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Reduction of NOx Emissions in a Single Cylinder Diesel Engine Using SNCR with In-Cylinder Injection of Aqueous Urea

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Reduction of NO_x Emissions in a Single Cylinder Diesel Engine

Using SNCR with In-Cylinder Injection of Aqueous Urea

by

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Redacted

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ABSTRACT

The subject of this study is the effect of in-cylinder selective non-catalytic reduction (SNCR) of NO_x emissions in diesel exhaust gas by means of direct injection of aqueous urea $((NH_2)_2CO)$ into the combustion chamber. A single cylinder diesel test engine was modified to accept an electronically controlled secondary common rail injection system to deliver the aqueous urea directly into the cylinder during engine operation.

Direct in-cylinder injection was chosen in order to ensure precise delivery of the reducing agent without the risk of any premature reactions taking place. Unlike direct in-cylinder injection of neat water, aqueous urea also works as a reducing agent by breaking down into ammonia (NH_3) and Cyanuric Acid $((HOCN)_3)$. These compounds serve as the primary reducing agents in the NO_x reduction mechanism explored here. The main reducing agent, aqueous urea, was admixed with glycerol $(C_3H_8O_3)$ in an 80-20 ratio, by weight, to function as a lubricant for the secondary injector.

The aqueous urea injection timing and duration is critical to the reduction of NO_x emissions due to the dependence of SNCR NO_x reduction on critical factors such as temperature, pressure, reducing agent to NO_x ratio, Oxygen and radical content, residence time and NH_3 slip. From scoping engine tests at loads of 40 percent and 80 percent at 1500 rpm, an aqueous urea injection strategy was developed. The final injection strategy chosen was four molar ratios, 4.0, 2.0, 1.0 and 0.5 with five varying injection timings of 60, 20, 10, 0, and -30 degrees after top dead center (ATDC). In addition to the base line and aqueous urea tests, water injection and an 80-20 water-glycerol solution reduction agent tests were also conducted to compare the effects of said additives as well. The comparison of baseline and SNCR operation was expected to show

that the urea acted as a reducing agent, lowering NO_x emissions up to 100% (based on exhaust stream studies) in the diesel exhaust gas without the aid of a catalyst.

The data collected from the engine tests showed that the aqueous urea-glycerol solution secondary had no effect on the reduction of NO_x and even resulted in an increase of up to 5% in some tests. This was due to the low average in-cylinder temperature as well as a short residence time, prohibiting the reduction reaction from taking place. The neat water and water-glycerol solution secondary injection was found to have a reduction effect of up to 59% on NO_x production in the emissions due to the evaporative cooling effect and increased heat capacity of the water.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBREVIATIONS

ATDC – After Top Dead Center
BL – Baseline
BMEP – Brake Mean Effective Pressure
BSFC – Brake Specific Fuel Consumption
BTE – Brake Thermal Efficiency
$C_3H_8O_3$ – Glycerol
CFD – Computational Fluid Dynamics
CFR – Code of Federal Regulations
CH – Methylene Radicals
CH_2 – Methylene
CH_2NH_2 – Methenamine Radical
CH_2NH_2OO – Oxygenated Methenamine Radical
CH_3NH_2 – Methylamine
CH_4 – Methane
CI – Compression Ignition
CN – Cyanide
CO – Carbon Monoxide
$CO(NH_2)_2$ – Urea
CO_2 – Carbon Dioxide
CuZSM5 - Zeolite Socony Mobil–5
DAQ – Data Acquisition
DEF – Diesel Exhaust Fluid
DWI – Direct Water Injection
E10 – 10% Ethanol-Diesel Blend
E15 – 15% Ethanol-Diesel Blend
EGR – Exhaust Gas Recirculation
EPA – Environmental Protection Agency
FTP – Federal Test Procedure
GHG – Green House Gasses
H_2CN – Methyleneaminyl Radical
H_2O – Water
HC – Hydrocarbon
HCCI – Homogeneous Charge Combustion Ignition
HCN – Hydrogen Cyanide
HNCO – Isocyanuric Acid
HNO_2 – Nitrous Acid
HNO_3 – Nitric Acid
$(HOCN)_3$ – Cyanuric Acid
HSDI – High Speed Direct Injection
LNT – Lean NO_x Trap
LOI – Length of Injection
N and N_2 – Nitrogen
N_2H – Diazenylium
N_2O – Nitrous Oxide

Na_2CO_3 – Sodium Carbonate
NAC – NO_x Absorber Catalyst
NCO – Cyanate
NH – Imidogen
NH_2 – Amidogen
NH_2CH_2OOH – Aminomethanol
NH_3 – Ammonia
NO – Nitrogen Monoxide
NO_2 – Nitrogen Dioxide
NO_x – Oxides of Nitrogen
NSR – Normalized Stoichiometric Ratio
O and O_2 – Oxygen
O_3 – Ozone
OH – Hydroxide
PM – Particulate Matter
PPR – Pulses Per Revolution
SCR – Selective Catalytic Reduction
SET – Supplemental Emissions Test
SI – Spark Ignition
SNCR – Selective Non-Catalytic Reduction
SO_3 – Sulfur Trioxide
SOI – Start of Injection
V_2O_5 – Vanadium Pentoxide
VEFEL - Vehicles, Engines, Fuels, and Emissions Laboratory
WO_3 – Tungsten Trioxide

