Report Title: Selective NOx Recirculation for Stationary Lean-Burn Natural Gas Engines

Type of Report: Technical Progress Report (Annual)

Reporting Period Start Date: September 30, 2004

Reporting Period End Date: September 30, 2005

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Date Report was Issued: December 28, 2005

DOE Award Number: DE-FC26-02NT41608

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Abstract

The research program conducted at the Center for Alternative Fuels, Engine and Emissions (CAFEE) at West Virginia University is directed towards the verification and optimization of an approach to remove oxides of nitrogen (NOx) from the exhaust gas of stationary lean-burn natural gas engines. This program is sponsored by the US Department of Energy, National Energy Technology Laboratory (NETL) under contract number: DE-FC26-02NT41608.

Selective NOx Recirculation (SNR) involves cooling the engine exhaust gas and then adsorbing the oxides of nitrogen (NOx) from the exhaust stream, followed by the periodic desorption of NOx. By returning the desorbed, concentrated NOx into the engine intake and through the combustion chamber, a percentage of the NOx is - decomposed during the combustion process. An initial study of NOx decomposition during lean-burn combustion was concluded in 2004 using a 1993 Cummins L10G 240hp natural gas engine. It was observed that the air/fuel ratio, injected NO (nitric oxide) quantity and engine operating points affected NOx decomposition rates of the engine. Chemical kinetic modeling results were also used to determine optimum NOx decomposition operating points and were published in the 2004 annual report. A NOx decomposition rate of 27% was measured from this engine under lean-burn conditions while the software model predicted between 35-42% NOx decomposition for similar conditions.

A later technology 1998 Cummins L10G 280hp natural gas engine was procured with the assistance of Cummins Inc. to replace the previous engine used for 2005 experimental research. The new engine was equipped with an electronic fuel management system with closed-loop control that provided a more stable air/fuel ratio control and improved the repeatability of the tests. The engine was instrumented with an in-cylinder pressure measurement system and electronic controls, and was adapted to operate over a range of air/fuel ratios. The engine was connected to a newly commissioned 300hp alternating current (AC) motoring dynamometer.

The second experimental campaign was performed to acquire both stoichiometric and slightly rich (0.97 lambda ratio) burn NOx decomposition rates. Effects of engine load and speed on decomposition were quantified, but Exhaust Gas Recirculation (EGR) was not varied independently. Decomposition rates of up to 92% were demonstrated. Following recommendations at the 2004 ARES peer review meeting at Argonne National Laboratories, in-

cylinder pressure was measured to calculate engine indicated mean effective pressure (IMEP) changes due to NOx injections and EGR variations, and to observe conditions in the cylinder.

The third experimental campaign gathered NOx decomposition data at 800, 1200 and 1800 rpm. EGR was added via an external loop, with EGR ranging from zero to the point of misfire. The air/fuel ratio was set at both stoichiometric and slightly rich conditions, and NOx decomposition rates were calculated for each set of runs. Modifications were made to the engine exhaust manifold to record individual exhaust temperatures. The three experimental campaigns have provided the data needed for a comprehensive model of NOx decomposition during the combustion process, and data have confirmed that there was no significant impact of injected NO on in-cylinder pressure.

The NOx adsorbtion system provided by Sorbent Technologies Corp. (Twinsburg, OH), comprised a NOx adsorber, heat exchanger and a demister. These components were connected to the engine, and data were gathered to show both the adsorption of NOx from the engine, and desorption of NOx from the carbon-based sorbent material back into the engine intake, using a heated air stream.

In order to quantify the NOx adsorbtion/desorption characteristics of the sorbent material, a bench top adsorption system was constructed and instrumented with thermocouples and the system output was fed into a NOx analyzer. The temperature of this apparatus was controlled while gathering data on the characteristics of the sorbent material. These data were required for development of a system model. Preliminary data were gathered in 2005, and will continue in early 2006. To assess the economic benefits of the proposed SNR technology the WVU research team has been joined in the last quarter by Dr Richard Turton (WVU - Chemical Engineering), who is modeling, sizing and costing the major components. The tasks will address modeling and preliminary design of the heat exchanger, demister and NOx sorbent chamber suitable for a given engine. A simplified linear driving force model was developed to predict NOx adsorbtion into the sorbent material as cooled exhaust passes over fresh sorbent material. This aspect of the research will continue into 2006, and the benefits and challenges of SNR will be compared with those of competing systems, such as Selective Catalytic Reduction..

Chemical kinetic modeling using the CHEMKIN software package was extended in 2005 to the case of slightly rich burn with EGR. Simulations were performed at 10%, 20%, 30% and 40% of the intake air replaced with EGR. NOx decomposition efficiency was calculated at the point in time where 98% of fuel was consumed, which is believed to be a conservative approach. The modeling data show that reductions of over 70% are possible using the “98% fuel burned” assumption. Both the CHEMKIN and experimental data will be used for the construction of a NOx decomposition model in FY2006.

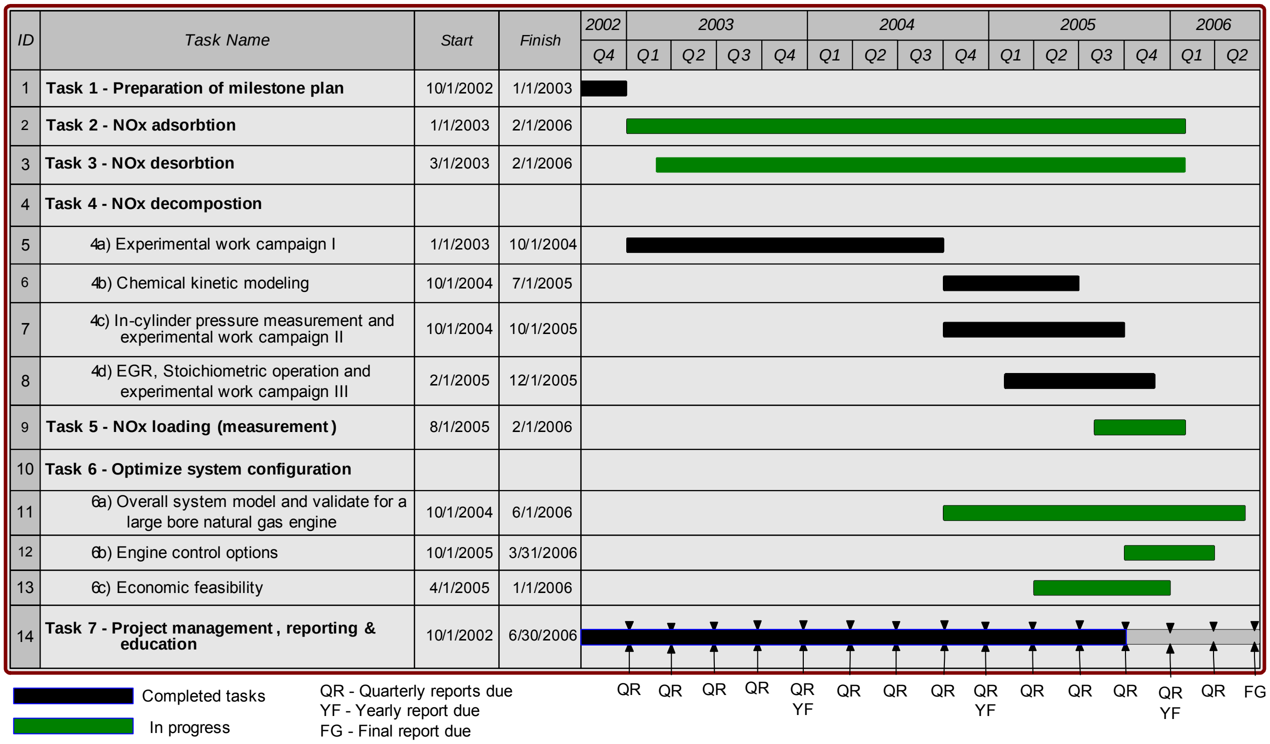
A study of possible system configurations commenced in 2005, and will be incorporated into the model. It was clear that the system could not be designed on a two phase adsorption/desorption assumption, but must account for four phases: cooling, adsorbing, heating, and desorbing. Exhaust gas appears to be the most suitable desorbing stream.

Updates to the project Gantt chart

New milestones were added to the Gantt chart in FY2005 (Figure 1). The modified Gantt chart and subtasks are described below.

TASK 1.0 Prepare milestone plan - Completed
TASK 2.0 NOx Adsorbtion - Deadline is extended to complete industrial partner tasks, and to deduce effectiveness from Task 4 work. – In progress
TASK 3.0 NOx Desorption - Deadline is extended to complete industrial partner tasks, and to deduce effectiveness from Task 5 work. - In progress
TASK 4.0 NOx Decomposition
    4a) Experimental work campaign I – Completed
    4b) CHEMKIN Modeling (requested at the 2004 ARES review at Argonne National Laboratory) – Completed
    4c) In-cylinder pressure measurement (requested at the 2004 ARES review at Argonne National Laboratory) and experimental work campaign II – Completed
    4d) Stoichiometric with EGR operation (to satisfy much higher destruction ratios) and experimental work campaign III - Completed
TASK 5.0 NOx Loading (Measurement) - In progress
TASK 6.0 Optimize system configuration
    6a) Overall system model – In progress
    6b) Engine control options – In progress
    6c) Economic feasibility (new task added in FY2005, following the 2005 ARES review at Argonne National Laboratory) – In progress
TASK 7.0 Project management, reporting and education – On schedule

Project Gantt-chart



ID	Task Name	Start	Finish
1	**Task 1 - Preparation of milestone plan**	10/1/2002	1/1/2003
2	**Task 2 - NOx adsorbtion**	1/1/2003	2/1/2006
3	**Task 3 - NOx desorbtion**	3/1/2003	2/1/2006
4	**Task 4 - NOx decompostion**		
5	4a) Experimental work campaign I	1/1/2003	10/1/2004
6	4b) Chemical kinetic modeling	10/1/2004	7/1/2005
7	4c) In-cylinder pressure measurement and experimental work campaign II	10/1/2004	10/1/2005
8	4d) EGR, Stoichiometric operation and experimental work campaign III	2/1/2005	12/1/2005
9	**Task 5 - NOx loading (measurement)**	8/1/2005	2/1/2006
10	**Task 6 - Optimize system configuration**		
11	6a) Overall system model and validate for a large bore natural gas engine	10/1/2004	6/1/2006
12	6b) Engine control options	10/1/2005	3/31/2006
13	6c) Economic feasibility	4/1/2005	1/1/2006
14	**Task 7 - Project management, reporting & education**	10/1/2002	6/30/2006

Figure 1. SNR Project Gantt-chart

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Introduction

Stationary natural gas fueled engines are usually operated in a lean burn mode to achieve high thermal efficiency and to control in-cylinder temperatures. However, in most circumstances this causes natural gas engines to produce an unacceptable level of NOx emissions. These emissions may be reduced least expensively by changing the in-cylinder combustion parameters or by equipping the engine with NOx abatement aftertreatment systems. The goals of the ARES (Advances Reciprocating Engines Systems) program is to develop technology to allow natural gas engines for power generation to operate at 0.1 g/bhp-hr NOx with an efficiency of 50% by 2010.

One method for NOx reduction is to operate lean-burn natural gas engines with high air/fuel ratios. However, this region of operation is relatively narrowly defined – the lower end ($\lambda \approx 1.3$) produces comparatively elevated levels of NOx, while operating in the upper end ($\lambda \approx 1.7$) leads to incomplete combustion and high unburned hydrocarbon (HC) emissions due to misfire, with corresponding loss of power density. Some further NOx reductions can be effected by retarding the ignition timing and introducing EGR. Again, applying these methods too harshly results in power reduction and durability problems.

Selective NOx Recirculation (SNR) technology, discussed in this report, proposes a NOx emissions reduction technique that can be used in stationary lean-burn natural gas engines. SNR incorporates the cooling of exhaust gas, followed by adsorption of NOx from the exhaust stream. NOx is then desorbed periodically from the adsorber, and returned at a high concentration to the engine intake. A substantial fraction of the returned NOx is decomposed by the in-cylinder combustion process.

Emissions control options

The two main approaches to control NOx are by altering the in-cylinder combustion process, and by the use of post-combustion aftertreatment systems. In automotive (primarily transit bus) applications, heavy-duty natural gas lean-burn engines have used wide-range oxygen sensor feedback to approach 1g/bhp-hr NOx, but further significant reductions are unlikely for lean-burn operation without exhaust gas aftertreatment. Currently the following technologies are proposed to reduce the NOx output.

Three-Way Catalyst (TWC)

A three-way catalyst (TWC) is primarily used in engines that maintain the air/fuel ratio at or near stoichiometric operation. It reduces the three major pollutants, namely NOx, CO and HC. A TWC is able to reduce NOx emissions by 90% and CO and HC by 80% [1]. The reactions that convert NOx to N_2 and CO and hydrocarbons to CO_2 and H_2O cannot take place if the exhaust gas contains more than 0.5% oxygen. For this reason, a TWC is not directly applicable for lean-burn engines. While a TWC may be applied to a stoichiometric natural gas engine, the stoichiometric operation usually implies a loss of thermal efficiency and would therefore be employed only if emissions standards cannot be met economically by competing systems.

Selective Catalytic Reduction (SCR)

The SCR technology selectively reduces NOx to N_2 from lean-burn exhaust gas when it passes through a catalyst in the presence of a reducing agent such as ammonia (NH_3), which can be injected directly or created by decomposition of urea ($(NH_2)_2CO$). NOx reductions of 80 to 90% are achievable with SCR, and higher reductions are possible with the use of more catalyst area and volume of reducing agent. Urea decomposes in the hot exhaust gas and SCR reactor, releasing ammonia. Approximately one mole of ammonia is required per mole of NOx at the SCR reactor inlet in order to achieve an 80 to 90% NOx reduction [2].

Johnson Matthey is one of the largest suppliers of SCR catalysts. On their webpage [3] they state that in general SCR catalysts are used in lean-burn applications where oxygen content is greater than 1% in the exhaust gas stream. The basic reaction steps in an SCR catalyst are shown below, where NO and NO_2 are converted to N_2 and H_2O using ammonia as a reducing agent [2][4].

$$4NO + 4NH_3 + O_2 \Rightarrow 4N_2 + 6H_2O \qquad \text{Equation 1}$$

$$2NO_2 + 4NH_3 + O_2 \Rightarrow 3N_2 + 6H_2O \qquad \text{Equation 2}$$

$$NO + NO_2 + 2NH_3 \Rightarrow 2N_2 + 3H_2O \qquad \text{Equation 3}$$

In Equation 3, the NOx conversion rate becomes faster when there is a mixture of NO and NO_2 present in the exhaust gas as the reactions in Equations 1 and 2 occur in parallel.

Depending on the application and operating temperature, various types of base metals are used in the catalyst. The most commonly used metals/oxides of metals in SCR systems made by Johnson Matthey are vanadium (V), tungsten (W), and titania (Ti), as well as silica, and zeolite which can be framed into a honeycomb structure or coated on to a ceramic support. The optimal operating temperatures where 95% or more of NOx is converted are listed below:

265 – 425°C: V/Ti/W on high-density honeycomb

345 – 590°C: zeolite on ceramic substrate

The amount of NOx converted greatly depends on the substrate volume, reductant concentration, operating temperature and activity of the SCR catalyst. The complexities of the system includes hazardous liquid agent storage, air and reactants monitoring, controls, catalyst poisoning, and reductant slip that can contribute to additional environmental concerns.

SCR systems add a significant cost to the installation and maintenance when integrated to an existing engine system (Table 1). A SCR system can be retrofitted on a 2300hp IC engine for approximately $158,000 [5] . The annual operating costs of the system can be as high as $67,000 per year. This includes ammonia or urea, catalyst washing, replacing sensors, thermocouples, and labor. The annual operating costs of an SCR system are significantly affected by the size of the engine system on which it is implemented and by the engine-out NOx level. Additional operating costs may be incurred if a reserve catalyst is required.

Table 1. SCR cost analysis (Krishnan et al [5])

Variables	For 90% NOx reduction	For 50% NOx reduction
Engine (hp)	2336	2336
Annual operation (hours)	8000	8000
Fuel consumptions (lb/bhp-hr)	0.34	0.34
Engine speed (rpm)	1800	1800
Engine load (%)	100	100
NOx (ppm)	687	687
Urea wt% with balance water	0.32	0.32
NOx emissions (tons/year)	101	101
NOx Reduction (%)	90	50
Tons of NOx reduced	91	50
Capital cost for system ($)	157,590	142,290
Annual operating cost ($)	66,882	46,116

Since the difference in capital cost for the 50% and 90% installations are relatively small, it is preferable to use a 90% reduction system.

The cost of the reducing agent (urea) greatly effects the implementation of an SCR system. A study was conducted by Fable et al, [6] to evaluate the cost of delivering aqueous urea to service stations. The study showed that the production cost of 32% of aqueous urea solution could range from $0.12 to $0.30 per gallon. But the cost to the end customer would be dominated by the distribution cost which could range anywhere from $0.70 to $35 per gallon. This wide range is mainly due to storage tank and delivery injection nozzle investments, infrastructure development and the impact of quality specifications. For applications involving large stationary engines, the distribution cost would be lower than for automotive use.

A study conducted by Fable et al, [6] mentions that the cost to purchase and manufacture urea to SCR systems is influenced by the price of natural gas. Figure 2 shows the manufacturing cost of urea vs natural gas prices. In 2002 the average price for natural gas was $3/million Btu.

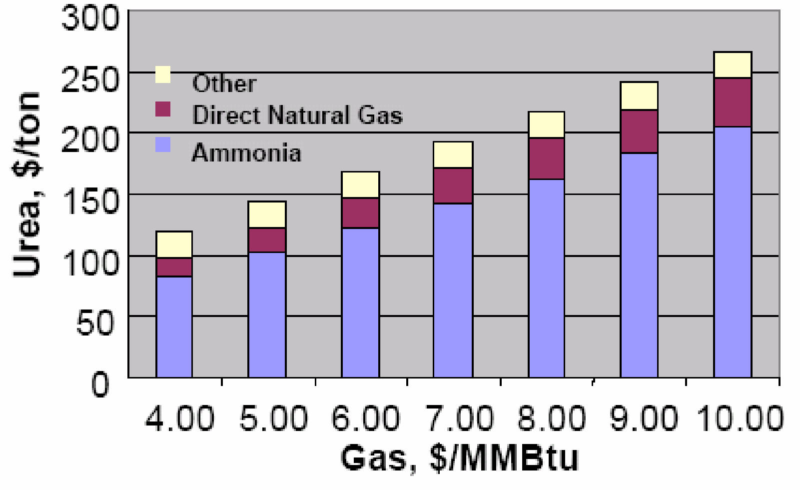


Figure 2. Urea manufacturing cost $/ton vs natural gas price $/million Btu [6]

Another study conducted by NREL/DOE showed that about 1 gallon of urea would be consumed for each 18 gallons of diesel fuel on heavy diesel vehicles equipped with SCR systems in order to reach the 2007 NOx targets [7].

