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Principal Author(s): Dr. Nigel Clark, Dr. Gregory Thompson, Richard Atkinson,
Chamila Tissera, Matt Swartz, Emre Tatli, Ramprabhu Vellaisamy

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Name and Address of Submitting Organization: West Virginia University
Office of Sponsored Programs
886 Chestnut Ridge Road
PO Box 6845
West Virginia University
Morgantown, WV 26506-6845

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Abstract

The research program conducted at the West Virginia University Engine and Emissions Research Laboratory (EERL) is working towards the verification and optimization of an approach to remove nitric oxides from the exhaust gas of lean burn natural gas engines. This project was sponsored by the US Department of Energy, National Energy Technology Laboratory (NETL) under contract number: DE-FC26-02NT41608.

Selective NO_x Recirculation (SNR) involves three main steps. First, NO_x is adsorbed from the exhaust stream, followed by periodic desorption from the aftertreatment medium. Finally the desorbed NO_x is passed back into the intake air stream and fed into the engine, where a percentage of the NO_x is decomposed. This reporting period focuses on the NO_x decomposition capability in the combustion process.

Although researchers have demonstrated NO_x reduction with SNR in other contexts, the proposed program is needed to further understand the process as it applies to lean burn natural gas engines. SNR is in support of the Department of Energy goal of enabling future use of environmentally acceptable reciprocating natural gas engines through NO_x reduction under 0.1 g/bhp-hr.

The study of decomposition of oxides of nitrogen (NO_x) during combustion in the cylinder was conducted on a 1993 Cummins L10G 240 hp lean burn natural gas engine. The engine was operated at different air/fuel ratios, and at a speed of 800 rpm to mimic a larger bore engine. A full scale dilution tunnel and analyzers capable of measuring NO_x, CO₂, CO, HC concentrations were used to characterize the exhaust gas. Commercially available nitric oxide (NO) was used to mimic the NO_x stream from the desorption process through a mass flow controller and an injection nozzle. The same quantity of NO_x was injected into the intake and exhaust line of the engine for 20 seconds at various steady state engine operating points. NO_x decomposition rates were obtained by averaging the peak values at each set point minus the baseline and finding the ratio between the injected NO amounts.

It was observed that the air/fuel ratio, injected NO quantity and engine operating points affected the NO_x decomposition rates of the natural gas engine. A highest NO_x decomposition

rate of 27% was measured from this engine. A separate exploratory tests conducted with a gasoline engine with a low air/fuel ratio yielded results that suggested, that high NO_x decomposition rates may be possible if a normally lean burn engine were operated at conditions closer to stoichiometric, with high exhaust gas recirculation (EGR) for a brief period of time during the NO_x decomposition phase and with a wider range of air/fuel ratios.

Chemical kinetic model predictions using CHEMKIN were performed to relate the experimental data with the established rate and equilibrium models. NO_x decomposition rates from 35% to 42% were estimated using the CHEMKIN software. This provided insight on how to maximize NO_x decomposition rates for a large bore engine. In the future, the modeling will be used to examine the effect of higher NO₂/NO ratios that are associated with lower speed and larger bore lean burn operation.

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Introduction

Spark ignited natural gas engines of all sizes are able to achieve acceptable efficiencies at part load only if operated in a lean burn mode because this allows for a reduction of throttling losses. Lean burn is also desirable to extend engine life by reducing the thermal load. Engines operated at stoichiometric air/fuel ratios with aftertreatment can offer very low tailpipe emissions levels but suffer throttling losses at part load. Although lean burn operation is still typical, Bhargava et al. [1] showed that use of exhaust gas recirculation offered NO_x reduction benefits.

