figure 54 Schematic of Bench-Flow Reactor System - Including Three-Way Branching Valve

LNT Experimental Procedure

Every experiment begins with the safety checkup of the exhaust fan and carbon monoxide detector in the laboratory. After the checkup, the first step of an experiment is started by switching on the main power of the BFR cabinet, computer installed with LabVIEW, analyzers, water condenser in the Horiba analyzer bench, and exhaust fan connected to the downstream of the Horiba analyzer bench. At the same time, Horiba and California NO_x analyzers require oxygen regulated at 0.9 bar (13 psig) and 1.72bar (25 psig) pressures to generate enough ozone inside for NO_x detection. Approximately, one hour of preheating time should be applying for

analyzers and the water condenser to be fully functional. Next, all gas bottles to be used in the experiment must be open and regulated to a supply pressure of 1.72 bar (25 psig), and the reactor branching valves must be lined-up for the LNT reactor. The outlet of the LNT reactor is to be connected to the inlet of Horiba analyzer bench and the power of the sample pump to be switched on. At the same instance, the MFC of N_2 is to be open with a certain flow rate to purge the BFR system and to stabilize desired analyzers for one hour before an actual experiment begins. The gas flow to appropriate analyzers can be selected by analyzer matrix switches, located on the front panel of the analyzer cabinet. During the time of the purgation, all heat components of the BFR system are switched on in order to reach a steady state temperature profile across the LNT reactor. In addition, a careful observation is required to not have a large pressure or vacuum develop across the BFR system when gases are presented by MFCs. A low pressure profile can be achieved by monitoring the pressure displays indicating before and after the LNT reactor and by regulating the pressure of the sample pump inside the analyzer bench.

Description of EmeraChem LNTs

Since the washcoat formulation of the LNT samples obtained from EmeraChem was unknown due to proprietary, three surface characterization techniques such as X-ray transmission electron microscope (TEM), X-ray diffraction (XRD) and Electron Probe Microanalysis (EPMA) were carried out to identify the formulation. XRD was used to identify the washcoat formulation and also to obtain average diameter of crystallites such as Pt, $BaCO_3$, $\gamma-Al_2O_3$ present in the washcoat. TEM was conducted to obtain Pt particle size distribution as well as to confirm the results obtained from XRD. On the other hand EPMA was performed to obtain concentration maps of Pt, Ce, Ba, and K and concentration profiles of elements (linescans) in LNT washcoat.

The average diameter of Pt, $\gamma-Al_2O_3$ and $BaCO_3$ crystallites in the fresh EmeraChem LNT sample was evaluated from the full-width at half-maximum (FWHM) of the corresponding peaks in the XRD spectra using the Scherrer equation. To avoid confusion only the highest peaks of the crystallites present in the LNT washcoat are labeled in XRD spectra shown in Figure 55. XRD peak for the Pt crystallites at $2\theta=39.76^\circ$, denoted as (o), is indiscernible in fresh LNT, which indicates that the average diameter of Pt crystallites was less than 2 nm -- the minimum size detected by XRD. The peak of $BaCO_3$, denoted as (•), at $2\theta = 24.09^\circ$ is observed to be highest in the spectra, and its average diameter of crystallite is calculated to be 48 nm. The spectral line at $2\theta = 66.6^\circ$, denoted as (♦), was assigned to $\gamma-Al_2O_3$, which is the dominant support in the washcoat. The average diameter of $\gamma-Al_2O_3$ crystallite is calculated to be 6 nm in fresh LNT. The peaks of CeO_2 , cerium mixed oxide, $KAl_2(Si_3Al)O_{10}(OH)_2$ and K_2O are observed at $2\theta = 28.5$, 29.41, 34.73 and 39.47° , respectively, and denoted as *, Δ , ∇ and ‡.

Figure 55 XRD Spectra of Fresh EmeraChem LNT

TEM image obtained from the powder of fresh EmeraChem is shown in Figure 56. The dark, relatively round objects in this image are Pt particles, and the image displays a rather wide distribution of Pt particle sizes. The diameters of most of Pt particles are found to be less than 2 nm, which are confirmed by the results obtained from XRD.

EPMA maps of elements present in the washcoat of fresh EmeraChem LNT are shown in Figure 57, while the linescan, which measures element concentration as a function of washcoat depth in the direction perpendicular to the washcoat, is shown in Figure 58. The back scatter image of Figure 57 (a) shows all possible elements present in fresh LNT, in which brighter spots in the image represent heavier atomic weight elements. The brighter spots appearing in the images of Figures 57 (b) to (e) are elemental maps of Pt, Ba, K and Ce, respectively. Linescans of Al and Si, shown in Figure 58, are used to identify the interface between the washcoat and substrate since Al and Si are the dominant elements in the γ -Al₂O₃ washcoat and the cordierite substrate, respectively. As seen in Figure 58 (b), Pt is not well dispersed in the washcoat with a thin layer of Pt particles observed at the top surface of the washcoat. It is not clear whether it was the intention of EmeraChem to deposit a layer of Pt particles on the top surface of the washcoat or it was due to a major manufacturing defect. Similarly, the low-temperature NO_x storage medium Ba is not well dispersed as can be seen in the form of agglomerations of Ba throughout the washcoat. On the other hand the high-temperature NO_x storage medium K was well dispersed in the washcoat of fresh EmeraChem LNT. The atomic fraction of K in the washcoat was ten times higher than Ba, as seen in the linescan of Figure 58. Negligible amount of Ce was detected in both EPMA map and linescan.

Figure 56 TEM Image of Pt particles in Fresh EmeraChem LNT with Magnification of 100,000 X

Figure 57 EPMA maps of (a) back scatter, (b) Pt, (c) Ba, (d) K and (e) Ce for fresh EmeraChem LNT

Figure 58 EPMA line scan for K, Ba, Pt, Ce, Al, and Si for fresh EmeraChem LNT

Therefore, the washcoat composition of EmeraChem LNT was identified with XRD, TEM, and EPMA. It consists of Pt, the precious metal component (PM), and two NO_x storage media of Ba and K, impregnated in γ -Al₂O₃ washcoat. In addition, a larger amount of K—the high-temperature NO_x storage component—was incorporated in the washcoat than Ba—the low-temperature NO_x storage media—in the EmeraChem LNTs.

Absorption Isotherm Experiment

A series of isothermal absorption experiment were carried out at different temperatures and gas hourly space velocities (GHSV) in order to investigate the effect of temperature and GHSV on the NO_x trapping capacity of EmeraChem LNT catalysts. From the isothermal absorption experiments the optimum operating temperature of the EmeraChem LNT catalysts can be determined. Consequently, experiments were conducted at three different gas hourly space-velocities of 25,000, 50,000, and 75,000 hr⁻¹ and five temperatures of 250, 300, 350, 400 and 500 °C. All experiments were performed at a concentration of 500 ppm NO with the composition of lean and rich excursions shown in Table 10. The rich excursion was used only to restore the original trapping capacity of the LNT at the end of the isothermal absorption experiments.

A typical absorption isotherm at 300°C and a GHSV of 25,000 hr⁻¹ is shown in Figure 59, in which the outlet concentration of NO_x is plotted versus time. For discussion purposes this concentration profile can be conveniently divided into three separate stages. The first stage, which lasts approximately 400s for this particular experiment, no NO_x is observed at the exit of the LNT catalyst, which indicates that the inlet NO_x has been completely trapped on the surface of the LNT. This is one of the primary attractions of the LNT technology for NO_x emission control applications in lean-burn engines. At the end of the first stage breakthrough or NO_x slip begins, and in the second stage rapid uptake of NO_x occurs. In the absorption isotherm experiment illustrated by Figure 4.5, this second stage lasts approximately from 400 to 2500s. As the NO_x storage sites are gradually filled up, the rate of NO_x trapping decreases, which leads to a slower NO_x uptake in the third stage. This later stage can last for a period of time; for this particular experiment the duration of the third stage is approximately 6500s. At the end of the third stage, the LNT is regenerated by subjecting to a rich excursion of 100s in duration. The rich

excursion with composition given in Table 10, consisting of 1.33% H₂ and 4.0% of CO, induces NO_x release as indicated by a sharp NO_x spike in Figure 59, and subsequent reduction to N₂. As a result of the rich excursion the LNT has been restored to restore its original trapping capacity.

Results obtained for other absorption isotherms at a GHSV of 25,000 hr⁻¹ are shown in Figure 60. Absorption isotherms at GHSVs of 50,000 and 75,000 hr⁻¹ are shown in Figures 61 and 62, respectively. As seen in these figures the absorption isotherms are qualitative similar at all GHSVs investigated in the present study. In addition, at any given GHSV the breakthrough or NO_x slip and the time to reach saturation occur much earlier for the absorption isotherms at 250 and 500C. The reasons for the discrepancies between isotherms at 250 and 500C and at other temperatures will be discussed later.

Table 10 Gas Composition Used in Isothermal Absorption and Regeneration Experiments

Gas	Fuel Lean	Fuel Rich
NO (ppm)	500	500
CO ₂ (%)	5	5
CO (ppm)	0	40,000
H ₂ (ppm)	0	13,333
O ₂ (%)	10	0
H ₂ O (%)	10	10
Lambda	2.07	0.89

Figure 59 NO_x concentration versus time at a temperature of 350 °C and a

Figure 60 NOx concentration versus time at various temperature and

Figure 61 NOx concentration versus time at various temperature and

Figure 62 NOx concentration versus time at various temperature and 500 ppm of inlet NOx concentration at SV=75,000h-1

Typical temperature and NOx concentration histories during the regeneration phase of absorption isotherm experiment performed at 400 °C and a GHSV of 25,000 hr⁻¹ are shown in Figure 63. The fuel rich excursion consisting of 1.33% of H₂ and 4% of CO was used to reduce NOx to N₂. Since the reduction reactions are highly exothermic, the maximum temperature always occurs inside the LNT during the generation phase as can be seen in Figure 63. In this particular isothermal absorption experiment an increase of 130 °C in catalyst temperature is observed. No significant temperature change is seen for the gas phase at the inlet, which indicates that gas-phase reactions are insignificant. On the other hand due to the heat transfer from the catalyst, the exit temperature of the gas phase has increased approximately 100 °C. The increase in the exit temperature of the gas phase always lags behind the increase in catalyst temperature. Since the NOx analyzer was set in the range of 0 to 1000 ppm, any NOx excursion above 1000 ppm was recorded as a straight line. As can also be seen in Figure 61 the rich excursion has successfully recovered all of the original NOx trapping capacity of the LNT.

Figure 63 Temperature and NOx concentration histories during regeneration phase of absorption isotherm performed at 400 °C and GHSV of 25,000 hr⁻¹

NOx Storage Capacity of LNT

From the isothermal absorption experiments the NOx storage capacity as a function of temperature is obtained. The area enclosed by the inlet and the outlet NOx concentration profiles is proportional to the amount of NOx absorbed by the catalyst during the fuel-lean condition, as shown in Figure 64. The area under the outlet NOx concentration profile is numerically integrated using Matlab, and from which the amount of NOx absorbed during the fuel-lean condition is estimated by the following equation.

Amount of NOx Stored [ppm.s]

$$= \text{Amount of NOx Injected} - \text{Amount of NOx Released}$$

The volumetric flow rate is used to convert from [ppm of NOx .s] to [L of NOx], then ideal gas law is applied to convert from [L of NOx] to [mole of NOx].

$$N = PV / RT,$$

where N= mole number of NOx, P= pressure, V= volume, R= universal gas constant, and T= temperature

Finally, NOx storage capacity per gram of catalyst is obtained by dividing moles of stored NOx by the weight of the LNT catalyst.

Figure 64 Area of NOx storage obtained from the plot of NOx outlet concentration versus time

The effect of temperature and GHSV on the NOx storage capacity of EmeraChem LNTs is shown in Tables 11 through 13 and plotted in Figure 65. As seen in Figure 65 at a given GHSV the NOx storage capacity exhibits a volcano-type dependence on the temperature, with a maximum in storage capacity of 3.2×10^{-3} gmol NOx/g catalyst occurring at 350°C. As discussed previously the NOx storage capacity below 350 is limited by chemical kinetics; on the other hand the decrease in the NOx storage capacity at temperatures above 350 is due to equilibrium-limited. proportional to GHSV because the resident time of NOx molecules to be stored decreases as the GHSV increases. Based on the results of the present study the optimum operating temperature for the EmeraChem LNT is 350°C at all GHSVs investigated.

Table 11 NOx Storage Capacities at 25,000hr-1

Temperature, C	NOx Storage, mol/g
250	0.0223
300	0.0283
350	0.0323
400	0.0312
500	0.0084

Table 12 NOx Storage Capacities at 50,000hr-1

Temperature (C)	NOx Storage.(mol/g)
250	0.015
300	0.0172
350	0.0191
400	0.0182
500	0.0082

Table 13 NOx Storage Capacities at 75,000hr-1

Temperature (C)	NOx Storage (mol/g)
250	0.0135
300	0.0165
350	0.0174
400	0.0166
500	0.0073

Figure 65 NOx storage capacity as a function of temperature and GHSV

Breakthrough Time

In the present investigation breakthrough time is defined as the time at which the concentration of NO_x in the simulated exhaust gas starts to increase, i.e., the onset of NO_x slip. The effect of temperature and GHSV on the breakthrough time are summarized in Tables 14 through 16 and are plotted in Figure 66. Similar to the NO_x storage capacity the breakthrough time exhibits a similar volcano-type dependence on the temperature, and a maximum in breakthrough time occurs at a temperature of 400 °C for all three different GHSVs investigated in the present study. However, the temperature at which the maximum breakthrough times occur is approximately 50 °C higher than the temperature at which the maximum NO_x storage occurs. In order to confirm the repeatability of the data two sets of breakthrough time experiments were conducted at a GHSV of 25,000 hr⁻¹, and the difference in the breakthrough time is within the experimental error.