Lean NOx Traps (LNT) or NOx Trap Catalyst

NOx Trap Catalysts or Lean NOx Traps have been installed on direct injection engines to reduce NOx emission. The temperature window for the catalysts that provide NOx conversions is between 200-550°C [8]. The lean NOx catalyst stores NOx under exhaust lean conditions and converts the stored NOx into N_2 under rich exhaust conditions. The catalysts are sensitive to sulfur poisoning and therefore require fuels with extremely low sulfur content. A NOx-Trap catalyst will gradually lose its NOx storage function with sulfur deposition and requires regular desulfations at high temperature and rich operating conditions. Much has been written on the durability and poisoning issues of NOx- Trap catalysts [9]-[25].

Evaluation on competing emissions reduction technologies (U.S. Air Force [26])

A study was conducted by the U.S. Air Force to evaluate available NOx reduction technologies on 148hp Detroit Diesel engine powered generators. The authors devised a numerical rating system to evaluate the merits of competing technologies. The system was divided into five criteria for a total of 100 points based on emissions reduction capability (25 points), cost (25 points), reliability and maintenance (20 points), deployability (20 points) and fidelity of data (10 points). Three pre-combustion and three post-combustion NOx reduction technologies were evaluated.

Only the emission reduction capability of each technology is discussed in this report. A maximum of 10 points were allocated for NOx reduction capability and were scored based on comparative NOx reductions demonstrated by each technology. Technologies that achieved greater than 90% reduction over all loads earned maximum points, followed by those achieving reductions in the 70 to 80% range. Points were prorated for systems with greater than 69% that varied with load, while systems with less than 69% NOx reduction scored 0. Each technology was further evaluated on increase in carbon monoxide (CO), particulate matter (PM), hydrocarbons (HC), or secondary emissions. Furthermore, the technologies had to be deployable on or before 2000. Since the study was geared toward diesel engine NOx reduction, two of the pre-combustion technologies were not applicable to stationary natural gas engines, but the aftertreatment systems could be applied.

Pre-combustion NOx reduction technologies

1. Water-in-Fuel Firing (WFF) – water was emulsified with the fuel to act as a detergent and injected into the engine thereby lowering the combustion temperature to reduce NOx formation.
2. Oxygen-Enriched Air (OEA) - Intake air was enriched with oxygen up to 21% to improve combustion.

3. Dual-Fuel Firing (DFF) – Natural gas was used a second fuel in a diesel engine and was injected into the intake manifold. Natural gas was chosen since it has lower NOx production than diesel fuel.

Post-combustion NOx reduction technologies

1. Selective-Catalytic Reduction (SCR) - Ammonia was used a reductant on a vanadia-coated titanium honeycomb catalyst.
2. NOx-Sorbent Filtering (NSF) – A granular activated carbon material was used to adsorb NOx from cooled exhaust gas.
3. Non-Thermal Discharge (NTD) - An electrically driven process that used high dielectric fields and a chemical agent to promote the conversion of NOx into NO_2 . The NO_2 was then cooled and a scrubber was used to remove the water soluble compounds from the exhaust gas.

The evaluation criteria for emissions reduction capability with numerical ratings are shown in Table 2. It was concluded in the study that, based on the criteria of emissions-reduction, cost, reliability, maintainability, deployability, the Water-in-Fuel Firing method, Selective-Catalytic Reduction, and NOx-Sorbent Filtering technologies are viable to attain overall environmental compliance. However, the study mentions that these three systems are not turnkey solutions, and therefore need further development.

Table 2. Numerical ratings for emission reduction technologies [26]

RATING ELEMENT/TECHNOLOGY	DFF	NTD	OEA	SCR	WFF	NSF
NOx Reduction	0	6	0	5	10	8
Impact on CO	0	1	2	3	1	3
Impact on PM	3	1	3	1	3	1
Impact on HC	0	2	3	2	0	3
Secondary Emissions	2	2	2	1	3	3
Deployment Schedule	3	0	1	3	3	2
TOTAL: EMISSIONS REDUCTION (25)	8	12	11	15	20	20

The NOx-Sorbent Filtering (NSF) method was one of the highest scored under the emissions reduction category in this review and received 8 out of 10 for NOx reduction. In this method the exhaust gas was first cooled using an air-to-air heat exchanger and then filtered to remove PM. In the next step the NOx was physically adsorbed on to a filter containing granular activated carbon material. The NSF system used in this study was similar to the first two steps in the Selective NOx Recirculation (SNR) system proposed in this report. However, the SNR system adds further steps, where NOx is desorbed from the carbon material and is recirculated back into the engine for decomposition.

Advanced Reciprocating Engine Systems (ARES)

The ARES program, which includes the present SNR study, was launched by the US Department of Energy (DOE) to develop a new class of cost effective gas fueled internal combustion (IC) engines by 2010 for stationary power generation applications. Its main objectives are to achieve fuel-to-electricity conversion efficiency of at least 50%, lower NOx emissions to under 0.1 g/bhp-hr, and lower operating cost by 10%, all the while maintaining reliability. The phase I ARES goals are to improve the current lean-burn technology with an emphasis on improving engine efficiency up to 44%. The future phase II goals are concentrating on stoichiometric burn engines with alternate aftertreatment technologies to reach the ARES NOx target.

Various NOx control strategies can be used achieve the required NOx emission in natural gas engines depending on whether it is run rich, stoichiometric, or lean. Typical NOx emission levels from natural gas fueled internal combustion engines are shown Table 3.

Table 3. NOx emission for a typical natural gas IC engine [27]

Air/fuel ratio: Lambda (λ)	NOx (g/bhp-hr)
0.98	8.3
0.99	11.0
1.06	18.0
1.74	0.7

Lean-burn combustion IC gas engines

The first phase in choosing a key technology to increase efficiency and lower NOx was by improving lean-burn spark ignition engine operation. In the ARES program, Cummins Inc. opted for engine enhancements that included increasing effective expansion ratio, improving air handling, using advanced engine controls, using long life spark plugs, and reducing friction [28]. NOx emissions were controlled by using SCR to achieve the 0.1 g/bhp-hr target.

Stoichiometric combustion IC gas engines

The second phase in natural gas fueled IC engine technology chosen by Cummins Inc. proposes stoichiometric operation that would allow the use of a three way catalyst (TWC). A stoichiometric engine using cooled EGR with a TWC aftertreatment system gives the ability to reduce NOx to under 0.1 g/bhp-hr without the use of a urea based SCR system [28].

Caterpillar Inc. is also developing a high BMEP (Brake Mean Effective Pressure) stoichiometric combustion concept utilizing EGR and a passive 3-way catalyst (SC-3: Stoichiometric, Clean exhaust induction, 3 way catalyst) for low NOx emissions while simultaneously reducing CO and non-methane HCs to low levels [29].

Waukesha Engine Dresser, Inc. is proposing a cooled-EGR stoichiometric engine with a TWC as an aftertreatment system. The added EGR, acting as a diluent, lowers the combustion temperature to reduce engine-out NOx. Lack of excess oxygen in the exhaust gas allows use of a conventional TWC [30].

Lean-burn operation in natural gas engines was originally used as a fuel saving technique. It can be seen that the requirement of low emissions production may supersede fuel economy in the future, and it may prove that the most economical method for emissions reduction is to allow stoichiometric combustion with a suitable aftertreatment system, even if thermal efficiency is sacrificed.

Selective NOx Recirculation (SNR) Approach

Selective NOx Recirculation (SNR) involves four main steps in NOx reduction. The first two steps are to cool the exhaust and to adsorb NOx from the exhaust stream, followed by periodic desorption from the aftertreatment medium. The final step passes the desorbed NOx gas into the intake air stream and feeds into the engine. A percentage of the NOx is expected to be decomposed during the combustion process. The motivation for this research was to clarify the reduction of NOx from large stationary engines.

Research Progress

In 2005 the researchers have addressed several topics essential to the understanding and optimization of SNR, namely in-cylinder NOx decomposition, adsorption and desorption, and system design and modeling. Two different set of tests were conducted in 2005, namely second and third campaigns, details of which are shown in Table 4 (the table also includes the first campaign conducted in 2004). The details for the two campaigns conducted in 2005 are explained in detail later in the report.

Table 4. Engines and test descriptions for the three campaigns

Campaign	Engine	Test Description	Variables
1 (2004)	1993 Cummins L10G	Lean w/o EGR	Speed, load and injection quantities
2 (2005)	1998 Cummins L10G	Slightly rich w/ limited EGR control: in-cylinder pressure measurement	Speed, load
3 (2005)	1998 Cummins L10G	Rich to stoichiometric w/ full EGR control: in-cylinder pressure measurement	Speed, load, EGR %, and injection quantities

Over the past year, the WVU researchers have considered several SNR system arrangements. The most likely arrangement for an application is presented here. The SNR technique does not use a catalytic converter to reduce NOx, but rather uses a cool NOx adsorber to collect a substantial fraction of the exhaust NOx onto the sorbent material by first cooling the engine exhaust gas. Once the adsorber is saturated (which may be determined by breakthrough measurement), the desorption process recirculates a concentrated stream of NOx into the intake of the engine facilitating thermal NOx decomposition [31]. Figure 3 shows a schematic of the SNR aftertreatment system, operating in an adsorbtion mode, coupled to a lean-burn engine. Control valve #2 shown in Figure 4 is used to direct the hot exhaust stream into the heat exchanger and demister to reduce the temperature and remove moisture before the exhaust gases enter the NOx adsorber.

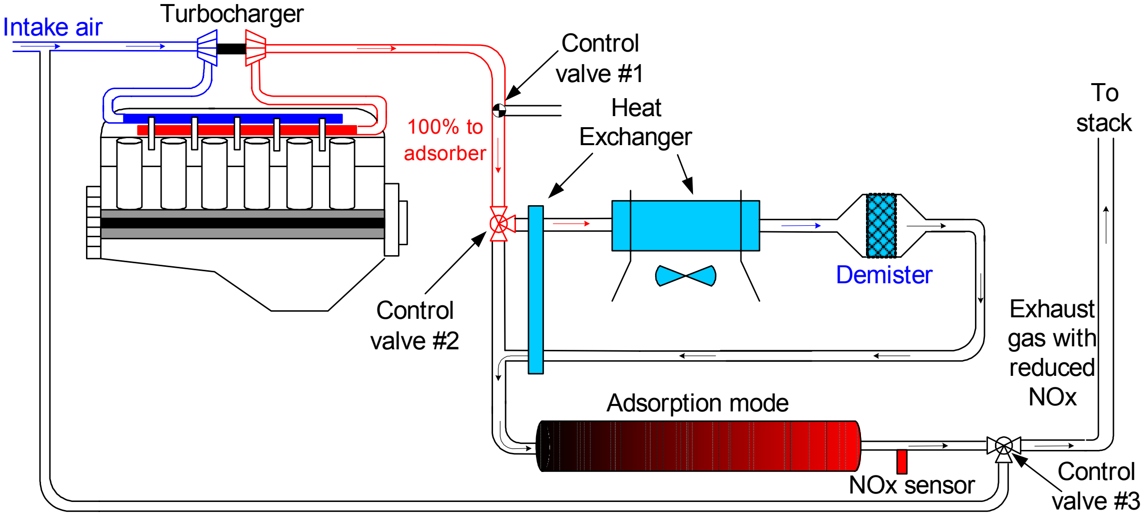


Figure 3. SNR aftertreatment system operating in adsorbtion phase

Figure 4 shows the schematic of the SNR system operating in a desorption mode. After the adsorber is saturated, a large portion of the exhaust gas is switched away from the adsorber initiating the desorption mode. The first control valve is used to direct 15-20% of the hot exhaust stream directly into the NOx adsorber to supply heat to the sorbent material and cause NOx desorption. The third valve, located downstream of the adsorber, directs the concentrated NOx stream into the intake line of the engine initiating NOx decomposition.

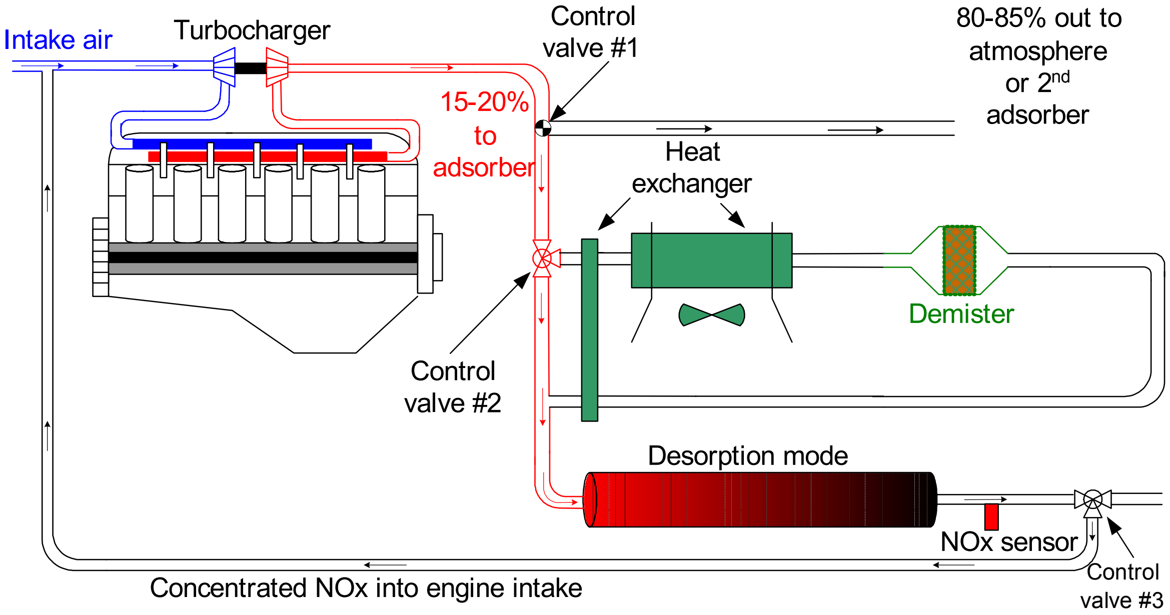


Figure 4. SNR aftertreatment system operating in desorption phase

The NOx adsorbtion quantity greatly depends on the exhaust gas temperature and the adsorber material used. High temperature NOx adsorbers employing alkaline earths have received substantial attention for diesel engine application, but the present SNR research has targeted a cool carbon-based sorbent. Since the SNR approach separates the process of NOx adsorbtion and decomposition, a wide range of sorbents could be considered for SNR application.

Evaluation of In-cylinder NOx Decomposition

The purpose of this section is to describe the evaluation of the decomposition of NOx, based on NO injections into the intake of a natural gas engine. In the early stages of the program, decomposition research was conducted using a 1993 Cummins L10G engine that included a mechanical fuel metering system with no feedback control. This system had limitation in changing the air/fuel ratio and emissions stability. Using this engine, it was verified that decomposition rates were around 27% at most during lean-burn operation. These low decomposition rates at lean burn have encouraged the researchers to run the engine at stoichiometric or slightly rich conditions for maximum NOx decomposition. This decision, which was also verified by CHEMKIN modeling presented later in this report. In 2004, the 1993 engine was replaced with an electronically managed 1998 Cummins L10G engine, and this engine was used to acquire the data discussed below in 2005. Modifications were made to the engine cylinder head of the new engine (see Table 5 and Figure 5) by Cummins Inc. to incorporate an in-cylinder pressure sensor. A Kistler Type 6067C water cooled precision cylinder pressure sensor pictured in Figure 6 was installed in cylinder #1. Various views of the cylinder head and pressure sensor installation are shown in Figures 7 and 8. To gain information on cylinder-to-cylinder combustion variations due to NOx injections, the exhaust manifold of the engine was instrumented with a K type thermocouple that can measure up to 2282°F at each exhaust valve to record temperatures.

Table 5. 1998 Natural gas engine specifications

Displacement	10 liters
Number of cylinders	6 (inline)
Firing order	1-5-3-6-2-4
Bore	125 mm (4.921 in)
Stroke	136 mm (5.354 in)
Compressions ratio	10.5 : 1
Horsepower	280 hp
Cummins Part List (CPL#)	2190
Rated speed	2100 rpm

Figure 5. 1998 Cummins L10G

Figure 6. Kistler type 6067C pressure sensor

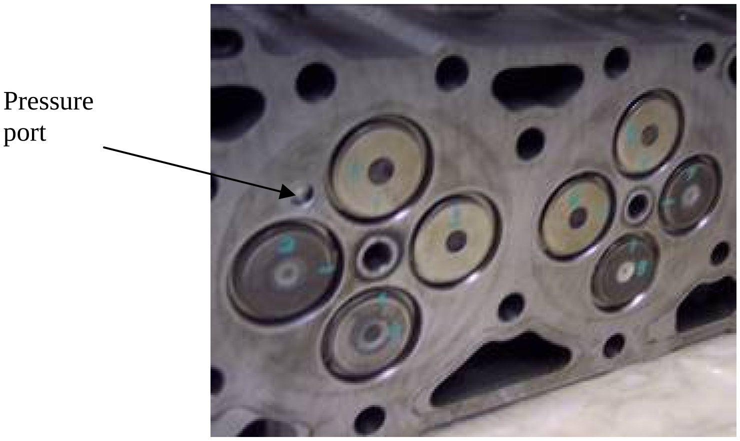


Figure 7. Bottom view of the cylinder head with pressure sensor port

Figure 8. Top view of the cylinder head with pressure sensor port

Exhaust Gas Recirculation (EGR) was introduced into the intake air through a two inch diameter pipe connecting the main exhaust line downstream of the turbocharger to the intake line upstream of the turbocharger intake. EGR was employed with the stoichiometric operation to allow in-cylinder temperature variation, and because in a real application, EGR would be desirable to increase part load efficiency and to control potential knock. This setup is referred to as a low pressure EGR arrangement. A butterfly valve downstream in the exhaust provided back pressure to drive the EGR flow, which was only used for the third campaign runs (its position was fixed for second campaign runs). EGR quantity was increased until engine misfire occurred to determine maximum practical EGR flow and the EGR percentage was calculated by taking the ratio of the CO_2 concentration measured in both the raw exhaust line and the intake manifold using a California Analytical CO_2 analyzer.

