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Nitric Oxide Conversion in a Spark Ignited Natural Gas Engine

Matthew M. Swartz

Thesis submitted to the
College of Engineering and Mineral Resources
at West Virginia University
in partial fulfillment of the requirements
for the degree of

Master of Science
in
Mechanical Engineering

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ABSTRACT

Nitric Oxide Conversion in a Spark Ignited Natural Gas Engine

Matthew M. Swartz

Reducing NO_x emissions from natural gas engines has become increasingly important from an environmental standpoint. A large percentage of stationary engine applications are natural gas fueled. The cleanest of these large bore engines currently produce on the order of one gram of NO_x per brake-horsepower hour (g/bhp-hr) of work done. The goal of this work is to reduce these emissions to 0.1 g/bhp-hr levels. Selective NO_x Recirculation (SNR), a technology which will help achieve these 0.1 g/bhp-hr levels, is currently being studied at West Virginia University. SNR has been proven in gasoline and diesel engines, with up to 90% NO_x conversion rates being achieved, but not much is known about its overall efficiencies when used with natural gas engines. This technique involves adsorbing NO_x from an exhaust stream, then selectively desorbing the NO_x into a concentrated NO_x stream, which is fed back into the engine's intake, thereby converting a percentage of the concentrated NO_x stream into harmless gases. Understanding the NO (a component of NO_x) conversion process plays a major role in optimizing the SNR technology.

The emphasis of this thesis is on the unique chemical kinetic modeling problem that occurs with high concentrations of NO_x in the intake air of a spark ignited natural gas engine with SNR. NO conversion experiments were performed on a Cummins natural gas engine, and CHEMKIN, a chemical kinetic solver software package was used to simulate

this process. A closed homogeneous batch reactor model was used to model the concentration of NO_x versus time for an initial mixture of NO , O_2 , N_2 , and CH_4 . A zero-dimensional model was used to model the NO_x conversion properties of a natural gas engine. The molar fraction of NO_x was monitored on small time scales, on the order of the time for complete combustion, and on large time scales, on the order of minutes. Predicting the mole fraction of NO_x as a function of time using a closed homogenous batch reactor model on small time scales allowed estimates of the percentage of NO converted locally during the combustion process. These percentages were then compared with experimental values, which were acquired from a Cummins 10 liter spark ignited natural gas engine. The model predicted conversion rates, based on percentage mass conversion, varying between 20% and 26%, and experiments showed conversion rates between 18% and 23% for a constant intake NO concentration of 25,000 ppm. Predicting NO_x concentration on large time scales, steady state, confirmed that the NO_x conversion phenomenon, over the in-cylinder time period in which combustion temperatures are maintained, is rate limited rather than equilibrium limited. This gives insight into how to maximize these conversion efficiencies for the SNR process. If the process is rate limited rather than equilibrium limited combustion temperature will play a larger role in NO conversion.

Once the experimental setup was modeled, CHEMKIN was then used to predict the effects of EGR and varying air-to-fuel (A/F) ratios on SNR efficiencies. CHEMKIN demonstrated that under ideal conditions, increasing the air to fuel ratio and adding EGR will increase NO conversion efficiency by up to 90%.

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NOMENCLATURE

A/F	Air-Fuel Ratio
Ar	Elemental Argon
ARES	Advanced Reciprocating Engine Systems
Ba(NO ₃) ₂	Barium Nitrate
BaO	Barium Oxide
C	Elemental Carbon
CH ₄	Methane
CO	Carbon Monoxide
CO ₂	Carbon Dioxide
D.O.E.	Department of Energy
EGR	Exhaust Gas Recirculation
g/bhp-hr	Grams per Brake Horsepower Hour
H	Elemental Hydrogen
H ₂ O	Water
HC	Hydrocarbon
HCCI	Homogenous Charge Compression Ignition
λ	Relative Air-Fuel Ratio
LNC	Lean NO _x Catalyst
LNT	Lean NO _x Trap
min	Minutes
N	Elemental Nitrogen
N ₂	Nitrogen
NGE	Natural Gas Engine
NO	Nitric Oxide
NO ₂	Nitrogen Dioxide
NO _x	Oxides of Nitrogen
NSRC	NO _x Storage Reduction Catalyst
O	Elemental Oxygen
O ₂	Oxygen
PFR	Plug Flow Reactor
PM	Particulate Matter
Pt	Platinum
ppm	Parts per Million
rpm	Revolutions per Minute
RSS	Root Sum of Squares
s	Seconds
SCR	Selective Catalytic Reduction
SI	Spark Ignited
SNR	Selective NO _x Recirculation
slpm	Standard Liters per Minute
slps	Standard Liters per Second
TWC	Three Way Catalyst

1 OBJECTIVES

- Measure, experimentally, the NO conversion properties of a lean burn, spark ignited natural gas engine operated at low speed steady state conditions, which mimic large bore engine operation and reaction time scales
- Develop a chemical kinetic model that will predict these conversion properties.
- Predict, using the chemical kinetic model, the conversion properties of a natural gas engine for various air-fuel ratios and with exhaust gas recirculation.
- Find the highest theoretical in-cylinder NO_x conversion that can be achieved.
- Show that 90% overall NO_x reductions can be achieved in lean burn natural gas engines with an optimized NO_x adsorber system.

2 INTRODUCTION

In heavy-duty lean-burn natural gas engines, NO_x control may be achieved by using wide range oxygen sensor feedback to control the air fuel ratio [1]. Further reductions of NO_x call for exhaust gas aftertreatment. Large bore natural gas engines, even with careful control, emit an order of magnitude higher NO_x than the 0.1 g/bhp-hr NO_x target set by the Department of Energy funded project ARES (Advanced Reciprocating Engine Systems). Conventional NO_x reduction catalysts cannot be used effectively because the lean-burn exhaust contains excess oxygen, which leads to unfavorable reaction conditions.

SNR involves cooled exhaust gas NO_x removal by NO_x adsorption, periodic heating and desorption of NO_x from the adsorber, and subsequent selective external recirculation and conversion of NO_x in the cylinder. The exhaust gas must first be cooled to increase the adsorption efficiency of the NO_x adsorber, and the adsorber heating allows NO_x to be released from the adsorbent material. The advantages of SNR are that it has no by-products and does not require a catalyst to reduce NO_x . The NO_x adsorbers used in the SNR process are also not as susceptible to sulfur poisoning as other competing technologies, which will be discussed in detail in the literature review. A schematic of the SNR process is shown below in Figure 1. The solid black pathways represent the high concentration NO_x stream that feeds back into the engine, and the exhaust switch is used to divert exhaust flow during the desorption process. This is a basic schematic; other variations include use of a second adsorber, which adsorbs the exhaust diverted during

desorption of the first adsorber, and the addition of exhaust gas recirculation (EGR). An analysis of the overall efficiency will show that with a two adsorber system overall conversion efficiencies of up to 90% can be achieved.

Figure 1: Schematic of SNR process

The SNR technology is in support of the U.S. Department of Energy's goal of reducing NO_x production rates to 0.1 g/bhp-hr levels, enabling future use of environmentally acceptable large bore reciprocating natural gas engines. In 1998, Krutzsch et al. [2, 3], found trends similar to those presented in this paper for NO_x conversion in gasoline and naturally aspirated and turbocharged diesel engines. These researchers achieved NO_x conversion rates exceeding 50% in a turbocharged diesel engine operating with direct fuel injection, and conversion rates of up to 90% in a spark ignited gasoline engine. However, little is known of the potential to convert NO_x in lean burn natural gas engines.

Chemical kinetic modeling was executed using the CHEMKIN software package from Reaction Design [4]. This software has been used to model spark ignited natural gas engine combustion characteristics [5], and HCCI combustion and emissions [6, 7]. The CHEMKIN version 4.0 software package makes use of the well tested GRIMech version 3.0 reaction mechanism developed by the Gas Research Institute [8]. CHEMKIN uses fundamental heat transfer relationships, reaction rates in the form of a reaction mechanism input file, which includes rates dependent on species, partial pressures, and various coefficients, and temperature dependent thermodynamic transport properties. With this information CHEMKIN solves the equation of state and the energy equation for given initial and boundary conditions supplied by the user. The equations are then solved for time steps specified by the user. The GRIMech reaction mechanism and thermodynamic property CHEMKIN input files includes gas phase chemistry, transport, and thermodynamic data, which are used as input files for the CHEMKIN software. The GRIMech reaction mechanism files include five elements C, H, O, N, and Ar, 53 chemical species, and 325 reactions [4]. The GRIMech reaction mechanism was suitable for this simulation because it captures essential details of methane combustion and NO_x formation. A list of the species and reaction mechanism are shown in Appendix A.

3 LITERATURE REVIEW

The three-way-catalyst (TWC) has long been used for NO_x reduction in gasoline engines, which operate under stoichiometric or slightly rich conditions. But the TWC is not an effective tool for reducing NO_x emissions from lean burn engines, such as the spark ignited natural gas engine being discussed in this thesis. This is due to excess oxygen and lowered HC and CO emissions in the exhaust of lean burn engines [9]. Because of this problem, other means of reducing NO_x emissions need to be developed. An overview and comparison of the various lean burn spark ignition natural gas engine emission reduction technologies was performed by Manivannan et al. [10].

Exhaust gas recirculation, which is a widely used technology in spark ignited natural gas engines, can be used to reduce NO_x emissions by reducing the flame temperature, and oxygen partial pressure that encourages NO_x formation [11 - 14]. Some studies have also shown that natural gas engines operating under stoichiometric conditions with the use of a TWC, EGR, and turbo-charging exhibit lower NO_x emissions, and fuel economy that rivals state-of-the-art lean operating engines [15, 16]. Similar strategies involving short time period stoichiometric operation are being developed for lean NO_x trap (LNT) and NO_x adsorber technologies in diesel and natural gas engines [17, 18].

Aftertreatment technologies competing with SNR in an attempt to reach the 0.1 g/bhp-hr goal include Lean NO_x Catalysts (LNC), NO_x adsorbers, and Selective Catalytic Reduction (SCR). These technologies are currently being tested and used on lean burn

natural gas and diesel fueled engines. LNC's selectively promote the reduction of NO_x by use of hydrocarbons. In the selective catalytic reduction of NO_x, catalysts are used to promote HC reactions with NO_x rather than O₂, to form N₂, CO₂, and water [19].

In lean exhaust gas HC must be added either by injecting fuel directly into the exhaust gas stream, or by opening the intake valve late thereby letting some unburned fuel pass through the exhaust valve. Even with this HC enrichment the conversion efficiencies remain in the 30 – 50% range with realistic HC/NO_x ratios [19]. LNC's also only operate effectively in a small temperature range, which does not always correspond to exhaust temperature, and resistance to catalyst poisons needs to be improved.

NO_x adsorbers, sometimes referred to as LNT's, NO_x storage/reduction catalysts (NSRC), or NO_x adsorber catalysts (NAC), reduce NO_x by reacting NO and O₂ on a catalyst surface (e.g. platinum) to form NO₂ which may still be susceptible to catalyst poisoning. The NO₂ is then stored on a storage material, for example barium oxide, as an inorganic nitrate [20].

The NO_x adsorber technology is similar to LNC, because it stores NO_x on a catalyst surface. However, the LNC must continuously supply HC to convert NO_x . The NO_x adsorber adsorbs NO_x onto a storage material during lean operation, and then converts the NO_x by passing a rich exhaust stream or HC enriched exhaust through the adsorber for a short period of time. The conversion mechanisms also differ for these two technologies. The LNC attempts to selectively convert the NO_x with HC, whereas the NO_x adsorber uses other species as well as HC to react with the stored NO_x . Attempts have been made to model the different reaction paths to better understand the NO_x adsorber chemistry [21].

SCR is similar to LNC technology. However, SCR uses nitrogen compounds such as urea or ammonia as a reductant to convert NO_x being held on the catalyst surface. With SCR, precise control of reductant injection is required along with continuous feedback from a NO_x sensor, or a reasonable NO_x engine model. Using ammonia as a reductant can cause undesirable ammonia emissions, known as ammonia slip, if too much is injected [22]. Urea, normally injected into the exhaust stream in an aqueous solution, presents less of a toxicity issue, but ammonia can still be formed from the hydrolysis of urea. Urea or ammonia must also be continuously supplied, and there are cost issues as well as maintenance issues involved with this [23].