Table 14. Breakthrough Time at 25,000hr⁻¹

Temperature, C°	Breakthrough Time, s	Second, s	Third, s
250	164.5	151.05	160.55
300	213.6	225	200
325	234	-	-
350	254.2	251.6	245.55
400	262.5	268.85	250.3
500	162.9	158.55	156.55

Table 15. Breakthrough Time at 50,000hr⁻¹

Temperature, C°	Breakthrough Time, s
250	28.4
300	50.9
350	63.4
400	66.8
500	24.8

Table 16. Breakthrough Time at 75,000hr-1

Temperature, C°	Breakthrough Time, s
250	20
300	31.05
350	36.6
400	42
500	12

Figure 66 Breakthrough time as a function of temperature and gas hourly space-velocity

Ratio of NO₂ to NO

The most important role of precious metal during the storage process is to oxidize NO to NO₂, which in turn is stored in the storage compound in the form of nitrates. Consequently the NO_x storage capacity of LNT is strongly depending on NO₂ conversion on Pt sites. The effect of temperature on the ratio of NO₂ to NO obtained from the isothermal absorption experiment performed at a GHSV of 75,000 hr⁻¹ is shown in Figure 66. The curve exhibits a volcano-shape dependency on the temperature with a maximum NO₂ /NO occurring at 400 . Chemical equilibrium between NO and NO₂ shows that NO₂ is the dominant species below 220 , and the amount of NO₂ decreases with increasing temperature. The result suggests that NO oxidation is kinetically limited below 400 , after that, the oxidation reaction is suppressed by NO₂ equilibrium. Since the maximum NO_x storage of EmeraChem LNTs was found to occur at 350 , the difference between temperatures for the maximum NO_x storage capacity and NO oxidation must be possibly due to the instability of nitrite or nitrate compounds above 400 .

Figure 67 Ratio of NO₂ to NO outlet concentration during absorption isotherm experiments performed at a GHSV of 75,000 hr⁻¹ and equilibrium ratio

Desorption Experiment

There are two primary mechanisms of NO_x desorption from the LNT surface. The first mechanism is thermal in nature in which NO_x is desorbed due to the exothermic oxidation of the reductants by O₂, either in the gas stream or absorbed on the LNT surface. As the temperature of the catalyst increases NO_x is released, since the stability of nitrates decreases with an increase in temperature. In the second mechanism NO_x is desorbed in the absence of O₂ in the gas stream. Since the trapping of NO_x is driven by equilibrium, the stability of nitrites species is significantly reduced. Thus, the shutting off of O₂ in the gas stream will provide a driving force for the decomposition of nitrate species with subsequent release of NO_x from the LNT surface. The second mechanism is predominant in the regeneration phase in which rich excursion is introduced, resulting in a net reducing environment. The NO_x desorption experiments were conducted at two different temperatures of 350 and 500 °C and at a GHSV of 25,000 hr⁻¹ in which the flow of O₂ and NO_x shut off at the end of the NO_x absorption period. The primary objective of the desorption experiment is to ascertain the thermal nature of the NO_x desorption mechanism. As shown in Figures 68 and 69, LNT catalysts in both experiments are fully saturated after 8000 s, and immediately after which the flows O₂ and NO_x are shut off around 9000 s. As can be seen in Figures 68 and 69 NO_x desorption is greater at 500 °C than 350 °C, and the result suggests that more NO_x is desorbed at higher temperature due to the higher decomposition rate of nitrite or nitrate compounds.

Figure 68 Desorption experiment performed at T = 350C and GHSV = 25,000 hr-1

Figure 69 Desorption experiment performed at T = 500 and GHSV = 25,000 hr-1

Cycling Lean and Rich Condition in Main Stream

The effects of lean and rich duration and reductant species on the regeneration of the LNT catalyst were investigated at an operating temperature of 350 °C and a space velocity of 50,000 hr⁻¹. The operating temperature was selected to be 350 °C since the catalyst was determined previously to have a maximum NOx storage capacity at that temperature. The experiments were performed for two different cases. In the first case, the time duration of the lean and rich phases were varied at a fixed concentration of CO and H₂. In the second case, the reductant concentrations-- CO and

H₂ -- were varied at constant time duration of the lean and the rich phases. The objectives of the first case are to investigate the effect of time duration of fuel lean and rich on the performance of the LNT catalyst and to determine the optimum time durations to regenerate the LNT catalyst with the minimum amount of reductants. On the other hand, the objective of second case is to investigate the effect of the reductant concentrations on the NO_x conversion efficiency using the optimum time durations obtained from the first case.

Varying Time Duration

Three different lean/rich cycles-- 50s lean and 10s rich, 50s lean and 5s rich, and 100s lean and 5s rich-- were selected to investigate the effect of lean and rich durations on the NO_x conversion of the EmeraChem LNT catalysts. The rich phase of the three investigated cycles consists of 4% CO and 1.33% H₂. As seen in Figures 70, 71 and 72, more than 99.9% NO_x conversion is obtained for the first two lean/rich cycles, whereas the NO_x conversion decreases to 93.3% for the last cycle. Since there is not much difference in NO_x conversion between the three different lean/rich cycles, a lean/rich cycle of 100s lean and 5s rich hereafter is selected since this cycle would offer the best fuel efficiency in regenerating the LNT catalysts.

Figure 70 NO_x Conversion versus time with 500ppm of NO_x inlet concentration (50s lean and 10s rich, CO=4%, H₂=1.33%, T=350C, SV=50K)

Figure 71 NOx Conversion versus time with 500ppm of NOx inlet concentration (50s lean and 5s rich, CO=4%, H2=1.33%, T=350C, SV=50K)

Figure 72 NOx Conversion versus time with 500ppm of NOx inlet concentration (100s lean and 5s rich, CO=4%, H2=1.33%, T=350C, SV=50K)

Varying the Concentration of Reductant

Experiments were performed at 350 C, the optimum operating temperature of the EmeraChem LNT catalyst, using two different concentrations of the reductants in the regeneration phase. One composition of the rich pulse consists of 4% and 1.33% H₂, while the other 2% CO and 0.67% H₂. COductants at the optimum time durations of 100s lean and 5s rich. Results are shown in Figures 73 to 75. The NO_x and CO conversion efficiencies are listed in Table 17. As seen in Table 17, it is apparent that H₂ is a slightly better reductant in reducing NO_x than CO.

Table 17 Result of Cycling 100sec lean and 5sec rich experiment with T=350 C and SV=50,000hr-1

Reductants	NO _x Conversion (%)	CO Conversion (%)	Temperature excursion during fuel rich (C)
4% CO & 1.33% H ₂	93.2	97.5	32.6
2% CO & 0.67% H ₂	90.9	100.0	33.7
4% H ₂	99.4	-	30.3
4% CO	97.7	98.7	34.3

Figure 73 NO_x Conversion versus time with 500ppm of NO_x inlet concentration (100s lean and 5s rich, CO=2%, H₂=0.67%, T=350C, SV=50K)

Figure 74 NOx Conversion versus time with 500ppm of NOx inlet concentration (100s lean and 5s rich, CO = 4%, T=350C, SV=50K)

Figure 75 NOx Conversion versus time with 500ppm of NOx inlet concentration (100s lean and 5s rich, H2 = 4%, T=350C, SV=50K)

Direct Fuel Injection (DFI)

Two separate DFI experiments were carried out: direct fuel injection in the absence and presence of oxygen in the simulated exhaust gases. These two types of experiments were used to simulate two different scenarios in which the rich excursions are generated in the operation of lean-burn natural gas engines. In the first scenario, the rich excursions are produced by running the engines under stoichiometric or rich conditions for a very short period. On the other hand in the second scenario the rich excursions are generated by injecting the reductants directly into the lean exhaust gases.

To duplicate the first scenario, at the beginning of the rich phase, oxygen was shut off and the reductant, either H₂ or CO, was directly injected into the reactor gas stream. In the second scenario, the rich excursions are generated by injecting the reductant into the lean exhaust gas stream. Both experiments were performed at the optimum operating temperature of 350 °C and a space velocity of 50,000 hr⁻¹ with an optimum lean/rich cycle of 100s lean and 5s rich.

Tables Figures 76 and 77 show the effect of the concentration of reductant species on the NO_x concentration profiles at the exit of the LNT catalysts with and without the presence of O₂. CO and H₂ were selected as the reductants, and the results are listed in Table 18 and 19. As seen in Figure 76, at a concentration of 2% CO the amount of NO_x slip at the end of the lean phase and the NO_x excursion at the end of the rich phase increase with each successive cycle. The NO_x conversion decreases significantly in the presence of oxygen in the fuel-rich condition. The results suggest that the reductant was consumed by directly reacting with oxygen rather than by the reduction reactions. The exothermic oxidation reaction results in an increase of 52.8 °C in the catalyst temperature (4% CO injection with O₂). Further observation of the results indicates that the NO_x conversion efficiency when injecting 4% CO in the absence of oxygen is less than that in cycling experiment with 4% CO. But the NO_x conversion efficiency was found to be the same for both direct injection and cycling experiment with 4% H₂. It was observed that H₂ was the best reductant for both LNT regeneration methods. In addition, the direct injection of H₂ as the reductant was slightly better than the lean / rich cycling method. Results of Direct Fuel Injection with both CO and H₂ as reductants at different concentrations for two different cases - with and without oxygen in the simulated exhaust gases, are shown in Tables 76-79.

Table 18 Results from Direct Fuel Injection Without O₂ (100s lean /5s rich cycle at T=350C & SV=50K)

Reductant	NO _x Conversion (%)	CO Conversion (%)	Mid Temp Jump (C)
2% CO injection	84.0	99.2	22.1
3% CO injection	92.3	98.0	22.1
4% CO injection	92.0	96.6	24.4
2% H ₂ injection	90.5	-	22.7
3% H ₂ injection	99.3	-	25.6
4% H ₂ injection	99.6	-	27.9

Table 19 Result from Direct Fuel Injection With O₂ (5s rich & 100s lean at T=350C & SV=50K)

Reductants	NO _x Conversion (%)	CO Conversion (%)	Mid Temp Jump (C)
2% CO injection with O ₂	56.0	99.6	22.7
3% CO injection with O ₂	56.4	99.7	36.1
4% CO injection with O ₂	53.3	99.8	52.8
2% H ₂ injection with O ₂	56.2	-	14
3% H ₂ injection with O ₂	56.7	-	26.2
4% H ₂ injection with O ₂	58.1	-	40.1

Figure 76 NO_x Conversion versus time for various CO injections using DFI in the absence of O₂ with 500ppm of NO_x inlet concentration (100s lean and 5s rich, T=350C, GHSV=50,000 hr⁻¹)

Figure 77 NOx Conversion versus time for various H2 injections using DFI with 500ppm of NOx inlet concentration (100s lean and 5s rich without oxygen, T=350C, SV=50K)

Figure 78 NOx Conversion versus time for various CO injections using DFI with 500ppm of NOx inlet concentration (100s lean and 5s rich with oxygen, T=350C, and SV=50K)

Figure 79 NOx Conversion versus time for various H2 injections using DFI with 500ppm of NOx inlet concentration (100s lean and 5s rich with oxygen, T=350C, SV=50K)

Conceptual Design of a Partial Flow LNT Regeneration and Gas Divider System Review

System Concept

The difficulties of using methane as a reductant in LNT strategies necessitates the development of a NO_x reduction catalyst coupled with an oxidation catalyst in a system capable of maintaining a high reaction temperature. A possible solution of maintaining a high reaction temperature in the converter is to use a reversing flow catalytic converter, which is capable of maintaining temperatures superior to the adiabatic temperature rise. Periodic flow reversal oxidation is a heat trap that performs active heat recovery on the top of the heat retention capability of the catalyst bed. The conception of the catalyst with reciprocating flow was discussed theoretically and verified experimentally[1, 3-6], but the problem of the deep investigation of more appropriate operational regimes of the such kind of reciprocating system over a broad range of conditions is not solved yet. The idea of the reversing flow catalyst is quite simple. The feed is periodically switched between the two ends of the catalytic converter. The operation of the reverse flow catalytic converter is controlled using valves, as shown schematically in the Fig. 80.

Figure 80 Schematic of rotating gas divider

In the Figure 80 (a) the control valves 1 & 4 are opened and engine exhaust flows to the catalytic converter from left to right (forward flow mode). In Figure 80 (b) the control valves 2 & 3 are opened and engine exhaust flows to the catalytic converter from right to left (reverse flow mode). Total time of the cycle equals to the sum of the times of the forward and reverse mode.

Such a concept provides a heat trap effect that can be used to achieve and maintain an enhanced reactor temperature as compared to a single direction flow mode operation. Figure 81 (a) illustrates a reactor temperature profile that might be observed in conventional unidirectional flow operation due to exothermic reaction. The temperature initially rises slowly as the reaction commence, and then more sharply as the heat released in the reaction accelerates the rate owing to the exponential temperature dependence of the rate constant. If the temperature pattern is established (Figure 81 (b)), the reverse mode can be used to take advantage of the high temperatures near the exit top rehear the reactor feed. During the the reverse mode the energy, stored in the catalytic converter during the forward mode, is effectively used to preheat the feed, that provides the opportunity to achieve the temperatures higher than the adiabatic temperature rise, based on the fresh feed inlet temperature. Depending on the duration of the modes one can achieve the autothermal converter operation at feed temperatures below those required for autothermal operation with unidirectional flow. In such a case, a quasi-steady –state operation may be achieved in which the reactor temperature profile has maximum near the center of the reactor (Figure 81 (e)).

Figure 81 The heat trap effect for reverse flow catalytic converter (a, b – forward mode; c, d – reverse mode, e - temperature profile at the quasi-steady-state)

Four-Way Single Diversion Valve Conceptual Schematic and Operation

The four-valve arrangement shown in Figure 80 may prove to be a less favorable system for vehicle installations. Because it is reasonable to expect a high level of leakage of exhaust gases with the current industrial shut-off valves, alternative design concepts had also been proposed to use rotary catalyst substrates [8]. Although the integrated design set forth in traditional rotary design was a conceptual improvement, the complication involved inhibited its use in automotive applications. An improved method [5] that combines both previous concepts is a “four-way single valve” system shown in the Figure 82.

Figure 82 Four-way single valve system: (a) - forward mode; (b) reverse mode

The advantages of this conceptual scheme are a relatively simple design, the opportunity to minimize the leakage, and it requires a small operational torque, which is required for the valve's rotor rotation. The reverse flow catalyst mechanism (PRFCM), showed in Fig. 82 consists from three main systems, a catalytic converter (CC), four-way single diversion valve (FWSDV) and exhaust pipe system (EPS).