The 1998 engine came equipped with a wide-band exhaust gas oxygen sensor and its proprietary controller interface. In order to operate the engine at air/fuel ratios other than those provided by the stock ECU, another NGK wide-band exhaust gas oxygen sensor was installed and a circuit was constructed to emulate the signal from the OEM oxygen sensor controller. The output from this circuit was connected to the ECU. This forced the ECU to control the fuelling of the engine at pre-settable values. The air/fuel ratio (λ) was measured to be between 0.94 – 1.02 for near-stoichiometric runs. EGR was used to control cylinder temperatures to avoid knocking and thermal problems during these rich burn conditions.

The exhaust gas from the engine was directed to an EPA compliant full-scale dilution tunnel [32]. Sample probes for the gas analyzers were located 15 feet from the entrance of the tunnel. The nominal flow in the dilution tunnel was set to 3000 scfm. The gas analyzer bench was capable of quantifying THC (total hydrocarbon), CO, CO_2, and NOx emissions. For each of the gases characterized, background corrections were performed. The tunnel, bench and analyzers are the same as those described in the prior annual report.

Test description (engine mapping runs)

To identify the optimal NOx decomposition operating points, the engine was run at wide open throttle to obtain maximum torque and power as a function of speed, know as an engine map. The OEM wide-band oxygen sensor held the lambda around 1.30. No EGR was introduced during this set of runs, and the engine was not observed to knock. Three engine maps were run, and NOx emissions were recorded under the following conditions (Figure 9):

1. First run without NO supply (baseline NOx)
2. Second run with continuous NO supply into the air intake line (NOx in intake)
3. Third run with continuous NO supply into the exhaust gas line (NOx in exhaust)

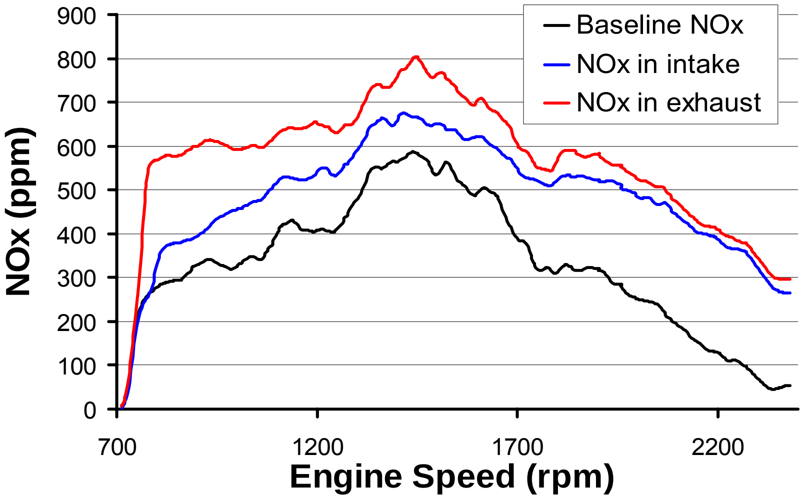


Figure 9. NOx measured during three engine maps

Baseline engine-out NOx was compared with NO introduced into the intake and exhaust lines. The power output of the engine was calculated and compared to the case where NO was introduced into the intake (Figure 10). It can be seen that NOx injections have a minimal effect on engine power output. It can also be noted that the highest NOx decomposition occurred at low speed and high load operating conditions (Figure 11).

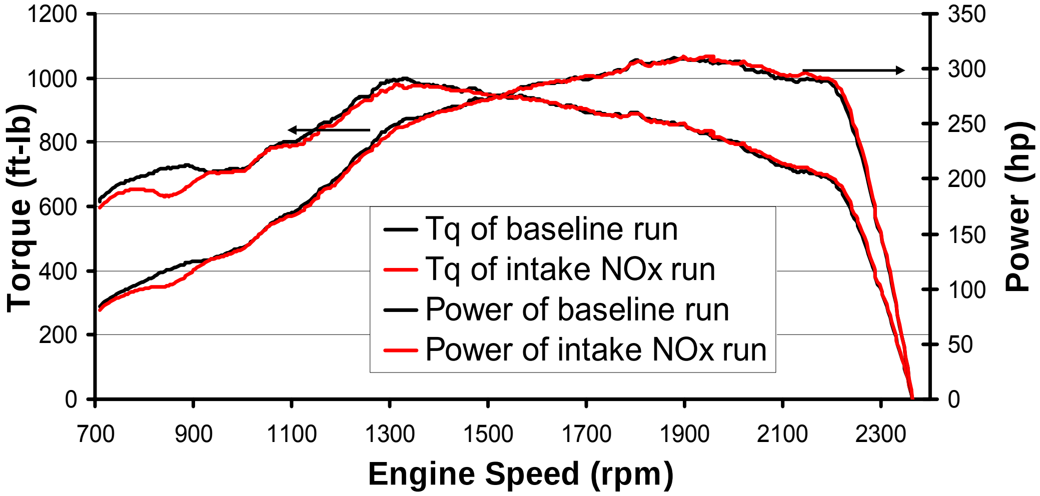


Figure 10. Engine map: continuous NOx supply effects on torque and power

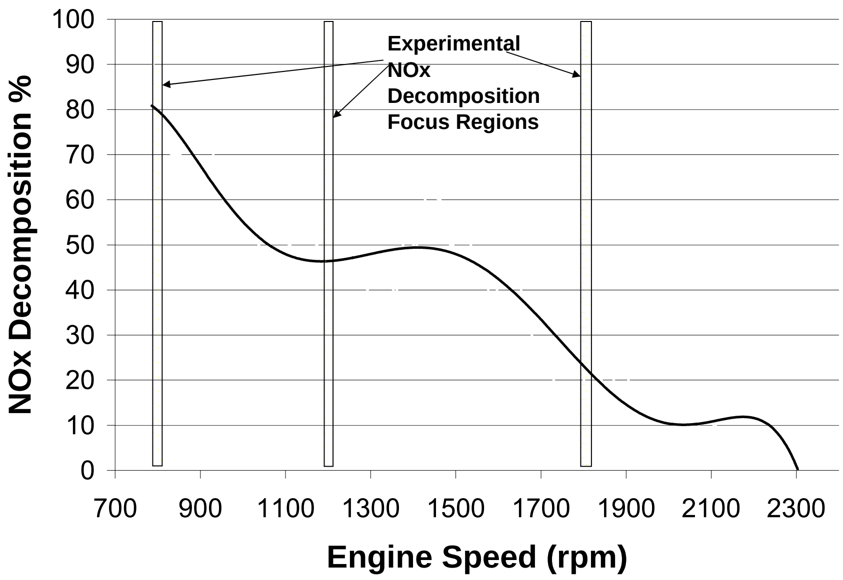


Figure 11. NOx decomposition % (spline fit) throughout the engine map

Establishing NOx decomposition rates during intermittent NOx injections

The initial NOx injection system was constructed in 2004 and was later upgraded in 2005 with a computer-managed mass flow controller in order to inject identical quantities of NO (nitric oxide 98.8%) into the intake and exhaust stream. Figure 12 shows the NOx injection system integrated with the engine and analyzers.

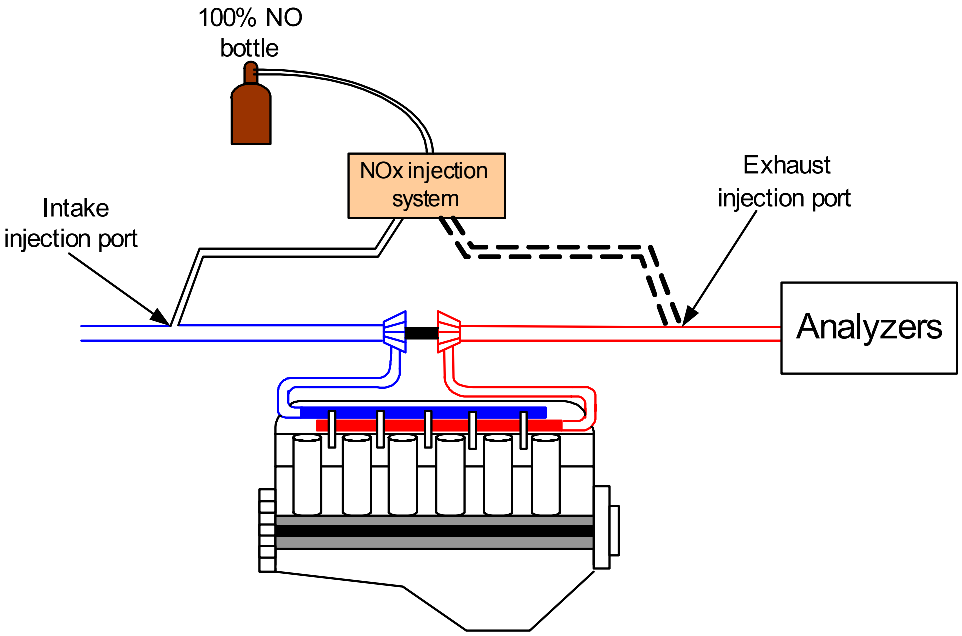


Figure 12. NOx injection system setup

NOx decomposition percentage was quantified by comparing 20-second injections into the exhaust versus intake (Figure 13). The peak value was for the central-averaged 10 seconds of injection. For every engine operating point, NO was injected at the exhaust line and at the intake line upstream of the turbocharger. It was necessary to rely only on the repeatability of the mass flow controller and not its accuracy for the calculation of NO decomposition percentages. The mass controller value was later used to infer the concentration of NO in the intake. It was assumed that the exhaust flow was too cold to react significantly with the NO injected directly into the exhaust, so that this served as a faithful representation of the NO quantity entering the engine.

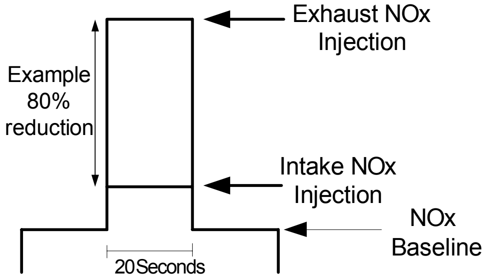


Figure 13. Establishing NOx decomposition rates

The percentage of injected NO that was decomposed during the combustion process was calculated for each operating condition as follows. The amount of NO injected into the exhaust line was the highest peak $NOx_{Peak\_Exhaust}$. The amount of NO seen by the NOx analyzer due to the injection after decomposition had occurred in the combustion was designated as NOx_{Peak_Intake}. The average of the baseline NOx emissions, $NOx_{Baseline}$, for a given mode was subtracted from the peak values. The decomposition efficiency (η) was calculated as a percentage of NO decomposed at each load (Equation 4) [31][33][34].

$$\eta = 1 - \frac{\left(NOx_{Peak\_Intake} - NOx_{Baseline}\right)}{\left(NOx_{Peak\_Exhaust} - NOx_{Baseline}\right)} \qquad \text{Equation 4}$$

Test description (NO injection runs)

As presented in Table 4, two different set of tests (second and third campaigns) were conducted in 2005. The engine was operated at 800, 1300, and 2100 rpm for the second campaign and the EGR percentage was not controlled. For the third campaign, the engine was run at 800, 1200, and 1800 rpm, with full control over EGR percentage directed into the intake. Emphasis was placed on running the engine slightly rich and closer to stoichiometric for this set of runs because previous lean burn tests in 2004 with lambda greater than 1.30 (first campaign) demonstrated that NOx decomposition percentages were not economically viable for field applications. Injected NOx amounts were one order of magnitude larger than the baseline emissions for the natural gas engine. One of the test matrices is shown in Table 6.

Table 6. Test matrix used during third campaign runs

Speed (rpm)	Load (ft-lb)	Engine Power (hp)	Air/Fuel Ratio (λ)	EGR Variation
800	200	30	0.94	0 – 16%
800	550	84	0.95	0 – 20%
1200	550	126	0.98	0 – 20%
1800	600	206	1.02	0 – 18%

Experimental results and discussion

Figure 14 shows NOx injections into the intake line and exhaust line at different engine speeds and loads during the second campaign. For this set of runs the NOx injection amount was held constant at 2.5% of the engine intake volume flow and the air/fuel ratio was kept constant at 0.97. The EGR percentages for each operating point are given in Figure 15 and the NOx decomposition percentages are given in Figure 16.