Using methane combustion as a NO_x reduction technique was initially suggested for regenerable flue gas clean up processes. In large coal fired power plants NO_x emissions can be reduced by injecting natural gas and O_2 into the hot flue gas that comes from coal

combustion. This process is very similar to the SNR process discussed in this thesis in that the main purpose of this gas reburning is to reduce NO_x emissions in the flue gas. In 1987 Yeh et al. [24] modeled the NO_x conversion process using an early version of CHEMKIN, which at the time was being developed by Sandia National Laboratories. The equilibrium-based CHEMKIN solver was used to calculate the thermodynamic feasibility of the gas reburning technology. Equilibrium calculations were performed for various flame temperatures, and varying NO injection quantities. The results showed that natural gas reburning in flue gas could be implemented to reduce over 90% of the NO_x emissions [24]. In 1998 the U.S. D.O.E. released a final report on retrofit gas reburning technology in coal fired boilers for flue gas NO_x reduction [25]. These researchers achieved a cost effective solution with over 60% NO_x reduction in various types of coal fired boilers. A chemical kinetic solver was also used in these simulations. The solver used 60 chemical species and 209 reaction mechanisms that define coal devolatilization and combustion. In this case a boiler heat transfer model was used for temperature profiles when modeling NO_x conversion and equilibrium values were not investigated. A Plug Flow Reactor (PFR) was used to model the flow of gases with varying temperature profiles.

The SNR process, developed in 1998 by Krutzsch et al. [2, 3] for diesel and gasoline engines, found similar trends for NO_x conversion. In 2005, Vellaisamy et al. [26, 27], confirmed these conversion properties in a 1992 DDC series 60 diesel engine, with detailed effects of the SNR process on PM and other regulated emissions. These researchers achieved NO_x conversion rates exceeding 50% in turbocharged diesel engines operated with direct fuel injection. They used similar techniques for finding the

NO_x conversion efficiencies, and also performed constant concentration NO_x conversion studies as will be described in detail in the following sections. A form of the following equation was also taken from [2], which describes the NO_x conversion efficiency as the flux of NO_x in the exhaust.

$$\eta_{NO_x} = 1 - \frac{(NO_{x1} - NO_{x2})}{NO_{xfeed}} \quad \text{Equation 4}$$

Here NO_{x1} and NO_{x2} represent the NO_x concentration with and without NO injection respectively, and NO_{xfeed} is the quantity of NO injected. Krutzsch et al. [2] found that increased engine load enhanced the conversion efficiency, and also found that the influence of engine speed was small.

Figure 2, taken from Krutzsch et al. [2], represents NO_x conversion for varying relative air-fuel ratio (λ) in a spark ignited (SI) gasoline engine. It was found that running the SI gasoline engine under lean conditions, with a relative air-fuel ratio of 1.45, the NO_x conversion efficiency dropped to 20%. This drop in conversion efficiency as the air fuel mixture became leaner in an SI gasoline engine was also predicted for the Cummins L10 natural gas engine used for this research using the CHEMKIN software package.

Figure 2: NO_x conversion percent for varying λ [2]

4 EXPERIMENTAL SETUP

The testing procedures and data reduction techniques presented in this thesis are similar to those used by Tissera et al. [28]. NO was injected in varying quantities to represent the concentrated NO_x stream that would come from the exhaust gas NO_x adsorber. CHEMKIN was then used to model the chemical kinetics of the NO_x conversion process. The goal of this modeling was to be able to match experiment and theory. If a correspondence between experiment and theory were found, then CHEMKIN could be used to model other variations of this process, including the addition of EGR and other engine operating conditions, without the expensive cost of experimentation, as with any computational model.

4.1 ENGINE AND INSTRUMENTATION

The specifications for the Cummins spark ignited natural gas engine used in this study are listed in Table 1.

Table 1: Test engine specifications

Engine serial #	34683888
Displacement	10 liters
Number of cylinders	6 (in-line)
Firing order	1-5-3-6-2-4
Bore	125 mm (4.921 in)
Stroke	136 mm (5.354 in)
Compression ratio	10.5 : 1
Rated power	240 hp
Rated speed	2100 rpm

A 300 hp Mustang eddy current dynamometer, controlled by a DYN-LOC IV Digital Dynamometer Controller, was used to absorb power output from the engine. The engine-out emissions were characterized by directing the exhaust gas to a full-scale dilution tunnel, and employing research grade analyzers to quantify concentrations of the species. All gas measurements taken during this testing followed the procedures outlined for a constant volume sampling system (CVS) in CFR Title 40 part 86 [30]. The dilution tunnel measured 18 inches in diameter, 20 feet in length and was constructed of stainless steel. The dilution tunnel mixing orifice diameter of 10 inches was located 3 feet from the entrance to the tunnel for a uniform mixing of gases. Sample probes for the gas analyzers were located 15 feet, or 10 diameters, from the entrance of the tunnel. The flow in the dilution tunnel was set to 3000 scfm.

The gas analyzer bench was capable of quantifying HC, CO, CO₂ and NO_x. The individual gas detection methods and manufacturers of each gas analyzer are shown in Table 2.

Table 2: Bench analyzers

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

The gas analyzers were calibrated with $\pm 1.0\%$ accuracy research grade calibration gases. The Rosemount Analytical Chemiluminescent Model 955 NO/NO_x analyzer used had an accuracy of $\pm 0.5\%$ of full scale. Since the NO_x injections were mostly over 50% of full scale measurement this yielded an overall NO_x measurement accuracy of $\pm 2.0\%$. The tunnel flow was calculated using the following relationship:

$$V_{mix} = \frac{K \cdot P}{\sqrt{T}} \quad \text{Equation 5}$$

where V_{mix} is the dilution tunnel flow, K is the venturi coefficient found during calibration, P is the pressure at the venturi throat, and T is the absolute venturi throat temperature. Using the root sum of squares (RSS) method of calculating experimental error:

$$\Delta V_{mix} = \sqrt{\left(\frac{\partial V_{mix}}{\partial K} \Delta K\right)^2 + \left(\frac{\partial V_{mix}}{\partial P} \Delta P\right)^2 + \left(\frac{\partial V_{mix}}{\partial T} \Delta T\right)^2} \quad \text{Equation 6}$$

yielded an uncertainty of $\pm 0.5\%$ for the tunnel flow when accounting for pressure and temperature measurement device inaccuracies. Using the RSS method of final time yielded an inaccuracy of $\pm 2.5\%$ for the NO_x measurements. Due to the nature of this study, steady state comparative study between NO_x readings operated under the same conditions for each data set, dynamometer and engine setting inaccuracies were not included in this analysis, and since NO_x is the major relevant species involved in this work, only the uncertainty analysis for NO_x is shown here. For a detailed uncertainty analysis of the WVU emissions testing laboratory's measurement systems refer to [29].

4.2 TEST DESCRIPTION

Baseline emissions were taken for HC, NO_x, CO and CO₂, at operating conditions shown in Table 3. These emissions data were taken one day prior to the NO injection tests that were performed. These operating conditions were chosen to mimic reaction time scales associated with low speed large stationary engine operation. The sampling rate for the gas analyzers was set to 1 Hz, and the engine operating conditions were set and then allowed to stabilize for 60 s periods. The emissions were then averaged over 50 s modes for each operating condition. The NO_{x1} and NO_{x2} data were taken from two separate NO_x analyzers at the same time to verify the accuracy of the NO_x readings. Standard deviation of λ was less than 0.015 for each engine operating condition. Having small variations in the relative air-fuel ratio (λ) were considered important, because λ plays a major role in NO_x production and conversion.

Table 3: Baseline emissions for HC, CO, CO₂, and NO_x for varying loads

	100 ft-lbs @ 800 rpm	175 ft-lbs @ 800 rpm	250 ft-lbs @ 800 rpm	325 ft-lbs @ 800 rpm	400 ft-lbs @ 800 rpm
HC (g/bhp-hr)	3.60	3.43	2.92	2.83	3.17
CO (g/bhp-hr)	2.59	1.79	1.52	1.43	1.38
CO ₂ (g/bhp-hr)	670	573	498	440	413
NO _x (g/bhp-hr)	1.82	0.68	0.61	0.84	1.09
NO _{x2} (g/bhp-hr)	1.75	0.64	0.59	0.80	1.07
HC (g/s)	0.0158	0.0250	0.0317	0.0388	0.0519
CO (g/s)	0.0114	0.0130	0.0165	0.0196	0.0227
CO ₂ (g/s)	2.93	4.17	5.41	6.04	6.76
NO _x (g/s)	0.0080	0.0049	0.0066	0.0115	0.0178
NO _{x2} (g/s)	0.0076	0.0047	0.0064	0.0110	0.0175
Lambda (λ)	1.26	1.36	1.40	1.41	1.40

Figure 3 shows the NO_{x1} and NO_{x2} analyzer readings for each of the 50 s modes, and Figure 4 shows the set and measured load. The sharp variations in the NO_x readings were

due to the data acquisition procedures used in this testing. The NO_x analyzers were zeroed and spanned based on the peak NO_x values reached during NO injections. This gave a low resolution measurement for the baseline NO_x values shown in Figure 3. The accuracy of this measurement does not significantly effect the overall NO_x conversion calculation, since the baseline engine emissions are all at least one order of magnitude smaller than the NO injection quantities. NO_x readings for the 800 rpm, 400 ft-lb set point appear to rise slightly over time relative to the initial NO_x reading at this engine set point, with a standard deviation about the mean for this set point still less than 9%. This may be due to an increase in the combustion temperature throughout the test, which can also be seen in the load plot in Figure 4. Continuous exhaust gas temperature was not monitored during this test but later measurements showed temperature rises on the order of 20 °F when changing from 325 to 400 ft-lb load. During initial testing the set point of 400 ft-lb and 800 rpm was attained, but when λ was increased to 1.4, the engine only attained an average of 384 ft-lb. Figures 5, 6, and 7 show the baseline HC, CO, and CO_2 emissions, respectively.

Figure 3: Baseline NO_x emissions for the Cummins L10 G test engine, reported as g/s of NO₂, for varying loads at 800 rpm

Figure 4: Set and measured load for the 800 rpm set point

Figure 5: Baseline HC emissions for the Cummins L10 G test engine for varying loads at 800 rpm

Figure 6: Baseline CO emissions for the natural gas engine for varying loads at 800 rpm

Figure 7: Baseline CO₂ emissions for the natural gas engine for varying loads at 800 rpm

To simulate the SNR process, commercially available nitric oxide (NO, 98.8% purity) injected into the engine air intake was used to mimic the NO_x recirculation process. To inject a precise quantity of NO into the engine's intake air, a mass flow controller capable of injecting up to 100 slpm, or approximately 2 g/s, of NO was used. The NO_x analyzers mentioned in Table 2 were employed to quantify the amount of NO_x produced by the engine, with varying quantities of NO being injected, and also to validate the injection quantities and determine if noticeable percentages of NO are being converted after combustion has occurred. It should be noted that the NO_x analyzers reported all values of NO_x in terms of mass NO₂ as per CFR regulations [30]. All values of NO_x throughout this paper, other than those listed in Table 3 and Figure 3, which are reported as mass of NO₂, are reported in terms of mass of NO, which is a deviation from the CFR due to the makeup of the injection gas.

During the first test, varying concentrations of NO were injected at an engine speed of 800 rpm and load of 400 ft-lb, Table 4. The engine was allowed to stabilize at 400 ft-lb and then NO was injected at rates varying from 0.39 g/s to 1.82 g/s for 20 second periods into the engine's air intake upstream of the fuel mixer (gas carburetor). Injecting for 20 second periods allowed the flow and the analyzer output to stabilize, while still minimizing the NO usage for each test. NO injection quantities in Table 4 represent the quantities as calculated by the mass flow controller.

Table 4: 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	5,100	62
800	400	0.78	10,000	62
800	400	1.17	15,000	62
800	400	1.56	20,000	62
800	400	1.96	25,000	62

On the second set of tests, engine speed and intake NO concentrations were kept constant, while varying the engine load, as seen in Table 5. At constant engine speed and varying loads, it is clear that the intake air flow rate fluctuates. To keep the percentage of NO in the intake air constant, the injected NO mass flow was altered accordingly. In doing this, it was predicted that better correlation between intake injection concentrations could be seen than by only holding the injection quantity constant. This held the molar fraction of NO in the intake constant for varying loads, which gave insight as to how conversion rates vary with temperature, knowing that higher loads lead to higher temperatures.