As was discussed before, the FWSDV seems to be an attractive option for the reverse flow catalyst design. The conceptual schematic of the FWSDV handles the reverse flow with two cylinders organized in a rotor (inner cylinder) and stator (outer cylinder) configuration. The stator has four openings arranged at right angles. The four fixed path options are the exhaust gas inlet from the LNT; to/from the oxidation catalyst and a system outlet. The rotor, which sits inside the stator acts as a divider to direct the flow of the exhaust gas. The rotor also has four path options. However, a divider plate placed across the middle separates the rotor in half. Furthermore there are four perforated openings each machined between a regular opening. In total, each side of the divider has two openings and two perforated openings alternating with each other. With the rotor placed inside the stator and with no offset, exhaust gas can enter from the LNT and is directed into the oxidation catalyst. As it exits the oxidation catalyst it re-enters the other side of the stator/rotor assembly and is directed out of the system as treated exhaust. A close-up view can be seen in Figure 83.

Figure 83 Exploded View of the Stator and Rotor Assembly

As the rotor is rotated, the flow directions are reversed and the oxidation exit becomes the entrance. The perforated openings provide a smooth transition period from forward and backward flow modes, minimizing the back pressure during the mode switching. At the same time, they prevent the leakage of the gases between the neighbor openings of the stator. To further prevent leakage, the gap between the rotor and stator walls will be minimized, yet have low enough friction to provide a smooth transition. The system can be operated in two modes, the rotor can rotate in only one direction (unidirectional) or back and forth (bidirectional). A detailed explanation of each is described in the next section.

Unidirectional Rotation

The total cycle of the RFC can be represented in two steady-state flow modes and transient transitional modes. Starting with no offset (0 degree), exhaust enters the assembly from the LNT and is directed to the entrance of the oxidation catalyst. This mode can be represented as Mode A. After some operation time period, the exit of the catalyst substrate is heated due to chemical reactions. At this time, the rotor is rotated to direct the LNT exhaust into the exit of the oxidation catalyst. The total motion for this operation requires that the rotor be rotated 90 degrees. During this rotation, a perforation in the rotor wall allows some exhaust to enter the rotor/stator assembly. This “slip” of exhaust is designed to reduce the back pressure effect on the engine. This transition period can be represented as Mode B. After the rotor is rotated 90 degrees, the exhaust from the LNT is now directed into the exit of the oxidation catalyst where it momentarily utilizes the reversed thermal profile to increase the catalytic reaction. This steady-state mode is represented as Mode C. As the temperature profile inside the catalyst returns to a normal profile, the rotor is again rotated another 90 degrees through a second perforation. This transient mode is represented as Mode D. As the rotor travels towards 360 degrees total rotation, the system returns to Mode A with no rotor/stator offset. A diagram of this action is represented in Figure 84. Figure 85 shows the predicted flow rate through the system for each mode.

Figure 84 Four-Way Single Diversion Valve Conceptual Schematic with Unidirectional Rotation

Figure 85 Flow Rate/Rotation Diagram for Four-Way Single Diversion Valve with Unidirectional Rotation

Multidirectional rotation

In addition to the unidirectional rotation option of the FWSDV, a multidirectional operation can be used. It differs from the previous option in that the rotor would rotate in two directions. When compared to the unidirectional method, the operation of Modes A, B, and C are the same. However at the end of Mode C, instead of rotating in the same direction towards Mode D, the rotor will reverse direction and travel back through the perforated Mode B to Mode A. For comparison Mode D can re-represented as Mode B'. A diagram of the operation can be seen in Figure 86 and a diagram of the flow rate effects can be seen in Figure 87.

Figure 86 Four-Way Single Diversion Valve Conceptual Schematic with Multidirectional Rotation

Figure 87 Flow Rate/Rotation Diagram for Four-Way Single Diversion Valve with Multi-directional Rotation

Conceptual Design of a Partial Flow LNT Regeneration and Gas Divider System Progress

Estimation of the Main Dimensions of the Periodical Reverse Flow Catalyst Mechanism

Catalyst Space Velocity Calculation

The Space Shared Lean NO_x Trap and Reverse Flow Catalyst Mechanism should be sized for the testing with CG-280 natural gas engine that has the exhaust parameters shown in Table system: There are several oxidation catalysts available for various applications but studies and experiments show that the Palladium catalyst has high conversion ratio for methane. Refer [3] Palladium catalyst with alumina wash coat is recommended for methane oxidation. The standard size of 9.5 inches diameter and 6 inches length of Palladium catalyst is used and the space velocity for this kind of catalyst equals 50,000 hr⁻¹. So, the standard residence time for the entire catalyst brick could be calculated as:

$$T_{rs} = 1 / 50,000 = 0.00002 \text{ hr}$$

Table 20 Natural Gas Engine Exhaust Parameters

			Rated Power	Peak Torque
Exhaust gas flow rate	V_e	Liter/sec	817	539
Exhaust gas temperature	T_e	$^{\circ}\text{C}$	643	587
Exhaust pipe diameter	D_e	Inches	4	4

The original space velocity of the system with the mentioned catalyst brick could be calculated for rated power as:

$$SV_{643} = V_e / V_c = 422,235.95 \text{ hr}^{-1}$$

Where, V_c is the catalyst volume; SV_{643} is the space velocity for outlet gas temperature condition.

Recalculating the original space velocity at standard temperature (25°C) yields:

$$SV_{25} = SV_{643} / (\rho_{25} / \rho_{643}) = SV_{643} / (916.15 \text{ K} / 298.15 \text{ K}) = 137,410.8 \text{ hr}^{-1}$$

The original residence time could be calculated as $1 / 137,410.8 \text{ hr}^{-1} = 0.000007277 \text{ hr}$, that is less than standard residence time for the existing catalyst brick of 0.00002 hr . However with an arrangement of two catalysts in line, the original space velocity equals to:

$$SV_{25(2)} = SV_{25} / 2 = 68,705.4 \text{ hr}^{-1}$$

and original residence time equals to:

$$T_{ro} = 1 / 68,705.4 \text{ hr}^{-1} = 0.0000145549 \text{ hr}$$

This is more than the standard residence time for two catalysts bricks arranged in line at 0.00001 hr .

Calculations at peak torque conditions demonstrate the following results:

$$SV_{643} = V_e / V_c = 278,563.17 \text{ hr}^{-1},$$

$$SV_{25} = SV_{643} / (\rho_{25} / \rho_{587}) = SV_{643} / (860.15 \text{ K} / 298.15 \text{ K}) = 96,559.038 \text{ hr}^{-1}$$

The original residence time could be calculated as $1 / 96,559.038 \text{ hr}^{-1} = 0.000010356 \text{ hr}$, which is less than standard residence time for the existing catalyst brick.

For two bricks in line:

$$SV_{25(2)} = SV_{25} / 2 = 48,279.519 \text{ hr}^{-1}$$

and the original residence time equals to:

$$T_{ro} = 1 / 48,279.519 \text{ hr}^{-1} = 0.0000207127 \text{ hr},$$

This again is more than standard residence time for two catalysts breaks arranged in line at 0.00001 hr.

In conclusion, calculations show that two 6" × 9 1/2" catalyst breaks could provide the appropriate CH₄ oxidation for both rated power and peak torque conditions.

Calculation of the Dimensions of the Rotor and Stator Openings

As shown in the Fig. 83, the FWSDV is required to have four manifolds. An engine of this rating usually requires four inch exhaust piping. Taking this in to consideration, it can be expected that the FWSDV diameter could reach up to 14-15 inches. In order to decrease the diameter of the FWSDV two approaches were considered:

- i. to decrease the area of the openings in two times
- ii. to switch the round shape of the openings to the elliptical one.

The cross section area of the engine's 4-inch exhaust manifold equals to 81,032 cm². With the maximum exhaust gas velocity at rated power, the maximum exhaust flow rate can be calculated to be could be estimated at rated power regime (that corresponds to the maximum flow rate of the exhaust gases) exhaust gas flow rate as:

$$\text{liters/sec} / 0.81032 \text{ dm}^2 = 100.8 \text{ m/s}$$

Following the first approach, the cross section area of the valve's manifolds should be roughly of 40.5 cm² that corresponds to the diameter of the round opening of 7.2 cm. The ellipse with the same cross section area could have the following dimensions of the axes: 10.8 cm and 4.8 cm. The velocity of the exhaust gases through the existing elliptical opening will be of 201.6 m/s. The FWSDV rotor has four perforated openings (Fig. 83). As will be shown later each perforated

opening consists of 43 round holes with diameter of 0.8 cm. So exhaust gas velocity could be calculated as:

$$V_{exh} = 812 \text{ liters/sec} \times 4 / (3.14 \times 0.08^2 \text{ dm}^2 \times 43) = 375.87 \text{ m/s}$$

Thermodynamic calculations of the fuel-lean combustion of natural gas and air with an equivalence ratio of 1.7 were performed in order to estimate the velocity of sound in the exhaust gases and compared with the calculated velocity of the gases that pass through the perforated opening. The following conditions were used for the estimation of the sound velocity:

Temperature of combustion products: $T=1642 \text{ K}$;

Molecular mass of combustion products: $\mu=28.2$

Specific heat ratio: $\gamma=1.272$

Taking into account the relaxation of the combustion products temperature up to $643 \text{ }^{\circ}\text{C}$ ($\approx 946 \text{ K}$), the velocity of sound is calculated to be:

$$a = (\gamma \times R \times T / \mu)^{1/2} = 595.62 \text{ m/s}$$

From this it is concluded that the velocity of the exhaust gases in the perforated opening will not exceed the velocity of sound. As a result, the dimensions for the stator's and rotor's regular and perforated openings were established. In addition, these dimensions became the base for the estimation of the rough outer diameter of the valve, which is to be 165 mm.:

Ellipse's axes: $108 \text{ mm} \times 48 \text{ mm}$;

The diameter of the holes in the perforated opening: 8 mm ;

The quantity of holes: 43.

Permissible Valve Leakage Calculation

Inherent to the reverse flow valve design is that a small amount of exhaust gas will by pass the oxidation catalyst untreated during the flow reversal. In order to still meet future federal regulations, a calculation needed to be performed to determine the allowable leakage rate. Since the reversing valve is after the NO_x adsorber, we are only interested in the effect of the oxidation catalyst. Therefore only the leakages of HC and CO are studied and since the ARES goal is geared toward stationary natural gas engines, the emission regulations set forth in the Code of Federal Regulation Part 40 for non-road engine are used. New terminology in the CFR allows lean burn natural gas fueled engines to be classified and tested as compression ignition engines. Therefore the following calculations were made using the Tier 4 regulations for non-road engines in the $175 \leq \text{hp} \leq 750 \text{ hp}$ range. These emission standards are to take effect in the 2011 to 2013 timeframe. The Tier 4 says that the emission reductions can be achieved through the use of control technologies; including advanced exhaust gas after treatment. The allowable limits are given as follows:

NMHC $\rightarrow$ 0.14 gms/hp-hr.

CO $\rightarrow$ 2.6 gms / hp-hr.

Data are obtained corresponding to the engine speed of 1800 rpm and the leakage calculations are made for various engine speeds (10%, 25%, 50%, 75% and 100%).

Since the leakage is largely affected by exhaust flow and engine backpressure, the leakage (both volumetric and mass flow) rates are calculated at rated speed and load conditions. To match other ARES work on the test engine, an engine speed of 1800 rpm is used for these conditions. At rated conditions, the exhaust composition downstream of LNT (Lean Nox Trap) is 1117 ppm of HC and 546 ppm of CO. With the engine at 100% load (252 hp), the amount of Hydrocarbon (HC) and Carbon monoxide (CO) allowed from emission standards in terms of grams per minute is calculated as

HC = $0.588 \frac{\text{gms}}{\text{min.}}$ and $10.92 \frac{\text{gms}}{\text{min.}}$ respectively. Now, it is required to find out the amount of

HC and CO that are allowed to by pass the catalyst for the same engine load and speed. The calculation involves various steps including finding out the volumetric flow rate, temperature, partial pressure, density and mass flow rate of the exhaust compositions.

Step 1: Finding out the volumetric flow rate of HC and CO:

Knowing the diameter and the length of catalyst the total volume for 2 catalysts is found to be 0.4922 cubic feet. The space velocity corresponds to 1800 rpm is $68,409 \text{ hr}^{-1}$. Now, the Exhaust flow rate = space velocity X Volume of catalysts

$$= 68,409 \times 0.4922$$

$$= 561.1818 \text{ cubic feet per minute.}$$

Volumetric flow rate = mole fraction X exhaust flow rate

$$(\text{Volumetric flow rate})_{\text{HC}} = 1117 \times 10^{-6} \times 561.1818$$

$$= 0.0177 \text{ cubic meter per minute.}$$

$$(\text{Volumetric flow rate})_{\text{CO}} = 546 \times 10^{-6} \times 561.1818$$

$$= 0.3064 \text{ cubic meter per minute.}$$

Step 2: Partial pressure of HC and CO:

The pressure of the exhaust composition down stream of the LNT is 2 atm. So the partial pressure of Hydro carbon (HC) and Carbon monoxide (CO) is calculated as follows:

$$P_p (\text{HC}) = 16.7 \times 1117 \times 10^{-6} = 0.01865 \text{ psi} = 128.587 \text{ N/m}^2$$

$$P_p (\text{CO}) = 16.7 \times 546 \times 10^{-6} = 0.00912 \text{ psi} = 62.868 \text{ N/m}^2.$$

Step 3: Density of HC and CO:

The density of HC is $\rho_{HC} = \frac{Pp(HC)}{R_{HC} \times T}$ and the density of CO is $\rho_{CO} = \frac{Pp(CO)}{R_{CO} \times T}$.