Unfortunately, engines operated at fairly high air/fuel ratios produce prodigious amounts of NO_x. Although increasing the air/fuel ratio further reduces NO_x, it also leads to incomplete combustion, high unburned methane emissions and a loss of power density. In the automotive world, heavy duty high speed natural gas lean burn engines have used wide range oxygen sensor feedback to approach 1g/bhp-hr of NO_x, but further significant reductions are unlikely for lean burn operation and call for exhaust gas aftertreatment. Large bore lean burn natural gas engines, even with careful control, are an order of magnitude off the 0.1 g/bhp-hr NO_x target. Conventional NO_x reduction catalysts, used widely to tame stoichiometric burn automobile emissions, cannot be employed because the lean-burn exhaust of large natural gas engines contain excess oxygen, which leads to unfavorable reaction conditions. This report addresses an emissions reduction technique that is proposed to reduce NO_x while allowing lean burn operation.

More recently, Caterpillar has proposed the SC-3 system, where clean exhaust gas is used as a combustion diluent, and a three way catalyst is enabled [2]. Approaches for reduction of large bore natural gas engine emissions have been presented in numerous recent papers, for example ([3] – [10]). A literature review on the topic of emissions from natural gas engines was performed at the inception of this program and was updated in the past year ([11] – [23]).

Description of the NO_x Reduction Approach–SNR

The Selective NO_x Recirculation (SNR) technique does not use a catalytic converter to reduce NO_x, but rather uses a NO_x adsorber to collect a substantial fraction of the NO_x from the exhaust gas. Once the adsorber is saturated (which may be determined by modeling or by

breakthrough measurement), the desorption process recirculates a concentrated stream of NO_x into the intake of the engine facilitating thermal NO_x decomposition [24]. Figure 1 shows a schematic of the SNR after-treatment system coupled to a lean burn engine. An exhaust gas control valve is used to separate the exhaust stream from the adsorber.

Figure 1. SNR after-treatment system

The following steps describe the NO_x decomposition process used in the SNR technique. Initially raw exhaust gas is directed to the adsorber. NO_x adsorption quantity greatly depends on the exhaust gas temperature and the adsorber material used. NO_x adsorbers employing alkaline earth metals have received substantial recent attention for diesel engine application. Material such as Barium has been developed as NO_x adsorbers for lean-burn applications [25]. However, since this SNR approach separates the process of NO_x adsorption and NO_x decomposition, a wider variety of sorbents can be used, and the NO_x is not destroyed in the vicinity of the sorbent material [24][26].

After the adsorber saturates the exhaust gas is switched away from the adsorber for a relatively short time period initiating the desorption mode. Once again, the quantity of NO_x desorbed depends on the temperature and type of material used. A concentrated stream of desorbed NO_x is directed into the intake air of the engine where it is reduced by the combustion process. In 1998 Krutzsch et al., achieved more than 50% NO_x decomposition in the combustion process with a turbocharged diesel engine [24]. They also found similar trends for NO_x conversion in naturally aspirated and turbo-diesel engines.

Experimental Setup

The natural gas engine experimental program commenced with the installation of a 10 liter Cummins lean burn natural gas engine on a test stand at West Virginia University, Engine and Emissions Research Laboratory (EERL). Engine specifications are listed in Table 1. The engine setup diagrams and initial experiments were detailed in the previous annual report [27]. A 300hp Mustang Eddy current dynamometer was used to absorb power output from the engine. It was controlled by a DYN-LOC IV Digital Dynamometer Controller. The fuel injection system of the older engine consisted of a mechanical fuel metering system with no feedback control. This had limitation in changing the air/fuel ratio and emissions stability.

Table 1. 1993 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	240 hp
Cummins Part List (CPL#)	1390
Rated speed	2100 rpm

At the end of this reporting period, two newer 1998 Cummins L10G engines were procured from Bell Power Systems with the assistance of Cummins Engine Company. These engines, the specifications of which are given in Table 2, were not employed in experimental research in this year, but are anticipated to permit leaner operation for experimental research in the next period. The injection system of these new engines consisted of an electronic fuel injection system with closed-loop control. This would provide a more stable air/fuel ratio and improve repeatability of the tests.