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

Speed	Load	NO injected	NO in intake	Engine intake flow
Rpm	ft-lb	g/s	ppm	slps
800	100	0.64	25,000	21
800	175	1.13	25,000	36
800	250	1.44	25,000	47
800	325	1.8	25,000	57
800	400	1.94	25,000	62

5 EXPERIMENTAL RESULTS

5.1 VARIED CONCENTRATION AND CONSTANT CONCENTRATION RESULTS

Figure 8 and Figure 9 show the results for the two tests. From these data it was clear that NO was decomposed during the combustion process at varying loads and injection quantities (note that the exhaust data represents the amount of NO before conversion). NO was injected into the exhaust to validate the injection quantities. This means that the data labeled Exhaust in Figure 8 and Figure 9 represent the engines emissions plus the NO injection without any conversion of NO, whereas the Intake data represents the amount of NO after conversion.

Figure 8: NO_x, reported as NO, for lean combustion, at constant 800 rpm engine speed and 400 ft-lb load, with varying NO injection quantities into the intake and exhaust

Figure 9: NO_x, reported as NO lean combustion at constant 800 rpm engine speed and intake air NO injection concentrations of 25,000 ppm

The percentage of injected NO that was converted to oxidized products during the combustion process was calculated for each operating condition as follows. First, the average of the “flat” (steady state) portion of the two peaks, at each load, was calculated. The averages were taken over a ten second period, starting when the values came within 4% of the peak value. Then the average of the baseline (the NO_x produced by the engine during normal operation) NO_x emissions, NO_{xbaseline}, at that load were calculated. Subtracting the NO_{xbaseline} from the NO_{xpeak_exhaust} value represents the amount of NO injected by the NO mass flow controller. These value show good correlation with the values from the mass flow controller for both the varying and constant concentration

cases, as seen in Table 6 and Table 7. They also show that an insignificant percent of NO is being reduced in the exhaust line and dilution tunnel measurement system.

Table 6: Comparison of mass flow controller and gas analyzer NO values for the constant load and varied concentration experiment

Speed	Set load	NO _{Xpeak_exhaust} - NO _{Xbaseline} analyzer reading	Mass flow controller	Percent difference
rpm	ft-lb	g/s	g/s	%
800	400	0.42	0.39	6.0
800	400	0.79	0.78	1.2
800	400	1.16	1.17	0.9
800	400	1.55	1.56	1.1
800	400	1.85	1.96	5.6

Table 7: Comparison of mass flow controller and gas analyzer NO values for the constant concentration and varied load experiment

Speed	Set load	NO _{Xpeak_exhaust} - NO _{Xbaseline}	Mass flow controller	Percent difference
rpm	ft-lb	g/s	g/s	%
800	100	0.66	0.65	1.9
800	175	1.13	1.13	0.3
800	250	1.48	1.48	0.2
800	325	1.79	1.80	0.1
800	400	1.91	1.94	1.3

Next the NO_{Xbaseline} was subtracted from the NO_{Xpeak_exhaust} value. This value represents the amount of NO_X that was seen by the NO_X analyzer due to the injection with conversion during the combustion process. This value was then taken as a percentage of the original amount of NO that was injected, to find the percentage of NO converted (η_c)

at each load and injection quantity as seen below in Equation 7. This is a similar method to that used by Krutzsch et al. [2].

$$\eta_c = 1 - \frac{(NO_{X_{peak_intake}} - NO_{X_{baseline}})}{(NO_{X_{peak_exhaust}} - NO_{X_{baseline}})} \quad \text{Equation 7}$$

The NO decomposition percentages for the data given in Figure 8 and Figure 9 are shown in Figure 10 and Figure 11, respectively. Error bars represent $\pm 2.5\%$ inaccuracy in the NO measurement, which sums to $\pm 5.0\%$ overall inaccuracy when subtracting these values as shown in Equation 7. It was observed that the NO conversion rates varied between 14 to 20% as seen in Figure 10 for varying injection quantities, and between 18 to 23% for a constant 25,000 ppm NO concentration at 800 rpm and varying loads, as seen in Figure 11.

Figure 10: NO decomposition for varying NO quantities at constant engine speed and load

Figure 11: NO decomposition vs. engine load for constant concentration and engine speed

The results shown in Figure 11 suggest NO conversion is not a strong function of engine load. The inability to hold the air-fuel ratio at the 100 and 175 ft-lb load levels may have skewed these results. The richer air-fuel ratios may have given more NO conversion than would have been seen at leaner levels, due to the increased HC levels. NO injection effects on other emissions are represented in Figure 12 and Figure 13. These results show 20% reductions in HC emissions and a decrease in CO emissions during NO injections.

Figure 12: Result of varying concentration NO injections on other emissions for the constant 800 rpm and 400 ft-lb load experiment

Figure 13: Result of NO injections on other emissions for the 800 rpm constant concentration and varied engine load experiment

5.2 REPEATABILITY

Figure 14 shows the 800 rpm 400 ft-lb engine set point data for each of the NO injection experiments shown in Figure 8 and Figure 9. The Exhaust 1 and Intake 1 data represent the varied NO concentration test, and Exhaust 2 and Intake 2 represent the constant concentration test. This set point was chosen to show repeatability, because the same quantity of NO was injected in each separate test on different test days. The λ variation for the 5 experiments (baseline and exhaust and intake injections for each NO injection experiment) was 1.38 to 1.42 and the day-to-day average engine torque variation was 385 to 402 ft-lb. These variations also represent the maximum variation of λ and torque

throughout all of the testing. Therefore, the percentage variation in the NO conversion efficiency due to day-to-day testing variations should not exceed what is shown here for any other test points. The reason for the large torque variation at this set point, as shown in Figure 4, was discussed previously. λ and torque were measured over the entire mode for each engine set point. NO injections did slightly affect λ , but λ remained within this range. Engine speed variation from day-to-day was negligible. The NO conversion for the varied concentration experiment and constant concentration experiment were 17% and 21% respectively.

Figure 14: Two sets of NO injections at 800 rpm and 400 ft-lb load on different test days

6 CHEMICAL KINETIC MODELING

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. In this work, it was assumed that a packet was initially at the temperature and pressure due to compression; clearly little reaction occurs at this temperature. The temperature was modeled to rise rapidly with the flame temperature, and the pressure 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 was 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 acknowledged, therefore, that this modeling represents a simplification, but it can provide trends.

CHEMKIN was used to model these packets of gas in a simulation of a closed homogenous batch reactor held at constant volume. A range of temperatures were used with the assumption that the highest temperature of any packet would not exceed the adiabatic flame temperature of 1900 K as calculated below. This type of model is zero-dimensional because it models a single packet of gases, and does not account for flame front motion or volume change due to piston motion. One-dimensional models use measured in-cylinder pressure as a function of time or crank angle to find an average

temperature trace. The unburned gas temperature history is calculated assuming the unburned fuel-air mixture is adiabatically compressed and expanded. These temperatures and pressures are then used to model the chemical reaction kinetics [31]. Two-zone models involve a burned and unburned gas region. One-dimensional two-zone models use the average pressure and calculated average temperature as a function of time to find heat transfer correlations for the two-zones [32]. A zero-dimensional model was preferred over the two-zone because the assumption of average temperature and pressure necessary for this type of model would not increase the overall accuracy of the model over a zero-dimensional one as described here. If detailed spatial relationships for temperature and pressure were known then a symmetric two-dimensional model may be of use. The fact that this packet is modeled over a range of actual combustion temperatures allows the model to be valid over the entire cylinder volume when a range of values is being considered. 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.

6.1 FLAME TEMPERATURE CALCULATION

To estimate the temperature and pressure at which these reactions occur, an adiabatic flame temperature calculation was performed for each of the varying A/F ratios and EGR cases. 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. The initial pressure of 1 atm was chosen to be representative of an engine operating without turbo boost pressure. This is the case for the Cummins L10 when operating under low speed, 800 rpm conditions. To account for

valve timing, a 90% volumetric efficiency was assumed, which yielded a pressure of 21.5 atm, before reactions have occurred.

6.1.1 LEAN BURN CASE

Emissions data at 800 rpm and 400 ft-lb load were used as shown in Table 3, to calculate the adiabatic flame temperature for the engine test point used for simulation. NO injections only further decreased the calculated flame temperature, but by an amount less than 2%, which was considered negligible by the author. An energy balance was performed assuming an adiabatic flame. Enthalpy values for reactants and products were taken from the JANAF tables [34], and Table 8 and Table 9 show the enthalpies and temperatures used in calculating the adiabatic flame temperature of 1910 K. This temperature was rounded down to 1900 K during modeling, to evenly distribute the data. 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.

Table 8: Reactant enthalpies (intake composition)

	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 9: Product enthalpies (exhaust composition)

	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 (gas)	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

6.1.2 STOICHIOMETRIC CASE

To find an estimate of the maximum flame temperature reached during the stoichiometric combustion of methane (CH₄), an adiabatic flame temperature calculation was performed assuming no dissociation of molecules. Again, the contribution of NO in the initial mixture was assumed negligible in the calculation of stoichiometric flame temperature.

Table 10: Reactant enthalpies for stoichiometric combustion of CH₄

	mole fraction	h (kcal/mol) @ 679 K	h (kcal)
CH ₄	0.09	-10.8	-1.03
O ₂	0.20	3.03	0.60
N ₂	0.71	3.17	2.24
		sum	1.82

Table 11: Reactant enthalpies for stoichiometric combustion of CH₄

	mole fraction	h (kcal/mol) @ 2342 K	h (kcal)
CO ₂	0.10	-60.1	-5.8
H ₂ O (gas)	0.19	-29.4	-5.6
N ₂	0.71	18.6	13.2
		sum	1.83

6.1.3 EGR AND RICH CASES

For the rich case the maximum flame temperature was calculated to be 2374 K based on no dissociation of products. For the lean burn with 20% EGR case, the flame temperature was calculated assuming no dissociation and only CO_2 and H_2O as the EGR constituents. The values used for CO_2 and H_2O for this case will be discussed in subsequent sections. For 20% EGR the flame temperature calculated was 1990 K. It should be noted that EGR should lower the flame temperature, but the flame temperature appears to have increased from the lean burn case to the lean burn with EGR case. This is because of the assumptions that were made, and the use of actual data for the lean with no EGR case. The value of 1900 K was taken when modeling both lean burn and lean burn with EGR, to simplify the test matrices.

6.2 CHEMKIN MODELING

6.2.1 LEAN BURN CASE

The closed homogeneous batch reactor within CHEMKIN was used to model chemical reactions occurring at a constant specific volume. CHEMKIN computations were performed in two sets, both at a relative air-fuel ratio of 1.4, corresponding to an air-fuel ratio of 24. First the concentration of NO in the initial mixture of gases was varied while holding the temperature at 1700 K and constant volume. To model this process completely a temperature range varying from 1300 K to the adiabatic flame temperature of 1900 K should be modeled, but in this case since only the general trend of NO_x conversion with varying concentration is being examined, only one mid-range

temperature was modeled. 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 a constant volume 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, note the injection amount in ppm is before fuel is added.

Table 12: Mole fractions of 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

Second, 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, and is shown in Table 13 for

each temperature. For this large range of temperatures, and therefore reaction rates, the time step for the CHEMKIN solver was varied for each temperature, along with the end time of each solution. To find a representative time in which complete combustion could be defined for each temperature, plots of CH_4 versus time were examined in the chemical kinetic modeling results section of this thesis. After the CH_4 levels dropped to near zero values at each temperature, the time for this reaction to occur was then at least doubled when finding an appropriate end time for the solution. The end times, the time at which at least 98% of the CH_4 has been depleted, and solver time step, the time step used in the CHEMKIN code finite difference approximations, used for lean combustion modeling are shown in Table 13. Note, that at 1300 K and 1450 K, the end time and time step were increased by one order of magnitude when NO was modeled as part of the initial mixture of gases for the stoichiometric and EGR cases. This is because of the reduced reaction rates of CH_4 and NO_x that modeling exhibits.

Table 13: Temperature and initial pressure with CHEMKIN solver time step and end times for lean combustion

Temperature (K)	Initial Pressure (atm)	End time (s)	Solver time Δt (s)
1300	41.2	1.00E-02	1.00E-07
1450	46.0	1.00E-03	1.00E-08
1600	50.7	1.00E-03	1.00E-08
1750	55.5	1.00E-04	1.00E-09
1900	60.3	1.00E-04	1.00E-09

Figure 15: Check for solution independence of time step

Figure 15 shows CH_4 as a function of time for a lean ($\lambda = 1.4$) mixture without NO. The solver time step was decreased until the solution showed solver time step independence.