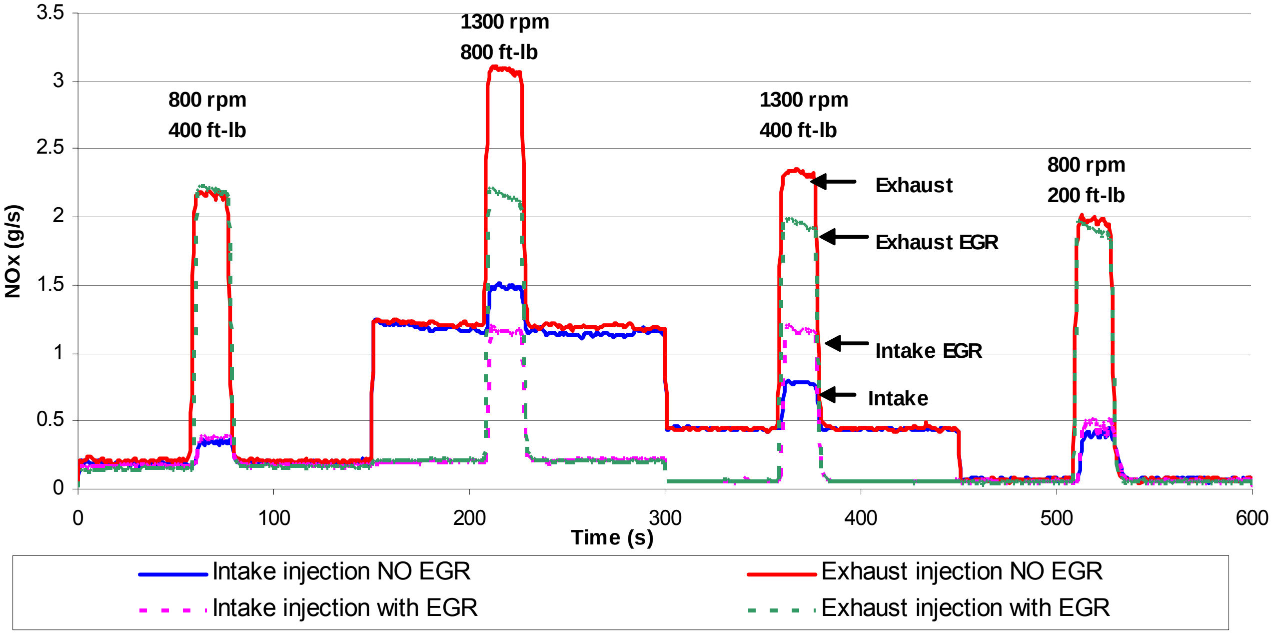


Figure 14. NOx injection runs during second campaign

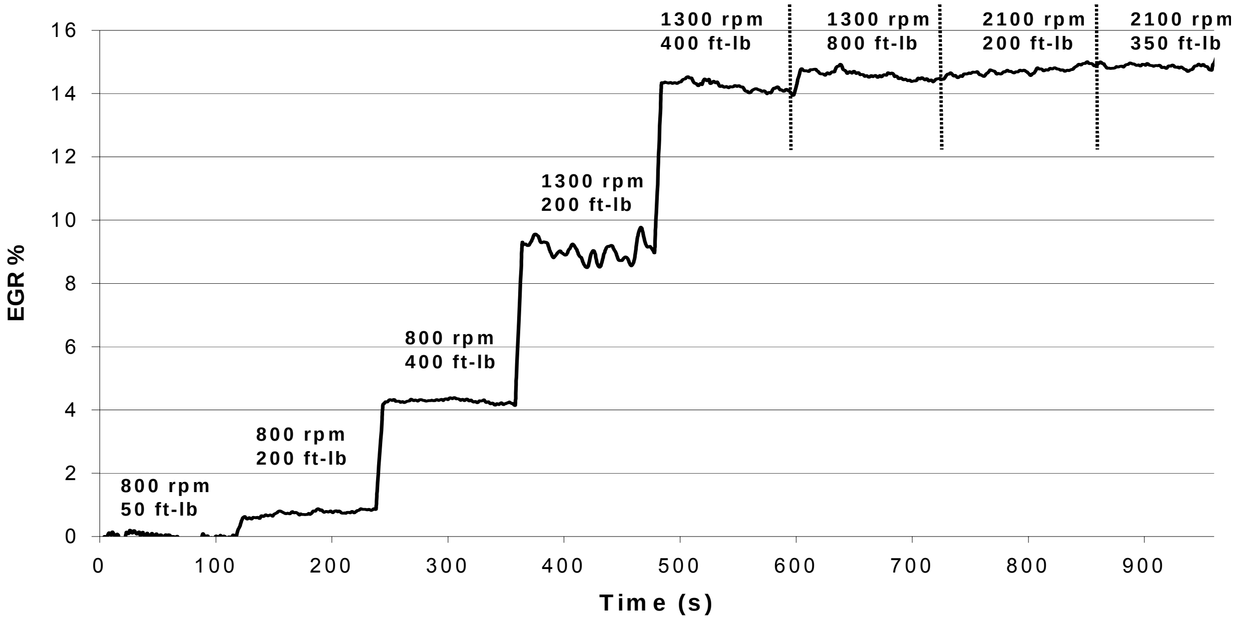


Figure 15. EGR percentages for the second campaign

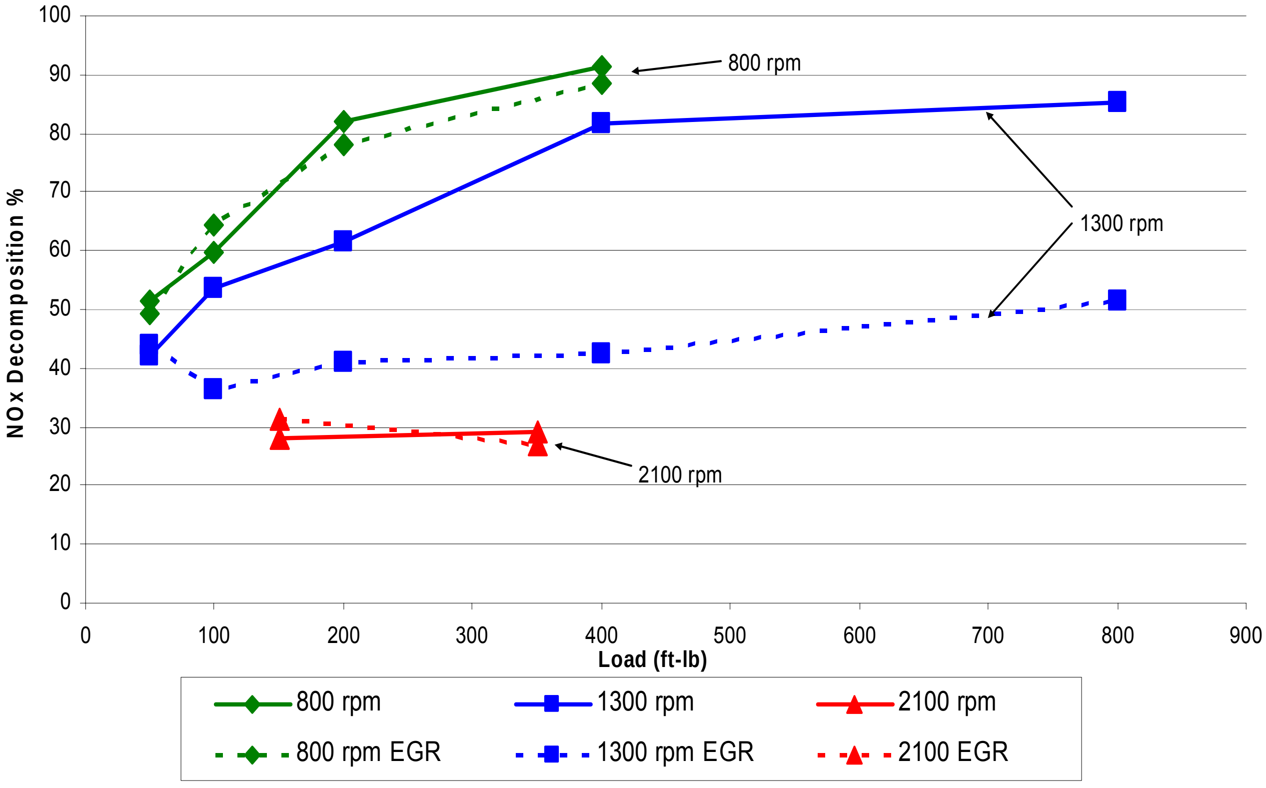


Figure 16. NOx decomposition percentages for the second campaign

During the third campaign, three different NOx quantities (1.2%, 3.0% and 4.1% of intake volume flow) were injected for each run to verify the effects of NOx concentration. Figure 17 shows these NOx injections for 800rpm and 200ft-lbs. Different from the second campaign, the EGR quantities were independently controlled in the third campaign and the resulting NOx decomposition rates for three different NOx injection amounts and five different EGR percentages for 800rpm and 200ft-lb are shown in Figure 18.

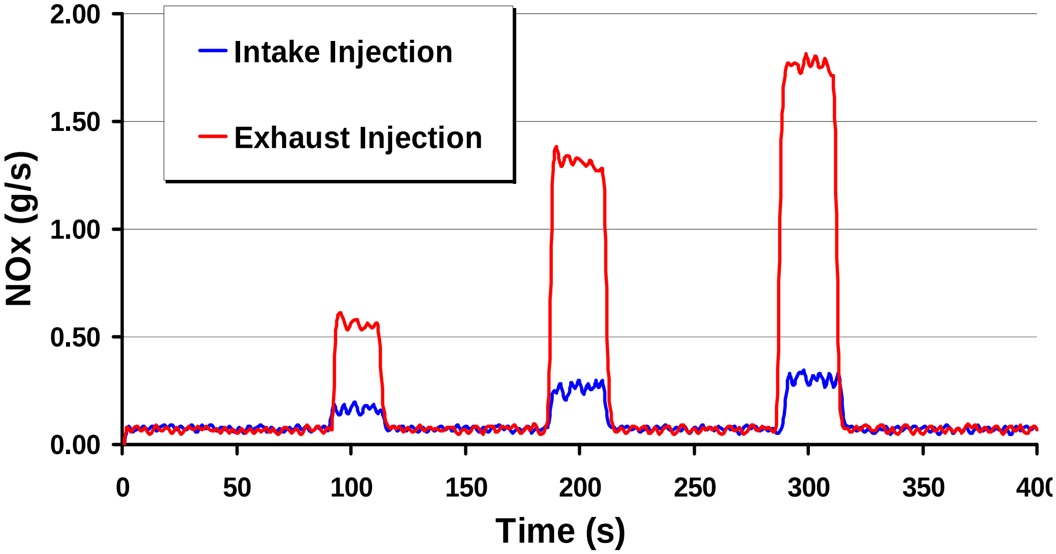


Figure 17. NOx injection runs with no EGR at 800 rpm and 200 ft-lb engine operating point

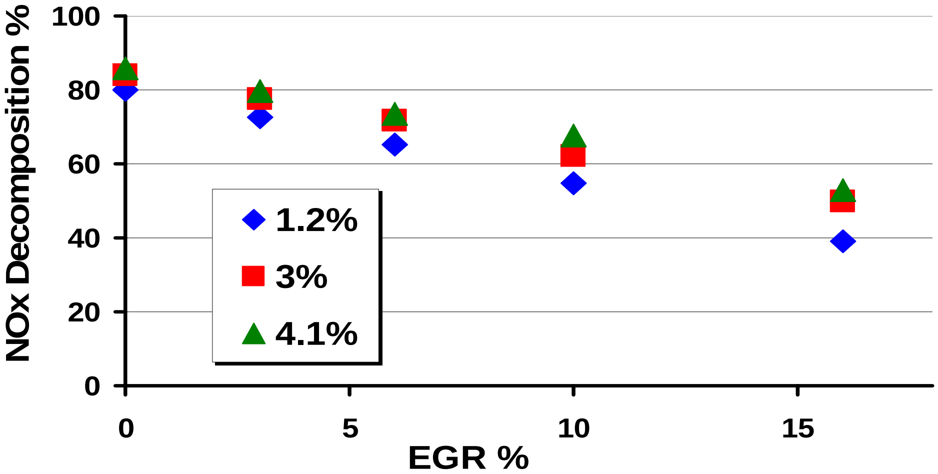


Figure 18. Effects of EGR on NOx decomposition

For the third campaign, the exhaust manifold temperatures were also measured. The temperature at each exhaust valve showed an increase during the NO injection time period. Further increase in temperature was observed as the intake NO concentration was increased from 1.2 – 4.1% (Figure 19). It can be speculated that the dissociation of NO into nitrogen (N_2)

and oxygen (O_2) made the combustion mixture leaner and therefore raised the exhaust gas combustion temperature. Variably in temperatures between cylinders can be attributed to variations in volumetric efficiency and air/fuel ratio. It is likely that the degree of NO decomposition is varying from cylinder to cylinder, so that the values acquired for decomposition may not represent the performance of the "best" cylinder. This suggests that higher reductions may be attainable by injecting the NO into the intake to feed a single cylinder and by managing the conditions in that cylinder closely.

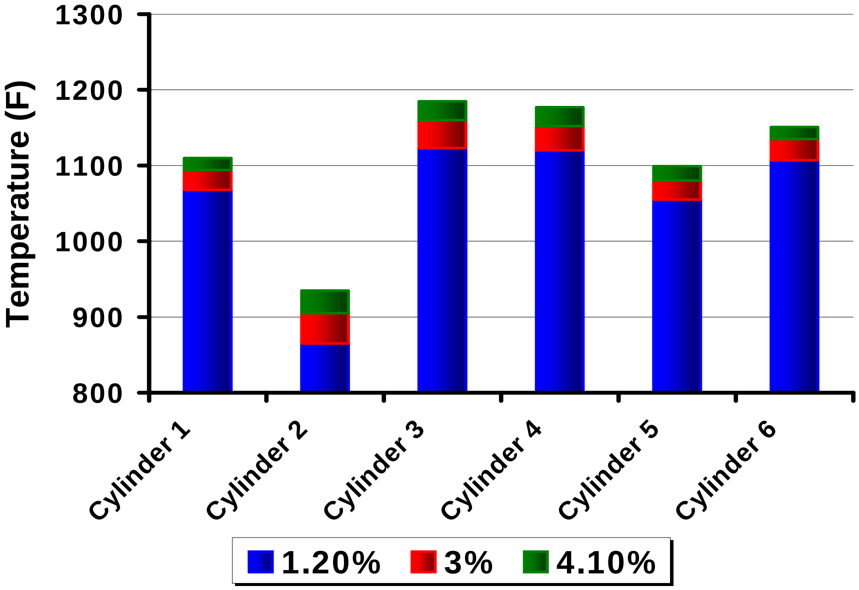


Figure 19. Cylinder-to-cylinder combustion temperature variation due to NO injections

Figure 20 shows the average of approximately 250 pressure traces taken in cylinder #1 of the engine during the third campaign for 800rpm and 200ft-lb. These data showed no measurable effect on in-cylinder pressure due to NO injections. More pressure traces, PV (pressure – volume) diagrams, and piston work (Indicated Mean Effective Pressure - IMEP) plots are presented in the Appendix of this report.

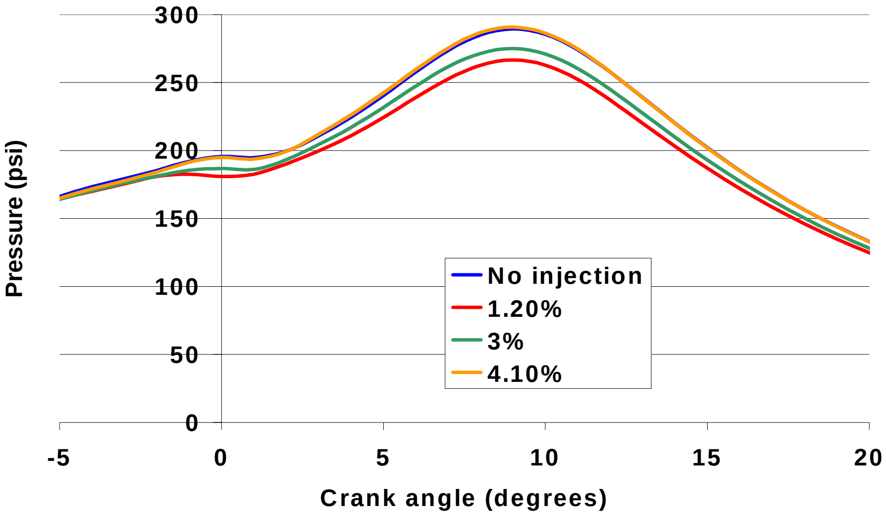


Figure 20. In-cylinder pressure variation due to NOx injections*

*note that the axis has been expanded to show pressure at top dead center

The NOx decomposition values shown in Figures 16 and 18 are available for subsequent system modeling and they show that the levels of NO decomposition are high enough to facilitate use of SNR provided that the adsorption system is sufficiently effective and economical.

Chemical kinetic modeling

Previously in the program the researchers executed CHEMKIN runs [35] to quantify the effects of air/fuel ratio and EGR, but runs for a slightly rich burn with EGR were not executed. The CHEMKIN modeling, as shown in Figures 21 through 25, was extended to the case of "slightly rich burn with EGR." When modeling rich combustion with NO in the intake air stream, the initial NO concentration was held constant at 20,000 ppm, while varying the temperature of reaction from 1450 K to 2350 K (an upper bound used previously). In this particular case, rich combustion was assumed to have a relative air/fuel ratio of 0.97. The models were simulated at 10%, 20%, 30% and 40% of the intake air replaced with EGR. The NOx decomposition efficiency was calculated when 98% of the CH_4 has been consumed. However, the investigators have also considered estimating the decomposition based on a time period associated with piston motion, and this generally yields higher decomposition percentages.

The modeling data show that reductions of over 70% are possible by the "98% fuel burned" method, but that it will be necessary to identify a temperature window as determined by the burn mixture and EGR content, to facilitate high reductions. The temperature must be high enough to cause a rapid reaction rate, but no so high as to establish an elevated NO equilibrium. Both the CHEMKIN data and experimental data will be used for the construction of a NOx decomposition model to be used in a system model in the next quarter.

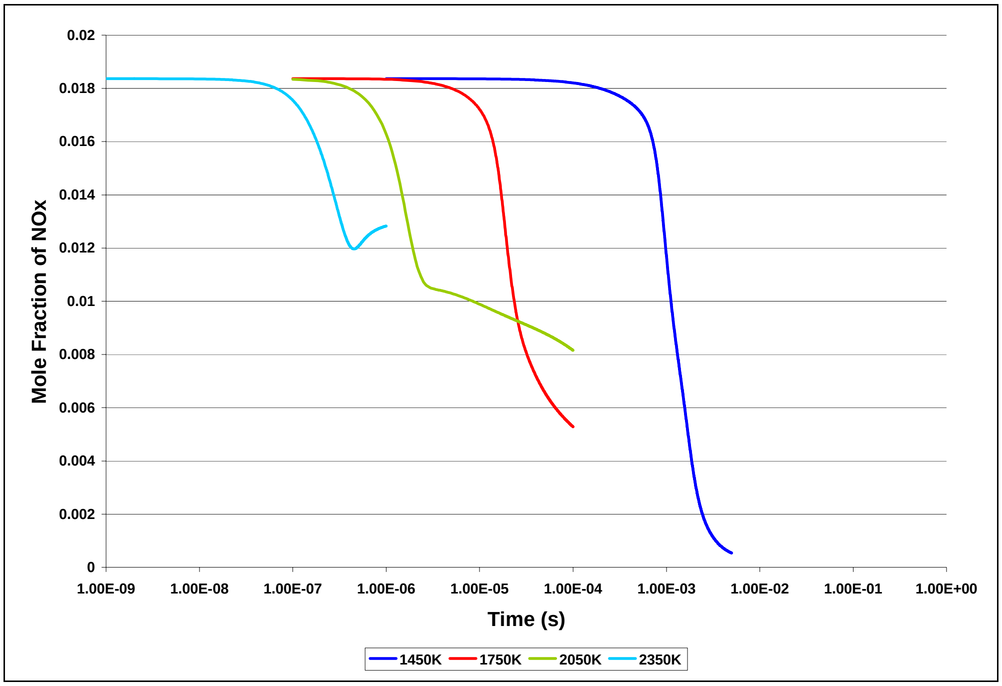


Figure 21. NOx decomposition% for 10% EGR for different flame temperatures

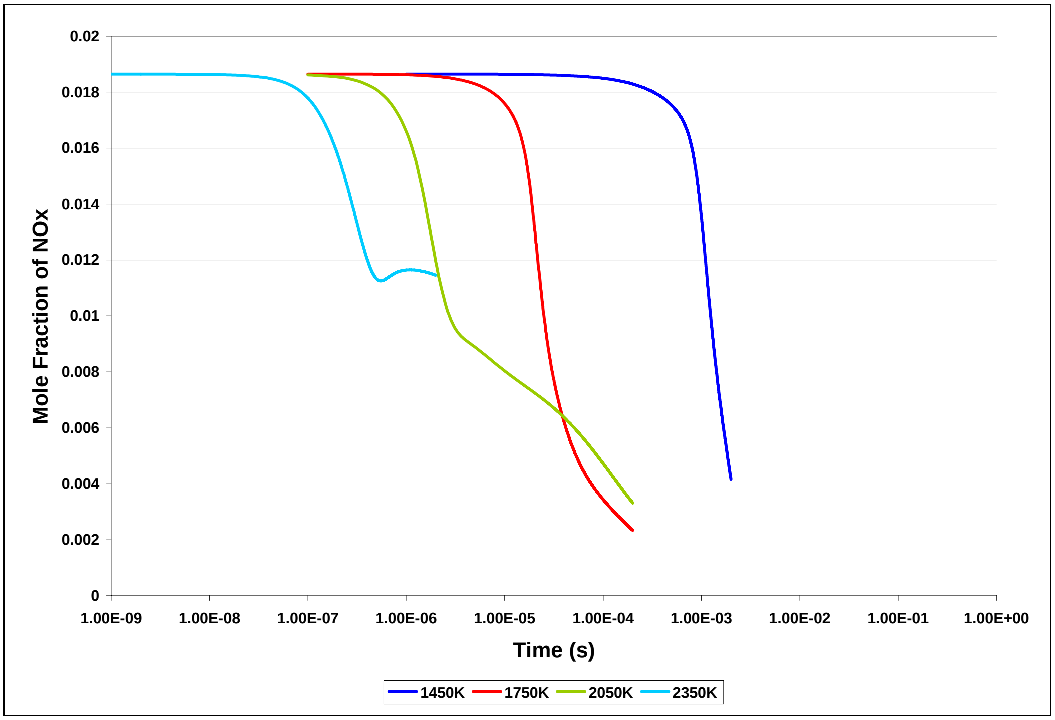


Figure 22. NOx decomposition percentage for 20% EGR for different flame temperatures