The temperature of HC and CO downstream of LNT is 873 K and the gas constants for HC and CO are 0.6395 J/gm- K and 0.297 J/gm- K respectively. Now,

$$\text{Density of HC is } \rho_{HC} = \frac{128.587}{0.6395 \times 873} = 0.2303 \text{ grams per cubic meter.}$$

$$\text{Density of CO is } \rho_{CO} = \frac{62.868}{0.297 \times 873} = 0.2425 \text{ grams per cubic meter.}$$

Step 4: Mass flow rate for HC and CO:

$$\begin{aligned} \text{a. Mass flow rate of HC is } \dot{m}_{HC} &= \rho_{HC} \times (\text{Volumetric flow rate})_{HC} \\ &= 0.2303 \times 0.0177 \\ &= 0.00407 \text{ grams per minute} \end{aligned}$$

$$\begin{aligned} \text{b. Mass flow rate of CO is } \dot{m}_{CO} &= \rho_{CO} \times (\text{Volumetric flow rate})_{CO} \\ &= 0.2425 \times 0.3064 \\ &= 0.002104 \text{ grams per minute} \end{aligned}$$

Step 5: Leakage rate:

It is required that the mass flow rate allowed from the CFR should be greater than or equal to the mass flow rate of the gas coming out of the system, which is given by

$$\begin{aligned} \dot{m}_{law}^* &\geq \dot{m}_{(outofcatalyst)}^* + \dot{m}_{(pastthecatalyst)}^* \\ &\geq (1 - \text{conversion efficiency}) \dot{m}_{engine}^* + \dot{m}_{(leakage)}^* \end{aligned}$$

Leakage rate for HC:

$$\begin{aligned} \dot{m}_{(leakageHC)}^* &\leq - (1 - \text{conversion efficiency}) \dot{m}_{engine}^* \\ &\leq 0.5 \dot{m}_{law}^* - (1 - 0.90) \times 0.00409 \\ &\leq 0.5875 \text{ grams per minute} \end{aligned}$$

Leakage rate for CO:

$$\begin{aligned} \dot{m}_{(leakageCO)}^* &\leq \dot{m}_{law}^* - (1 - \text{conversion efficiency}) \dot{m}_{engine}^* \\ &\leq 60.48 - (1 - 0.90) \times 0.002104 \\ &\leq 10.919 \text{ grams per minute} \end{aligned}$$

Thus, it is calculated that the maximum leakage that is allowed to by pass the catalyst for Hydrocarbon (HC) is 0.5875 grams per minute and that of Carbon monoxide (CO) is 10.919 grams per minute

Four-Way Single Diversion Valve Design

Valve Assembly Description

The concept of multidirectional rotation was used to simplify the design of the valve drive system. The design of the diversion valve consists of two cylinders, one rotating inside the other, which is stationary. A partition plate is welded to the inner cylinder and the alternating rotation of inner cylinder causes periodic flow reversal. The valve assembly also includes a top plate, a top cap, a top flange, a gasket and a steel washer. A diagram of the four-way single diversion valve is provided in Figure 88.

To simplify construction, the outer cylinder (1) and inner cylinder (2) are fabricated from standard dimensional pipe available through retail. Although the gap between the inner and outer cylinders is very small, the leakage through this gap can have an effect on the system performance. To accommodate the required seal and the rotation of the valve a labyrinth type seal will be used. Furthermore at the center of the outer cylinder, an arrangement for sleeve seating is provided on which the inner cylinder will rest and rotate. This prevents the direct surface-to-surface contact between the inner and outer cylinder and hence avoids possible wearing during rotation.

Figure 88 Four-Way Single Diversion Valve – (1)Outer cylinder; (2) Inner cylinder; (3) Partition Plate; (4) Top cap; (5) Top flange

Description of the Outer Cylinder

For the outer cylinder, the outer diameter is 166.275mm and the inner diameter is 160.275mm. Four elliptical openings are provided at 90-degree increments in order to facilitate both forward and reverse flow. A small seating arrangement lip is provided near the upper surface of the outer cylinder. This has been provided to maintain accuracy when assembling the flange and other parts. Figure 31 shows the snap shot of the outer cylinder.

As a requirement for assembly, a flange will be seated around the top of the outer cylinder at the flange seating (item 2 in Figure 89). The flange is provided in order to connect the outer cylinder with a assembly top cap. The flange is also provided with a seating arrangement for a copper gasket and a steel washer used to seal the assembly. The steel washer provides a small gap between the plate and the cap and leaves room for the valve to rotate. Figure 90 shows the top flange

Figure 89 Outer Cylinder/Stator – (1) Elliptical hole; (2) Flange seating; (3) Labyrinth sealing; (4) Sleeve seating

Figure 90 Flange – (1) Flange Seating; (2) Assembly Bolt Holes; (3) Gasket Groove

Description of Inner Cylinder

While the outer cylinder remains stationary, the inner cylinder rotates 90 degrees alternatively to provide the full cycle that includes one forward and one reverse mode. As with the outer cylinder, the inner cylinder has four elliptical holes and four perforated opening. The elliptical patterns are provided in order to avoid the complete blockage of the exhaust gas while the inner cylinder is rotating inside the outer cylinder. For clarity, the snap shot of inner cylinder is provided in Figure 91.

A base plate (item 4 in Figure 91) is positioned flush with the bottom of the inner cylinder and provides a slot for the partition plate. This plate will be press fit into the inner cylinder. The bottom of the base plate provides the top surface of the lower labyrinth seal. Once the lower plate is in place, the partition plate is press fit into its slot. To complete the inner cylinder assembly, a top plate is press fit flush with the top of the inner cylinder and the partition plate. A diagram of the top plate can be seen in Figure 92.

Figure 91 Inner Cylinder – (1)Elliptical opening; (2) Perforated in elliptical opening; (3) Labyrinth sealing; (4) Lower Base plate with groove for partition plate; (5) Projection to maintain gap

Figure 92 Top Plate - (1) Labyrinth sealing; (2) Slot for partition plate; (3) Shaft Hole

Description of the Top Cap

After the inner cylinder has been assembled and placed inside the outer cylinder assembly a top cap plate is bolted to the flange of the outer cylinder. The plate is shown in Figure 93. The labyrinth sealing surface on the bottom side of the top cap is mated with the sealing surface on the top of the inner cylinder to provide a leak proof seal. A circular hole is provided at the center and is where the rotation shaft passes through to the inner cylinder. The other end of the shaft is connected to the cylinder piston arrangement and will be discussed in the next section. However a sectional view of the assembled valve can be seen in Figure 94.

Figure 93 Top Cap - (1) Hole for Rotation Shaft; (2) Labyrinth Sealing

Figure 94 Valve Assembly - (1) Outer Cylinder; (2) Inner Cylinder; (3) Top Plate; (4) Top Cap; (5) Assembly Bolt Holes; (6) Copper Gasket; (7) Steel Washer

Description of Elliptical-to-Circular Pipe Connector

Since the valve openings are elliptical, an adapter is required to go from circular exhaust pipe to the elliptical opening. The specially fabricated pipe connector has a circular opening at one end and elliptical opening at another end. The exhaust pipe is connected to the circular opening using standard Marman flanges and the elliptical opening is welded with the outer cylinder of the valve. Four such pipe connectors are used, two at the inlets to the valve and two at the outlets from the valve. Figure 95 shows the pipe connector.

Figure 95 Pipe Connector

Operation of Valve Drive Mechanism

The multidirectional rotation of the valve is achieved through a reciprocating mechanism. The mechanism consists of an air piston and a drive arm. The piston end is connected to the rotational shaft, which is connected to the inner cylinder of the four way single diversion valve. Figure 96 shows the schematic diagram of the assembly and the estimated dimensions of the piston stroke based on the dimension of the valve, the valve's rotation and dimensions of the air cylinder. The linear movement of the piston rotates the inner cylinder and each full stroke of the piston rotates the inner cylinder 90 degrees.

Since the air cylinder turns from the axial position during the displacement of piston, tie rods are used to connect the piston end to the arm. The male tie rod is connected to the steel arm and the female tie rod is connected to the piston rod. The two tie rods are coupled so that the piston cylinder arrangement rotates the steel arm 90 degrees. Therefore the steel arm makes alternate rotation through 90 degree in both clock wise and anti-clock wise direction, which in turn rotates the inner cylinder of the valve through 90 degree alternatively. The inner cylinder shaft is fabricated with two steps, one having the diameter of 0.275 inches for the length of 2.00 inches. This end goes through the hole in the top cap and is secured to the top plate. The other end has the diameter of 0.50 inch for the length of 0.75 inches. A steel coupler is fabricated that couples the shaft with the steel arm. For clarity, the pictures of the shaft, coupler and the steel arm are provided in Figure 97. Figure 98 shows the complete motion control arm assembled.

Figure 96 Schematic Diagram of the Motion Control Mechanism

Figure 97 (A) Shaft; (B) Coupler; (C) Steel arm

Figure 98 Schematic of Assembled Motion Control Arm

Lean Burn Natural Gas Engine Testing and NO_x Reduction Strategy Review

Test Bed Development

The test bed was developed to allow both The University of Tennessee and the Oak Ridge National Lab (ORNL) to evaluate their unique LNT systems, applied to a lean burn natural gas engine. The development of the test bed, including installation of the engine and setup of all controls and data acquisition for LNT management, has been completed and was reported in Report 1. Table 21 shows a summary of the engine specifications. While this engine is not in the size range of interest to the ARES program it serves as a practical starting point for assessing the catalyst technology.

Table 21 Cummins Engine Specifications

C Gas Plus General Engine Data		
Name	C Gas Plus	
Model	CG-280	
Type	4 Cycle; In-Line 6 Cylinder	
Bore x Stroke (mm)	114 x 135	
Displacement (L)	8.3	
General Performance Data	Peak Power	Peak Torque
Engine Speed (rpm)	2400	1400
Engine Power (kW)	209	169
Engine Torque (N-m)	831	1153
Inlet Air Flow (L/sec)	293	205
Exhaust Gas Flow (L/sec)	817	539
Exhaust Gas Temperature (C)	643	587
Nominal Fuel Consumption (kg/hr)	47	34
Inlet Air Restriction (mm H ₂ O)	445	
Exhaust Restriction (mm Hg)	102	

Currently the LNT system for ORNL and UTK is installed on the test bed to allow for an initial catalyst evaluation and development of regeneration parameters. This LNT system consists of a dual path NO_x adsorbing catalyst system shown below in Figure 99. One leg of the dual path system is regenerated while the other is in the adsorption stage. Methane is injected into the exhaust stream ahead of the catalyst to create the fuel rich environment necessary for regenerating the LNT, and a set of pneumatically actuated exhaust brake valves are used to control the space velocity. The catalyst system consists of an oxidation, reformer and LNT catalyst developed by EmeraChem.

Figure 99 Dual leg Catalyst System Schematic

Initial Engine Baseline

The baseline performance and emissions of the 8.3-liter natural gas engine have been characterized at a matrix of operating points. Some initial catalyst volume estimates have been made based on exhaust flow, NO_x level and temperature data. Baseline results were also used to determine the validity of translating data from bench flow studies to full-scale engine data. This baseline data also allowed us to investigate the scalability of the 8.3-liter engine compared to the larger genset engines of interest to the ARES program. Figure 100 shows a matrix of engine out NO_x levels for the C Gas Plus.

Development of LNT Regeneration Strategy

Methane will be used as the reducing agent for the LNT. Before the storage sites of the catalyst become saturated methane will be injected into the exhaust directly upstream of the catalyst. Control over the injection rate will allow for control of the exhaust composition entering the catalyst. In addition, during regeneration the space velocity must be controlled across the catalyst to allow enough time for NO_x release and subsequent reduction. This was accomplished by throttling the exhaust flow with a set of exhaust brake valves.

Figure 100 NOx Rating

Lean Burn Natural Gas Engine Testing and NO_x Reduction Strategy Progress

Exhaust Aftertreatment System

Aftertreatment of lean burn natural gas NO_x was achieved through implementation of a dual path NO_x adsorbing catalyst system as shown in Figure 101. The dual path system allows for NO_x reduction by managing the LNT catalyst on a time-shared schedule. By periodically alternating the flow, the catalyst leg can flow the majority of the exhaust while in its adsorption mode. When it is time to regenerate the catalyst, the majority of the flow is diverted through the bypass leg. Restricting the flow across the catalyst during regenerating serves two purposes; the lower catalyst space velocity allows enough time for the release and reduction of stored NO_x and the lower mass flow rate of lean exhaust gasses reduces the amount of reductant needed to create the correct stoichiometry for regeneration. This consequently reduces the fuel penalty.

Figure 101 Exhaust Aftertreatment System Photograph

For the purpose of simplifying the experiment, only one leg of the system contains catalyst bricks. In an actual application, both legs of the system would contain catalysts. However, the single chamber system was used here to evaluate the lean NO_x trap's ability to store and reduce NO_x as well as the reforming catalyst's ability to break down methane into a usable source for regeneration. Projections of the conversion efficiencies and fuel penalties for a two chamber system were made from measurements of the one chamber system.

For this research, the same compressed natural gas supplied to the engine was used as the reducing agent. Shown in Figure 102, a pair of automotive injectors introduced the reductant directly upstream of the catalyst can. The injectors were actuated by a 75 Hz square wave signal. Adjusting the duty cycle of this signal controlled the amount of reducing agent introduced. The natural gas supplied was primarily methane. However, efficient regeneration of an LNT requires hydrogen or carbon monoxide in an oxygen free environment. Thus, an oxidation catalyst and reforming catalyst, placed upstream of the LNT, served to burn out the excess oxygen from the lean exhaust and reform the methane to a usable source for regeneration.

The oxidation catalyst, reforming catalyst and two lean NO_x trap catalyst bricks were each 9.5" in diameter by 6" in length. Each of the catalysts, developed by EmeraChem, were deposited on a cordierite honeycomb with 300 cells/in². The LNT catalyst contained a loading of 1.6 g/in³ Al₂O₃, 100 g/ft³ of Platinum and 0.14 g/in³ of barium oxide. The oxidation catalyst had a coating of 1.8 g/in³ alumina and 50 g/ft³ of palladium metal. The reformer catalyst was prepared with a 1.59 g/in³ 6:1 Platinum-Rhodium washcoat with a precious metal loading of 40 g/ft³ and 3.9% cerium oxide on alumina. An additional 20 g/ft³ of Rhodium was deposited on the surface

Figure 102 Natural Gas Injectors

Figure 103 Flow Control Valves

A set of pneumatically actuated exhaust brake valves designed by US Gear was used to control the flow of the exhaust gasses. Shown in Figure 103, one valve is mounted in each leg of the exhaust system and are alternately opened and closed to redirect the exhaust flow. A computer based control system controlled the auxiliary fuel injection, the exhaust valves and allowed the capability of either manual or automatic control of the system.