6.2.2 STOICHIOMETRIC CASE

When modeling stoichiometric combustion with NO in the intake air stream, the NO concentration was held constant at 25,000 ppm (before fuel was added), while varying the temperature of reaction from 1300 K to the adiabatic flame temperature for stoichiometric combustion of 2350 K. Stoichiometric combustion has a relative air-fuel ratio of 1, which corresponds to an air-fuel ratio of 17.3 for methane combustion. These values were used when calculating the initial mole fractions of the initial mixture of gases for modeling purposes. For this large range of temperatures, and therefore reaction rates, the time step for the CHEMKIN solver was varied for each temperature, along with the

end time of each solution, as was described previously. The end times and solver time steps used for stoichiometric combustion modeling are shown in

Table 14: Temperature and initial pressure with CHEMKIN solver time step and end times for stoichiometric combustion

Temperature (s)	Initial Pressure (atm)	End time (s)	Solver time Δt (s)
1300	41.2	1.00E-02	1.00E-07
1450	46.0	1.00E-03	1.00E-08
1600	50.7	1.00E-03	1.00E-08
1750	55.5	1.00E-04	1.00E-09
1900	60.3	1.00E-04	1.00E-09
2050	65.0	1.00E-04	1.00E-09
2200	69.8	1.00E-05	1.00E-10
2350	74.5	1.00E-06	1.00E-11

6.2.3 EGR CASE

Before modeling it was not clear as to how EGR will affect the SNR process. Plans to run the natural gas engine with EGR and the SNR process have been put into place at the time of completion of this thesis. The purpose of this modeling is to predict if EGR will increase the NO_x conversion efficiency, and therefore increase the overall efficiency of the SNR process.

6.2.4 LEAN BURN WITH EGR CASE

To model the SNR process with EGR exhaust gas composition data was taken from the Cummins L10 natural gas engine, Table 3. It was assumed that SNR, or the simulated NO injections, will not play a major role in the exhaust gas composition from a steady state

standpoint, but it should be noted that this will affect exhaust gas composition. To simplify the computational matrices only the 20% EGR case was modeled. This is a general estimate of the amount of EGR that may be needed to maximize the conversion efficiencies, and values ranging from 0 to 40% have been shown to be acceptable levels in a spark ignited engine [14]. 20% of the intake air was assumed to be replaced with EGR at standard conditions. The air-fuel ratio was then based on assuming that the 20% EGR would not displace a significant amount of O₂ in an engine operating under lean conditions. Therefore a relative air-fuel of 1.4 would result in the same amount of fueling as the lean burn case without EGR. Tables 15, 16, and 17 show the resulting mixtures of EGR, intake air, NO, and CH₄. These tables together represent the method for calculating the initial mixture of gases that would be entering an engine cylinder with EGR and SNR. This method was defined in this manner to model the methods of injecting NO and mixing fuel that are already in place for experimentation on the Cummins L10 natural gas engine. Table 17 represents the mixture of gases that was modeled in CHEMKIN.

Table 15: EGR and intake air mixture for lean combustion with EGR

Species	Mole fraction
NO	4.44E-05
CH ₄	2.60E-04
O ₂	1.91E-01
N ₂	7.69E-01
CO	7.14E-05
CO ₂	1.18E-02
H ₂ O	2.86E-02
NO ₂	7.83E-06

Table 16: EGR, intake air, and NO mixture for lean combustion with EGR

Species	Mole fraction
NO	2.50E-02
CH ₄	2.53E-04
O ₂	1.86E-01
N ₂	7.49E-01
CO	6.96E-05
CO ₂	1.15E-02
H ₂ O	2.79E-02
NO ₂	7.63E-06

Table 17: EGR, intake air NO, and fuel mixture for lean combustion with EGR

Species	Mole fraction
NO	2.27E-02
CH ₄	9.31E-02
O ₂	1.69E-01
N ₂	6.80E-01
CO	6.32E-05
CO ₂	1.05E-02
H ₂ O	2.53E-02
NO ₂	6.92E-06

6.2.5 RICH BURN CASE

For rich burn a relative air-fuel ratio of 0.9 was used. This yielded the following initial mixture of gases, Table 18.

Table 18: Initial mixture of gases for the rich burn case

Species	Mole fraction
NO	0.022
CH ₄	0.102
O ₂	0.193
N ₂	0.683

7 CHEMICAL KINETIC MODELING RESULTS

7.1 LEAN BURN CASE

Using a complete engine stroke yields a time reference on the order of milliseconds. NO mole fraction versus time is shown in Figure 16 for a time scale much longer than this. The curve shows varying amounts of initial NO concentration, which are held at 1700 K and 53.9 atm for 50 s, 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 s.

Figure 16: Mole fraction of NO_x , reported as NO, for varying initial gas mixtures on a large time scale

The highest line represents and initial concentration of NO in a mixture of CH₄, O₂, N₂, 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 is 1.4 and the concentrations of N₂ and O₂ in air were 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 CH₄, air, and no initial NO concentration.

In each of the curves shown in Figure 16, excluding the zero and 625 ppm NO concentration levels, the mole fraction of NO drops, 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 17. 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. The objective of this varied NO concentration model was to compare the varied concentrations experiments of Figure 8 and Figure 10. The experimental results do show slightly lower conversions at lower injection concentrations, but since the modeling was done after the experimentation quantities below this equilibrium level of .0016 mole fraction level were not tested.

After the effects of varying in cylinder concentration were modeled in CHEMKIN, the effects of constant concentration and varied temperature on NO conversion rates were explored in more detail, similar to experimental data in Figure 9. One method of determining the conversion rate of NO in the CHEMKIN models proposed by the author is the “line method.” This is a simple method that is based on the assumption that there is

a certain time interval in which all reactions are occurring, and after that all reactions will freeze. The second method proposed by the author is the “CH₄ Method.” This method assumes that after a certain percent of the CH₄ is consumed, then the NO_x conversion has also ceased.

7.1.1 LINE METHOD

More refined time steps and shorter end times were then 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 CH₄, O₂, N₂, and NO at a relative air-fuel ratio of 1.4. As with all models, the solutions were checked for solver time step independence. Figure 17 to Figure 20 show NO, NO₂, CH₄, and NO_x as a function of time for these small time scales, and Figure 21 shows NO_x as a function of time on a larger time scale. These figures indicate that NO₂ is being formed on the same time scale in which complete combustion of CH₄ occurs. NO₂ levels then decrease significantly. Conversely, NO levels drop rapidly then rise slightly as NO₂ is depleted. This behavior leads to the conversion of NO_x as seen in Figure 20.

The vertical dashed line in Figure 20 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° before and 10° after 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 NO_x 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 20, but can easily be seen in Figure 21.

Figure 17: Mole fraction of NO for constant temperature processes

Figure 18: Mole fraction of NO_2 for constant temperature processes

Figure 19: Mole fraction of CH_4 for constant temperature processes

Figure 20: Mole fraction of NO_x, reported as NO, for constant temperature processes on a small time scale

Figure 21: Mole fraction of NO_x , reported as NO for constant temperature processes on a large time scale

Figure 22: Conversion percentage at various temperatures

Figure 22 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 22.

7.1.2 PERCENT CH₄ METHOD

This method of calculating the NO_x conversion efficiency assumes that when 98% of the CH₄ has been consumed, the reactions freeze, and NO_x is no longer being converted. Another method that may have been used would be to assume different percentage conversion for each temperature. This value of 98% was chosen because it is representative of the time at which the CH₄ reaction rates slowed to rates that were

considered negligible as seen in Figure 23. This assumption was necessary because 100% combustion is not reached within CHEMKIN's solver, reaction rates are just slowed to near zero levels, and CH₄ levels are reduced to 10⁻¹⁰ mole fraction or less. 99% and 97% CH₄ burn percentages were also tested, with variations in the conversion percentage of less than 5%. Another method that may have been used would be to assume different percentage conversion for each temperature. This would then require knowledge of in cylinder temperature distributions that is beyond the scope of this work. A simple logic statement was written to find the time at which 98% of the initial quantity of CH₄ was consumed, for the lean case this corresponds to 98% of 0.07 mole fraction, or 0.0014 mole fraction of CH₄. The time frame for this percentage of CH₄ to be consumed varies with temperature, as can be seen in Figures 23, 25, 27, and 29 for the varying mixtures of gases. This time was then used to find the mole fraction of NO_x, shown in Figures 24, 26, 28, and 30, in the mixture at that time, which then gave the NO_x conversion.

The percent CH₄ method was chosen when evaluating EGR and stoichiometric characteristics. Since the in cylinder pressure is not yet measured, the time frame in which reactions are actually occurring is not yet known. This does not discredit the line method, but just means that more information is needed to make it a useful tool. In actuality a composite of the two methods may predict the NO_x conversion efficiencies more accurately than either method alone.

Figure 23: Mass depletion of CH₄ for a lean (λ equals 1.4) mixture, with 25,000 ppm NO

Figure 24: Mass conversion of NO_x for a lean (λ equals 1.4) mixture, with 25,000 ppm
NO

7.2 STOICHIOMETRIC CASE

Stoichiometric burn represented in Figure 25 and Figure 26 occurs at much higher flame temperatures than the lean burn case. Just as higher temperatures cause higher baseline NO_x values from increased reaction rates, the reverse rates of reaction when elevated concentrations of NO are present in the intake air are also increased, leading to higher NO conversion than for the lean case.

Figure 25: Mass depletion of CH_4 for the stoichiometric (λ equals 1) mixture, with
25,000 ppm NO

Figure 26: Mass conversion of NO_x for the stoichiometric (λ equals 1) mixture, with 25,000 ppm NO

7.3 EGR CASE

With an exhaust gas mixture in the intake air, the conversion rates have increased from those of the lean case. Even at the same combustion temperatures as the lean case the reaction rates are significantly higher. This leads to the conclusion that the added intake species CO, CO_2 , and H_2O are causing an increased rate of reaction and depletion of NO.

Figure 27: Mass depletion of CH₄ for a lean (λ equals 1.4) mixture, with 20% EGR and 25,000 ppm NO and

Figure 28: Mass conversion of NO_x for a lean (λ equals 1.4) mixture, with 20% EGR and 25,000 ppm NO and

7.4 RICH BURN CASE

The rich burn case exhibits the highest overall modeled conversion efficiencies. Conversion efficiencies ranging from 35 to 50% are shown here using the CH_4 method. This rich burn model shows that heightened levels of CH_4 in the intake air give the largest overall reduction in NO. This also leads the author to believe that by increasing the dwell time of the gasses in the engine cylinder, and allowing lower combustion temperatures will yield conversion rates exceeding 90%. This is demonstrated by the vertical dashed line in Figure 30, which shows that at combustion temperatures of 1450 K 90% conversion will be achieved if the gasses are kept at these elevated temperature

(increased dwell time). The vertical dashed line is drawn at 4 ms, which corresponds to the time it takes the piston to go from 10° before to 10° after TDC at 800 RPM.

Figure 29: Mass depletion of CH₄ for the rich (λ equals .9) mixture with 25,000 ppm NO

Figure 30: Mass conversion of NO_x for a rich (λ equals .9) mixture with 25,000 ppm NO

7.5 SUMMARY OF CHEMICAL KINETIC MODELING RESULTS

The chemical kinetic modeling attempts to show that for a given initial mixture of gases in an engine cylinder, reacting at varying in cylinder temperatures, the NO conversion rate can be modeled by a single packet of gases reacting at varying temperatures, and the conversion rate of the gases in the cylinder should lie within the bounds of the conversion rates of the individual packets, as seen in Figure 31, which shows the NO conversion rates using the CH_4 method of calculation. The upper bound for the combustion temperature range was set by the theoretical adiabatic flame temperature, and the lower bound of 1300 K was based on plots of CH_4 and NO_x for temperatures lower than 1300 K. The plots of NO_x versus time for each of the cases show that for 1300 K combustion

temperatures, the reactions take on the order of .1 seconds to occur. This is much larger than the time in which reactions are actually occurring in the engine cylinder, so temperatures less than this value were neglected. Although NO_x conversion may not have time to occur when considering the actual time scales for combustion when compared to the time scales for reaction at 1300 K, the percentage of gases that are reacting at this temperature in the engine cylinder are relatively low, and the trend of increasing NO_x conversion with added EGR and more fuel rich mixtures should still be valid. These modeling results lead to the conclusion that heightened combustion temperatures and excess CH_4 associated with rich and stoichiometric burn increase NO conversion efficiencies. EGR components of CO, CO_2 , and H_2O also increase NO reaction rates and conversion efficiencies. These results also lead the author to believe that conversions up to 90% can be achieved with proper management air-fuel ratio as shown in Figure 30, which is similar to the results obtained for a gasoline engine operating under stoichiometric conditions [2].