Table 2. 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

Bench Analyzers

The exhaust gases from the Cummins engine were directed to a full-scale dilution tunnel (Figure 2) as outlined by the CFR title 40 part 86 [28]. The dilution tunnel was 18 inches in diameter, 20 feet in length and was constructed of stainless steel. It had a mixing orifice, with diameter 10 inches, located 3 feet from the entrance to the tunnel to promote a uniform mixing of gases. Sample probes for the gas analyzers were located 15 feet from the entrance of the tunnel. The nominal flow into the dilution tunnel was set to 3000 scfm. The gas analyzer bench was capable of quantifying HC, CO, CO₂ and NO_x emissions (Table 3).

Figure 2. Dilution tunnel and gas analyzer setup

Table 3. Bench analyzers

Analyzer	Detection Method	Manufacturer
Hydrocarbon analyzer	Flame ionization	Rosemont Analytical
NO _x analyzer	Chemiluminescent	Rosemont Analytical
CO	Non-dispersive infrared absorptiometry	Horiba Instruments
CO ₂	Non-dispersive infrared absorptiometry	Horiba Instruments

NO_x Injection System

The NO_x injection system comprised of a compressed NO gas bottle (98.8% NO), a mass flow controller capable of injecting a maximum flow of 1.58 liters per second (lps) with $\pm 1\%$ error, and an injection nozzle. The tests were conducted with 20 second injections in each mode to avoid excessive consumption of NO as compared to continuous NO injections.

For every engine run, NO was injected at the exhaust pipe and at the intake line upstream of the turbo charger Figure 3. The reason for injecting into the exhaust was to assess the amount of NO_x decomposed by comparing with NO injected into the intake manifold. It was necessary to rely only on the precision of the mass flow controller and not its accuracy for the NO decomposition calculation. It was assumed that the exhaust flow was too cold to react significantly with the NO injected directly into the exhaust.

Figure 3. NO_x injection system setup

Test Description

The engine was run in stock configuration (with air/fuel ratio set manually) to determine its baseline emissions. Based on the engines full load vs. speed trace (engine map) a steady state test matrix was created for each engine. The controlled variables were engine speed and load, air/fuel ratio and NO_x injection flow rates. Injected NO_x amounts were one order of magnitude larger than the baseline emissions for the natural gas engine. Engine intake air flow rates for all engines were measured using a laminar flow element (LFE). This intake air flow rate and the mass flow rate of NO injected were used to calculate NO concentration before decomposition. This NO flow rate calculation did rely on the accuracy of the NO mass flow controller.

Engine speed was kept constant at 800 rpm to approximate the reaction time constants of a large bore natural gas engine. During the first set of tests, engine speed and intake NO concentrations were kept constant while varying the engine load (Table 4). At constant engine speed and varying load the intake air flow rate fluctuated. In order to keep the NO

concentration in the intake air constant, injected NO amount had to be altered accordingly. In other words, the molar fraction of NO in the intake was held constant at varying loads.

Table 4. Varying engine load at constant engine speed

Speed	Load	NO Injected	NO in Intake	Intake Flow Rate
rpm	ft-lb	g/s	ppm	slps
800	100	0.64	25,000	21
800	175	1.13	25,000	36
800	250	1.47	25,000	47
800	325	1.8	25,000	57
800	400	1.95	25,000	63

In the second round of tests for the Cummins L10G, varying concentrations of NO were injected at an engine speed of 800 rpm and load of 400 ft-lb (Table 5) in order to assess the NO concentration effect on NO_x decomposition.

Table 5. Varying injection quantities of NO at constant engine speed and load

Speed	Load	NO Injected	NO in Intake	Engine Intake Flow
rpm	ft-lb	g/s	ppm	slps
800	400	0.39	5,000	64
800	400	0.78	10,000	64
800	400	1.17	15,000	64
800	400	1.5	19,000	64
800	400	1.82	23,000	64

Engine out emissions were taken for HC, NO_x, CO and CO₂. These were found to be sensitive to the relative air/fuel ratio (λ). Two more sets of engine runs were formed to observe the effects of λ on NO_x decomposition. In the first test, λ was held between the range 1.35 to 1.37, and 1.38 to 1.41 in the second test. Note that this is as lean as this engine can be operated reliably. Misfire could occur during leaner operation, possibly due to cylinder-to-cylinder variations.