Complete Baseline Testing

Following the development of the experimental test bed, the first objective was to fully characterize the engine through a series of baseline tests. These tests would serve to provide pertinent performance and emissions data necessary for the development of the exhaust aftertreatment system. While the 210 kW engine does not fall into the 0.5 to 6.5 MW range of interest to the ARES program, it serves as a practical starting point for assessing the catalyst technology. Thus, baseline testing not only evaluates the performance and emissions characteristics, but it was also necessary to determine the scalability of the 8.3 liter engine compared to larger gensets of interest to ARES. A complete set of baseline data also serves to support further experimental results and aids in the comparison to other published data. In accordance with ARES goals, baseline testing was focused on a fixed speed of 1800 rpm. The baseline map was then extended to include a full load torque curve from 800 to 2400 rpm as well as a 45-point test matrix. This chapter serves to outline the details and present the results of all baseline testing. In addition, estimations of the catalyst's performance are made for certain test modes.

Before conducting baseline tests, a procedure was followed for engine warm up and calibration of the emissions analyzers. The same engine warm up procedure was followed throughout the research to maintain consistency and to ensure repeatability of results. Following engine warm up, the inlet and exhaust restrictions at rated conditions were set at 17.5" H₂O and 4" Hg. The following list outlines the standard engine warm up procedure as specified in CFR 40, Part 89, Subpart E (89.407), for constant speed engines:

For constant-speed engines:

Operate the engine at minimum load for 2 to 3 minutes.

Operate the engine at 50 percent load for 5 to 7 minutes.

Operate the engine at maximum load for 25 to 30 minutes.

Start test cycle within 20 minutes of the end of the warm up. A mode begins when the speed and load are stabilized within $\pm 2\%$. A mode ends when valid emission sampling for that mode ends. For a mode to be valid, the speed and load requirements must be maintained continuously during the mode. The torque modal points were calculated from the torque value with the engine warm and at rated conditions. All data was recorded during a minimum of the last 60 seconds of each mode. The emissions instruments were turned on at least one hour before calibration. Each analyzer was first zeroed with purge air, then calibrated with bottled span gasses. The span drift was checked at the end of testing to ensure zero and span difference did not exceed $\pm 3\%$ of full scale as specified by CFR 40, Part 89, Subpart E (89.408).

The first step in the baseline test procedure was to generate a 9 point full load torque curve from 800 rpm to 2400 rpm. This full load curve was then used to determine the 45-point test matrix for baseline testing. Modes for the test matrix included 10%, 25%, 50%, 75% and 100% load for each of the 9 speeds used to develop the full load torque curve. After warm up, testing began at

the highest speed and load point then moved through each of the 5 load points at this fixed speed. Data was collected at five-minute intervals between each mode to allow temperatures and engine out emissions to stabilize. Each mode in the test matrix was logged for 120 seconds at a sampling frequency of 10 Hz. The full test matrix is shown in Table 22.

Table 22 Baseline Test Matrix

	Torque (ft-lbs)								
	800 rpm	1000 rpm	1200 rpm	1400 rpm	1600 rpm	1800 rpm	2000 rpm	2200 rpm	2400 rpm
100%	468	546	665	841	809	753	712	630	580
75%	351	410	499	631	607	565	534	473	435
50%	234	273	333	421	405	377	356	315	290
25%	117	137	166	210	202	188	178	158	145
10%	47	55	67	84	81	75	71	63	58

The exhaust flow, brake specific fuel consumption (BSFC), brake mean effective pressure (BMEP) and the NOx rating were calculated using the experimental data. The equations and assumptions used for calculating each of these are described below. The bubble plots in Figures 104 through 110 represent emissions maps of the engine. All other pertinent data collected during baseline testing is summarized in Tables 23 through 33.

The overall NOx rating for an engine is calculated in accordance with CFR 40, Part 89, Subpart E, where the NOx rating for each of five modes is weighted and summed per the weighting factors shown in Table 34. Using the NOx rating data for 1800 rpm, the engine's rating is 1.73 g/hp-hr. The goal for the ARES program is to achieve a NOx rating of 0.1 g/hp-hr. Using this engine as an example, the exhaust aftertreatment system must reduce the NOx levels by greater than 94% to meet this goal.

$$\dot{V}_{exh} = \dot{V}_{fuel} + \dot{V}_{air}$$

$$\dot{V}_{fuel} = \frac{\dot{m}_{fuel} * SV}{MW_{fuel}}$$

Where :

$$\dot{V}_{exh} = \text{calculated volumetric exhaust flow } \left(\frac{\text{Liters}}{\text{min}} \right)$$

$$\dot{V}_{fuel} = \text{calculated volumetric fuel flow } \left(\frac{\text{Liters}}{\text{min}} \right)$$

$$\dot{V}_{air} = \text{measured volumetric inlet air flow } \left(\frac{\text{Liters}}{\text{min}} \right)$$

$$\dot{m}_{fuel} = \text{measured mass fuel flow } \left(\frac{\text{lb}}{\text{min}} \right)$$

$$SV = \text{standard volume } \left(22.414 \frac{\text{Liters}}{\text{mole}} \right)$$

$$MW_{fuel} = \text{molecular weight } \left(16.499 \frac{\text{g}}{\text{mole}} \right)$$

$$NOx \text{ Rating} = \frac{\dot{m}_{NOx}}{P}$$

$$\dot{m}_{NOx} = \frac{X_{NOx} * \dot{V}_{exh} * MW_{NO_2}}{SV}$$

Where :

$NOx \text{ Rating}$ = calculated NOx rating ($\frac{g}{hp-hr}$)

$\dot{m}_{NOx}$ = calculated mass NOx flow ($\frac{g}{hr}$)

P = measured power (HP)

X_{NOx} = measured NOx concentration (ppm)

MW_{NO_2} = molecular weight ($46 \frac{g}{mole}$)

$$BMEP = \frac{2 * P}{N * V_{swept}}$$

Where :

$BMEP$ = calculated brake mean effective pressure (bar)

P = measured power (kW)

N = measured engine speed ($\frac{rev}{sec}$)

V_{swept} = engine swept volume ($.0083 m^3$)

$$BSFC = \frac{\dot{m}_{fuel}}{P}$$

Where :

$BSFC$ = calculated brake specific fuel consumption ($\frac{lb}{hp-hr}$)

$\dot{m}_{fuel}$ = measured mass fuel flow ($\frac{lb}{hr}$)

P = measured power (HP)

Figure 104 Engine CO Map

Figure 105 Engine NOx Map

Figure 106 Engine NO Map

Figure 107 Engine THC Map

Figure 108 Engine Methane map

Figure 109 Engine CO₂ Map

Figure 110 Engine O2 Map

Table 23 Baseline Power Map

Power (hp)									
	800 rpm	1000 rpm	1200 rpm	1400 rpm	1600 rpm	1800 rpm	2000 rpm	2200 rpm	2400 rpm
100%	66	95	137	213	239	252	264	276	276
75%	50	71	103	161	179	188	198	209	208
50%	33	48	69	106	121	126	131	138	138
25%	16	24	34	53	59	61	65	67	68
10%	7	10	13	22	24	25	26	27	27

Table 24 Baseline Boost Pressure Map

Boost Pressure (psig)									
	800 rpm	1000 rpm	1200 rpm	1400 rpm	1600 rpm	1800 rpm	2000 rpm	2200 rpm	2400 rpm
100%	2.79	5.70	11.63	21.21	21.34	20.04	19.65	19.49	18.09
75%	1.61	3.24	7.33	13.91	14.13	13.99	14.21	14.73	14.35
50%	0.63	1.50	3.47	7.58	9.38	9.74	10.85	11.80	12.44
25%	0.01	0.28	0.88	2.38	3.27	4.23	5.60	6.70	7.68
10%	-0.16	-0.05	0.12	0.52	0.87	1.31	1.87	2.42	3.27

Table 25 Baseline Inlet Air Flow Map

Inlet Air Flow (scfm)									
	800 rpm	1000 rpm	1200 rpm	1400 rpm	1600 rpm	1800 rpm	2000 rpm	2200 rpm	2400 rpm
100%	112	158	268	446	498	524	563	602	615
75%	95	122	191	338	377	403	437	477	491
50%	81	97	130	207	252	282	324	356	372
25%	70	78	91	119	137	153	176	194	211
10%	64	69	75	85	95	103	113	123	136

Table 26 Baseline Fuel Flow Map

Fuel Flow (lb/hr)									
	800 rpm	1000 rpm	1200 rpm	1400 rpm	1600 rpm	1800 rpm	2000 rpm	2200 rpm	2400 rpm
100%	23.5	33.2	47.8	72.4	81.0	86.5	93.4	100.5	103.7
75%	18.5	25.7	37.1	56.2	62.7	67.7	73.8	80.3	83.2
50%	13.7	19.0	26.5	38.4	44.6	49.0	54.7	59.1	62.3
25%	8.8	12.2	16.6	22.8	26.1	28.8	32.6	35.7	38.5
10%	6.2	8.5	10.8	14.1	16.3	18.2	20.5	22.8	25.4

Table 27 Baseline Exhaust Flow Map

Exhaust Flow (L/min)									
	800 rpm	1000 rpm	1200 rpm	1400 rpm	1600 rpm	1800 rpm	2000 rpm	2200 rpm	2400 rpm
100%	3421	4826	8066	13367	14921	15739	16901	18070	18481
75%	2882	3709	5798	10159	11320	12101	13130	14338	14749
50%	2439	2938	3960	6245	7600	8483	9740	10685	11160
25%	2061	2326	2741	3594	4144	4619	5313	5871	6382
10%	1875	2040	2227	2562	2844	3094	3416	3728	4113

Table 28 Baseline BSFC Map

BSFC (lb/hp-hr)									
	800 rpm	1000 rpm	1200 rpm	1400 rpm	1600 rpm	1800 rpm	2000 rpm	2200 rpm	2400 rpm
100%	0.355	0.349	0.349	0.341	0.338	0.343	0.354	0.364	0.376
75%	0.371	0.362	0.361	0.348	0.350	0.360	0.373	0.385	0.400
50%	0.414	0.398	0.384	0.362	0.370	0.389	0.417	0.429	0.450
25%	0.553	0.514	0.486	0.430	0.445	0.472	0.502	0.533	0.570
10%	0.954	0.849	0.814	0.646	0.680	0.740	0.778	0.847	0.929

Table 29 Baseline BMEP Map

BMEP (bar)									
	800 rpm	1000 rpm	1200 rpm	1400 rpm	1600 rpm	1800 rpm	2000 rpm	2200 rpm	2400 rpm
100%	8.90	10.25	12.31	16.37	16.12	15.09	14.23	13.52	12.38
75%	6.73	7.65	9.23	12.43	12.07	11.25	10.67	10.22	9.34
50%	4.44	5.14	6.20	8.16	8.12	7.55	7.07	6.76	6.22
25%	2.16	2.57	3.06	4.07	3.95	3.65	3.49	3.29	3.04
10%	0.88	1.08	1.20	1.69	1.62	1.47	1.42	1.32	1.23

Table 30 Baseline Exhaust Back Pressure Map

Exhaust Back Pressure (psig)									
	800 rpm	1000 rpm	1200 rpm	1400 rpm	1600 rpm	1800 rpm	2000 rpm	2200 rpm	2400 rpm
100%	0.67	0.78	1.03	1.57	1.80	1.99	2.23	2.52	2.59
75%	0.64	0.72	0.88	1.23	1.38	1.54	1.71	1.94	1.98
50%	0.62	0.67	0.75	0.91	1.01	1.12	1.26	1.37	1.42
25%	0.60	0.63	0.67	0.72	0.76	0.79	0.85	0.90	0.93
10%	0.58	0.60	0.63	0.66	0.66	0.69	0.71	0.73	0.75

Table 31 Baseline NOx Rating Map

NOx Rating (g/hp-hr)									
	800 rpm	1000 rpm	1200 rpm	1400 rpm	1600 rpm	1800 rpm	2000 rpm	2200 rpm	2400 rpm
100%	19.02	11.57	3.62	2.70	2.88	3.09	2.66	2.43	2.31
75%	18.58	13.96	3.62	2.24	1.93	1.53	1.38	1.29	1.43
50%	15.01	12.36	5.70	2.67	1.71	1.20	0.76	0.79	0.89
25%	9.00	8.29	6.49	3.69	2.27	1.67	1.12	1.10	1.18
10%	6.22	6.06	5.30	5.75	3.94	3.32	2.65	2.78	2.69

Table 32 Baseline Air to Fuel Ratio Map

Air to Fuel Ratio									
	800 rpm	1000 rpm	1200 rpm	1400 rpm	1600 rpm	1800 rpm	2000 rpm	2200 rpm	2400 rpm
100%	20.5	21.4	23.1	24.3	24.6	24.8	24.9	25.0	25.3
75%	20.1	20.8	22.9	24.1	24.6	24.7	24.8	24.9	24.8
50%	19.9	20.2	21.0	23.6	24.1	24.4	24.6	24.6	24.5
25%	19.7	19.9	20.5	20.7	20.6	21.9	22.8	23.6	23.6
10%	19.3	19.5	19.8	20.5	21.3	21.5	21.4	20.9	20.7

Table 33 Baseline Turbo Out Temperature Map

Turbo Out Temp (C)									
	800 rpm	1000 rpm	1200 rpm	1400 rpm	1600 rpm	1800 rpm	2000 rpm	2200 rpm	2400 rpm
100%	527	579	604	586	590	604	621	638	656
75%	519	573	599	598	600	614	630	645	655
50%	489	543	580	585	590	606	636	640	649
25%	453	506	553	564	574	586	604	615	624
10%	411	455	507	539	549	569	586	595	614

Table 34 Weighting Factors

Mode #	% of Full Load	Time in Mode (min)	Weighting Factors
1	100%	5	0.05
2	75%	5	0.25
3	50%	5	0.30
4	25%	5	0.30
5	10%	5	0.10

LNT Capacity Estimation

Baseline data is useful in predicting the performance of the lean NOx trap system at particular engine modes. Using baseline engine data along with bench flow reactor data provided by EmeraChem, estimates of the NOx storage capacity were made. The trapping capacity of the catalyst is highly dependent on temperature as was demonstrated by the bench flow reactor studies. Data from these studies gives the capacity of the catalyst after 10% and 50% NOx breakthrough (τ_{10} and τ_{50}) over a range of temperatures. The conditions of the experiment along with bench flow data are listed in Tables 35 and 36.