Figure 31: Summary of NO conversion percentages for all cases

8 OVERALL SNR EFFICIENCY

8.1 ADSORBER CHARACTERISTICS

Sorbent Technologies Corporation of Twinsburgh, OH completed initial testing of the carbon based NO_x adsorbent material [35]. Shown below in Figure 32 and Figure 33 are the results of this testing.

Figure 32: Adsorption efficiency as a function of the cooled exhaust gas temperature for varied concentrations of NO and NO₂ averaged over 60 minutes [35]

Quantities of NO and NO₂ mixed with air were fed through the adsorber at 100 and 500 ppm levels and varying inlet gas temperature. The objective of this experiment was to mimic typical large bore stationary engine exhaust NO and NO₂ emissions, and test the adsorbers efficiency for removing NO_x at these levels. Figure 32 shows that increasing

NO and NO₂ concentration only slightly increase adsorber efficiency, and that exhaust gas temperature plays a major role in adsorber efficiency.

Figure 33: Desorption efficiency as a function of desorb time for NO and NO₂ [35]

In the second set of tests, shown in Figure 33, the adsorber was first exposed to 1000 ppm NO laden air, in which the adsorber adsorbed 2.0 weight percent NO in the first cycle before the adsorption efficiency dropped below 85%. The bed then desorbed 90% of the adsorbed gas when air heated to 300 °C was passed through the adsorber. Subsequent cycles showed the adsorber to adsorb 2.0 weight percent NO and desorb effectively all off it during the heated air adsorber regeneration. Secondly the effects of NO₂ on the adsorption and desorption process were investigated [35].

8.2 TWO ADSORBER SYSTEM EFFICIENCY

To obtain an estimate of the maximum overall process conversion a two adsorber system was chosen. The advantage of this being that when one adsorber is in desorption mode, and passing concentrated NO_x through the engine for conversion, the other adsorber will be adsorbing the concentrated NO_x stream as it is leaving the engine. The baseline engine out NO_x, $\dot{m}_{engine_out}$, for this overall process conversion efficiency model was assumed to be 0.018 g/s (value reported as g/s NO₂), that of the Cummins L10G at the steady state engine operating point of 800 rpm and 400 ft-lb load, Table 3. At this operating condition the intake flow is 62 slps, Table 5. For a first approximation, the intake flow was assumed to be equal to the exhaust flow, which yielded a concentration of 144 ppm. The adsorber's adsorption efficiency, η_a , is approximately 90% for this concentration with the appropriate exhaust gas temperature. The NO_x capacity of the adsorber, m_a , was assumed to be 0.2 kg of NO_x, and the desorption time, t_d , which is a function of the thermal transients of the adsorbent material and residence time of the exhaust gas in the adsorber, was assumed to be 10 minutes. The adsorber was modeled to completely desorb all of the adsorbed NO_x. In reality, the adsorber would have to be sized to hold slightly more NO_x than this to account for residual NO_x that was not desorbed. Finally, the engine conversion, η_c , was assumed to be 50%, which CHEMKIN modeling has shown can be reached with EGR and slightly rich operation.

Assuming the two adsorber system starts with the first adsorber full and desorbing into the second adsorber, the flow out of the first adsorber, $\dot{m}_{adsorber_out}$ would be:

$$\dot{m}_{adsorber_out} = \frac{m_a}{t_d}$$

Equation 8

The engine then converts a percentage of this flow, and the amount of NO_x going into the second adsorber, $\dot{m}_{adsorber_in1}$, is the adsorption efficiency, times the sum of the baseline engine out NO_x plus this desorbed flow after conversion:

$$\dot{m}_{adsorber_in1} = \eta_a [\dot{m}_{engine_out} + (1 - \eta_c)(\dot{m}_{adsorber_out})]$$

Equation 9

The adsorber also allows a percentage of the flow to pass through the adsorber during this time:

$$\dot{m}_{adsorber_out1} = (1 - \eta_a) [\dot{m}_{engine_out} + (1 - \eta_c)(\dot{m}_{adsorber_out})]$$

Equation 10

Once the first adsorber has completed desorption, the adsorber finishes adsorbing baseline engine out NO_x, $\dot{m}_{engine_out}$, until the adsorption capacity, m_a , is reached. The amount of NO_x entering the adsorber during this time can be expressed as:

$$\dot{m}_{adsorber_in2} = \eta_a \cdot \dot{m}_{engine_out}$$

Equation 11

The flow allowed to pass through the adsorber during this time can be expressed as:

$$\dot{m}_{adsorber_out2} = (1 - \eta_a) \dot{m}_{engine_out}$$

Equation 12

The total adsorption time, t_a , can then be expressed as the desorption time plus the remaining time to reach the adsorption capacity.

$$t_a = t_d + \left[m_a - \dot{m}_{adsorber_in1}(t_d) \right] / \dot{m}_{engine_in2} \quad \text{Equation 13}$$

Figure 34 shows the resulting NO_x emissions after the two adsorber system has been applied. The dashed line represents the real time system out NO_x. This was then time averaged to investigate overall process conversion.

Figure 34: NO_x emissions for the two adsorber model, with 0.018 g/s engine out emissions without aftertreatment and 90% adsorber efficiency

The periodic spikes in the dashed line of Figure 34 represent the time periods in which concentrated desorbed gas is being passed through the engine for conversion. This process will be repeated until the adsorbent material is degraded to the point that it needs replaced. The time averaged line Figure 34 represents an average overall conversion of 82% for the two adsorber system. As the engine conversion efficiency approaches 100% overall conversion approaches the adsorber efficiency. If an adsorber efficiency of 90% could be achieved through close exhaust gas temperature control, and close NO_x concentration control through adsorption and desorption timing, and engine conversion efficiencies of 90% were achieved through slightly rich operation, as the CHEMKIN modeling suggests may be possible, overall NO_x conversions exceeding 90% could be achieved.

9 CONCLUSIONS

In conclusion it is possible to convert NO into harmless gases by passing it through a spark ignited natural gas engine at sufficiently high concentrations and engine loads. It was found that the NO conversion rates varied only slightly as load increased, as seen in Figure 11. This behavior may be linked to that of Figure 22, 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 11. Although Figure 22 represents the conversion percentage in a packet of gases at particular temperatures, a continuum of packets with temperatures in the same range would also exhibit the same behavior, as in an engine cylinder. Conversion rate predictions from 35% to 42% were estimated using the line method and 20% to 26% using the CH₄ method, and conversions of 18% to 23% were observed experimentally. The overestimate of NO conversion by using the line method comes from not knowing the actual time period in which reactions are occurring in the engine cylinder. The CH₄ method predicts the range of values for NO_x conversion that occurred in experiments within $\pm 3\%$. Knowledge of in-cylinder pressure measure may prove to be a very useful tool in determining a better estimate for the time frame in which reactions are occurring. The NO conversion for slightly rich operation, shown in Figure 30, of 90% may be achieved with close control of combustion temperatures and timing.

The data to the left of the vertical dashed line in Figure 20 represent the time frame in which NO conversions would actually occur in an internal combustion engine. Since the mixture has not yet reached equilibrium, the NO_x 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 NO_x production. This also gives insight into why Figure 10 only showed modest increases in the NO conversion rate as the initial concentration of NO was increased.

It was observed that the air-fuel ratio had little effect on CO_2 and a modest effect on CO and HC baseline emissions during actual engine testing, but it had a substantial effect on NO_x . This effect is widely acknowledged [36]. CHEMKIN showed similar trends when reaction rates with varying air-fuel ratios were compared, and showed that increasing λ lead to increased reaction rates of NO, leading to increased conversion rates. Addition of EGR also showed increased NO reaction and conversion rates. The variations in air fuel ratio may have effected some of the conversion percentage trends that were shown in the experimental data, but even at the set points where constant air-fuel ratio was achieved, NO_x conversion remained relatively constant for varying injection quantities and loads.

With proper control of a two adsorber system and management of air-fuel ratio and EGR 90% overall NO_x conversion efficiencies should be achieved with the SNR process. If a normally lean burn natural gas engine is operated under stoichiometric or slightly rich conditions with EGR for short periods of time, long enough to convert the desorbed NO, 90% engine conversion should be achieved.

REFERENCES

- [1]. R. W. Weeks and J. J. Moskwa, "Transient Air Flow Rate Estimation in a Natural Gas Engine Using a Nonlinear Observer," SAE 940759, Society of Automotive Engineers, Warrendale, PA 1994.
- [2]. B. Krutzsch, G. Wenninger, M. Weibel, P. Stapf, A. Funk, D. E. Webster, E. Chaize, B. Kasemo, J. Martens, and A. Kiennemann, "Reduction of NO_x in Lean Exhaust by Selective NO_x – Recirculation (SNR -Technique), Part II: NO_x Storage Materials," SAE 982592, Society of Automotive Engineers, Warrendale, PA 1998.
- [3]. E. Chaize, D. E. Webster, B. Krutzsch, G. Wenninger, M. Weibel, S. Hodjati, C. Petit, V. Pitchon, A. Kiennemann, R. Loenders, O. Monticelli, P. A. Jacobs, J. Martens, and B. Kasemo, "Reduction of NO_x in Lean Exhaust by Selective NO_x – Recirculation (SNR -Technique), Part I: System and Conversion Process," SAE 982592, Society of Automotive Engineers, Warrendale, PA 1998.
- [4]. R. J. Kee, F. M. Rupley, J. A. Miller, M. E. Coltrin, J. F. Grcar, E. Meeks, H. K. Moffat, A. E. Lutz, G. Dixon Lewis, M. D. Smooke, J. Warnatz, G. H. Evans, R. S. Larson, R. E. Mitchell, L. R. Petzold, W. C. Reynolds, M. Caracotsios, W. E. Stewart, P. Glarborg, C. Wang, O. Adigun, W. G. Houf, C. P. Chou, S. F. Miller, P. Ho, and D. J. Young, CHEMKIN Release 4.0, Reaction Design, Inc., San Diego, CA 2004.
- [5]. S. Rousseau, B. Lemoult, and M. Tazerout, "Combustion Characterization of Natural Gas in a Lean Burn Spark-Ignition Engine," Proceedings of the Institution of Mechanical Engineers Part D-Journal of Automobile Engineering 213(D5):481-489, Département Systèmes Energétiques et Environnement, Ecole des Mines de Nantes, France 1999.
- [6]. S. C. Kong and R. D. Reitz, "Application of Detailed Chemistry and CFD for Predicting Direct Injection HCCI Engine Combustion and Emissions," Proceedings of the Combustion Institute 29:663-669, Chicago, IL 2003.
- [7]. S. C. Kong and R. D. Reitz, "Use of Detailed Chemical Kinetics to Study HCCI Engine Combustion with Consideration of Turbulent Mixing Effects," Journal of Engineering for Gas Turbines and Power-Transactions of the ASME 124(3):702-707, American Society of Mechanical Engineers, New York, NY 2002.
- [8]. G. Smith, D. Golden, M. Frenklach, N. Moriarty, B. Eiteneer, M. Goldenberg, C. Bowman, R. Hanson, S. Song, W. Gardiner, V. Lissianski, and Z. Qin, http://www.me.berkeley.edu/gri_mech, Berkely, CA 2004.