Experimental Results

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 NO_{x,feed}. The amount of NO seen by the NO_x analyzer due to the injection after decomposition had occurred in the combustion was designated as

NO_{X_intake} . This was obtained by visually identifying and averaging the steady state portion of the peaks at each load. The average of the baseline NO_x emissions, $NO_{Xbaseline}$, at that load was subtracted from the peak values. The decomposition efficiency (η) was calculated as a percentage of NO decomposed at each load (Equation 1) [24].

$$\eta = 1 - \frac{(NO_{X_intake} - NO_{Xbaseline})}{NO_{Xfeed}} \quad \text{Equation (1)}$$

The baseline emissions are shown in table 6.

Table 6. L10-G baseline emissions at varying loads at 800 rpm

	250 ft-lb @ 800 rpm	325 ft-lb @ 800 rpm	400 ft-lb @ 800 rpm
CO ₂ (g/s)	4.34	5.91	7.32
HC (g/s)	0.022	0.033	0.051
CO (g/s)	0.017	0.023	0.029
NO _x (g/s)	0.012	0.055	0.122

Figures 4 show the results for the test conducted corresponding to table 4.

Figure 4. Varying load at constant NO concentration: Table 5

It can be seen that the NO_x peak while injecting into the intake manifold was less than the NO_x peak while injecting into the exhaust. The same test was conducted for the air/fuel ratio (λ) between the range 1.35 to 1.37. It can be seen that a slight change in air/fuel ratio had a significant effect on NO_x decomposition. The NO decomposition percentage is given in figure 5 along with the effects of load and λ on the NO decomposition at each mode.

Figure 5. Effects of load and λ on NOx decomposition

The results from the second set of test corresponding to table 5 are shown in Figure 6. NOx decomposition increased slightly with increasing NOx concentration in the engine. This phenomenon is summarized in Figure 7.

Figure 6. Varying NO quantities at constant engine speed and load: Table 5

Figure 7. Effects of λ and injected intake NOx percentages on NOx decomposition

In addition to NOx emissions data, emissions of CO, CO₂ and HC at the corresponding operating points were recorded as shown in Figure 8 and Figure 9. For each of the gases characterized, background corrections were made for accuracy. Background corrections take into account the concentration of species in the dilution air according to the methodology presented in the code of federal regulations (CFR), Title 40 [28].

Figure 8. Effects on CO and HC emissions due to intake NO injection

Figure 9. Effects on CO₂ emissions due to intake NO injection

There were no significant changes in CO and CO₂ emissions due to NO injections. It can be seen that HC level dropped by 0.01 grams during NO injections made into the intake. Even though it is still an insignificant amount the fluctuation can be due to the fact that NO increases the O₂ content in the combustion aiding more fuel to be burned.

Experimental Testing Discussion

NOx decomposition percentages vs. amount of NO injected into the intake is shown in Figure 7. The lack of data points at higher intake NO concentrations were due to the limitations of the NOx injection system. On the Cummins engine, it was observed that the air/fuel ratio had a modest effect on CO, CO₂ and HC baseline emissions, but it had a substantial effect on NOx. NOx decomposition was also affected by altering the air/fuel ratio. In other words, NOx decomposition was higher when engine was run in a leaner fashion. It is conceded that wall quench effects and volume specific heat transfer rates are higher for this engine used in this study than for a large bore engine.

Exploratory Work

Some exploratory work on stoichiometric burn NOx decomposition was performed using a gasoline engine that was available. The intent was to evaluate the NO decomposition at higher in cylinder temperatures and lower available oxygen concentrations before proceeding with similar research on a natural gas engine. A brief overview of the engine specifications and

NO_x decomposition results are given below. A Honda GX390 13 hp gasoline engine (Table 7) was also used to obtain NO_x decomposition rates at various steady state engine operating points. This engine was part of a Hercules brushless 6.5 KW generator and load was added through a panel of electrical loads.