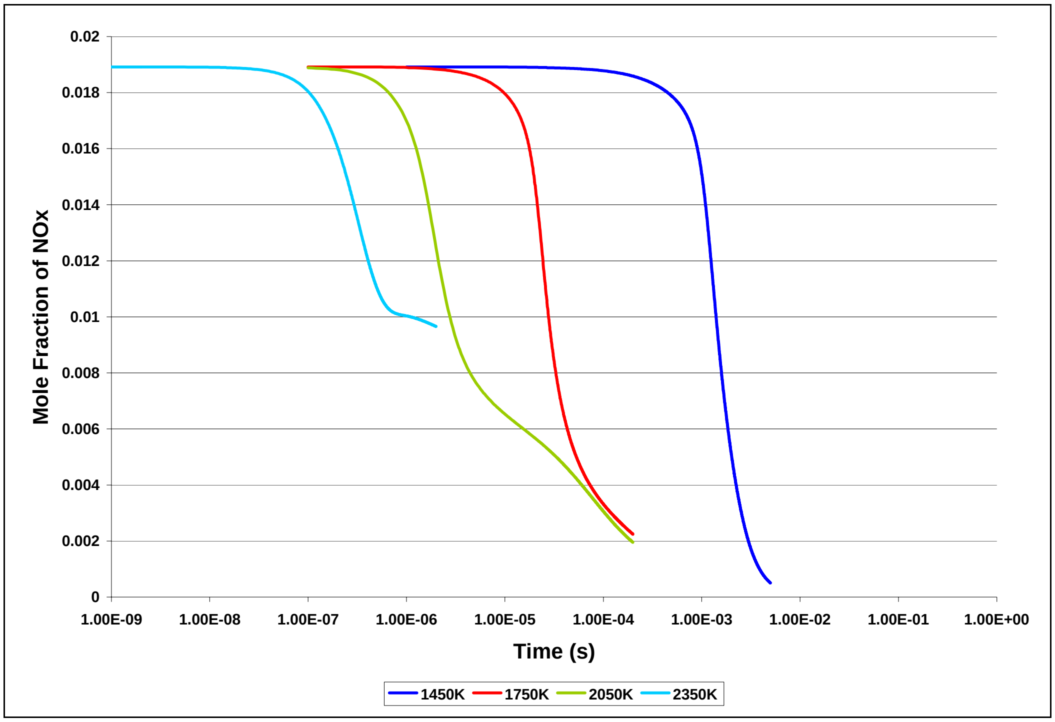


Figure 23. NOx decomposition% for 30% EGR for different flame temperatures

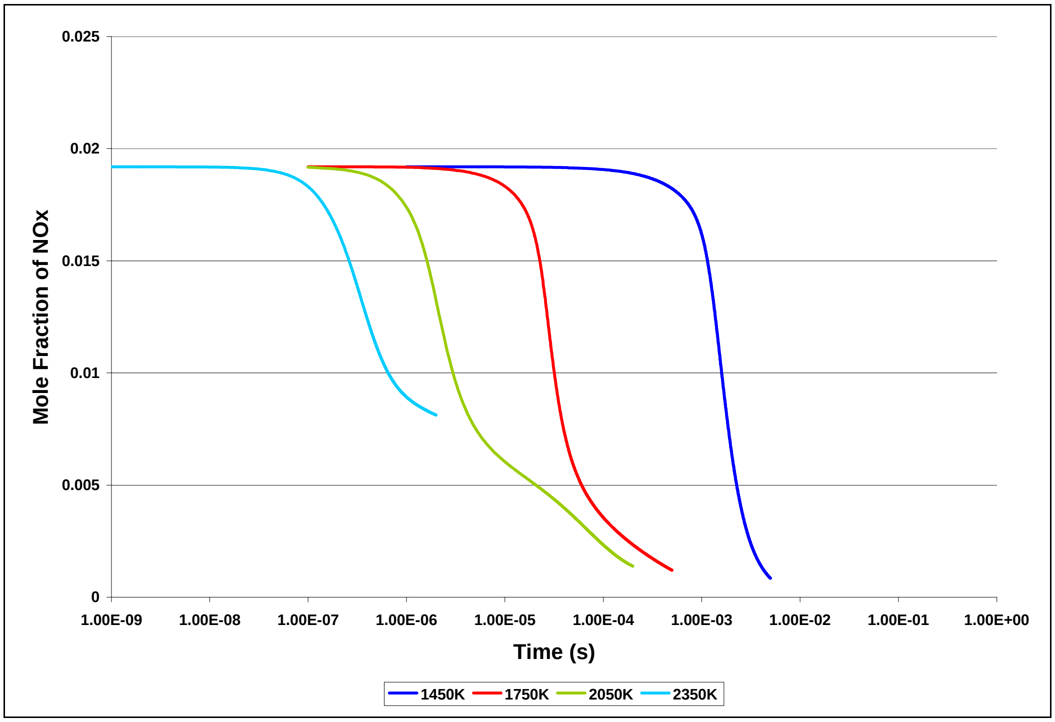


Figure 24. NOx decomposition% for 40% EGR for different flame temperatures

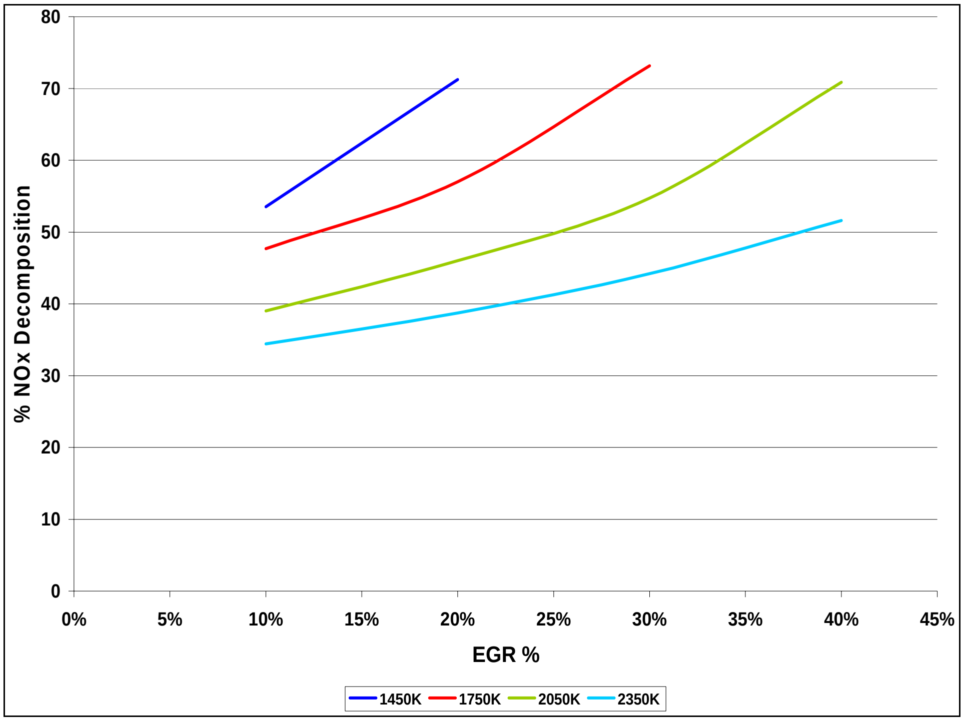


Figure 25. NOx decomposition% for different EGR % flame temperatures when 98% fuel is burned

NOx adsorbtion system

This report presents two separate efforts to examine the properties of the sorbent and adsorber system. Firstly, a full scale system was used in conjunction with the Cummins engine and secondly a bench top apparatus was constructed to gain more information on sorbent material. The NOx adsorbtion system (Figure 26) was acquired from Sorbent Technologies, who have provided industrial assistance on the program, and was integrated with the test engine. The system consists of the rectangular sorbent bed (L-32", W-13", H-34") shown in Figure 26, a demister, and two heat exchangers. A hot air blower was added for desorption of NOx from the sorbent bed in this set of tests. It is understood that in a field application, utilizing the heat of the exhaust would be a preferred method for desorption, to minimize system energy demands.

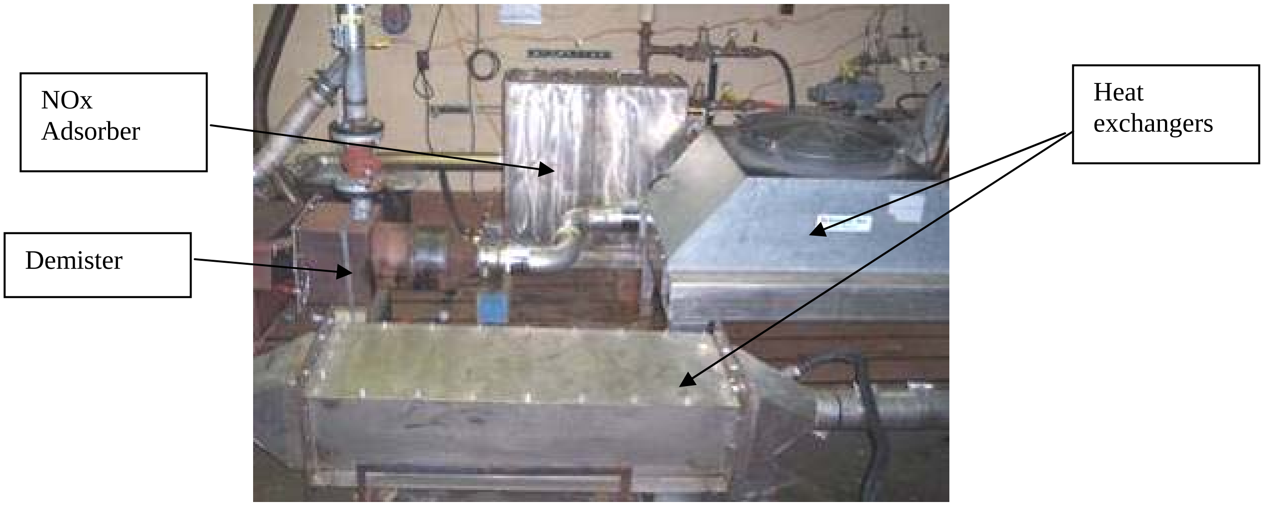


Figure 26. NOx adsorbtion system

Figure 27. NOx adsorber

The NOx adsorber as supplied was capable of handling exhaust flow rates up to 400 cfm. The Cummins L10G was operated at 800 rpm and 200 ft-lb load, so that the exhaust flow rate was approximately 100 cfm. This operating point did not produce substantial back pressure that would result in internal EGR.

In an initial test to verify adsorber function, the adsorber was filled with 60 lb of carbon-based adsorbent material provided by Sorbent Technologies. Cooled raw exhaust from the engine was directed into the adsorbtion system for 120 minutes. The exhaust temperature entering the bed was maintained under 100°F to increase adsorbtion efficiency. The gas leaving the adsorber was directed into the dilution tunnel and analyzed for its NOx content. Figure 28 shows a comparison between the baseline NOx emissions output of the engine and NOx output from the adsorber at the same engine operating point. The NOx adsorbtion percentage declined from an initial efficiency of 80% down to 48% as the adsorbent material gradually saturated with NOx.

The average adsorbtion percentage was 64% for 120 minutes of adsorber loading. The “NOx adsorbtion %” line in Figure 28 is a best-fit line based on the measured NOx data. It should be noted that this adsorber was not matched specifically for the Cummins L10G engine application, and the researchers believe that a different adsorber geometry would be desirable to minimize NOx breakthrough.

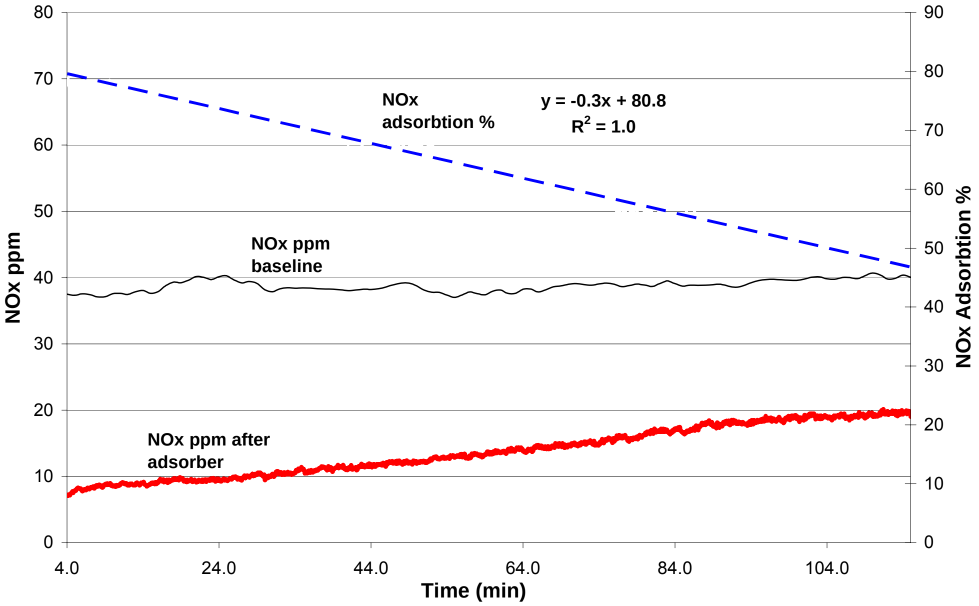


Figure 28. NOx adsorbtion data

The engine was shut down during the desorption phase. The NOx adsorber was desorbed by using an electrical hot air blower and the desorbed NOx was sampled at the dilution tunnel. The hot air flow rate was set at 170 cfm and after approximately 30 minutes, the internal temperature of the adsorber reached 300°F. Figure 29 shows the desorption process conducted for 80 minutes with a peak NOx output of 65 ppm seen in the dilution tunnel. In order to make the desorption process more efficient, a more rapid rate and higher initial concentration of NOx desorption is desirable, suggesting that more rapid heating is required. However, these data presented above serve to give confidence in the adsorbtion/desorption technique.

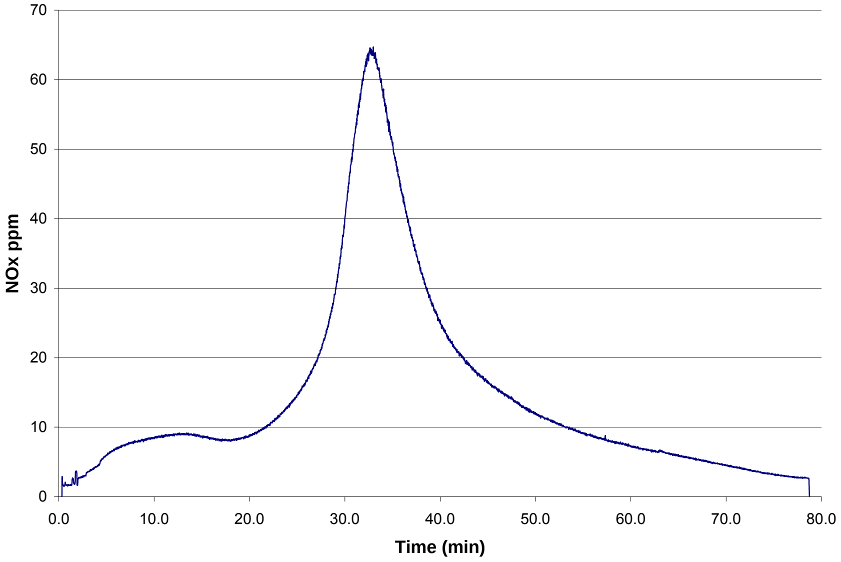


Figure 29. NOx desorption process

Bench top study on NOx adsorbtion and desorption process

It was clear that the full scale adsorber used in the engine tests was unsuited to characterizing the adsorption and desorption processes, and the characteristics of the sorbent material to support system design. Therefore, a new bench scale NOx sorbent chamber was designed and constructed to measure performance of the carbon-based adsorbtion material. A 24" long, 3" diameter stainless steel cylinder was chosen as the sorbent chamber (Figure 30). Temperatures were measured at three locations in the cylinder by thermocouples placed at 4", 12", and 20" from the inlet of the chamber. NO was introduced into the bed at one end and output from the bed at the other end was measured by an Eco-Physics NOx analyzer.

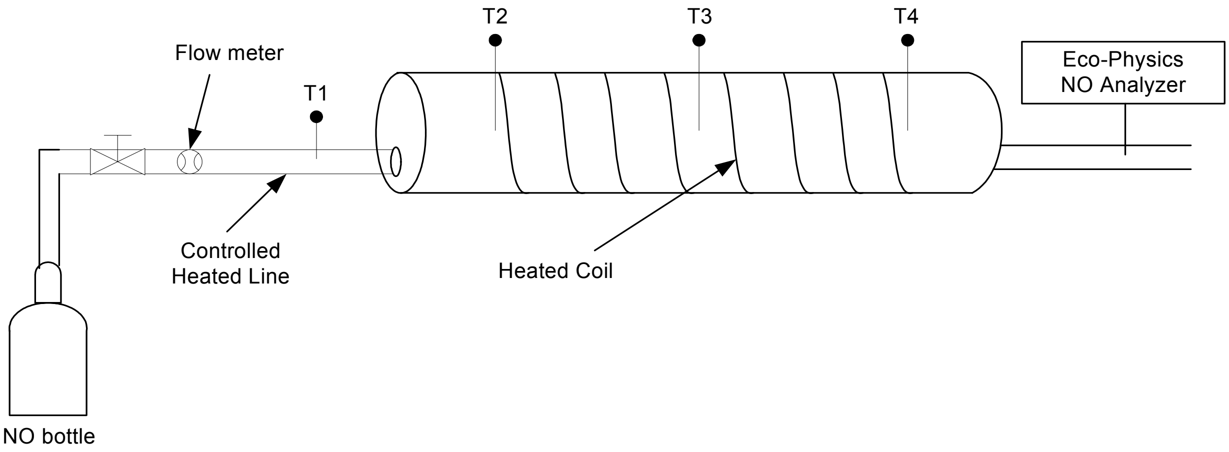


Figure 30. Schematic of the bench top NOx sorbent chamber

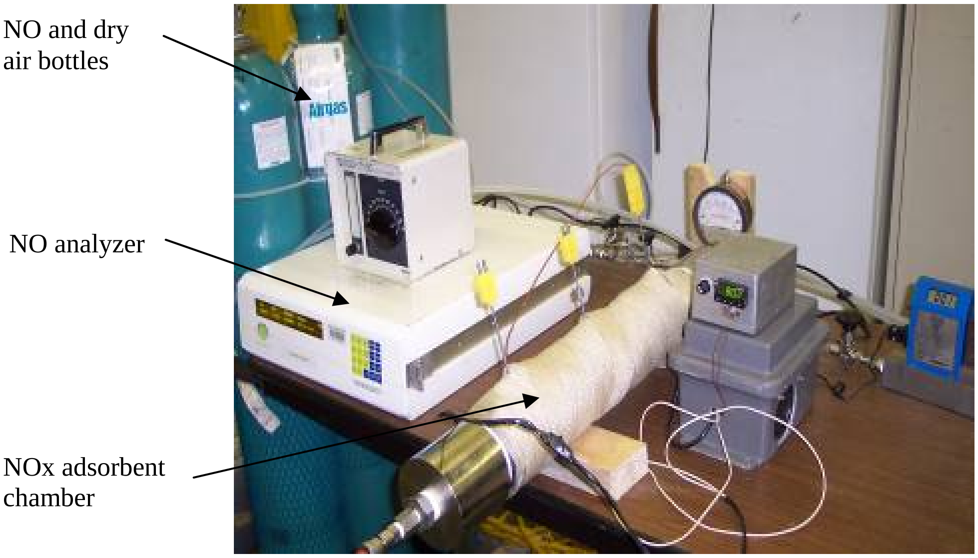


Figure 31. Bench top NOx sorbent setup

Adsorbtion phase

In the adsorption phase, the chamber was fed by pressure-regulated gas from NO (nitric oxide) cylinders at 100, 500, and 1000 ppm concentrations at room temperature (77°F). Calibration gas was used rather than pure NO in order to establish a satisfactory volumetric flow for a defined NO flow. This gas was introduced through a heated line to preheat the sample, as bed cooling had been observed during initial runs in the desorption phase. Gas flow was controlled by a valve and measured with a flowmeter. Three different flow rates for each NO concentration were chosen and fed into the chamber until the adsorbent material was saturated and NO breakthrough had occurred. For the adsorbtion phase, the heated line was set to room temperature to maximize the adsorbtion efficiency. The adsorbtion phase test matrix is shown in Table 7. In these preliminary runs, there was no attempt to assess the effect of temperature on adsorption.