- [9]. K. S. Varde, J. C. Cherng, C. J. Bailey, and W. A. Majewski, "Emissions and Their Control in Natural Gas Fueled Engines," SAE 922250, Society of Automotive Engineers, Warrendale, PA 1992.
- [10]. A. Manivannan, P. Tamil porai, S. Chandrasekaran, and R. Ramprabhu, "Lean Burn Natural Gas Spark Ignition Engine – An Overview," SAE 2003-01-0638, Society of Automotive Engineers, Warrendale, PA 2003.
- [11]. S. Bhargarva, N. N. Clark, and M. W. Hildebrand, "Exhaust Gas Recirculation in a Lean-Burn Natural Gas Engine," SAE 922250, Society of Automotive Engineers, Warrendale, PA 1992.
- [12]. T. Sakonji and F. Shoji, "Study on Improvement of Natural Gas Fueled Spark Ignition Engines –Effect of EGR Utilization," SAE 971714, Society of Automotive Engineers, Warrendale, PA 1997.
- [13]. R. R. Raine, G. Zhang, and A. Pflug, "Comparison of Emissions from Natural Gas and Gasoline Fuelled Engines – Total Hydrocarbon and Methane Emissions and Exhaust Gas Recirculation Effects," SAE 970743, Society of Automotive Engineers, Warrendale, PA 1997.
- [14]. K. B. Looney, "EGR as an Emission Reduction Strategy in a Spark-Ignited Natural Gas Engine," M. S. Thesis, West Virginia University, Morgantown, WV 1995.
- [15]. C. Nellen and K. Boulouchos, "Natural Gas Engines for Cogeneration: Highest Efficiency and Near-Zero-Emissions through Turbocharging, EGR and 3-Way Catalytic Converter," SAE 2000-01-2825, Society of Automotive Engineers, Warrendale, PA 2000.
- [16]. G. R. Neame, D. P. Gardiner, R. W. Mallory, V. K. Rao, M. F. Bardon, and V. Battista, "Improving the Fuel Economy of Stoichiometrically Fuelled S.I. Engines by means of EGR and Enhanced Ignition – A Comparison of Gasoline, Methanol and Natural Gas," SAE 952376, Society of Automotive Engineers, Warrendale, PA 1995.
- [17]. B. West, S. Huff, J. Parks, S. Lewis, J. Choi, W. Partridge, and J. Storey, "Assessing Reductant Chemistry During In-Cylinder Regeneration of Diesel Lean NO_x Traps," SAE 2004-01-3023, Society of Automotive Engineers, Warrendale, PA 2004.
- [18]. O. H. Bailey, "NO_x Adsorbers for Diesel Applications: General Considerations and Operational Issues," DieselNet Technical Report, Ecopoint, Inc., Brampton, ON, Canada 1997.
- [19]. W. A. Majewski, "Lean NO_x Catalyst," DieselNet Technical Report, Revision 2004.01, Ecopoint, Inc., Brampton, ON, Canada 2004.

- [20]. W. A. Majewski, "NO_x Adsorbers," DieselNet Technical Report, Revision 2004.01, Ecopoint, Inc., Brampton, ON, Canada 2002.
- [21]. T. Kobayashi, T. Yamada, and K. Kayano, "Study of NO_x Trap Reaction by Thermodynamic Calculation," SAE 970745, Society of Automotive Engineers, Warrendale, PA 1997.
- [22]. R. M. Heck and R. J. Farrauto, "Catalytic Air Pollution Control: Commercial Technology," Van Nostrand Reinhold, New York, NY 1995.
- [23]. W. A. Majewski, "Selective Catalytic Reduction," DieselNet Technical Report, Revision 2003.11, Ecopoint, Inc., Brampton, ON, Canada 2003.
- [24]. J. J. Yeh, H. Pennline, and C. Drummond, "New Strategy to Decompose Nitrogen Oxides from Regenerable Flue Gas Cleanup Processes," 194th ACS National Meeting, American Chemical Society, New Orleans, LA 1987.
- [25]. "Enhancing the Use of Coals by Gas Reburning," Final Report, U.S. Department of Energy, Office of Fossil Energy, Federal Energy Technology Center, Morgantown, WV 1998.
- [26]. R. Vellaisamy, N. N. Clark, G. J. Thompson, R. J. Atkinson, C. A. Tissera, and M. M. Swartz, "Assesment of NO_x Destruction in Diesel Engines by Injecting NO in the Intake Manifold," SAE 2005-01-0379, Society of Automotive Engineers, Warrendale, PA 2005.
- [27]. R. Vellaisamy, "Assesment of NO_x Destruction in Diesel Engines by Injecting NO in the Intake," M. S. Thesis, West Virginia University, Morgantown, WV 1997.
- [28]. C. A. Tissera, M. M. Swartz, E. Tatli, R. Vellaisamy, N. N. Clark, G. J. Thompson, R. D. Nine, and R. J. Atkinson, "Selective NO_x Recirculation for Stationary Lean-Burn Natural Gas Engines," ICEF2004-839, ASME Fall 2004 Technical Conference, American Society of Mechanical Engineers, New York, NY 2004.
- [29]. J. A. Hoppie, "Defining Drivetrain Losses in Developing a Cycle for Engine and Chassis Dynamometer Test Compliance and Uncertainty Analysis of Emissions Test Facilities," M. S. Thesis, West Virginia University, Morgantown, WV 1997.
- [30]. Code of Federal Regulations, Title 40, Part 86, "Emission Regulations for New Otto-Cycle and Diesel Heavy-Duty Engines; Gaseous and Particulate Exhaust Test Procedures," Washington, D.C. 1998.
- [31]. W. S. Wayne, "A Parametric Study of Knock Control Strategies for a Bi-Fuel Engine," Dissertation, West Virginia University, Morgantown, WV 1997.

- [32]. J. Cowart, M. Haghgooeie, C. Newman, G. Davis, W. Pitz, and C. Westbrook, "The Intensity of Knock in an Internal Combustion Engine: An Experimental and Modeling Study," SAE 922327, Society of Automotive Engineers, Warrendale, PA 1992.
- [33]. L. Dodge, J. Kubesh, D. Naegeli, and P. Campbell, "Modeling NO_x Emissions from Lean-Burn Natural Gas Engines," SAE 981389, Society of Automotive Engineers, Warrendale, PA 1998.
- [34]. M. W. Chase and D. R. Lide, "JANAF Thermochemical Tables," Journal of Physical and Chemical Reference Data, American Chemical Society, Washington, D.C. 1986.
- [35]. B. W. Nelson, "Demonstration of a New Emission Control System for Stationary Diesel and Natural Gas Fired Engines," Final Report, California Air Resources Board, Sorbent Technologies Corporation, Twinsburgh, OH 2004.
- [36]. J. Heywood, "Internal Combustion Engine Fundamentals," McGraw Hill, New York, NY 1988.

APPENDIX A: GRIMECH VERSION 3.0 CHEMKIN INPUT FILE

The following description of the GRI-Mech input file, used as the chemical kinetics input file that describes methane combustion, was taken from the CHEMKIN user manuals [4]. “First, the file specifies the elements and species that appear in the mechanism, and then includes the reaction mechanism description. The input is essentially format free. The elements and species names need only be separated by blank spaces. The character string that describes the reaction appears on the left and is followed by the three Arrhenius coefficients (pre-exponential factor, temperature exponent, and activation energy). Enhanced third body efficiencies for selected species are specified in the line following that for a reaction which contains an arbitrary third body, M. Exclamation marks signify the beginning of comments and the remainder of the line is ignored.”

```
! GRI-Mech Version 3.0 7/30/99  CHEMKIN format
! See README30 file at anonymous FTP site unix.sri.com, directory gri;
! WorldWideWeb home page http://www.me.berkeley.edu/gri\_mech/ or
! through http://www.gri.org , under 'Basic Research',
! for additional information, contacts, and disclaimer
```

```
ELEMENTS
O  H  C  N  AR
END
```

```
SPECIES
H2      H      O      O2      OH      H2O      HO2      H2O2
C      CH      CH2      CH2(S)  CH3      CH4      CO      CO2
HCO      CH2O      CH2OH      CH3O      CH3OH      C2H      C2H2      C2H3
C2H4      C2H5      C2H6      HCCO      CH2CO      HCCOH      N      NH
NH2      NH3      NNH      NO      NO2      N2O      HNO      CN
HCN      H2CN      HCNN      HCNO      HOCN      HNCO      NCO      N2
AR      C3H7      C3H8      CH2CHO      CH3CHO
END
```

```
!THERMO
! Insert GRI-Mech thermodynamics here or use in default file
!END
```

REACTIONS

2O+M<=>O2+M	1.200E+17	-1.000	.00
H2/ 2.40/ H2O/15.40/ CH4/ 2.00/ CO/ 1.75/ CO2/ 3.60/ C2H6/ 3.00/ AR/ .83/			
O+H+M<=>OH+M	5.000E+17	-1.000	.00
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .70/			
O+H2<=>H+OH	3.870E+04	2.700	6260.00
O+HO2<=>OH+O2	2.000E+13	.000	.00
O+H2O2<=>OH+HO2	9.630E+06	2.000	4000.00
O+CH<=>H+CO	5.700E+13	.000	.00
O+CH2<=>H+HCO	8.000E+13	.000	.00
O+CH2(S)<=>H2+CO	1.500E+13	.000	.00
O+CH2(S)<=>H+HCO	1.500E+13	.000	.00
O+CH3<=>H+CH2O	5.060E+13	.000	.00
O+CH4<=>OH+CH3	1.020E+09	1.500	8600.00
O+CO(+M)<=>CO2(+M)	1.800E+10	.000	2385.00
LOW/ 6.020E+14 .000 3000.00/			
H2/2.00/ O2/6.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/3.50/ C2H6/3.00/ AR/ .50/			
O+HCO<=>OH+CO	3.000E+13	.000	.00
O+HCO<=>H+CO2	3.000E+13	.000	.00
O+CH2O<=>OH+HCO	3.900E+13	.000	3540.00
O+CH2OH<=>OH+CH2O	1.000E+13	.000	.00
O+CH3O<=>OH+CH2O	1.000E+13	.000	.00
O+CH3OH<=>OH+CH2OH	3.880E+05	2.500	3100.00
O+CH3OH<=>OH+CH3O	1.300E+05	2.500	5000.00
O+C2H<=>CH+CO	5.000E+13	.000	.00
O+C2H2<=>H+HCCO	1.350E+07	2.000	1900.00
O+C2H2<=>OH+C2H	4.600E+19	-1.410	28950.00
O+C2H2<=>CO+CH2	6.940E+06	2.000	1900.00
O+C2H3<=>H+CH2CO	3.000E+13	.000	.00
O+C2H4<=>CH3+HCO	1.250E+07	1.830	220.00
O+C2H5<=>CH3+CH2O	2.240E+13	.000	.00
O+C2H6<=>OH+C2H5	8.980E+07	1.920	5690.00
O+HCCO<=>H+2CO	1.000E+14	.000	.00
O+CH2CO<=>OH+HCCO	1.000E+13	.000	8000.00
O+CH2CO<=>CH2+CO2	1.750E+12	.000	1350.00
O2+CO<=>O+CO2	2.500E+12	.000	47800.00
O2+CH2O<=>HO2+HCO	1.000E+14	.000	40000.00
H+O2+M<=>HO2+M	2.800E+18	-.860	.00
O2/ .00/ H2O/ .00/ CO/ .75/ CO2/1.50/ C2H6/1.50/ N2/ .00/ AR/ .00/			
H+2O2<=>HO2+O2	2.080E+19	-1.240	.00
H+O2+H2O<=>HO2+H2O	11.26E+18	-.760	.00
H+O2+N2<=>HO2+N2	2.600E+19	-1.240	.00
H+O2+AR<=>HO2+AR	7.000E+17	-.800	.00
H+O2<=>O+OH	2.650E+16	-.6707	17041.00
2H+M<=>H2+M	1.000E+18	-1.000	.00
H2/ .00/ H2O/ .00/ CH4/2.00/ CO2/ .00/ C2H6/3.00/ AR/ .63/			
2H+H2<=>2H2	9.000E+16	-.600	.00
2H+H2O<=>H2+H2O	6.000E+19	-1.250	.00
2H+CO2<=>H2+CO2	5.500E+20	-2.000	.00
H+OH+M<=>H2O+M	2.200E+22	-2.000	.00
H2/ .73/ H2O/3.65/ CH4/2.00/ C2H6/3.00/ AR/ .38/			
H+HO2<=>O+H2O	3.970E+12	.000	671.00
H+HO2<=>O2+H2	4.480E+13	.000	1068.00
H+HO2<=>2OH	0.840E+14	.000	635.00