Table 7. Gasoline engine specifications

Manufacturer/Model	Honda GX390
Displacement	0.389 liters (389 cc)
Number of cylinders	1
Bore	88 mm (3.5 in)
Stroke	64 mm (2.5 in)
Horsepower	13 hp

The gasoline engine had a much lower intake air flow rate of 6.5 slps than the natural gas engine. The NO injection system was used to inject similar concentration of NO as in the natural gas engine, as well as inject up to 70% of NO into the intake. The first run kept the intake NO concentration constant at varying engine loads (Table 8). The second run was conducted at 75% engine load while varying the intake NO concentration from 1 to 5% (Table 9). Figure 8 and Figure 9 show NO injections into the exhaust and intake corresponding to Table 8, and Table 9.

Table 8. Varying engine load at constant NO concentration

Speed	Load	NO Injected	NO in Intake	Intake Flow Rate
rpm	ft-lb	g/s	ppm	slps
3600	1.0	0.27	50,000	4.4
3600	3.9	0.30	50,000	4.8
3600	7.8	0.36	50,000	5.8
3600	9.8	0.40	50,000	6.4

Table 9. Varying injection quantities of NO at constant electrical load

Speed	Load	NO Injected	NO in Intake	Intake Flow Rate
rpm	ft-lb	g/s	ppm	slps
3600	9.8	0.12	10,000	4.8
3600	9.8	0.21	20,000	4.8
3600	9.8	0.30	30,000	4.8
3600	9.8	0.41	40,000	4.8
3600	9.8	0.50	50,000	4.8

Figure 10. Varying load at constant NO concentration: Table 6

Figure 11. Varying injection quantities at constant engine speed and load: Table 7

Further results were obtained for higher intake NO concentrations that ranged from 1 to 70% of the intake air at constant speed and load (Figure 10). It was noted that the effect of intake NO concentration on decomposition efficiency had no significant effect on the gasoline fueled engine when compared with the natural gas engine. This result was further confirmed when intake NO concentration was increased from 5 to 70% of the intake air.

Figure 12. NO decomposition percentage vs. the amount of NO injected

Figure 13. Exhaust gas temperature during intake NO injections

It is noted that NO_x decomposition in a gasoline engine cannot be extended directly to NO_x decomposition in a natural gas engine because natural gas is usually acknowledged to be less reactive than gasoline. However, results obtained from these tests are encouraging for lower air/fuel ratio research. Exhaust gas temperature on the gasoline engine showed a significant temperature rise during the NO injection time period. As seen in Figure 13 the temperature raised 75 – 100 °F during NO injections. It is known that a typical gasoline spark ignited engine lies close to stoichiometric operation or on the slightly rich side [29]. The success of these runs would indicate further research on stoichiometric natural gas operation need to be investigated.

Chemical Kinetic Modeling

Feedback provided by reviewers at the ARES university program presentation in May 2004, included the suggestion that the researches employ reaction modeling as an additional tool to understand and optimize the NO_x decomposition behavior. Chemical kinetic behavior was modeled using the CHEMKIN software package from Reaction Design. This software has been used to model natural gas engine spark ignition combustion characteristics, and HCCI combustion and emissions ([30] – [32]). The CHEMKIN version 4.0 software package makes use of the well tested GRI_{mech} version 3.0 reaction mechanism developed by the Gas Research Institute [32]. The GRI_{mech} reaction mechanism includes gas phase chemistry, transport, and thermodynamic data, which are used as input files for the CHEMKIN software. These files include five elements C, H, O, N, Ar and 53 chemical species, and 325 reactions ([33] – [35]). The GRI_{mech} reaction mechanism was suitable for this simulation because it captures the essential details of methane combustion and NO_x formation.