Unfortunately, the catalyst temperatures on the engine test stand exceed the range of temperatures demonstrated in the bench flow study, thus the data was extrapolated to estimate capacities above

550 °C. The storage capacity was estimated, as a function of temperature, for 10%, 25%, 50%, 75% and 100% engine load at 1800 rpm. With knowledge of the catalyst's storage capacity (grams) and the engine's NOx flow rate (grams/sec), the 10% and 50% breakthrough times were estimated. Table 37 shows the results of these estimates based on a 14 liter LNT catalyst volume. Estimates for the 75% and 100% load points were not made, as interpolations of bench flow data showed trapping capacities falling off to zero at these temperatures.

Table 35 Conditions for Bench Flow Study

Parameter	Bench Flow Value
LNT catalyst space velocity	30,000 /hr
Oxidation catalyst space velocity	60,000 /hr
Reformer catalyst space velocity	60,000 /hr
Temperature	400, 450, 500, 550° C
NOx	500ppm
CO	500ppm
H2O	13.5%
CO2	6.7%
O2	6.0%
N2	balance

Table 36 Results from Bench Flow Study

Temperature (C)	Capacity @ t10 (g/L)	Capacity @ t50 (g/L)
400	2.1	3.5
450	1.4	2.5
500	0.6	1.3
550	0.3	0.4

Table 37 LNT Capacity Estimations

% Load	100%	75%	50%	25%	10%
Temperature (C)	600	580	560	510	440
NOx flow (g/sec)	0.192	0.067	0.037	0.030	0.018
t10 Capacity (g)	-	-	1.96	7.56	21.56
t50 Capacity (g)	-	-	3.08	15.68	37.8
t10 Time (sec)	-	-	53	252	1198
t50 Time (sec)	-	-	83	523	2100

Development of Regeneration Parameters

With lean NO_x trap technology, NO_x is trapped on the barium oxide storage sites in a lean (excess oxygen) environment, forming barium nitrate. In a rich (oxygen depleted) environment, the stored NO_x are released by reactions with excess CO and H₂ and is subsequently reduced over the catalyst's platinum loading. Injecting natural gas into the exhaust creates the conditions for the rich mode, termed "regeneration". The natural gas, which is primarily methane, reacts across an oxidation catalyst to burn out the excess oxygen. A reforming catalyst is then used to further promote the combustion of the highly stable methane into CO and H₂. In addition to controlling the exhaust composition during regeneration, it was also necessary to control the exhaust flow rate across the catalyst. Redirecting the majority of the exhaust through the bypass leg with a set of flow control valves did this. The ability to control both the exhaust composition and flow rate is critical to successful regeneration of the lean NO_x trap. Therefore, a series of experiments were conducted to help gain insight into exhaust flow rates and compositions under various engine conditions and injection parameters. The first of these experiments was designed to determine the flow rate across the catalyst, during regeneration, for a range of engine conditions. The second experiment was to map out the exhaust composition for a range of engine conditions and injection parameters. The final experiment was to determine the oxidation efficiency of methane across the catalysts for a range of exhaust temperatures. This chapter serves to outline the methods and results for each of these experiments.

Exhaust Flow Control

Controlling flow through the dual leg exhaust system was crucial for management of the catalyst. When the NO_x trap is in the adsorption stage the bypass leg must be closed off, thus directing most of the exhaust across the catalysts. Once the LNT begins to saturate, the majority of the lean exhaust gases must be redirected through the bypass leg and the reductant is injected. Diverting the majority of the exhaust for regeneration is crucial to LNT management for two reasons. It reduces the oxygen mass flow, thereby minimizing the amount of reductant needed, and consequently reducing the fuel penalty. It also reduces the space velocity across the catalyst, allowing enough time for release of the stored NO_x and their subsequent reduction. In bench flow reactor studies conducted at EmeraChem, a space velocity of 5,000 /hr was used during regeneration. Based on a total LNT volume of 14 liters the exhaust flow rate would have to be throttled to 1167 liters/min to achieve similar conditions. The following experiment was used to map out the exhaust flow rate across the catalyst, while the flow control valve was used to restrict the flow.

With the flow control valve in the closed position, the portion of the exhaust that is allowed to pass is termed "slip flow". It was desired to know the rate of this slip flow under various engine conditions. Thus, an experiment was designed to estimate the volumetric slip flow rate by diluting the flow with nitrogen and measuring the change in the exhaust composition.

As shown in Figure 111, with the flow control valve partially closed, nitrogen was injected into the throttled exhaust stream at a fixed flow rate. The fraction of the exhaust flow, which crosses the flow control valve, was diluted by the injected nitrogen flow. The dilution ratio could be determined by taking exhaust samples upstream and downstream of the injection. The slip flow rate could then be calculated from the known nitrogen flow rate and the measured dilution ratio. The following control volume analysis (Figure 112) was used to derive an equation for the volumetric slip flow rate.

Figure 111 Experimental Schematic for Slip Flow Estimations

Figure 112 Control Volume for Slip Flow Analysis

The volumetric flow rate of CO₂ into and out of the control volume can be calculated as follows.

$$CO_2_In\left(\frac{L}{min}\right) = \%CO_2_A \times [Slip\ Flow\left(\frac{L}{min}\right)]$$

$$CO_2_Out\left(\frac{L}{min}\right) = \%CO_2_B \times [Diluted\ Slip\ Flow\left(\frac{L}{min}\right)]$$

$$= \%CO_2_B \times [Slip\ Flow\left(\frac{L}{min}\right) + N_2\ Flow\left(\frac{L}{min}\right)]$$

Then an equation for the slip flow rate can be derived by equating the volumetric flow of CO₂ into and out of the control volume.

$$CO_2_In\left(\frac{L}{min}\right)=CO_2_Out\left(\frac{L}{min}\right)$$

$$\%CO_2_A \times [Slip\ Flow\left(\frac{L}{min}\right)] = \%CO_2_B \times [Slip\ Flow\left(\frac{L}{min}\right) + N_2\ Flow\left(\frac{L}{min}\right)]$$

$$Slip\ Flow\left(\frac{L}{min}\right) = N_2\ Flow\left(\frac{L}{min}\right) \times \left[\frac{\%CO_2_B}{\%CO_2_A - \%CO_2_B} \right]$$

These exhaust flow control experiments were used to determine the slip flow at 10%, 25%, 50%, 75% and 100% load for 1800 rpm. Measurements were taken at various nitrogen flow rates to verify repeatability of the test. Nitrogen flows were controlled with a Hastings mass flow controller. Bottled ultra high purity nitrogen was supplied to the mass flow controller at a constant 80 psi. The results of these tests are presented in Table 38 and Figure 113. Experimental results for estimating slip flow rates at 10% load are not presented, as they were highly inconsistent.

Table 38 Exhaust Flow Rates During Adsorption and Regeneration

% Load	Slip Flow During Adsorption (L/min)	Slip Flow During Regeneration (L/min)
100	14418	1298
75	11069	905
50	7814	603
25	4419	250

Figure 113 Exhaust Flow Rates During Adsorption and Regeneration

Exhaust Composition Control

As with controlling the flow rate across the catalyst, controlling the exhaust composition is also critical to regeneration. Enough reducing agent must be injected to fully burn out the excess oxygen and create the CO and H₂ necessary for regeneration. A universal exhaust gas oxygen sensor (UEGO) placed down stream of the injectors was used to determine the stoichiometry of the exhaust gasses entering the catalyst can. A stoichiometric air-fuel mixture for natural gas combustion has an A/F ratio of 17.2 while the lean burning C Gas Plus engine operates between 21.5 and 24.8 at 1800 rpm. In terms of lambda values, this is 1.25 to 1.44, where 1.00 represents a stoichiometric mixture and less than 1.00 would be rich. The goal of this experiment was to map out the injection parameters necessary to achieve lambda values of 0.5, 0.7 and 0.9 for each of the five load points at 1800 rpm. A 75Hz, 12-volt square wave signal was used to excite the injectors. The signal's duty cycle was the variable used to adjust the overall flow rate, thus controlling the exhaust composition. The following results present the number of injectors and the duty cycle used to achieve the desired equivalence ratio. As can be seen in Table 39, the two injectors at maximum duty cycle could not inject enough reductant to achieve the targeted equivalence ratio of 0.5 at 100% and 75% load. In addition, the fuel penalty was calculated, based on a cycling period of 25 second adsorption (lean operation) followed by a 5 second regeneration (rich operation) with a 3 second injection.

Table 39 Exhaust Composition Control

1800 rpm - 25 sec lean - 5 sec regen - 3 sec injection					
% Load	Number of Injectors	Duty Cycle %	Target Lambda	Actual Lambda	Fuel Penalty %
100	2	95	0.5	0.70	2.22%
100	2	95	0.7	0.70	2.22%
100	2	35	0.9	0.90	0.80%
75	2	95	0.5	0.57	3.17%
75	2	65	0.7	0.70	2.09%
75	2	25	0.9	0.90	0.82%
50	2	72	0.5	0.49	3.29%
50	2	38	0.7	0.70	1.71%
50	2	18	0.9	0.90	0.70%
25	2	27	0.5	0.48	2.32%
25	2	16	0.7	0.70	1.29%
25	1	8	0.9	0.91	0.53%
10	1	13	0.5	0.50	1.58%
10	1	8	0.7	0.72	0.80%
10	1	6	0.9	0.90	0.42%

Methane Oxidation

Successful regeneration of the LNT depends on the ability of the oxidation and reforming catalyst to combust methane with the excess oxygen present in the lean exhaust. The ability of the catalysts to combust the highly stable methane is partially dependent on the catalyst temperatures. Thus, at lower loads (i.e. lower temperatures), regeneration of the lean NO_x trap may become more difficult. The following experiment was intended to assess the dependence of methane oxidation on catalyst temperatures. Exhaust methane concentrations were sampled at three locations as depicted in Figure 114, Oxi Cat In, Oxi Cat Out and LNT Out. These samples were taken at 8 different load points for 1800 rpm. This gave a range of catalyst temperatures from 550° to 413° C. Table 40 gives the reduction efficiencies through the oxidation catalyst and through the end of the aftertreatment system for this range of temperatures. Also shown in the table are the engine out methane concentrations in parts per million. As can be seen in Figure 115, the reduction efficiency begins to fall off below 500° C, and the oxidation catalyst becomes nearly ineffective below 450° C. The inability to regenerate the catalyst at lower temperatures presents a challenge for the application of the lean NO_x trap aftertreatment system. This poor performance at lower temperatures coupled with the lower NO_x storage capacity at higher temperatures creates a narrow temperature window for optimizing system performance. These temperature issues are further illustrated with testing presented in the next chapter.

Figure 114 Sample Positions for Methane Oxidation Study

Table 40 Methane Oxidation Results

Temp (C)	Oxi Cat Out CH4 Reduction	LNT Out CH4 Reduction	Engine Out CH4 (ppm)
413	0.4%	19.5%	1180
452	6.7%	26.9%	1242
482	18.7%	34.6%	1212
508	26.7%	35.3%	1171
522	27.3%	33.3%	1219
538	26.0%	35.3%	1162
548	27.1%	34.6%	1134
550	28.8%	33.2%	1103

Figure 115 Methane Oxidation vs. Catalyst Temperatures

Lean NOx Trap Evaluation

The primary focus of this research was to evaluate the application of lean NOx trap catalysis to a lean burn natural gas engine. The key technical issues to be addressed were the utilization of natural gas for regeneration, as methane is difficult to catalytically combust, and the storage capacity of the catalyst under the high exhaust temperatures of natural gas combustion. As will be demonstrated in the following experiments, methane more readily reacts at higher temperatures, yielding better results for regeneration, while the LNT has higher storage capacities at lower temperatures. This leads to a narrow temperature window where the system will exhibit maximum performance. Testing of the aftertreatment system was conducted under steady state conditions at 1800 rpm with 10%, 25% and 50% engine loads; the catalyst temperatures under these conditions were 440, 510 and 560° C, respectively. Testing at 75% and 100% engine loads was avoided because high temperatures could potentially damage the catalysts. The remainder of this chapter serves to describe the procedures and results for these tests and concludes with an evaluation of the exhaust aftertreatment system.

Lean NOx Trap Cycle

Results of a typical test with the lean NOx trap system are shown in Figures 116. During this test, the engine was operated at 1800 rpm and 50% load. The catalyst was managed with 120 second sorption periods and 20 second regenerations. The exhaust flow rates were 297 scfm during sorption periods and 21 scfm during regeneration periods. This correlates to LNT space velocities of 36,042/hr and 2,550/hr based on 14 liters of catalyst. The 140 second catalyst management cycle, for which three periods are shown in the following figures, was repeated under steady state engine conditions. The first of these figures shows the NOx levels measured into and out of the dual leg system.

Figure 116 Typical NOx Profiles

Figure 117 Fuel Flow and Exhaust Stoichiometry

Figure 118 Catalyst Temperatures

The system in NO_x levels average 120 ppm, while the system out NO_x levels vary through the management cycle. Directly following the regeneration sequence, system out NO_x levels reach their lowest levels of 5 ppm. This represents an instantaneous trapping efficiency of 96%. As the sorption period continues, and storage sites on the catalyst become occupied, NO_x slip begins to occur. By the end of the 120-second sorption, the catalyst is only trapping 58%, with system out NO_x levels reaching 50 ppm. This is followed by the 20-second regeneration period. Of the 20-second regeneration period, fuel was injected for the first 10 seconds. The remaining 10 seconds was a delay in switching the valves. This valve delay throttles the exhaust flow across catalyst long enough for the reductant to completely pass through the catalysts. The geometry of the exhaust aftertreatment system is a dual leg system with one leg serving as a bypass during catalyst regeneration. This single chamber system allows the entire engine out NO_x to circumvent the LNT during the 20-second regeneration. In a single chamber system, this fraction of exhaust, which goes untreated inevitably, leads to a lower overall NO_x reduction efficiency. However, in an actual application this single chamber system could be expanded into a two-chamber system by adding a catalyst to the bypass leg.

For the purpose of this study the catalysts are evaluated by their trapping efficiencies. The trapping efficiency is defined as the percentage of NO_x stored by the catalyst during the sorption period. The catalyst's trapping efficiency varies with changes in engine conditions and catalyst management parameters.