H+H2O2<=>HO2+H2	1.210E+07	2.000	5200.00
H+H2O2<=>OH+H2O	1.000E+13	.000	3600.00
H+CH<=>C+H2	1.650E+14	.000	.00
H+CH2(+M)<=>CH3(+M)	6.000E+14	.000	.00
LOW / 1.040E+26 -2.760 1600.00/			
TROE/ .5620 91.00 5836.00 8552.00/			
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .70/			
H+CH2(S)<=>CH+H2	3.000E+13	.000	.00
H+CH3(+M)<=>CH4(+M)	13.90E+15	-.534	536.00
LOW / 2.620E+33 -4.760 2440.00/			
TROE/ .7830 74.00 2941.00 6964.00 /			
H2/2.00/ H2O/6.00/ CH4/3.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .70/			
H+CH4<=>CH3+H2	6.600E+08	1.620	10840.00
H+HCO(+M)<=>CH2O(+M)	1.090E+12	.480	-260.00
LOW / 2.470E+24 -2.570 425.00/			
TROE/ .7824 271.00 2755.00 6570.00 /			
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .70/			
H+HCO<=>H2+CO	7.340E+13	.000	.00
H+CH2O(+M)<=>CH2OH(+M)	5.400E+11	.454	3600.00
LOW / 1.270E+32 -4.820 6530.00/			
TROE/ .7187 103.00 1291.00 4160.00 /			
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/			
H+CH2O(+M)<=>CH3O(+M)	5.400E+11	.454	2600.00
LOW / 2.200E+30 -4.800 5560.00/			
TROE/ .7580 94.00 1555.00 4200.00 /			
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/			
H+CH2O<=>HCO+H2	5.740E+07	1.900	2742.00
H+CH2OH(+M)<=>CH3OH(+M)	1.055E+12	.500	86.00
LOW / 4.360E+31 -4.650 5080.00/			
TROE/ .600 100.00 90000.0 10000.0 /			
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/			
H+CH2OH<=>H2+CH2O	2.000E+13	.000	.00
H+CH2OH<=>OH+CH3	1.650E+11	.650	-284.00
H+CH2OH<=>CH2(S)+H2O	3.280E+13	-.090	610.00
H+CH3O(+M)<=>CH3OH(+M)	2.430E+12	.515	50.00
LOW / 4.660E+41 -7.440 14080.0/			
TROE/ .700 100.00 90000.0 10000.00 /			
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/			
H+CH3O<=>H+CH2OH	4.150E+07	1.630	1924.00
H+CH3O<=>H2+CH2O	2.000E+13	.000	.00
H+CH3O<=>OH+CH3	1.500E+12	.500	-110.00
H+CH3O<=>CH2(S)+H2O	2.620E+14	-.230	1070.00
H+CH3OH<=>CH2OH+H2	1.700E+07	2.100	4870.00
H+CH3OH<=>CH3O+H2	4.200E+06	2.100	4870.00
H+C2H(+M)<=>C2H2(+M)	1.000E+17	-1.000	.00
LOW / 3.750E+33 -4.800 1900.00/			
TROE/ .6464 132.00 1315.00 5566.00 /			
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .70/			
H+C2H2(+M)<=>C2H3(+M)	5.600E+12	.000	2400.00
LOW / 3.800E+40 -7.270 7220.00/			
TROE/ .7507 98.50 1302.00 4167.00 /			
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .70/			
H+C2H3(+M)<=>C2H4(+M)	6.080E+12	.270	280.00
LOW / 1.400E+30 -3.860 3320.00/			
TROE/ .7820 207.50 2663.00 6095.00 /			
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .70/			
H+C2H3<=>H2+C2H2	3.000E+13	.000	.00

H+C2H4(+M)<=>C2H5(+M)	0.540E+12	.454	1820.00
LOW / 0.600E+42 -7.620 6970.00/			
TROE/ .9753 210.00 984.00 4374.00 /			
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .70/			
H+C2H4<=>C2H3+H2	1.325E+06	2.530	12240.00
H+C2H5(+M)<=>C2H6(+M)	5.210E+17	-.990	1580.00
LOW / 1.990E+41 -7.080 6685.00/			
TROE/ .8422 125.00 2219.00 6882.00 /			
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .70/			
H+C2H5<=>H2+C2H4	2.000E+12	.000	.00
H+C2H6<=>C2H5+H2	1.150E+08	1.900	7530.00
H+HCCO<=>CH2(S)+CO	1.000E+14	.000	.00
H+CH2CO<=>HCCO+H2	5.000E+13	.000	8000.00
H+CH2CO<=>CH3+CO	1.130E+13	.000	3428.00
H+HCCOH<=>H+CH2CO	1.000E+13	.000	.00
H2+CO(+M)<=>CH2O(+M)	4.300E+07	1.500	79600.00
LOW / 5.070E+27 -3.420 84350.00/			
TROE/ .9320 197.00 1540.00 10300.00 /			
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .70/			
OH+H2<=>H+H2O	2.160E+08	1.510	3430.00
2OH(+M)<=>H2O2(+M)	7.400E+13	-.370	.00
LOW / 2.300E+18 -.900 -1700.00/			
TROE/ .7346 94.00 1756.00 5182.00 /			
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .70/			
2OH<=>O+H2O	3.570E+04	2.400	-2110.00
OH+HO2<=>O2+H2O	1.450E+13	.000	-500.00
DUPLICATE			
OH+H2O2<=>HO2+H2O	2.000E+12	.000	427.00
DUPLICATE			
OH+H2O2<=>HO2+H2O	1.700E+18	.000	29410.00
DUPLICATE			
OH+C<=>H+CO	5.000E+13	.000	.00
OH+CH<=>H+HCO	3.000E+13	.000	.00
OH+CH2<=>H+CH2O	2.000E+13	.000	.00
OH+CH2<=>CH+H2O	1.130E+07	2.000	3000.00
OH+CH2(S)<=>H+CH2O	3.000E+13	.000	.00
OH+CH3(+M)<=>CH3OH(+M)	2.790E+18	-1.430	1330.00
LOW / 4.000E+36 -5.920 3140.00/			
TROE/ .4120 195.0 5900.00 6394.00/			
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/			
OH+CH3<=>CH2+H2O	5.600E+07	1.600	5420.00
OH+CH3<=>CH2(S)+H2O	6.440E+17	-1.340	1417.00
OH+CH4<=>CH3+H2O	1.000E+08	1.600	3120.00
OH+CO<=>H+CO2	4.760E+07	1.228	70.00
OH+HCO<=>H2O+CO	5.000E+13	.000	.00
OH+CH2O<=>HCO+H2O	3.430E+09	1.180	-447.00
OH+CH2OH<=>H2O+CH2O	5.000E+12	.000	.00
OH+CH3O<=>H2O+CH2O	5.000E+12	.000	.00
OH+CH3OH<=>CH2OH+H2O	1.440E+06	2.000	-840.00
OH+CH3OH<=>CH3O+H2O	6.300E+06	2.000	1500.00
OH+C2H<=>H+HCCO	2.000E+13	.000	.00
OH+C2H2<=>H+CH2CO	2.180E-04	4.500	-1000.00
OH+C2H2<=>H+HCCOH	5.040E+05	2.300	13500.00
OH+C2H2<=>C2H+H2O	3.370E+07	2.000	14000.00
OH+C2H2<=>CH3+CO	4.830E-04	4.000	-2000.00
OH+C2H3<=>H2O+C2H2	5.000E+12	.000	.00
OH+C2H4<=>C2H3+H2O	3.600E+06	2.000	2500.00

OH+C2H6<=>C2H5+H2O	3.540E+06	2.120	870.00
OH+CH2CO<=>HCCO+H2O	7.500E+12	.000	2000.00
2HO2<=>O2+H2O2	1.300E+11	.000	-1630.00
DUPLICATE			
2HO2<=>O2+H2O2	4.200E+14	.000	12000.00
DUPLICATE			
HO2+CH2<=>OH+CH2O	2.000E+13	.000	.00
HO2+CH3<=>O2+CH4	1.000E+12	.000	.00
HO2+CH3<=>OH+CH3O	3.780E+13	.000	.00
HO2+CO<=>OH+CO2	1.500E+14	.000	23600.00
HO2+CH2O<=>HCO+H2O2	5.600E+06	2.000	12000.00
C+O2<=>O+CO	5.800E+13	.000	576.00
C+CH2<=>H+C2H	5.000E+13	.000	.00
C+CH3<=>H+C2H2	5.000E+13	.000	.00
CH+O2<=>O+HCO	6.710E+13	.000	.00
CH+H2<=>H+CH2	1.080E+14	.000	3110.00
CH+H2O<=>H+CH2O	5.710E+12	.000	-755.00
CH+CH2<=>H+C2H2	4.000E+13	.000	.00
CH+CH3<=>H+C2H3	3.000E+13	.000	.00
CH+CH4<=>H+C2H4	6.000E+13	.000	.00
CH+CO(+M)<=>HCCO(+M)	5.000E+13	.000	.00
LOW / 2.690E+28 -3.740 1936.00/			
TROE/ .5757 237.00 1652.00 5069.00 /			
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .70/			
CH+CO2<=>HCO+CO	1.900E+14	.000	15792.00
CH+CH2O<=>H+CH2CO	9.460E+13	.000	-515.00
CH+HCCO<=>CO+C2H2	5.000E+13	.000	.00
CH2+O2=>OH+H+CO	5.000E+12	.000	1500.00
CH2+H2<=>H+CH3	5.000E+05	2.000	7230.00
2CH2<=>H2+C2H2	1.600E+15	.000	11944.00
CH2+CH3<=>H+C2H4	4.000E+13	.000	.00
CH2+CH4<=>2CH3	2.460E+06	2.000	8270.00
CH2+CO(+M)<=>CH2CO(+M)	8.100E+11	.500	4510.00
LOW / 2.690E+33 -5.110 7095.00/			
TROE/ .5907 275.00 1226.00 5185.00 /			
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .70/			
CH2+HCCO<=>C2H3+CO	3.000E+13	.000	.00
CH2(S)+N2<=>CH2+N2	1.500E+13	.000	600.00
CH2(S)+AR<=>CH2+AR	9.000E+12	.000	600.00
CH2(S)+O2<=>H+OH+CO	2.800E+13	.000	.00
CH2(S)+O2<=>CO+H2O	1.200E+13	.000	.00
CH2(S)+H2<=>CH3+H	7.000E+13	.000	.00
CH2(S)+H2O(+M)<=>CH3OH(+M)	4.820E+17	-1.160	1145.00
LOW / 1.880E+38 -6.360 5040.00/			
TROE/ .6027 208.00 3922.00 10180.0 /			
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/			
CH2(S)+H2O<=>CH2+H2O	3.000E+13	.000	.00
CH2(S)+CH3<=>H+C2H4	1.200E+13	.000	-570.00
CH2(S)+CH4<=>2CH3	1.600E+13	.000	-570.00
CH2(S)+CO<=>CH2+CO	9.000E+12	.000	.00
CH2(S)+CO2<=>CH2+CO2	7.000E+12	.000	.00
CH2(S)+CO2<=>CO+CH2O	1.400E+13	.000	.00
CH2(S)+C2H6<=>CH3+C2H5	4.000E+13	.000	-550.00
CH3+O2<=>O+CH3O	3.560E+13	.000	30480.00
CH3+O2<=>OH+CH2O	2.310E+12	.000	20315.00
CH3+H2O2<=>HO2+CH4	2.450E+04	2.470	5180.00
2CH3(+M)<=>C2H6(+M)	6.770E+16	-1.180	654.00