In-cylinder temperature and composition are not homogeneous throughout the volume, nor are they even homogeneous in the ‘burned’ and ‘unburned’ gas zones in the cylinder. On a microscopic scale, one may consider the reduction of NO in a “packet” of gas as the flame front approaches, consumes, and leaves behind the reactants. The authors considered such a packet that was initially at the temperature and pressure due to compression; clearly little reaction occurs at this temperature. The temperature is modeled to rise rapidly with the flame temperature, and the pressure is modeled to rise in sympathy, by holding the specific volume of the gases constant. The reactions that occur during this time must consider both the flame chemistry (changing composition) and the elevated temperature. In the post-flame period, the gas composition will change less, but the temperature will remain elevated, which can be mimicked well by maintaining a constant specific volume. What is not modeled is the change in pressure (and hence temperature) due to the combustion of other packets of gas before and after the combustion of the packet in question. It is understood that this view is qualitative, but it can provide a basis for examining parameter effects on the decomposition.

CHEMKIN was used to model these packets of gas in a closed homogenous batch reactor held at constant volume. A range of temperatures was used with the assumption that the highest temperature of any packet would not exceed the adiabatic flame temperature of 1900 K as calculated below. In 1998 Dodge et al. [33] found that a similar zero-dimensional model well predicted the NO_x emission from lean burn natural gas engines.

Flame Temperature Calculation

To estimate the temperature and pressure at which these reactions occur, an adiabatic flame temperature calculation was performed. The compression stroke was modeled as an isentropic compression. The gases at an initial temperature and pressure of 298 K and 1 atm were compressed to a temperature of 679 K and pressure of 23.9 atm. To take care of valve timing, a 90% volumetric efficiency was assumed, which yielded a pressure of 21.5 atm, before reactions have occurred.

The flame temperature was calculated using actual emissions data from the Cummins natural gas engine to define the flame products of the combustion. Emissions data at 800 rpm and 400 ft-lb load were used, as seen in Table 4. This revealed the highest flame temperature for the engine test points used. NO injections only further decreased the flame temperature, by an amount considered negligible by the authors. An energy balance was performed assuming an adiabatic flame. Enthalpy values were taken from the JANAF tables [34] and Tables 10 and 11 show the enthalpies and temperatures used in calculating the adiabatic flame temperature of 1910 K.

Table 10. Reactant enthalpies

	g/s	h (kcal/mol) @ 679 K	h (kcal/s)
CH ₄	3.01	-10.8	-2.03
O ₂	17.2	3.03	1.63
N ₂	53.3	3.17	6.04
		Sum	5.63

Table 11. Product enthalpies

	g/s	h (kcal/mol) @ 1910 K	h (kcal/s)
CO	0.027	-12.2	-0.012
CO ₂	7.04	-70.3	-11.3
H ₂ O (g)	6.78	-36.2	-13.7
NO _x	0.212	30.0	0.138
CH ₄	0.039	22.2	0.055
N ₂	53.2	14.5	27.7
O ₂	5.87	14.7	2.70
		Sum	5.63

It should be noted that the enthalpy of NO₂ was used when calculating the enthalpy of NO_x, which gives a slightly higher flame temperature.

CHEMKIN Modeling

The closed homogeneous batch reactor within CHEMKIN was used to model chemical reactions occurring at a constant specific volume. The CHEMKIN computations were performed in two sets, both at a relative air/fuel ratio of 1.4. Firstly, the concentration of NO in the initial mixture of gases was varied while holding the temperature at 1700 K and constant volume. It should be noted that each packet of gas will react at a different temperature, but an initial choice for the temperature of an individual packet was needed. The initial pressure was chosen to be representative of the pressure which would occur from the isentropic compression of the gases in the engine cylinder, followed by an iso-volumetric process which brings the packet of gas up to the flame temperature, assumed here to be 1700 K, with no chemical reactions occurring. After assuming a 90% volumetric efficiency this yielded a pressure of 53.9 atm at 1700 K. The pressure was left to vary slightly as the molar quantity changed in the cylinder as a result of reaction. The initial mole fractions of each mixture of CH₄, O₂, N₂, and NO are shown in Table 12.