Figure 117 shows the air-fuel ratio measured directly upstream of the oxidation catalyst and the fuel flow to both the engine and injectors. With an air-fuel ratio of 17.1 representing stoichiometric conditions, it can be seen here that lean conditions exist through the sorption period. Following the injection and closing of the valve, an oxygen depleted/reductant rich exhaust condition is created in which the stored NO_x can be released and reduced. Another crucial parameter for system evaluation is the amount of fuel required for regeneration. As the

energy from this fuel supplies no power to the end user, it is considered a fuel penalty and is defined as the percentage of fuel injected to that which is supplied to the engine. During the injection, an instantaneous fuel penalty of 20% is measured. However, over a full cycle, this is only a 1.7% fuel penalty.

Figure 118 shows temperatures at the cores of the oxidation, reformer and lean NO_x trap catalysts as well as the exhaust temperature at the turbo outlet. The temperature oscillations of the catalyst bricks are due to the exothermic oxidation of the methane. The wide temperature difference between the turbo outlet and the catalyst bricks is due to heat loss along the exhaust pipe.

Optimizing Regeneration Parameters

The trapping efficiency as well as the associated fuel penalty are primary parameters for evaluating the aftertreatment system. These evaluation parameters are highly dependent on engine conditions (i.e. exhaust temperatures and NO_x flow rates) as well as the conditions used for catalyst management (i.e. injection rates and sorption period). The system was evaluated at a matrix of injection rates and sorption periods for 10%, 25% and 50% engine loads. The results from this test matrix revealed the optimal conditions for catalyst management at a given engine condition. The injection rate was used to control the exhaust stoichiometry during regeneration. Oxygen depleted exhaust with lambda values of 0.5, 0.6, 0.7 and 0.8 were targeted for the test matrix. A ten second injection duration was used for all testing. After the injection sequence, switching of the valves was delayed until the stoichiometry downstream of the catalyst reached lean conditions ($\lambda > 1.0$). This ensured enough time for the reductant to pass through the catalysts. The performance was allowed to stabilize with sorption periods of 30, 60, 120 and 240 seconds for each targeted lambda value.

Figures 119 through 121 below show the results of the test matrix for engine conditions at 50% load. The four sorption periods are shown across the x-axis and each curve represents a different injection rate. A sixty second sorption period yields greater than 90% trapping efficiencies for all lambda values. Beyond this period the trapping efficiencies begin to drastically fall off. A shorter sorption period of 30 seconds yields modest gains in trapping efficiencies, yet results in markedly higher fuel penalties. In optimizing the regeneration strategy it is often necessary to compromise one performance parameter for gains in another. Because the ARES program targets NO_x ratings of 0.1 g/hp-hr, this was the deciding factor in determining the optimal parameters for regeneration. Figure 121 shows that injecting for 0.6 lambda with a sorption period of 60 seconds achieves a 0.088 g/hp-hr NO_x rating. This was just within the ARES target, thus it was chosen as the optimal regeneration scheme. This optimal scheme for steady state conditions at 50% engine load results in a 2.84% fuel penalty. Figure 63 also shows the NO_x profiles through 5 cycles for this optimal regeneration scheme.

Figure 119 50% Load NOx Trapping Efficiencies

Figure 120 50% Load NOx Ratings and Fuel Penalties

Figure 121 50% Load NOx Profiles for Optimal Regen

Figures 122 through 124 below show the results of the test matrix for engine conditions at 25% load. A 120 second sorption period with injections for 0.5 lambda yields trapping efficiencies higher than 97% and NOx ratings as low as 0.05 g/hp-hr. These optimal regeneration conditions for steady state conditions at 25% engine load lead to a 1.62% fuel penalty. NOx profiles through 5 regeneration cycles for these optimal conditions are shown in Figure 124. It is important to note that the optimal adsorption period for 25% load (120 seconds) is twice what it was for 50% load (60 seconds). This is in part due to the lower catalyst temperatures at 25% load. The storage capacity of the lean NOx trap is a function of its temperature. Thus, as the exhaust temperatures increase with increasing load, the catalyst's storage capacity will decrease as will the effective adsorption period. This concept is explored in more detail later in this chapter.

Figure 122 25% Load NOx Trapping Efficiencies

Figure 123 25% Load NOx Ratings and Fuel Penalties

Figure 124 25% Load NOx Profiles for Optimal Regen

Figures 125 through 127 below show the results of the test matrix for engine conditions at 10% load. A 30 second sorption period with 0.5 lambda yields a 91% trapping efficiency. With an engine out NOx rating of 5.00 g/hp-hr, this trapping efficiency achieves an average rating of 0.47 g/hp-hr and instantaneous ratings of 0.36 g/hp-hr. These results fall well short of the ARES goal. These conditions resulted in a 3.66% fuel penalty. Besides not achieving high enough trapping efficiencies at 0.5 lambda, the catalyst would not regenerate beyond 120 second sorption periods. Trapping efficiencies dropped off to zero, thus the data is not presented in the following figures. Similar results occurred beyond 60 second sorptions for 0.6 lambda and beyond 30 second sorptions for 0.7 and 0.8 lambda. There are two explanations for this inability to regenerate the catalyst at 10% engine load. The first, is that low catalyst temperatures hinder the reforming of methane into the H₂ and CO necessary for regeneration.

Figure 125 10% Load NOx Trapping Efficiencies

Figure 126 10% Load NOx Ratings and Fuel Penalties

Figure 127 10% Load NOx Profiles for Optimal Regen

At 10% load catalyst temperatures are 440° C. At these low temperatures, the oxidation catalyst has not reached its light off temperature as indicated in Figure 127. Thus, not enough of the injected methane is being catalytically combusted to create the conditions necessary for regeneration. The second explanation for poor performance is that the mass flow of exhaust, which must slip past the closed valve for regeneration, becomes too low. Although the targeted lambda values are met, the mass of fuel injected is simply not enough to fully regenerate a saturated catalyst. This second explanation is explored with further testing and the results are presented in the following section.

Adjusting Flow Rates for Regeneration

The exhaust flow that slips past the valve during regeneration becomes very low at 10% load. This results in a low injection of reductant to attain the desired stoichiometry. The poor catalyst performance at 10% load could result from an insufficient mass of fuel injection to regenerate the catalyst. A potential solution to this problem would be to prevent the valve from fully closing, thus allowing higher mass flow rates of exhaust during regeneration. This would result in higher injection rates of fuel necessary to attain the desired stoichiometry. Segments of the test matrix were repeated for this scenario, in which the valve was left wide open during regenerations. Fuel injection rates were set to achieve 0.7 lambda for 60, 120 and 240 second sorption periods. Figures 128 through 130 show results from these tests.

As can be seen in Figure 128, the trapping efficiency reached 97.4% for 0.7 lambda and 120 second sorptions. As the original test matrix revealed the catalyst would not even regenerate under these conditions with the valve fully closed during regeneration. The 97.4% trapping efficiency achieved a 0.129 g/hp-hr NOx rating and instantaneous ratings as low as 0.10 g/hp-hr. These conditions resulted in a 2.62% fuel penalty. The catalysts trapping efficiency is maintained at 95.6% with 240 second sorptions. These conditions yielded fuel penalties as low as 1.05%.

These results prove that the position of the flow control valve during regeneration can play a role in further optimizing the system. This is particularly true for lower loads, and is recommended as a next step in LNT evaluation studies.

Figure 128 10% Load NOx Trapping Efficiencies with Full Slip Flow

Figure 129 10% Load NOx Ratings with Full Slip Flow

Figure 130 10% Load Fuel Penalties with Full Slip Flow

NOx Storage Capacities

The previous section outlined experiments designed to find the optimal injection rates and sorption periods for catalyst management, and presented an evaluation of the system based on trapping efficiencies and fuel penalties. Another critical characteristic in evaluating a LNT catalyst is its capacity to store NOx. NOx storage capacity is defined as the mass of NOx (as NO₂) stored on the catalyst during the sorption period, until trapping efficiencies fall below 90%. Typically, the capacity is normalized per catalyst volume, giving it units of grams per liter. As stated previously, the storage capacity of a Lean NOx Trap is a function of catalyst temperatures. Thus, thermal management becomes a key factor in optimizing the exhaust aftertreatment system. It is desirable to maximize capacities because this can decrease the catalyst volume required for a particular application, thus reducing capital costs. Higher capacities also result in longer periods between catalyst regeneration thus reducing fuel penalties. This section investigates NOx storage capacities as a function of catalyst temperatures.

For this experiment, the storage capacity of the LNT was tested at three different catalyst temperatures. The aftertreatment system was operated with the optimal regeneration parameters found from the test matrix for 10%, 25% and 50% engine loads until catalyst temperatures stabilized to their respective temperatures; 440° C, 510° C and 560° C. The regeneration sequence was then stopped and the catalyst was allowed to adsorb until trapping efficiencies fell

below 90%. Analysis of the results yielded Figure 131, which shows the dependence of the NO_x storage capacity on catalyst temperatures. The predicted storage capacity from bench flow reactor and baseline engine data is also shown. Because they were extrapolated from experiments with more controlled conditions, results for predicted storage capacities are higher than actual storage capacities. Nevertheless, both show the same general trend of decreasing capacities with increasing temperatures. Comparing the temperature dependence of the LNT for storage capacity (Figure 131), with the temperature dependence of the oxidation catalyst for methane oxidation (Figure 115), reveals a narrow temperature window for optimizing performance.

Figure 131 LNT Storage Capacity vs. Temperature

Fixed Temperature Adsorption

Because the LNT and the oxidation catalyst require different temperature ranges for optimal performance, one potential solution would be to physically separate the two catalyst bricks. Placing the oxidation catalyst closer to the outlet of the turbocharger would allow it to be maintained at higher temperatures for methane oxidation. Placing a waste heat recovery system in front of the LNT would allow it to be maintained at a lower temperature for higher NO_x storage capacities. Ideally, the LNT would be maintained at a constant temperature regardless of engine load. The following experiment was used to simulate such a scenario. Here, the aftertreatment system is operated with the optimal regeneration parameters for 25% engine load. Once the catalyst temperatures stabilize to 510° C, the engine load is changed to 50%, the regeneration sequence is stopped, and the catalyst immediately begins to adsorb. By doing this, the NO_x flux from the engine has been changed to that of the higher load, but the catalyst temperatures have not been given time to change. Thus, the catalyst is adsorbing NO_x at the higher engine load but with a constant 510° C. The same procedure was repeated for each engine load. The average NO_x rating for the 5 engine modes was calculated until the trapping efficiency fell below 90%. Figure 132 shows these average NO_x ratings, as well as minimum NO_x ratings

and NOx flux rates for each engine mode. These results show that when the LNT adsorbs at a constant 510° C, NOx reduction is possible at higher engine loads. Even with the high NOx flow rates an average NOx rating of 0.17 g/hp-hr and instantaneous ratings of 0.06 g/hp-hr are achievable at 75% load. At 100% load average ratings of 0.63 g/hp-hr and instantaneous ratings of 0.17 g/hp-hr are possible. These results demonstrate the potential improvements to be gained by a better thermal management system for the catalyst.

Figure 132 NOx Ratings with Fixed Temperature Adsorption

Methane Utilization

Experiments proved that the oxidation catalyst could successfully combust methane at high enough temperatures. However, in addition to burning out excess oxygen through methane combustion, the rich combustion products CO and H₂ must be formed. The following experiments explored the production and utilization of CO for the range of injection rates used in the test matrix. These experiments were conducted at 25% and 50% engine loads, where catalyst bricks are above their light off temperature. CO levels were measured at three positions along the catalyst chamber during the regeneration sequence; Oxi Cat In, Oxi Cat Out and LNT Out as indicated in Figure 114. Figures 133 and 134 show the grams of CO at each of these positions when injecting for lambda values of 0.5, 0.6, 0.7, 0.8 and 0.9. The results show an increase in CO levels measured at the Oxi Cat Out position as exhaust entering the catalyst becomes richer. For 50% load CO production stabilizes beyond 0.7 lambda. CO levels measured at the LNT Out position are consistently lower than those measured at the Oxi Cat In position. This indicates that the Lean NOx Traps are utilizing some of the CO for regeneration. For 50% engine load, the quantity of CO produced at 0.9 lambda, is small enough that it is entirely consumed by the regeneration mechanism. Similarly, for 25% engine load, all of the CO produced at 0.8 and 0.9 lambda is consumed. Unlike CO levels sampled at the Oxi Cat Out position, CO levels sampled at LNT Out do not taper off beyond 0.7 lambda. This indicates that the reformer catalyst is also

producing CO. Because of the catalyst can assembly, it was not possible to access a sample point between the reformer catalyst and the LNT. A more in-depth investigation of methane utilization would require sampling CO levels after the reformer, and is recommended as a next step in methane utilization studies.