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LOW / 3.400E+41 -7.030 2762.00/
TROE/ .6190 73.20 1180.00 9999.00 /
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .70/
2CH3<=>H+C2H5 6.840E+12 .100 10600.00
CH3+HCO<=>CH4+CO 2.648E+13 .000 .00
CH3+CH2O<=>HCO+CH4 3.320E+03 2.810 5860.00
CH3+CH3OH<=>CH2OH+CH4 3.000E+07 1.500 9940.00
CH3+CH3OH<=>CH3O+CH4 1.000E+07 1.500 9940.00
CH3+C2H4<=>C2H3+CH4 2.270E+05 2.000 9200.00
CH3+C2H6<=>C2H5+CH4 6.140E+06 1.740 10450.00
HCO+H2O<=>H+CO+H2O 1.500E+18 -1.000 17000.00
HCO+M<=>H+CO+M 1.870E+17 -1.000 17000.00
H2/2.00/ H2O/ .00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/
HCO+O2<=>HO2+CO 13.45E+12 .000 400.00
CH2OH+O2<=>HO2+CH2O 1.800E+13 .000 900.00
CH3O+O2<=>HO2+CH2O 4.280E-13 7.600 -3530.00
C2H+O2<=>HCO+CO 1.000E+13 .000 -755.00
C2H+H2<=>H+C2H2 5.680E+10 0.900 1993.00
C2H3+O2<=>HCO+CH2O 4.580E+16 -1.390 1015.00
C2H4(+M)<=>H2+C2H2(+M) 8.000E+12 .440 86770.00
LOW / 1.580E+51 -9.300 97800.00/
TROE/ .7345 180.00 1035.00 5417.00 /
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .70/
C2H5+O2<=>HO2+C2H4 8.400E+11 .000 3875.00
HCCO+O2<=>OH+2CO 3.200E+12 .000 854.00
2HCCO<=>2CO+C2H2 1.000E+13 .000 .00
N+NO<=>N2+O 2.700E+13 .000 355.00
N+O2<=>NO+O 9.000E+09 1.000 6500.00
N+OH<=>NO+H 3.360E+13 .000 385.00
N2O+O<=>N2+O2 1.400E+12 .000 10810.00
N2O+O<=>2NO 2.900E+13 .000 23150.00
N2O+H<=>N2+OH 3.870E+14 .000 18880.00
N2O+OH<=>N2+HO2 2.000E+12 .000 21060.00
N2O(+M)<=>N2+O(+M) 7.910E+10 .000 56020.00
LOW / 6.370E+14 .000 56640.00/
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .625/
HO2+NO<=>NO2+OH 2.110E+12 .000 -480.00
NO+O+M<=>NO2+M 1.060E+20 -1.410 .00
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .70/
NO2+O<=>NO+O2 3.900E+12 .000 -240.00
NO2+H<=>NO+OH 1.320E+14 .000 360.00
NH+O<=>NO+H 4.000E+13 .000 .00
NH+H<=>N+H2 3.200E+13 .000 330.00
NH+OH<=>HNO+H 2.000E+13 .000 .00
NH+OH<=>N+H2O 2.000E+09 1.200 .00
NH+O2<=>HNO+O 4.610E+05 2.000 6500.00
NH+O2<=>NO+OH 1.280E+06 1.500 100.00
NH+N<=>N2+H 1.500E+13 .000 .00
NH+H2O<=>HNO+H2 2.000E+13 .000 13850.00
NH+NO<=>N2+OH 2.160E+13 -.230 .00
NH+NO<=>N2O+H 3.650E+14 -.450 .00
NH2+O<=>OH+NH 3.000E+12 .000 .00
NH2+O<=>H+HNO 3.900E+13 .000 .00
NH2+H<=>NH+H2 4.000E+13 .000 3650.00
NH2+OH<=>NH+H2O 9.000E+07 1.500 -460.00
NNH<=>N2+H 3.300E+08 .000 .00
NNH+M<=>N2+H+M 1.300E+14 -.110 4980.00

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H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .70/			
NNH+O2<=>HO2+N2	5.000E+12	.000	.00
NNH+O<=>OH+N2	2.500E+13	.000	.00
NNH+O<=>NH+NO	7.000E+13	.000	.00
NNH+H<=>H2+N2	5.000E+13	.000	.00
NNH+OH<=>H2O+N2	2.000E+13	.000	.00
NNH+CH3<=>CH4+N2	2.500E+13	.000	.00
H+NO+M<=>HNO+M	4.480E+19	-1.320	740.00
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .70/			
HNO+O<=>NO+OH	2.500E+13	.000	.00
HNO+H<=>H2+NO	9.000E+11	.720	660.00
HNO+OH<=>NO+H2O	1.300E+07	1.900	-950.00
HNO+O2<=>HO2+NO	1.000E+13	.000	13000.00
CN+O<=>CO+N	7.700E+13	.000	.00
CN+OH<=>NCO+H	4.000E+13	.000	.00
CN+H2O<=>HCN+OH	8.000E+12	.000	7460.00
CN+O2<=>NCO+O	6.140E+12	.000	-440.00
CN+H2<=>HCN+H	2.950E+05	2.450	2240.00
NCO+O<=>NO+CO	2.350E+13	.000	.00
NCO+H<=>NH+CO	5.400E+13	.000	.00
NCO+OH<=>NO+H+CO	0.250E+13	.000	.00
NCO+N<=>N2+CO	2.000E+13	.000	.00
NCO+O2<=>NO+CO2	2.000E+12	.000	20000.00
NCO+M<=>N+CO+M	3.100E+14	.000	54050.00
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .70/			
NCO+NO<=>N2O+CO	1.900E+17	-1.520	740.00
NCO+NO<=>N2+CO2	3.800E+18	-2.000	800.00
HCN+M<=>H+CN+M	1.040E+29	-3.300	126600.00
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .70/			
HCN+O<=>NCO+H	2.030E+04	2.640	4980.00
HCN+O<=>NH+CO	5.070E+03	2.640	4980.00
HCN+O<=>CN+OH	3.910E+09	1.580	26600.00
HCN+OH<=>HOCN+H	1.100E+06	2.030	13370.00
HCN+OH<=>HNCO+H	4.400E+03	2.260	6400.00
HCN+OH<=>NH2+CO	1.600E+02	2.560	9000.00
H+HCN(+M)<=>H2CN(+M)	3.300E+13	.000	.00
LOW /	1.400E+26	-3.400	1900.00/
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .70/			
H2CN+N<=>N2+CH2	6.000E+13	.000	400.00
C+N2<=>CN+N	6.300E+13	.000	46020.00
CH+N2<=>HCN+N	3.120E+09	0.880	20130.00
CH+N2(+M)<=>HCNN(+M)	3.100E+12	.150	.00
LOW /	1.300E+25	-3.160	740.00/
TROE/	.6670	235.00	2117.00 4536.00 /
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ 1.0/			
CH2+N2<=>HCN+NH	1.000E+13	.000	74000.00
CH2(S)+N2<=>NH+HCN	1.000E+11	.000	65000.00
C+NO<=>CN+O	1.900E+13	.000	.00
C+NO<=>CO+N	2.900E+13	.000	.00
CH+NO<=>HCN+O	4.100E+13	.000	.00
CH+NO<=>H+NCO	1.620E+13	.000	.00
CH+NO<=>N+HCO	2.460E+13	.000	.00
CH2+NO<=>H+HNCO	3.100E+17	-1.380	1270.00
CH2+NO<=>OH+HCN	2.900E+14	-.690	760.00
CH2+NO<=>H+HCNO	3.800E+13	-.360	580.00
CH2(S)+NO<=>H+HNCO	3.100E+17	-1.380	1270.00
CH2(S)+NO<=>OH+HCN	2.900E+14	-.690	760.00

CH2 (S) +NO<=>H+HCNO	3.800E+13	-.360	580.00
CH3+NO<=>HCN+H2O	9.600E+13	.000	28800.00
CH3+NO<=>H2CN+OH	1.000E+12	.000	21750.00
HCNN+O<=>CO+H+N2	2.200E+13	.000	.00
HCNN+O<=>HCN+NO	2.000E+12	.000	.00
HCNN+O2<=>O+HCO+N2	1.200E+13	.000	.00
HCNN+OH<=>H+HCO+N2	1.200E+13	.000	.00
HCNN+H<=>CH2+N2	1.000E+14	.000	.00
HNCO+O<=>NH+CO2	9.800E+07	1.410	8500.00
HNCO+O<=>HNO+CO	1.500E+08	1.570	44000.00
HNCO+O<=>NCO+OH	2.200E+06	2.110	11400.00
HNCO+H<=>NH2+CO	2.250E+07	1.700	3800.00
HNCO+H<=>H2+NCO	1.050E+05	2.500	13300.00
HNCO+OH<=>NCO+H2O	3.300E+07	1.500	3600.00
HNCO+OH<=>NH2+CO2	3.300E+06	1.500	3600.00
HNCO+M<=>NH+CO+M	1.180E+16	.000	84720.00
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .70/			
HCNO+H<=>H+HNCO	2.100E+15	-.690	2850.00
HCNO+H<=>OH+HCN	2.700E+11	.180	2120.00
HCNO+H<=>NH2+CO	1.700E+14	-.750	2890.00
HOCN+H<=>H+HNCO	2.000E+07	2.000	2000.00
HCCO+NO<=>HCNO+CO	0.900E+13	.000	.00
CH3+N<=>H2CN+H	6.100E+14	-.310	290.00
CH3+N<=>HCN+H2	3.700E+12	.150	-90.00
NH3+H<=>NH2+H2	5.400E+05	2.400	9915.00
NH3+OH<=>NH2+H2O	5.000E+07	1.600	955.00
NH3+O<=>NH2+OH	9.400E+06	1.940	6460.00
NH+CO2<=>HNO+CO	1.000E+13	.000	14350.00
CN+NO2<=>NCO+NO	6.160E+15	-0.752	345.00
NCO+NO2<=>N2O+CO2	3.250E+12	.000	-705.00
N+CO2<=>NO+CO	3.000E+12	.000	11300.00
O+CH3=>H+H2+CO	3.370E+13	.000	.00
O+C2H4<=>H+CH2CHO	6.700E+06	1.830	220.00
O+C2H5<=>H+CH3CHO	1.096E+14	.000	.00
OH+HO2<=>O2+H2O	0.500E+16	.000	17330.00
DUPLICATE			
OH+CH3=>H2+CH2O	8.000E+09	.500	-1755.00
CH+H2 (+M) <=>CH3 (+M)	1.970E+12	.430	-370.00
LOW/ 4.820E+25 -2.80 590.0 /			
TROE/ .578 122.0 2535.0 9365.0 /			
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .70/			
CH2+O2=>2H+CO2	5.800E+12	.000	1500.00
CH2+O2<=>O+CH2O	2.400E+12	.000	1500.00
CH2+CH2=>2H+C2H2	2.000E+14	.000	10989.00
CH2 (S) +H2O=>H2+CH2O	6.820E+10	.250	-935.00
C2H3+O2<=>O+CH2CHO	3.030E+11	.290	11.00
C2H3+O2<=>HO2+C2H2	1.337E+06	1.610	-384.00
O+CH3CHO<=>OH+CH2CHO	2.920E+12	.000	1808.00
O+CH3CHO=>OH+CH3+CO	2.920E+12	.000	1808.00
O2+CH3CHO=>HO2+CH3+CO	3.010E+13	.000	39150.00
H+CH3CHO<=>CH2CHO+H2	2.050E+09	1.160	2405.00
H+CH3CHO=>CH3+H2+CO	2.050E+09	1.160	2405.00
OH+CH3CHO=>CH3+H2O+CO	2.343E+10	0.730	-1113.00
HO2+CH3CHO=>CH3+H2O2+CO	3.010E+12	.000	11923.00
CH3+CH3CHO=>CH3+CH4+CO	2.720E+06	1.770	5920.00
H+CH2CO (+M) <=>CH2CHO (+M)	4.865E+11	0.422	-1755.00
LOW/ 1.012E+42 -7.63 3854.0/			

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TROE/ 0.465 201.0 1773.0 5333.0 /
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .70/
O+CH2CHO=>H+CH2+CO2 1.500E+14 .000 .00
O2+CH2CHO=>OH+CO+CH2O 1.810E+10 .000 .00
O2+CH2CHO=>OH+2HCO 2.350E+10 .000 .00
H+CH2CHO<=>CH3+HCO 2.200E+13 .000 .00
H+CH2CHO<=>CH2CO+H2 1.100E+13 .000 .00
OH+CH2CHO<=>H2O+CH2CO 1.200E+13 .000 .00
OH+CH2CHO<=>HCO+CH2OH 3.010E+13 .000 .00
CH3+C2H5(+M)<=>C3H8(+M) .9430E+13 .000 .00
LOW/ 2.710E+74 -16.82 13065.0 /
TROE/ .1527 291.0 2742.0 7748.0 /
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .70/
O+C3H8<=>OH+C3H7 1.930E+05 2.680 3716.00
H+C3H8<=>C3H7+H2 1.320E+06 2.540 6756.00
OH+C3H8<=>C3H7+H2O 3.160E+07 1.800 934.00
C3H7+H2O2<=>HO2+C3H8 3.780E+02 2.720 1500.00
CH3+C3H8<=>C3H7+CH4 0.903E+00 3.650 7154.00
CH3+C2H4(+M)<=>C3H7(+M) 2.550E+06 1.600 5700.00
LOW/ 3.00E+63 -14.6 18170./
TROE/ .1894 277.0 8748.0 7891.0 /
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .70/
O+C3H7<=>C2H5+CH2O 9.640E+13 .000 .00
H+C3H7(+M)<=>C3H8(+M) 3.613E+13 .000 .00
LOW/ 4.420E+61 -13.545 11357.0/
TROE/ .315 369.0 3285.0 6667.0 /
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .70/
H+C3H7<=>CH3+C2H5 4.060E+06 2.190 890.00
OH+C3H7<=>C2H5+CH2OH 2.410E+13 .000 .00
HO2+C3H7<=>O2+C3H8 2.550E+10 0.255 -943.00
HO2+C3H7=>OH+C2H5+CH2O 2.410E+13 .000 .00
CH3+C3H7<=>2C2H5 1.927E+13 -0.320 .00
END

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