Secondly, the initial mole fractions of CH₄, O₂, N₂, and NO in the mixture were held constant throughout each computation. Reactions were constrained by maintaining a constant specific volume. An array of initial temperatures ranging from 1300 K to 1900 K was used as an input to model the NO versus time while the temperature during each computation was kept constant. Here the simulation pressure for each temperature was calculated in the same manner as mentioned previously.

Table 12. Mole fractions of initial mixtures used in modeling the constant volume process

NO injection amount (ppm)	Mole fractions of initial mixtures			
	NO	CH ₄	O ₂	N ₂
0	0	0.0697	0.2047	0.7256
625	0.0006	0.0697	0.2045	0.7252
1,250	0.0012	0.0697	0.2044	0.7248
1,720	0.0016	0.0696	0.2043	0.7244
2,500	0.0023	0.0696	0.2042	0.7239
5,000	0.0047	0.0694	0.2037	0.7222
10,000	0.0093	0.0691	0.2028	0.7188
20,000	0.0186	0.0684	0.2008	0.7121

Chemical Kinetic Modeling Results

NO mole fraction versus time shown in Figure 12 for a time scale much longer than the time reactions would occur in an engine cylinder. The curve shows varying amounts of initial NO concentration, which are held at 1700 K and 53.9 atm for 50 seconds, which was three orders of magnitude longer than the time it takes to complete a stroke of the piston. The solver time step used was 0.01 seconds.

Figure 14. Mole fraction of NO for varying initial gas mixtures on a large time scale

The highest line represents an initial concentration of NO in a mixture of CH_4 , O_2 , N_2 , and NO, with NO making up 20,000 ppm of this mixture. This concentration corresponds to a 0.0186 mole fraction of NO if the relative air fuel ratio λ is 1.4 and the concentrations of N_2 and O_2 in air are taken as 0.78 and 0.22, respectively. The lowest curve represents the normal initial conditions for a natural gas engine (excluding residual gases) with only CH_4 air and no initial NO concentration.

In each of the curves shown in Figure 12, excluding the zero NO concentration level, the mole fraction of NO drops significantly, within the first second of reaction time. The actual time in which these conversions occur, due to the computational error for the large time step used, is on the order of milliseconds as seen in Figure 13. After this initial drop, the rates of reaction

slow until equilibrium is reached. With this particular mixture the equilibrium level is approximately 0.0016 mole fraction.

Figure 15. Mole fraction of NO for constant temperature (K) processes

A more refined time step of 5×10^{-6} seconds and a shorter end time was tested for initial temperatures ranging from 1300 to 1900 K and initial NO concentration of 25,000 ppm or 0.0233 mole fraction for this particular initial mixture of CH_4 , O_2 , N_2 , and NO at a λ of 1.4. As with all models, the solutions were checked for solver time step independence. The runs can be repeated for different time steps and arrived at the same conclusion. Figures 13, 14, 15, and 17 show NO, NO_2 , NOx, and CH_4 as a function of time for these small time scales. These figures indicate that NO_2 is being formed on the same time scale in which complete combustion of CH_4 occurs. NO_2 levels then decrease significantly. Conversely, NO levels drop rapidly then rise slightly as NO_2 is depleted. This behavior leads to a steady conversion of NOx as seen in Figure 15.

The dashed line in Figure 15 was put in place to clarify the area of interest in the combustion process. The results to the left of the dashed line represent high reaction rates which are occurring in a time frame on the order of magnitude of 10 degrees before and after top dead center (TDC). For an engine running at 800 rpm this corresponds to a time of 4 milliseconds. The results to the right of the dashed line represent reactions that would theoretically occur if the gases stayed at high temperatures. Although on this time scale it may seem that reactions have stopped occurring and NOx levels have reached some equilibrium level, this is

not the case. The reactions rates have just slowed to a different rate which is not visible in Figure 15, but can easily be seen in Figure 16.