Table 7. Adsorbtion phase test matrix

NO concentration (ppm)	Flow rate (cfm)
100	1.0
	1.8
	2.8
500	1.0
	1.8
	2.8
1000	1.0
	1.8
	2.8

Desorption phase

An electrical heater coil was wrapped around chamber to heat the whole chamber and sorbent material. During the preliminary runs in the last quarter, in order to obtain a rapid desorption using dry air, higher gas flow rates than the ones used for the adsorbtion were chosen. Prior to each test, the chamber was heated to three different temperatures respectively before allowing the dry air to flow though the apparatus. The desorption test matrix is shown in Table 8. The internal chamber temperatures were recorded during this phase. The Eco-Physics NO analyzer was used to measure NO released from the chamber. When 90% of the stored NO had been released, at which point measurements were terminated.

Preliminary data were gathered to demonstrate the success of the experimental arrangement. Adsorption/desorption rates and sorbent loading (equilibrium) properties will be calculated as a function of temperature, flow rate and NO concentration based on data gained in the next quarter. The researchers have also acquired another carbon sample to evaluate in this apparatus.

Table 8. Desorption phase test matrix

Flow rate (cfm)	Temperature (°F)
5	250
	350
	450
10	250
	350
	450
15	250
	350
	450

Figure 32 shows the relative measured concentrations when 1000 ppm NO was introduced into chamber. The sorbent material temperature was set at 76° F. For the desorption phase, the sorbent chamber was heated to 300°F.

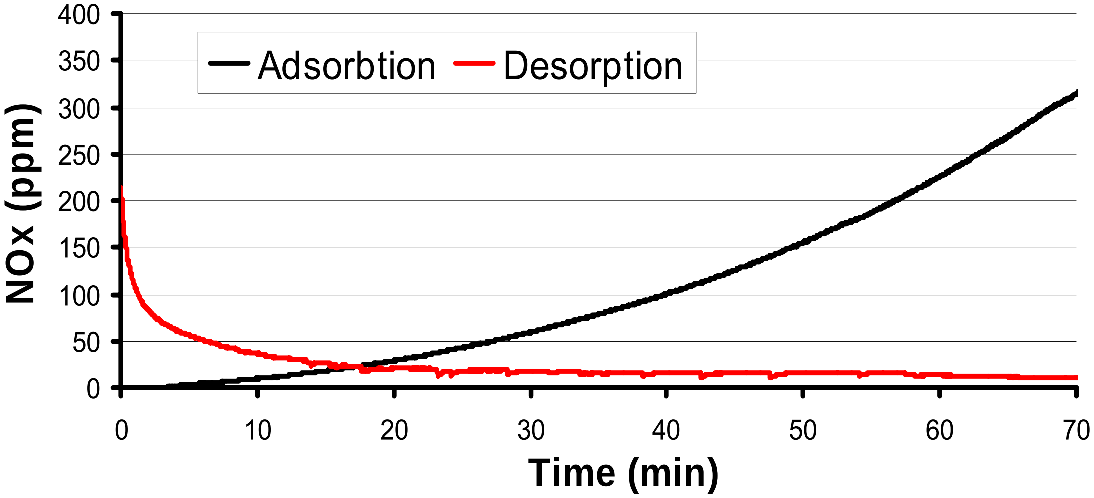


Figure 32. Benchtop adsorbtion and desorption curves for 1000ppm NO supply

SNR system configuration and challenges

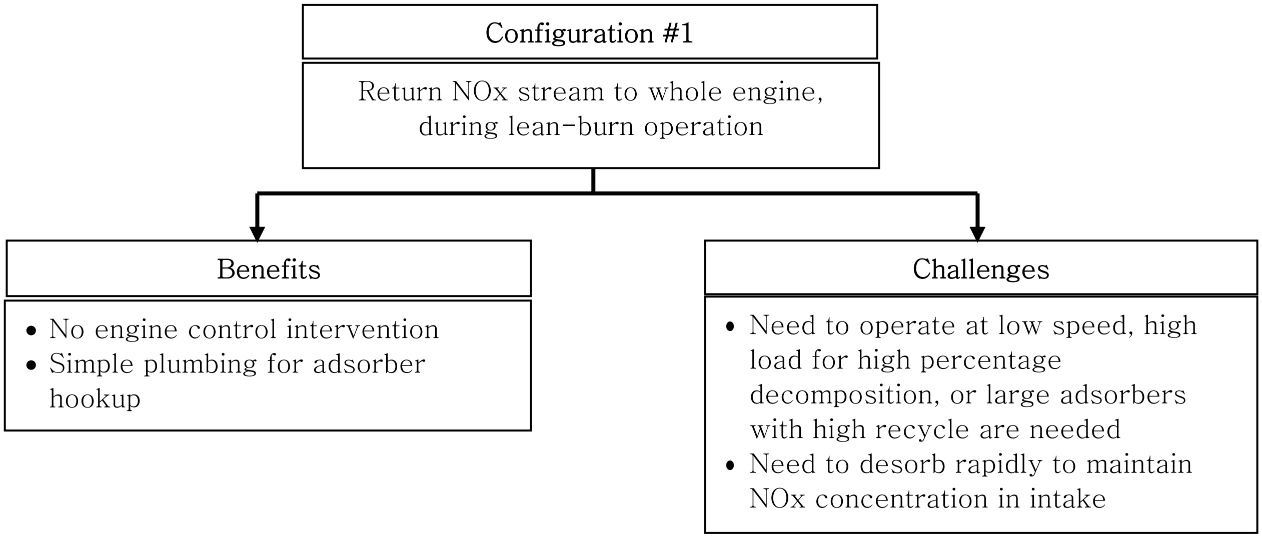
Interfacing with engine

The researchers investigated the feasibility of implementing the SNR system on a production engine. The main focus in this investigation was to achieve maximum NOx reduction from the engine/aftertreatment system and implement the system with minimum engine modifications.

Existing modeling and data have shown that for NOx decomposition, the engine must be operated with a stoichiometric or slightly rich mixture. However, stoichiometric operation implies high in-cylinder temperatures, leading to concerns over engine efficiency, longevity and excessive NOx production. The solution is to combine the stoichiometric operation with the recirculation of exhaust gas (EGR), to provide a mixture that encourages NOx decomposition chemically, and at a suitable in-cylinder temperature. The desired in-cylinder temperature must be low enough to discourage a high NOx equilibrium, but high enough to promote a fast rate of decomposition, as CHEMKIN model data have shown. The basic system design must therefore allow for the addition of EGR while operating the engine at a stoichiometric setting, even though the engine is normally intended to be lean in operation. The investigators also appreciate that excessive EGR can lead to slow and incomplete combustion, with high carbon monoxide and hydrocarbon emissions. Data from a prior program at WVU have confirmed this fact [35].

With mixer-equipped engines, the design assumes that the excess air in the intake must be replaced with exhaust gas. However, for very lean engines, where effects of full EGR replacement of excess air would be unacceptable, the intake must be throttled and augmented with exhaust gas during the decomposition. For engines with feedback control of lambda, it will be necessary to intervene between the wide range oxygen sensor and controller to cause the controller to operate the engine stoichiometrically during the decomposition phase. This type of operation has already been demonstrated with the electronically-managed Cummins L10G engine used in this research.

The following diagrams explain possible system configurations along with its benefits and challenges.



Configuration #1

Return NOx stream to whole engine, during lean-burn operation

Benefits

- No engine control intervention
- Simple plumbing for adsorber hookup

Challenges

- Need to operate at low speed, high load for high percentage decomposition, or large adsorbers with high recycle are needed
- Need to desorb rapidly to maintain NOx concentration in intake

Configuration #2

Return NOx stream to whole engine, during intermittent stoichiometric burn operation

Benefits

- The same fueling control is applied to the whole engine
- A wide operating range is possible for adequate NOx decomposition
- It is readily implemented on most electronically controlled engines
- A reducing catalyst could be used for additional NOx cleanup

Challenges

- Affects turbochargers because mass flow must be reduced
- Concern over engine thermal management and knock
- Transient may occur during changeover from lean burn
- Complex controls and fueling on mixer-type engines
- Need to desorb rapidly to maintain NOx concentration in intake
- Intermittent loss of thermal efficiency

Configuration #3

Return NOx stream to one cylinder, during lean burn operation

Benefits

- Concentration of NOx in cylinder aids rapid decomposition

Challenges

- Need to operate at low speed, high load for high percent decomposition, or large adsorbers with high recycle are needed
- Need to raise desorbed stream to intake runner pressure

Configuration #4

Return NOx stream to whole engine, during intermittent stoichiometric burn with EGR operation

Benefits

- The same control is applied to the whole engine
- A reasonable operating range is possible for adequate NOx decomposition
- If EGR replaces excess air, control of mixer-type engines is simplified
- Reducing catalyst could be used for additional NOx cleanup

Challenges

- Transient may occur during changeover from lean burn to stoichiometric burn
- EGR mass must match desorption requirements
- Plumbing can be more complex

Configuration #5

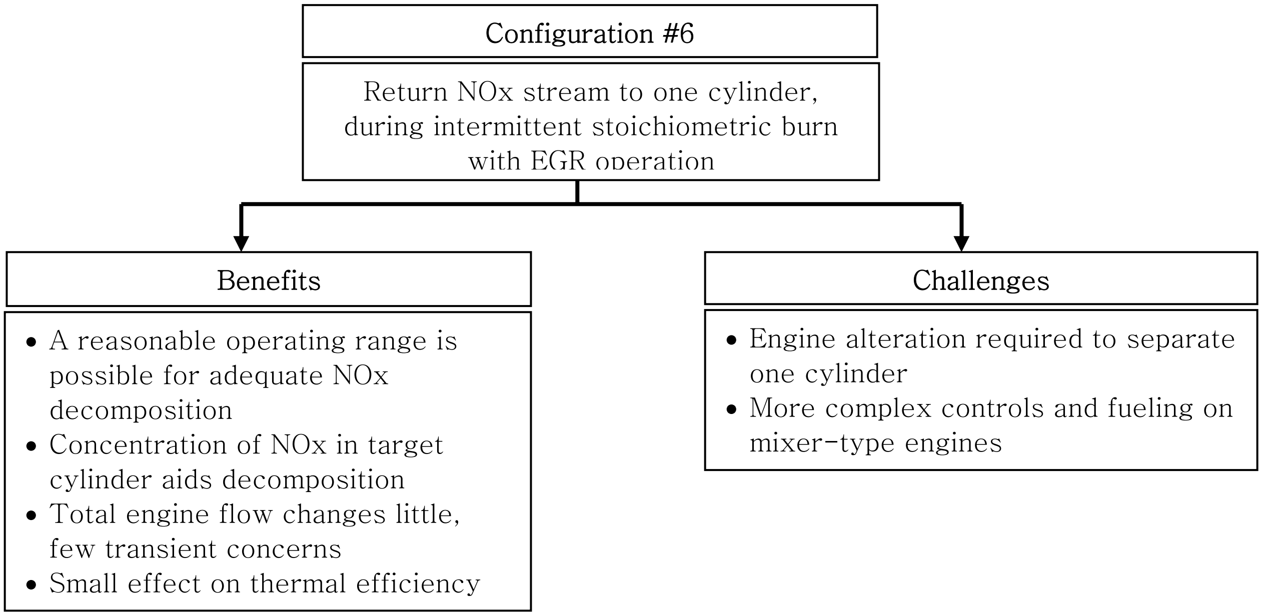
Return NOx stream to one cylinder, during intermittent stoichiometric burn operation

Benefits

- A wide operating range is possible for adequate NOx decomposition
- Concentration of NOx in target cylinder aids decomposition
- Total engine flow changes little, few transient concerns
- Small effect on thermal efficiency

Challenges

- Engine alteration required to separate one cylinder, ie. separate intake runner
- Concern over engine thermal management on one cylinder
- More complex controls and fueling on mixer-type engines



Configuration #6

Return NOx stream to one cylinder, during intermittent stoichiometric burn with EGR operation

Benefits

- A reasonable operating range is possible for adequate NOx decomposition
- Concentration of NOx in target cylinder aids decomposition
- Total engine flow changes little, few transient concerns
- Small effect on thermal efficiency

Challenges

- Engine alteration required to separate one cylinder
- More complex controls and fueling on mixer-type engines

System modeling

System modeling and design, originally to be conducted in conjunction with Sorbent Technologies, is now being conducted with the cooperation of Dr Richard Turton of the Dept of Chemical Engineering art West Virginia University. The purpose of this task is to model the adsorption of NOx, primarily nitric oxide (NO), from the exhaust gases of lean-burn stationary natural gas and diesel engines. Modeling, which leads to sizing of system components, is an essential precursor to assessing the capital cost of the SNR equipment.

In order to achieve efficient adsorption, the exhaust gases must be cooled prior to feeding to a bed of sorbent. The desorption process will be achieved by flushing the NOx laden cold sorbent bed with a hot gas. This temperature-swing process is common for a variety of commercial systems. The system design must consider the heating and cooling rates for the bed at the time that desorption and adsorption (respectively) are initiated. If the thermal inertia of the bed prevents rapid heating, the desorbed stream may be low in NOx concentration, leading to poor decomposition rates in the engine. The design should not consider an adsorption-desorption cycle, but rather a cycle of four modes, namely adsorption, heating, desorption and cooling. In a twin adsorber system, adequate time would be available for the heating, desorption and cooling phases between the adsorption phases. Also, there is freedom in determining the cycle time of the adsorbers, which determines adsorber size and heating/cooling behavior.

The basic process flow diagram showing the absorption and desorption cycles is shown in Figure 33. Hot exhaust gas is first cooled and then any water that is condensed is removed in the knock-out vessel (demister). The hot gas then enters one of the two absorbers acting in tandem, with one adsorbing and the other heating, desorbing, and cooling. Both beds operate in an unsteady mode. The sequence of operation follows three steps, first absorb the NOx from the cold exhaust gas stream, then desorb the NOx by passing a hot gas through the bed, and finally, cool the bed back down to ambient temperature ready to start the cycle again.

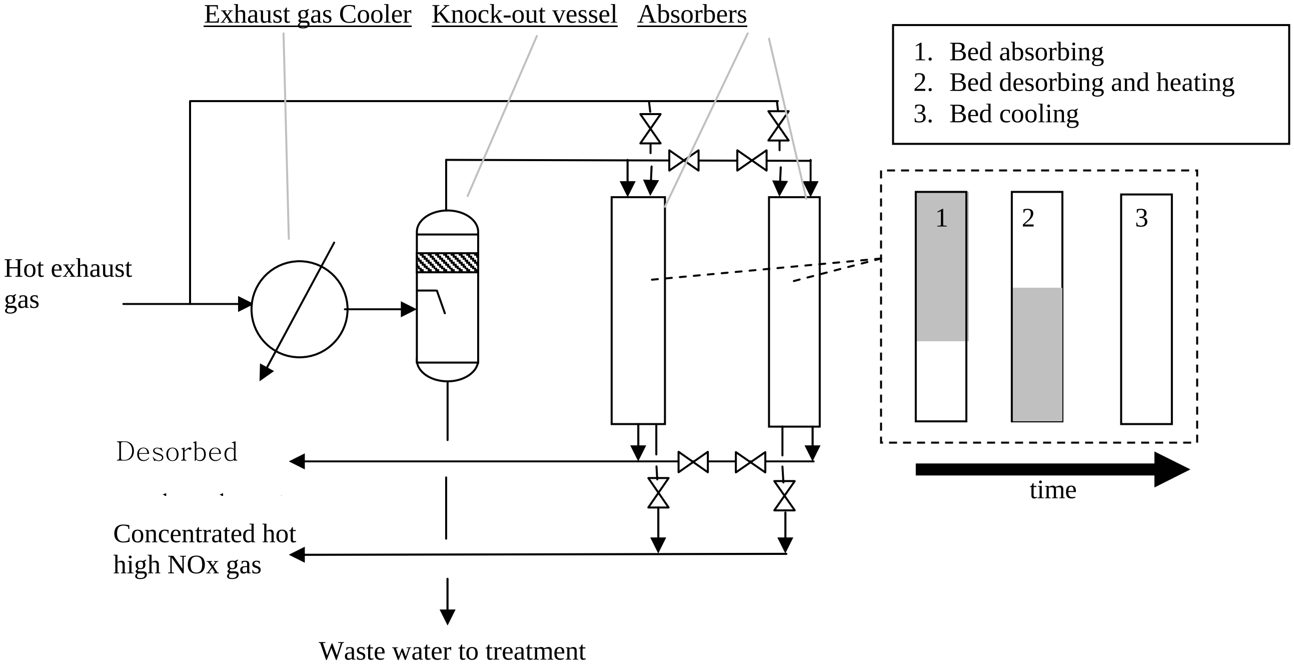


Figure 33. Process Flow Diagram showing flows of exhaust gas and operation of absorber

The current task will address the modeling and preliminary design of the exhaust gas cooler, knock-out vessel, and absorbers. Stream properties, both physical and transport, will be obtained by simulating the basic heat and cooling processes on the ChemCAD simulator.