Figure 133 50% Load CO Production and Consumption

Figure 134 25% Load CO Production and Consumption

Nomenclature

- $a(x)$ = Catalytic surface area per unit volume, $\text{cm}^2 / \text{cm}^3$
 A_v = Frontal area of the monolith, cm^2
 $C_{g,i}$ = Concentration of species i in the bulk gas stream, mole fraction
 $C_{s,i}$ = Concentration of species i in the solid phase, mole fraction
 D_i = Diffusivity of the species i in the relative mixture, cm^2 / s
 C_{pg} = Specific heat of gas, $\text{J} / \text{g.K}$
 C_{ps} = Specific heat of solid, $\text{J} / \text{g.K}$
 h = Heat transfer coefficient, $\text{J} / \text{cm}^2 . \text{s.K}$
 K_{mi} = Mass transfer coefficient of the species i , cm / s
 R_h = Hydraulic radius of channel, cm
 R_g = Universal gas const.
 $(R_a)_H$ = Specific reaction rate in gas phase for species i , $\text{mol} / \text{cm}^2 \text{Pd.s}$
 $(R_a)_{\text{surface}}$ = Specific surface reaction rate for species i , $\text{mol} / \text{cm}^2 \text{Pd.s}$
 S = Geometric surface area per unit volume, $\text{cm}^2 / \text{cm}^3$
 T_s = Solid Temperature, K
 T_{gas} = Gas Temperature, K
 v = Linear Superficial velocity of exhaust gas, cm / s
 W_g = Mass flow rate, g / s
 Y_{surface} = Mole fraction on the surface
 Y_{gas} = Mole fraction of species in gas phase

Symbols

- ϕ = Void fraction of the monolith
 λ_s = Thermal conductivity of the solid, $\text{J} / \text{cm.s.K}$
 ρ_g = Gas Density, g / cm^3
 ρ_s = Solid Density, g / cm^3

Bibliography

1. M.Zheng, E.Mirosh, W.Klopp, D.Ulan, M.Pardell, P.Newman, G.Bunimovich, Y.Matros, and A. Nishimura, "Development of a Compact Reverse-Flow Catalytic Converter for Diesel Dual Fuel LEV", SAE paper 1999-01-3558.
2. M.Zheng, E.Mirosh, D.Ulan, W .Klopp, M.Pardell, P .Newman, and A. Nishimura, "A Novel Reverse-Flow Catalytic Converter Operated on an ISUZU-6HH1 Diesel Dual Fuel Engine", 1999 ASME-IEC Fall Technical Conference, October 17-20,1999.
3. B. Liu, R. E. Hayes, M. D. Checkel, M. Zheng and E. Mirosh, "Reverse Flow Catalytic Converter for a Natural Gas/Diesel Dual Fuel Engine", Journal of Chemical Engineering Science, 56 (2001) 2641-2658, Oxford, New York, Pergamon Press.
4. V. Strots, G. Bunimovich, Y. Matros, M. Zheng, and E. Mirosh, 1998, "Novel Catalytic Converter for Natural Gas Powered Diesel Engines", SAE 980194.
5. R. McCormick, A. Newlin, D. Mowery, M. Graboski, and T. Ohno, 1996, "Rapid Deactivation of Lean-Burn Natural Gas Engine Exhaust Oxidation Catalysts", SAE paper 961976.
6. J. Lampert, M. Kazi, and R. Farrauto, "Palladium Catalyst Performance for Methane Emissions Abatement from Lean Burn Natural Gas Vehicles", Applied Catalyst B: Environmental 14, pp. 211-223, 1997.
7. Robert J. Farrauto and Kenneth E. Voss, "Monolithic Diesel Oxidation Catalysts", Applied Catalyst B: Environmental 10, pp. 29-51, 1996.
8. Cullis, C.F. and B.M. Willat. "Oxidation of methane over supported precious metal catalysts", J.Cat., 83 267-285, 1983.
9. Duggal, Vinod K., Roy Meyer, David Meyers, Syed M. Shahed. "Development of a Heavy Duty On-Highway Natural Gas-Fueled Engine". SAE Paper No. 922362, Warrendale, Pennsylvania: Society of Automotive Engineers, Inc., 2000.
10. Fussel, Lori M., Jeffrey W. Hodgson, and David K. Irick. "Automotive Engines and Vehicles" Encyclopedia of Environmental Analysis and Remediation, New York: John Wiley and Sons, Inc., 1998.
11. Hayes, R.E., Kolaczowski, S.T., Introduction to Catalytic Combustion. Amsterdam, The Netherlands: Gordon and Breach Science Publishers, 1997.
12. Helden, R., Verbeek, R., Aken, M., Genderen, M., Patchett, J., Straten, T., Kruithof, J., and Saluneaux, C., 2002, "Engine Dynamometer and Vehicle Performance of a Urea SCR-System for Heavy-Duty Truck Engines", SAE paper 2002-01-0286.
13. Heywood, John B. Internal Combustion Engine Fundamentals. New York, NY: McGraw-Hill, Inc., 1988.
14. Lisenby, Paul M., "An Experimental Investigation of Natural Gas Catalysts Using a Bench-Flow Reactor", M. Sc. Thesis, Department of Mechanical Engineering, The University of Tennessee – Knoxville, 1995.
15. Mital, R., S. C. Huang, B. J. Stroia, Robert C. Yu, and C. Z. Wan 2002, "A Study of Lean NOx Technology for Diesel Emission Control", SAE paper 2002-01-0956.
16. Quiros, Edwin N., Yasuhiro Daisho, Turo Yaeo, Takahisa Koseki, Takeshi Saito, Ryoji Kihara. "Combustion and Exhaust Emissions in a Direct-Injection Diesel Engine Dual

- Fueled with Natural Gas”, SAE Paper No. 950465, Warrendale, Pennsylvania: Society of Automotive Engineers, Inc., 2000.
17. Stone, Richard. Introduction to Internal Combustion Engines. Warrendale, Pennsylvania: Society of Automotive Engineers, Inc., 1999.
 18. Subramanian, S., Kudla, R.J., Chattha, M.S., “Treatment of Natural Gas Vehicle Exhaust”, SAE Paper No. 930223, Warrendale, Pennsylvania: Society of Automotive Engineers, Inc., 1993.
 19. Turns, Stephen R. An Introduction to Combustion, Concepts and Applications. New York, NY: McGraw-Hill, Inc., 2000.
 20. Zhang, G., Pflung, A., Raine, R.R., “Comparison of Emissions from Natural Gas and Gasoline Fuelled Engines – Total Hydrocarbon and Methane Emissions and Exhaust Gas Recirculation Effects”, SAE Paper No. 970743, Warrendale, Pennsylvania: Society of Automotive Engineers, Inc., 1997.
 21. Zheng, M., Mirosh, E., Liu, B., Checkel, M.D., Hayes, R.E., “Experimental and Modeling Study of Variable Cycle Time for a Reversing Flow Catalytic Converter for Natural Gas/Diesel Dual Fuel Engines”, SAE Paper No. 2000-01-0213, Warrendale, Pennsylvania: Society of Automotive Engineers, Inc., 2000.
 22. Zheng, Ming, Edward A. Mirosh, Vadim O. Strots, Grigorii A. Bunimovich, Yurii Sh. Matros. “Novel Catalytic Converter for Natural Gas Powered Diesel Engines”. SAE Paper No. 980194. Warrendale, Pennsylvania: Society of Automotive Engineers, Inc., 2000.
 23. M. van Sint Annaland, R. C. Nijssen, “A novel reverse flow reactor coupling endothermic and exothermic reactions: an experimental study,” Chemical Engineering Science pp. 4967-4985, 2002
 24. Krzysztof Gosiewski, Ulrich Bartmann, Marek Moszczynski, Leslaw Mleczko, “Effect of the intraparticle mass transport limitations on temperature profiles and catalytic performance of the reverse-flow reactor for the partial oxidation of methane to synthesis gas,” Chemical Engineering Science pp. 4589-4602, 1999
 25. F. Cunill, L. van de Beld, K. R. Westerterp, “Catalytic Combustion of Very Lean Mixtures in a Reverse-Flow Reactor Using an Internal Electric Heater,” Ind. Eng. Chem. Res. pp. 4198-4206, 1997
 26. Jason M. Keith, David T. Leighton, Jr., Hsueh-Chia Chang, “A New Design of Reverse-Flow Reactors with Enhanced Thermal Dispersion,” Ind. Eng. Chem. pp. 667-682, 1999
 27. M. van Sint Annaland, J. A. M. Kuipers, W. P. M. van Swaaij, “Safety analysis of switching between reductive and oxidative conditions in a reaction coupling reverse flow reactor,” Chemical Engineering Science, pp. 1517-1524, 2001
 28. B. Liu, R. E. Hayes, M. D. Checkel, M. Zheng, E. Mirosh, “Reversing flow catalytic converter for a natural gas/diesel dual fuel engine,” Chemical Engineering Science pp. 2641-2658, 2001
 29. H. Zufle, T. Turek, “Catalytic combustion in a reactor with periodic flow reversal. Part 1. Experimental results,” Chemical Engineering and Processing pp. 327-340, 1997
 30. H. Zufle, T. Turek, “Catalytic combustion in a reactor with periodic flow reversal. Part 2. Steady-state reactor model,” Chemical Engineering and Processing pp. 341-352, 1997

31. Moshe Ben-Tullilah, Einat Alajem, Rina Gal, Moshe Sheintuch, "Flow-rate effects in flow-reversal reactors: experiments, simulations and approximations," Chemical Engineering Science, 2002
32. Yu. Sh. Matros, G. A. Bunimovich, V. O. Strots, E. A. Mirosh, "Reversed flow converter for emission control after automotive engines," Chemical Engineering Science pp. 2889-2898
33. R. Quinta Ferreira, C. Almeida Costa, S. Masetti, "Reverse-flow reactor for a selective oxidation process," Chemical Engineering Science pp. 4615-4627
34. F. Moallemi, G. Batley, V. Dupont, T. J. Foster, M. Pourkashanian, A. Williams, "Chemical modeling and measurements of the catalytic combustion of CH₄/air mixtures on platinum and palladium catalysts," Catalysis Today pp. 235-244, 1999
35. Byung-Chul Choi, Geon-Seog Son, Eugene Kim, Kwi-Young Lee, "Effective Parameters on the Catalytic Reaction of NGV Catalytic Converter," SAE 960239, 1996
36. Athanasios G. Konstandopoulos, Margaritis Kostoglou, "Periodically Reversed Flow Regeneratino of Diesel Particulate Traps," SAE 1999-01-0469, 1999
37. Montiero, D. Zemlyanov, F.H. Ribiero., "Complete Methane Oxidation on Palladium Model Catalyst". G. Zhu, J. Han, R.S. 2003.
38. Viatcheslav I. Naoumov, Viktor G. Kriukov, Airat L. Abdullin., "Chemical Kinetics Software System for the propulsion and power engineering", 41st Aerospace Science Meeting and exhibit. 2003.
39. Warren R. Smith, Ludmilla N. Bobrova., "Mathematical modeling of a reverse flow reactor with catalytic surface dynamics". Chemical Engineering Science. 57, pp. 393 – 407, 2002.
40. Moshe Ben Tullilah, Einat Alajem, Rina Gal, Moshe Sheintuch, "Flow – Rate effects in flow reversal reactors: Experiments, simulation and approximations", Chemical Engineering Science. 2002.
41. Dragos Ciuparu, Maxim R. Lyubovsky, Eric Altman, Lisa D. Pfefferle and Abhaya Datye, "Catalytic Combustion of Methane over Palladium Based Catalysts", Catalytic Reviews. 44 (4), pp. 593 – 649, 2002.
42. Eduardo Lopez, Noemi S. Schbib, Carlos E. Gigola and Veronica Bucala, "Influence of the Methane Combustion Kinetic Model on the Operating Conditions of an Auto thermal Catalytic Reactor", Ind. Eng. Chem. Res, 40, pp. 5199 – 5205, 2001.
43. Roberts E. Hayes, Stan T. Kolaczowski, Paul K.C. Li, "The palladium catalyst oxidation of methane: reaction kinetics and the effect of diffusion barriers", Chemical Engineering Science. 56 (16), pp. 4815 – 4835, 2001.
44. R.S. Monteiro, D. Zemlyanov, J.M. Storey and F.H. Ribeiro, "Turnover Rate and reaction orders for the complete oxidation of methane on a palladium foil in excess oxygen", Journal of Catalysis. 199, pp. 291 – 301, 2001.
45. F. Moallemi, G. Batley, V. Dupont, T.J. Foster, M. Pourkashanian, A. Williams. Chemical modeling and measurements of the catalytic combustion of CH₄ / air mixtures on platinum and palladium catalysts. Catalysis Today. 47, pp. 235 – 244, 1999.
46. O. Deutschmann, R. Schmidt, F. Behrendt and J. Warnatz, "Numerical Modeling of Catalytic Ignition". 26th Symposium on combustion. pp. 1747 – 1754, 1996.

47. Pio Forzatti, Gianpiero Groppi, "Catalytic combustion for the production of energy", *Catalysis Today*. 54, pp. 165 – 180, 1999.
48. Quinta Ferreira, C. Almeida Costa. S. Masseti, "Reverse flow reactor with selective oxidation process", *Chemical Engineering Science*. 54, pp. 4615 – 4627, 1999.
49. Ruoyu Hong, Xin Li, Hongzhong Li, Weikang Yuan, "Modeling and simulation of SO₂ oxidation in a fixed bed reactor with periodic flow reversal", *Catalysis Today*. 38, pp. 47 – 58, 1997.
50. Robert Jahn, Dalimi Snita Milan Kubicek, Milos Marek, "3 – D modeling of monolith reactors", *Catalysis Today*. 38, pp. 39 – 46, 1997.
51. Robert Hayes, Stan T. Kolaczowski, W. John Thomas and James Titiloye, "Transient Experiments and Modeling of the catalytic combustion in a monolith reactor", *Ind. Eng. Chem. Res.*, 35(2), pp. 406 – 414, 1996.
52. Naktsuji, T., Yasukawa, R., Tabata, K., Sugaya, T., Ueda, K., and Niwa, M., "*Highly Durable NOx Reduction System and Catalysts for NOx Storage Reduction System*," SAE Technical Paper Series 980932, 1998.
53. Bragan, M. S., Clark, A. D., and Brisley, R. J., "*Recent Progress in Nox Trap Technology*," SAE Technical Paper Series 980933, 1998.
54. Mahzoul, H., and Brilhac, P. G., "*Experimental and Mechanistic Study of NOx Absorption over NOx Trap Catalysts*," *Applied Catalysis B: Environmental* 20 pp.47-55, 1999.
55. Larsson, M., Andersson, L., Fast, O., Litorell, M., and Mukuie, R., 1999, "*NOx Trap Control by Physically Based Model*," Society of Auto motive Engineers 1999-01-3503, 1999.
56. Fridell, E., Persson, H., Westerberg, B., Olsson, L., and Skoglundh, M., "*The Mechanism for NOx Storage*," *Catalysis Letters* 66 (2000) pp.71-74, 2000.
57. Lietti, L., Forzatti, P., Nova, I., and Tronconi, E., "*NOx Storage Reduction over Pt- Ba/γ-Al₂O₃ Catalyst*," *Catalysis Letters* 204 pp.175-191, 2001.
58. Laurent, F., Pope, C.J., Mahzoul, H., Delfosse, L., and Gilot, P., "*Modelling of NOx Adsorption over NOx Adsorbers*," *Chemical Engineering Science* 58 (2003) 1793-1803, 2002.
59. Wagner, G. J., Ph.D., "*Advanced Reciprocating Engine Systems Bench Flow Reactor Testing of NOx Absorber Catalyst for Lean- Burn Natural Gas Engine: Efficiency of Regeneration Process Utilizing Methane Oxidation and Reforming Catalysts*," Research Report for Oak Ridge National Lab., 2003.