Figure 16. Mole fraction of NO_2 for constant temperature (K) processes

Figure 17. Mole fraction of NO_x for constant temperature (K) processes on a small time scale

Figure 18. Mole fraction of NO_x for constant temperature (K) processes on a large time scale

Figure 19. Mole fraction of CH₄ for constant temperature (K) processes

Figure 18 is a representation of NO conversion rates for varying combustion temperatures. These values represent the amount of NO_x converted after 4 milliseconds, as seen by the vertical dashed line in Figure 15.

Figure 20. Conversion percentage at various temperatures

Conclusion

The experimental research was conducted on the Cummins natural gas engine and the modeling was conducted to closely represent the reactions of a natural gas combustion chamber. The experimental and modeling of the relative air/fuel ratios were coincided during the tests. It was found that the NO conversion rates varied slightly as load was increased, as seen in Figure 5. This behavior may be linked to that of Figure 18, which indicates at temperatures of 1400 K and above, the conversion rates varied only by 7% as compared to a variation of only 5% in Figure 5. Although Figure 18 represents the conversion percentage in a packet of gases at particular temperatures, a matrix of packets with temperatures in the same range would also exhibit the same behavior, as in an engine cylinder. Conversion rates from 35% to 42% were estimated using the CHEMKIN software, and conversions of 18% to 27% were observed experimentally. The overestimate of NO conversion shown by CHEMKIN may be attributed to incomplete combustion, incomplete mixing of NO and intake air, humidity, which was not accounted for in the model, or inaccurate chemical kinetic modeling.

The data to the left of the dashed line in Figure 17 represents the time frame in which NO conversions would actually occur in an internal combustion engine. Since the mixture has not yet reached equilibrium, the NOx conversion phenomenon can be labeled as a rate limited process, rather than equilibrium limited. This means that the NO conversion rate is a function of the reaction rates for the various reactions leading to NOx production. This also gives

insight into why the data from the natural gas engine in Figure 7 only showed modest increases in the NO conversion rate as the initial concentration of NO was increased.

List of Publications

1. Chamila A. Tissera, Matt M. Swartz, Emre Tatli, Ramprabhu Vellaisamy, Nigel N. Clark, Gregory J. Thompson, Ralph D. Nine, Richard J. Atkinson, "Selective NO_x 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

Pending Publications

1. Chamila A. Tissera, Matt M. Swartz, Emre Tatli, Ramprabhu Vellaisamy, Nigel N. Clark, Gregory J. Thompson, Ralph D. Nine, Richard J. Atkinson, "NO_x Decomposition in Natural Gas, Diesel and Gasoline Engines for Selective NO_x Recirculation," SAE 2005 Fuels and Lubricants meeting and exhibition, Rio de Janeiro, Brazil

Presentations

1. Distributed Energy Resources (DER) peer review, Washington D.C., December 02, 2003
2. DOE/ARES University Program peer review, Argonne National Laboratory, Argonne IL, May 11, 2004
3. ASME/ICED 2004 Fall Technical Conference, Long Beach CA, October 24, 2004

Future Work

In the future the authors plan to use real time in-cylinder pressure measurements as a constraint for reaction modeling in CHEMKIN, with aspirations that this will lead to a better correlation between experiment and theory. Pressure sensors will be installed on to the new Cummins L10G electronic control engine. This will also help determine the actual time frame in which reactions are occurring in the new natural gas engine. CHEMKIN will also be used to

model the effects of varying air/fuel ratios on CO, CO₂, HC, and NO_x emissions. It was observed that the air/fuel ratio had a modest effect on CO, CO₂ and HC baseline emissions during actual engine testing, but it had a substantial effect on NO_x. Further tests will be conducted to operate the normally lean burn engine closer to stoichiometric, with high exhaust gas recirculation (EGR) for a brief period of time during the NO_x decomposition phase.

A Combustion Fast NO_x analyzer equipped with a special spark plug adaptor will be used to measure in-cylinder NO formation. The NO_x adsorber and heat exchanger acquired from Sorbent Technologies will be installed in series with the natural gas engine. A test matrix of all the experiments is currently been designed. It was decided that the natural gas engine will be used for NO_x decomposition during the desorption period of the NO_x adsorber.

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