Evaluation of a base case

In order to illustrate the design method, a base case has been chosen. This uses operating conditions for a Cummins L10G natural gas engine, which are shown in Table 9. Future modeling will also address application to a larger engine, namely a Cummins QSV91.

Table 9. Conditions used to evaluate the Base Case

Speed (rpm)	Load (ft-lb)	Exhaust Temp (°F)	Exhaust Flow (scfm)	Exhaust NOx (ppm)	Ratio of $NO:NO_2$
800	400	975	95	3330	9:1
1300	800	1100	355	1060	9:1

The sorbent that will be used for the base case is a coconut-based activated carbon marketed by Calgon Carbon, Corp., for which data are available. This carbon has the properties shown in Table 10.

Table 10. Properties of Calgon Carbon Corp's coconut activated carbon, OVC4X8

Property	Value
Ash, wt%	3.0
Moisture, wt%	3.0
Hardness No.	97
Apparent density, g/cc	0.5
Average particle size, mm	3.7
Surface Area, m^2/g	1,200

The isotherm for the adsorption of nitrous oxide (N_2O) on this carbon was provided by Calgon at a temperature of 76°F (24.4°C) and pressure of 1 atmosphere. For the base case, it is assumed that the absorption data for NO and N2O are the same. Although this assumption is probably not valid, it will not effect the methodology of approach used in the following sections. The data from Calgon showed that the adsorbed amount of solute (*q*) is a linear function of the gas phase concentration of solute (*c*), when both are plotted on log-log scales. This relationship is consistent with a Freundlich-type isotherm of the form:

$$q = kp^{1/n} \quad \text{or} \quad \log q = \log k + (1/n)\log p \qquad \text{Equation 5}$$

For the current work, it is more convenient to express this relationship in terms of *q* and *c*, the appropriate equation becomes:

$$q = 127.6c^{0.6} \qquad \text{Equation 6}$$

where *q* is the loading of NO on the carbon (kg-NO/kg-carbon) and *c* is the gas phase concentration of NO, kg-NO/m3-air. As an example, consider 1000 ppm of NO in air at 24.4°C and 1 atm pressure,

$$\text{molar density of NO} = (ppm)\frac{P}{RT} = (10^{-3})\frac{(101.3\times10^{3})}{(8.314)(273.2+24.4)} = 0.04094\ \text{mol/m}^3$$

$$\text{concentration of NO} = (0.04094)(mw) = (0.04094)(0.016+0.014) = 1.2283\times10^{-3}\ \text{kg/m}^3$$

from Equation 6, we have $q = (127.6)(1.2283\times10^{-3})^{0.6} = 2.288$ kg-NO/m^3-carbon

The analysis of the adsorption-desorption cycles is critical to the successful operation of the NOx reduction system. During these cycles, many phenomena occur simultaneously and the overall process is highly complex. For example, as cold exhaust gas passes over the fresh sorbent, NO must diffuse from the bulk to the surface of the sorbent particles (carbon). Adsorption at active sites on the carbon and simultaneous diffusion and adsorption within the porous particles takes place. The result of these processes on the microscopic level is that at the macro-scale level a diffuse concentration wave is observed to pass down the bed. The non-linear absorption isotherm for the NO absorption further complicates the situation since the rates of adsorption will be different at different concentrations and at different locations within the diffuse wave front. With this in mind, a simplified analysis based on linear isotherms will be developed and the predictions of the model will be given. In the future work, experimental results for the sorbent of interest in this work will be compared with the predictions of the model, and parameters for the sorbent will be adjusted in order to correlate the results with the model predictions.

<u>Approximate solution of Klinkenberg [37]</u>

Using a linear driving force model, under the additional assumptions of constant fluid velocity and negligible axial dispersion, Klinkenberg [36] proposed an approximate solution of the form:

$$\frac{c(\tau,\zeta)}{c_F} = \frac{1}{2}\left[1 + erf\left\{\sqrt{\tau} - \sqrt{\zeta} + \frac{1}{8\sqrt{\tau}} + \frac{1}{8\sqrt{\zeta}}\right\}\right] \qquad \text{Equation 7}$$

where: c is the concentration in the bed, c_F is the feed concentration of the gas, τ is the dimensionless time, ζ is the dimensionless distance, and *erf* is the error function. The approximate solution given by Eqn. (4) is within 0.6% of the rigorous solution for values of $\zeta < 2$. Furthermore,

$$\tau = k\left[t - \frac{z}{u}\right] \qquad \text{Equation 8}$$

$$\zeta = \frac{kKz}{u}\left[\frac{1-\varepsilon_b}{\varepsilon_b}\right] \qquad \text{Equation 9}$$

where:

t is time

z is distance

u is fluid velocity

k is the overall (internal and external) mass transfer coefficient

K is the Henry's law constant for a linear absorption isotherm ($q = Kc$)

A relationship for the overall mass transfer coefficient is given by Eqn. (10),

$$\frac{1}{kK} = \frac{d_p}{6k_c} + \frac{d_p^2}{60D_e} \qquad \text{Equation 10}$$

where:

d_p is the volume equivalent spherical particle diameter

k_c is the external mass transfer coefficient

D_e is the effective diffusivity within the pores of the particle

The external mass transfer coefficient, k_c, can be evaluated using the correlation due to Wakao and Funazkri [38]:

$$Sh = \frac{k_c d_p}{D_i} = 2 + 1.1\mathrm{Re}^{0.6}\, Sc^{1/3} = 2 + 1.1\left[\frac{d_p G}{\mu}\right]^{0.6}\left[\frac{\mu}{\rho D_i}\right]^{1/3} \qquad \text{Equation 11}$$

where:

Re = Reynolds number

Sc = Schmidt number

Sh = Sherwood number

D_i = diffusivity of solute in bulk gas = 0.23 cm2/s for NO in air at ambient conditions

G = mass flux of gas = (gas density) x (gas velocity)

μ = gas viscosity

ρ = gas density

Finally, the effective diffusivity of the solute in the pores of the sorbent can be obtained from:

$$\frac{1}{D_{eff}} = \frac{\tau_m}{\theta}\left(\frac{1}{D_i} + \frac{1}{D_{Kn}}\right) \qquad \text{Equation 12}$$

where the Knudsen diffusivity, D_{Kn}, is given by Seader and Henley [39] as

$$D_{Kn} = 19,400\frac{\theta}{S\rho_p}\sqrt{\frac{T}{mw}} \qquad \text{Equation 13}$$

and where

Θ is the internal porosity of the particle $(1 - \rho_p/\rho_s)$

τ_m is the tortuosity of the internal pores (typically ~ 4)

ρ_p is the particle density (g/cm3)

ρ_s is the solid density (g/cm^3)

S is the specific surface area of the pellet (cm2/g)

T is the absolute temperature (K)

Example Calculation for Adsorption

In order to evaluate the method described above, a test example corresponding to the 1300 rpm-case shown in Table 9 was developed. The physical constants and parameters for this test case are listed below.

Length of adsorber, L = 4 m

Diameter of adsorber, D = 0.5 m

Volume of adsorber, V = 0.7854 m3

Bed voidage, Γ_b = 0.5

Solids density, ρ,ρ_p = 1.2 g/cm3 = 1,200 kg/m^3

Apparent density,ρ_a = 0.5 g/cm3 = 500 kg/m^3

Mass of carbon in absorber, M_a = 196.3 kg

Particle porosity, Θ = 0.5833

Tortuosity of pores, τ_m = 4.0

Bed temperature, T = 90°F = 305.4 K

Gas flow, Q_g = 355 scfm = 0.1746 m3/s

Gas velocity, u = 0.8895 m/s

Bed Reynolds no., Re = 219

Schmidt no., Sc = 0.652

Diffusivity of NO in CO2/N2, D_i = 0.23 cm2/s = 0.000023 m2/s

Particle diameter, d_p = 3.7 mm = 0.0037 m

Gas density, $\rho_g = 1.2$ kg/m^3

Gas viscosity, $\mu = 18.0\times10^{-6}$ kg/m.s

External mass transfer coefficient, k_c = 0.163 m/s

Internal surface area of carbon, S = 12,000,000 cm2/g = 1,200 m2/g

Knudsen diffusivity, D_{Kn} = 0.002508 cm2/s = 2.5075×10-7 m2/s

Effective pore diffusivity, D_{eff} = 0.000362 cm2/s = 3.6174×10-8 m2/s

Isotherm constant, K (assuming a linear isotherm) = 1091 m3-carbon/m3gas

Kk = 0.1584 s-1

Inlet Concentration of NO = 13.028×10^{-4} kg/m^3

Overall mass transfer coefficient, k = 14.5×10-5 m/s

Total capacity of bed = 0.5584 kg NO

Stoichiometric time for saturation = 40.9 min = 2454 s

ρ, (using t = 68 min and z = bed length = 4m)

$$\tau = k\left[t - \frac{z}{u}\right] = (14.5\times10^{-5})\left[2454 - \frac{4}{0.8895}\right] = 0.36$$

$$\zeta_{z=4\text{m}} = \frac{kKz}{u}\left[\frac{1-\varepsilon_b}{\varepsilon_b}\right] = \frac{(0.1584)(4)}{(0.8894)}\frac{(1-0.5)}{0.5} = 0.7124 < 2.0$$

Because the value of ζ is less than 2.0, the approximate solution of Eqn (7) is not valid. However, in order to illustrate the use of Eqn (7), the value of k was increased by a factor of 20 to 0.0029. The resulting concentration profiles are shown in Figure 33.

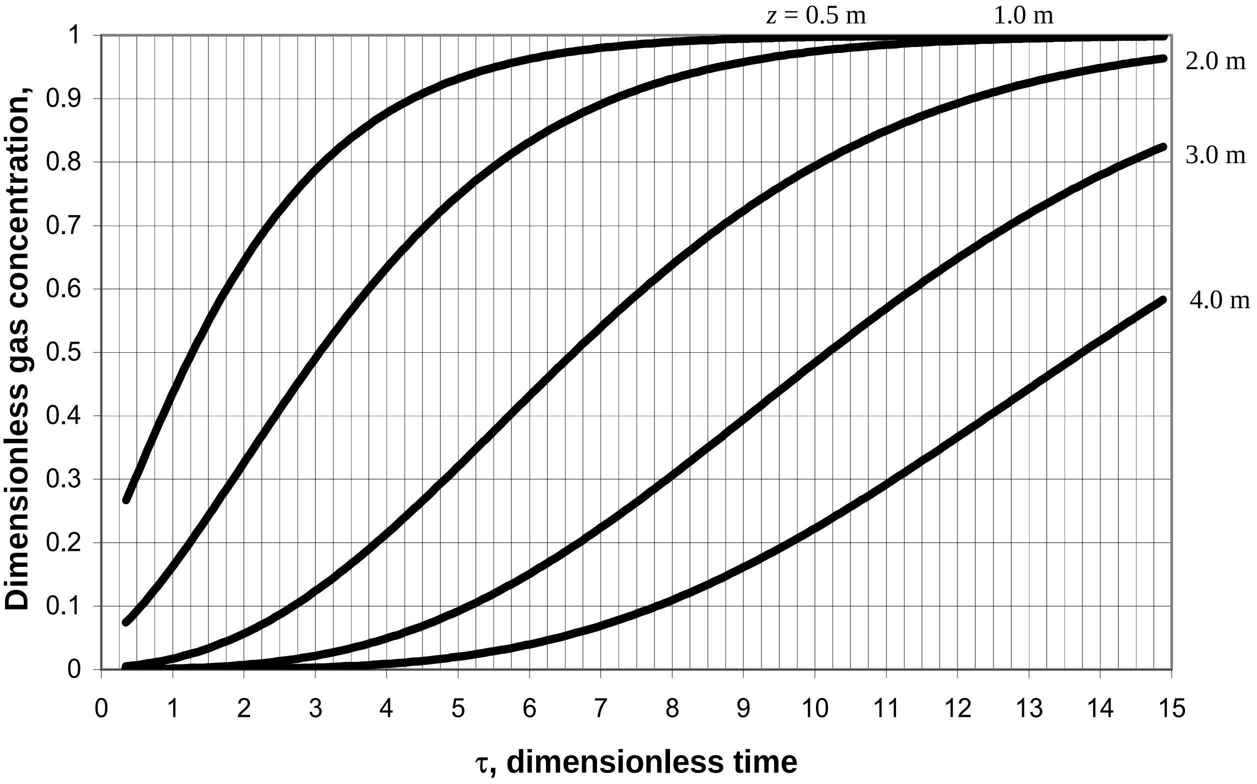


Figure 34. Gas phase concentration profiles for absorption on a bed of carbon with $k = 0.0029\ s^{-1}$

From Figure 34, the breakthrough of NO at the outlet of the absorber (z = 4m) occurs at a value of τ = 7, this is close to the stoichiometric break through time, which corresponds to about 41 minutes.

Future work will focus on evaluating the experimental results for the adsorption of NO on the commercial sorbent and reconciling the data with the predictions of the simplified analysis due to Klinkenberg[37].

Future work

All NOx decomposition data from the third campaign will be analyzed and the data from all three campaigns and CHEMKIN modeling will be used to develop a model to describe the NOx decomposition as a function of the intake NOx concentration and the engine operating parameters (speed, load, air/fuel ratio, EGR%). The most reasonable configurations for operating the engine-adsorber system will be identified, and these will be used as the basis for the creation of Matlab/Simulink models for each chosen system configuration. Performance of the systems will be compared using the models, and the optimum configuration will be identified. Engine and system control strategy will be chosen to suit the design for both mechanically and electronically managed engines.

Comprehensive adsorption and desorption data on carbon-based sorbents will be acquired using the bench top adsorber. An adsorption/desorption model that considers gas temperature and heat and mass transfer will be formulated based on these data.

NOx adsorbtion system components (sorbent chamber, heat exchanger) will be sized for two models of natural gas engines the Cummins L10G, and one of larger displacement: a Cummins QSV91-G lean-burn natural gas engine (Table 11) has been targeted for modeling purposes. Based on this sizing, an economic analysis will be used to determine capital and operating costs for the system. These costs will be contrasted with costs published for competing NOx reduction systems. System sizing of the heat exchanger and adsorber (ChemCAD simulator) is undertaken by Dr Richard Turton (Dept of Chemical Engineering, WVU).

Two journal papers on the natural gas SNR implementation will be authored to reach a wider constituency.

Table 11. Cummins QSV91 engine technical data

Displacement	91 liters
Number of cylinders	18 (V)
Bore	180 mm (7.086 in)
Stroke	200 mm (7.874 in)
Compressions ratio	12 : 1
Power	1700 hp (1250kW)
NOx emissions	0.7 g/bhp-hr (350mg/Nm^3)
Engine speed	1200-1500rpm

List of publications and presentations

1. Chamila A. Tissera, Matt M. Swartz, Emre Tatli, Ramprabhu Vellaisamy, Nigel N. Clark, Gregory J. Thompson, Ralph D. Nine, Richard J. Atkinson, “Selective NOX Recirculation for Stationary Lean-Burn Natural Gas Engines,” ASME Fall Technical Conference 2004, ICEF2004-839

2. Matt M. Swartz, Chamila A. Tissera, Emre Tatli, Ramprabhu Vellaisamy, Nigel N. Clark, Gregory J. Thompson, Richard J. Atkinson, “Nitric Oxide Conversion in a Spark Ignited Natural Gas Engine,” SAE World Congress 2005. 2005-01-0234

3. Chamila A. Tissera, Matt M. Swartz, Emre Tatli, Nigel N. Clark, Gregory J. Thompson, Richard J. Atkinson, “Selective NOX Recirculation for Stationary Lean-Burn Natural Gas

Engines," 2nd Annual Advanced Stationary Reciprocating Engines Conference, Hosted by, South Coast Air Quality Management District, Diamond Bar, CA. March 15-16, 2005

4. Chamila A. Tissera, Emre Tatli, Andy Zimmerman, Nigel N. Clark, Gregory J. Thompson, Richard J. Atkinson, "Selective NO_X Recirculation for Stationary Lean-Burn Natural Gas Engines," Presentation at the 2005 ARES University Program review held at Argonne National Laboratory, Argonne, Illinois on July 12, 2005

5. ARES catalysis group conference call organized by Oak Ridge National Laboratory, Knoxville TN, on August 19, 2005

6. Chamila A. Tissera, Emre Tatli, Andy Zimmerman, Nigel N. Clark, Gregory J. Thompson, Richard J. Atkinson, "Selective NOX Recirculation for Stationary Lean-Burn Natural Gas Engines," Poster presentation held at the 2005 Distributed Energy Peer Review held at Crystal City, Virginia, December 13-15, 2005

References

[1]. Energy Nexus Group, Arlington VA, "Technology Characterization: Reciprocating Engines," prepared for EPA - Climate Protection Partnership, Washington DC, February 2002.

[2]. G. Cox, K. DelVecchio, W. Hays, J. Hiltner, R. Nagaraj, C. Emmer, "Development of a Direct- Injected Natural Gas Engine System for Heavy-Duty Vehicles Final Report Phase II," Document no. NREL/SR-540-27501, February 2000.

[3]. Johnson Matthey, Selective Catalytic Reduction (SCR) deNOx Catalyst. URL http://ect.jmcatalysts.com/applications-ssec-na-products-scr.htm.

[4]. S. Saito, R. Shinozaki, A. Suzuki, H. Jyoutaki, Y. Takeda, "Development of Urea-SCR System for Commercial Vehicle - Basic Characteristics and Improvement of NOx Conversion at Low Load Operation," SAE paper no. 2003-01-3248.

[5]. R. Krishnan, RJM Corporation, Norwalk CT, "SCR Economics for Diesel Engines," Diesel and Gas Turbine Worldwide, July-August 2001.

[6]. S. Fable, M. Jackson, "Urea Infrastructure Hurdles: Report on TIAX Selective Catalytic Reduction Urea Infrastructure Study," Motor Fuels: Effects on Energy Efficiency & Emissions in the Transportation Sector October 10, 2002.

[7]. S. Fable, F. Kamakate, S. Venkatesh, "Selective Catalytic Reduction Urea Infrasturcture Study," National Renewable Energy Laboratory, Document no. NREL/SR-540-32689, July 2002.

[8]. D. Dou, S. Miyaura, T. Dogahara, S. Kikuchi, K. Okada, "NOx-Trap Catalyst Development for Mitsubishi 1.8L GDITM Application," SAE paper no. 2003-01-3078.

[9]. N. Fekete, R. Kemmler, D. Voigtländer, B. Krutzsch, E. Zimmer, G. Wenninger, W. Strehlau, J. van den Tillaart, J. Leyrer, E. Lox and W. Müller, "Evaluation of NOx Storage Catalysts for Lean Burn Gasoline Fueled Passenger Cars," SAE paper no. 970746, 1997.

[10]. M. Brogan, A. Clark, R. Brisley "Recent Progress in NOx-Trap Technology," SAE paper no. 980933.

[11]. J.M. Kisenyi, B. Cumming, R. Stark, R.A Marshall, E.F. Gibbons "Correlation between Dynaomometerand Vehicle-Aged Catalysts for Automotive Lean-Burn Applications," SAE paper no. 980934.

[12]. D. Dou; O.H. Bailey "Investigation of NOx Adsorber Catalyst Deactivation," SAE Paper no. 982594.

[13]. M. Dearth, J. Hepburn, E. Thanasiu, J. McKenzie, G. Horne, "Sulfur Interaction with Lean NOx-Traps: Laboratory and Engine Dynamometer Studies," SAE Paper no. 982595.

[14]. Y. Ikeda, K. Sobue, S. Tsuji, S. Matsumoto "Development of NOx Storage-Reduction Three-way Catalyst for D4 Engines," SAE paper no. 1999-01-1279.

[15]. U. Goebel, J. Hoehne, E. Lox, W. Mueller, A. Okumura, W. Strehlau, M. Hori "Durability Aspects of NOx Storage Catalysts for Direct Injection Gasoline Vehicles," SAE paper no. 99FL-103.

[16]. Sh. Hodjati, F. Semelle, N. Moral, C. Bert and M. Rigaud "Impact of Sulfur on the NOx-Trap Catalyst Activity-poisoning and Regeneration Behavior," SAE Paper no. 2000-01-1874.

[17]. I. Hachisuka, H. Hirata, Y. Ikeda, S. Matsumoto "De-activation Mechanism of NOx storage-Reduction Catalyst and Improvement of Its performance," SAE paper no. 2000-01-1196.

[18]. J. Asik, G. Meyer, D. Dobson "Lean NOx-Trap Desulfation Through Rapid Air Fuel Modulation," SAE paper no. 2000-01-1200.

[19]. O. Bailey, D. Dou, M. Molinier "Sulfur Traps for NOx Adsorbers: Materials Development and Maintenance Strategies for Their Application," SAE paper no. 2000-01-1205.

[20]. H. Ohno, T. Takanohashi, N. Takaoka, O. Kuroda, H. Iizuka "NOx Conversion Properties of a Mixed Oxide Type Lean NOx Catalyst," SAE paper no. 2000-01-1197.

[21]. K. Iwachido, H. Tanada, T. Wantanabe, N. Yamada, O. Nakayama, H. Ando, M. Hori, S. Taniguchi, N. Noda, F. Abe "Development of the NOx Adsorber Catalyst for Use with High-Temperature Conditions," SAE paper no. 2001-01-1298.

[22]. D. Dou, J. Balland "Impact of Alkali Metals on the Performance and Mechanical Properties of NOx Adsorber Catalysts," SAE paper no. 2002-01-0734.

[23]. D. Monroe, W. Li "Desulfation Dynamics of NOx Storage Catalysts," SAE paper no. 2002-01-2886.

[24]. J. Parks, A. Watson, G. Campbell, B. Epling "Durability of NOx Absorbers: Effect of Repetitive Sulfur Loading and Desulation," SAE paper no. 2002-01-2880.

[25]. C. Sluder, B. West "Effects of Regeneration Conditions on NOx Adsorber Performance," SAE paper no. 2002-01-2876.

[26]. J. Reuther, “Evaluation of Air Emissions-Reduction Technologies for Aerospace Ground Equipment,” Battelle Research Laboratories, Columbus OH, Document no. AFRL-HE-WP-TR-1998-0026, April 1998.

[27]. Manufacturers of Emission Controls Association, “Emissions Control Technology for Stationary Internal Combustion Engines,” Status report, 1660 L Street NW, Suite 1100, Wachinton DC 20036, July 1997.

[28]. L. Brandon, “Cummins’ Technology Strategy for ARES,” DOE Distributed Energy Peer Review, Arlington VA, December 13, 2005.

[29]. D. Baldwin, G. Gerber, “Advanced Reciprocating Engine Systems,” DOE Distributed Energy Peer Review, Arlington VA, December 13, 2005.

[30]. J. Drees, Waukesha Engine Dresser, Inc. “Stoichiometric Combustion Advances,” ARES-ARICE Contractor Conference, April 14-15, 2004.

[31]. G. Krutzsch, M. Wenninger, P. Weibel, A. Stapf, D. Funk, E. Webster, E. Chaize, B. Kasemo, J. Martens, A. Kiennemann, “Reduction of NOx in Lean Exhaust by Selective NOX – Recirculation (SNR -Technique), Part I: System and Conversion Process,” SAE paper no. 982592.

[32]. Code of Federal Regulations, Title 40, Part 86, Subpart N, “Emission Regulations for New Otto-Cycle and Diesel Heavy-Duty Engines; Gaseous and Particulate Exhaust Test Procedures,” Washington D. C., 1998.

[33]. E. Chaize, D. Webster, B. Krutzsch, G. Wenninger, M. Weibel, Sh. Hodjati, C. Petit, V. Pitchon, A. Kiennemann, R. Loenders, O. Monticelli, P. A. Jacobs, J. A. Martens, B. Kasemo, “Reduction of NO_X in Lean Exhaust by Selective NO_X Recirculation (SNR - Technique), Part II: NO_X Storage Materials,” SAE paper no. 982593.

[34]. C Tissera, M. Swartz, E. Tatli, R. Vellaisamy, N. Clark, G. Thompson, R. Nine, R. Atkinson, “Selective NOX Recirculation for Stationary Lean-Burn Natural Gas Engines,” ASME Fall Technical Conference 2004, paper no. ICEF2004-839.

[35]. M Swartz, C. Tissera, E. Tatli, R. Vellaisamy, N. Clark, G. Thompson, R. Atkinson, “Nitric Oxide Conversion in a Spark Ignited Natural Gas Engine,” SAE paper no. 2005-01-0234.

[36]. S. Bhargava, M. Hildebrand, N. Clark, “Exhaust Gas Recirculation in a Lean Burn Natural Gas Engine,” SAE Spring Fuels and Lubricants Meeting, Dearborn, MI, May 1998, SAE paper no. 981395.

[37]. A. Klinkenberg, “Heat Transfer in Cross-Flow Heat Exchangers and Packed Beds,” Industrial and Engineering Chemistry Research, 46, 2285-2289 (1954)

[38]. N. Wakao, T. Funazkri, “Effect of Fluid Dispersion Coefficients on Particle-to-fluid Mass Transfer Coefficients in Packed Beds,” Chemical Engineering Science, 33, 1375-1384 (1978)

[39]. J. Seader, E. Henley, “Separation Process Principles,” John Wiley and Sons, New York, NY (1998)

Appendix

Each of the following plots (in-cylinder pressure trace, PV diagrams, and piston work done plots) shows four curves corresponding to stock baseline trace, baseline with EGR trace, effect due to NOx injection, and effect due to NOx injections with added EGR. The engine operating point was 800 rpm with 200 ft-lb load.

In-cylinder pressure plots

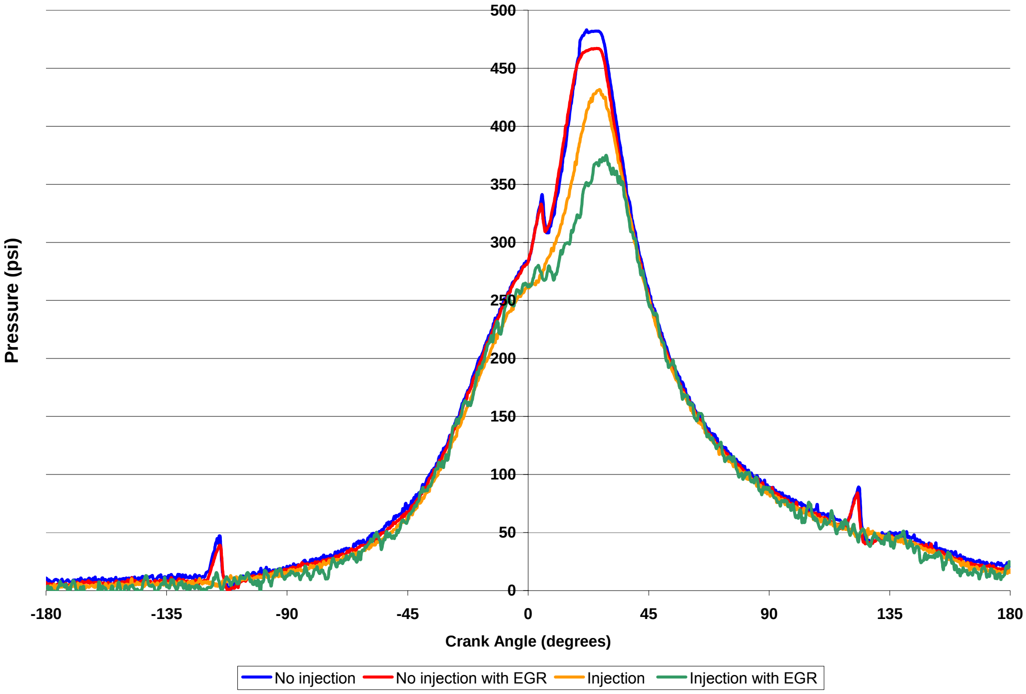


Figure A 1. Pressure plots

Pressure – volume plots

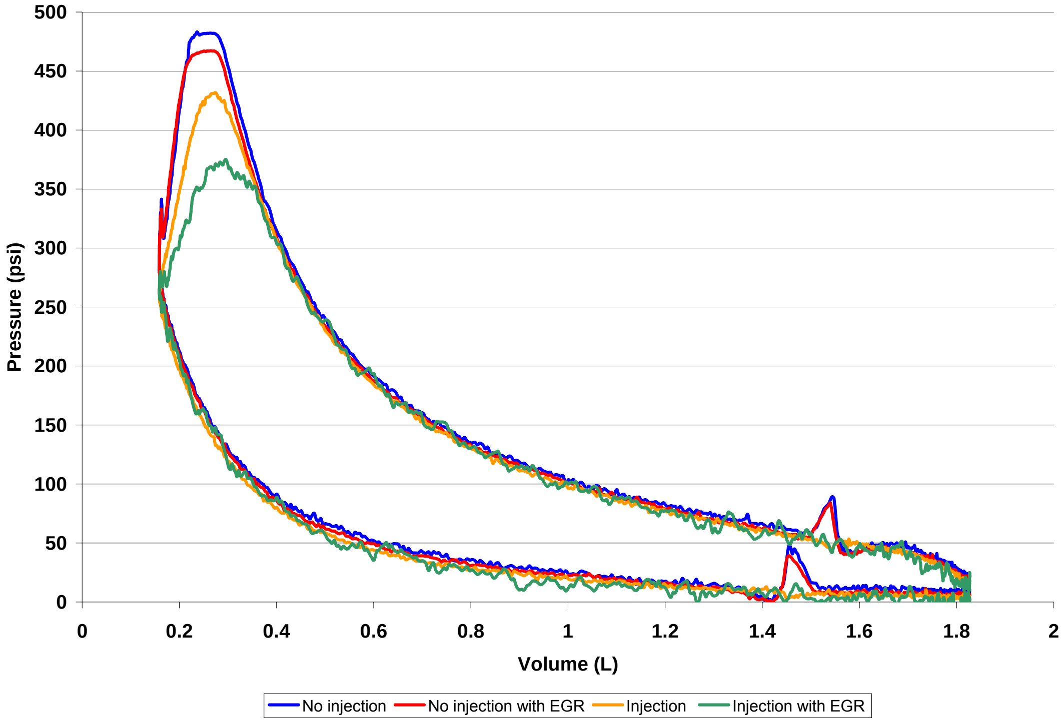


Figure A 2. PV diagrams

Piston work (IMEP) plots

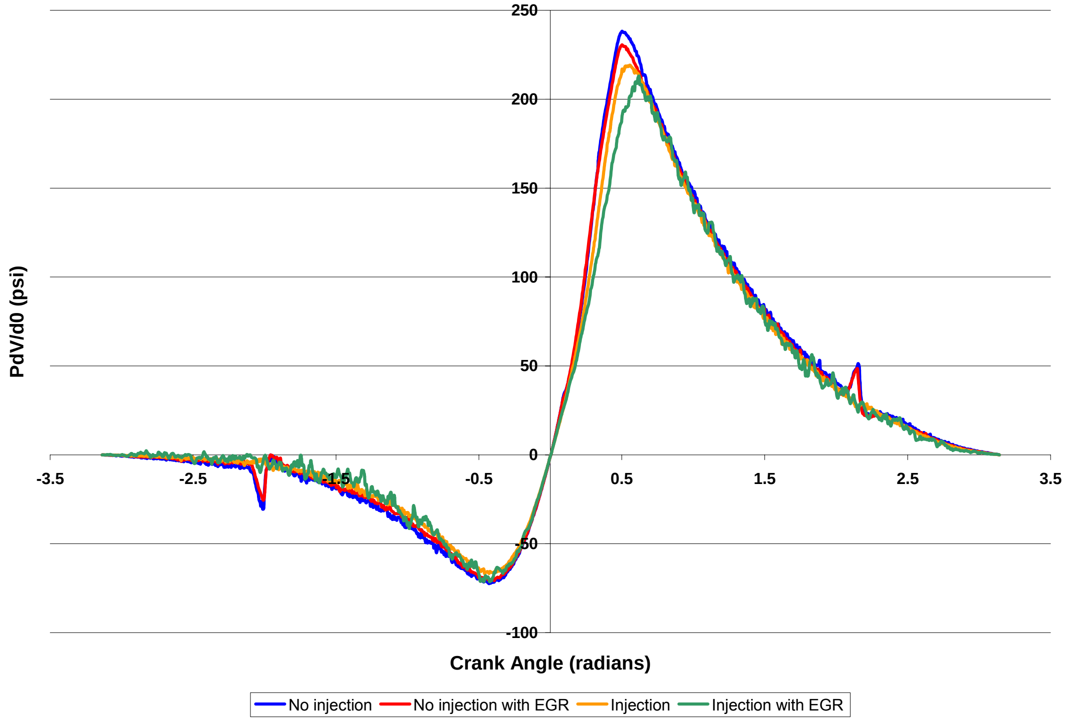


Figure A 3. Piston work diagrams

The figures show that the injections had very little effect on the in-cylinder pressures, and the EGR has lowered the peak values as was expected.

Influence of EGR on NOx decomposition

Figure A4 shows raw data from a test conducted at 1300rpm at 800ft-lb load to understand the effect of EGR on NOx decomposition. Region A represents the NOx output from the engine at a slightly rich condition. Region B represents the NOx output when 15% EGR was introduced into the engine, when an 83% reduction in NOx output was observed. Region C represents the exhaust NOx level during a NOx injection of 2 g/s into the intake. Region D represents the combination of 15% EGR and 2 g/s NOx injection at the same time. Although coincidently level D reached the engine baseline level A, it can be seen that NOx injection into the intake along with EGR can decompose a substantial fraction of NOx.

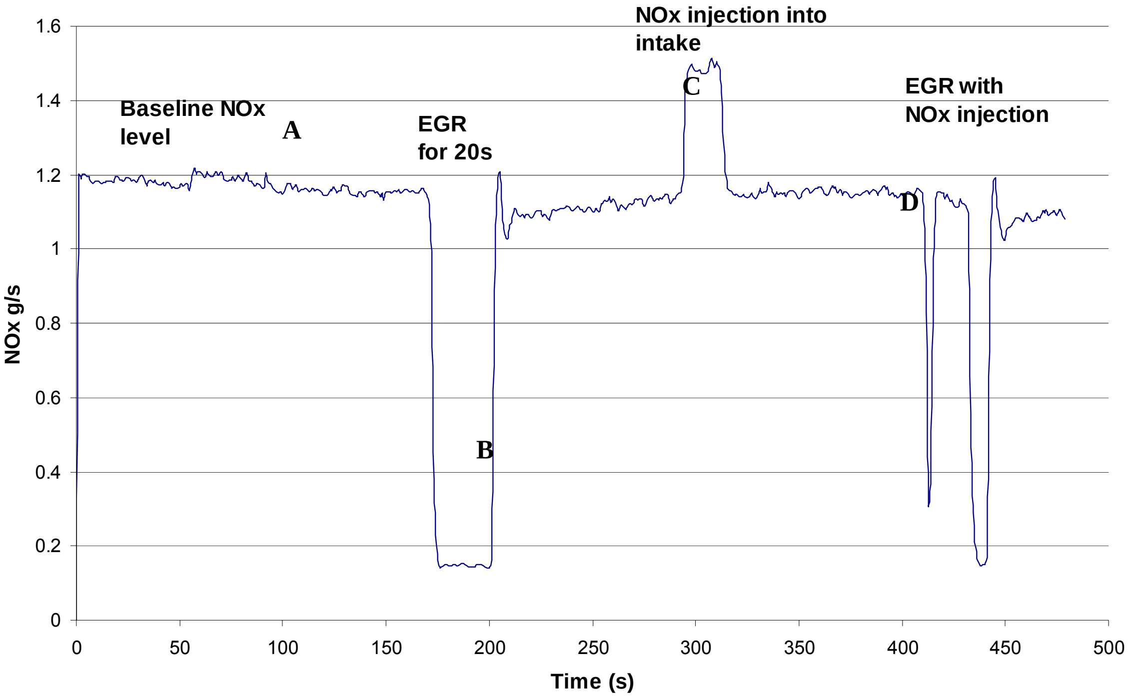


Figure A 4. Influence of EGR on NOx decomposition