LIST OF SYMBOLS

$\dot{n}$ – Molar flow rate
m – Mass
$\dot{m}$ – Mass flow rate
M – Molar weight
P – Pressure
R – Gas Constant
T_{cyl} - Temperature
V – Volume
x – Concentration

1   INTRODUCTION

Practically all fossil fuel combustion processes produce harmful gas byproducts and particulate matter (PM), mainly composed of unburned and radical Hydrocarbons (HC), that pollutes the air and other numerous organisms and ecosystems [1]. Despite efforts to find less harmful alternative fuels and power sources such as solar and wind power, the burning of fossil fuels like oil, natural gas and coal, still remains the leading source of the world's energy production [2].

In an attempt to reduce the amount of pollutants and other harm to the environment, governments and agencies around the world have implemented standards and regulations to control the amount of air pollution produced by the burning of fossil fuels. In the United States, the Environmental Protection Agency (EPA) is the federal authority on creating regulations that govern interaction with the environment. The EPA regulates emissions on all fossil fuel burning processes from coal power plants to consumer gasoline lawn mowers. The EPA has set regulations on the amounts of particular types of vaporous byproducts in combustion emissions such as carbon monoxide (CO), PM and oxides of nitrogen (NO_x).

The EPA considers NO_x to be nitric oxide (NO) and nitrogen dioxide (NO_2) [3]. In combustion, the main constituents of NO_x are NO and NO_2 [4]. These gases are toxic to most living creatures and are highly reactive in the atmosphere. NO_x combines with available reactants to form ground level O_3, which is also toxic to humans, plants and other organic materials [1]. NO_x can also react with water (H_2O) to form nitrous acid (HNO_2) and nitric acid (HNO_3) in acid rain [4]. Photochemical smog can also occur when NO_x reacts with unburned HC and sunlight [1]. Current EPA NO_x emission standards for light-duty and heavy-duty automobiles can be found at the EPA's website [5].

NO_x is one of the key focuses of emission reduction in all combustion processes. The reduction of NO_x in diesel engines, specifically, has received worldwide attention due to its harmful health and environmental effects. Over the years, many NO_x reduction strategies have been tested and implemented. As emissions regulations become more stringent, more effective and efficient methods of reduction of NO_x will be necessary. One such method is the selective reduction of NO_x by the means of specialized reducing agents and injection techniques. Selective non-catalytic reduction (SNCR), unlike selective catalytic reduction (SCR), can achieve selective NO_x reduction without the addition of expensive and complicated secondary mechanisms like catalysts, and instead perform NO_x reduction directly in the cylinder. The object of this study was to reduce NO_x emissions in a single cylinder diesel engine by the secondary injection of aqueous urea directly into the cylinder.

2   LITERATURE REVIEW

2.1   NO$_x$ Formation

In stoichiometric or theoretical complete combustion, hydrocarbon fuel reacts with oxygen in air (O$_2$ and N$_2$) to release heat and form H$_2$O and CO$_2$, while the N$_2$ passed through unreacted. This of course is ideal and unfortunately, incomplete combustion occurs which leads to the additional formation of undesirable byproducts such as NO$_x$, CO, unburned HC, and PM. There are three mechanisms in which NO$_x$ is formed in the burning of fossil fuels: Thermal NO$_x$, Prompt NO$_x$, and Fuel NO$_x$ [6].

2.1.1   Thermal NO$_x$

The main mechanism of NO$_x$ formation in the combustion process occurs from the burning of fuel at high temperatures in a process known as Thermal NO$_x$. In heat engines, higher temperatures mean higher efficiency and the differences in temperatures at different states is what drives the cycle, typically from a hot state (high energy) to a lower heat state (low energy). Unfortunately, it is at these higher temperatures, typically above 1873 K, in which the strong triple bond in the atmospheric nitrogen (N$_2$) are broken to react with available oxygen (O and O$_2$) to form NO$_x$ [7]. The primary reactions of NO$_x$ formation were derived by Zeldovich in 1971 [6]. Equations 2.1 through 2.3 show the chemical reactions of N$_2$ breaking down and combining with radicals of O and Hydroxide (OH).

$$N_2 + O \rightarrow NO + N \hspace{4cm} \text{Equation 2.1}$$
In high temperatures the strong triple bond between the nitrogen atoms is broken and one nitrogen finds a radical oxygen atom and easily bond.

$$N + O_2 \rightarrow NO + O \hspace{4cm} \text{Equation 2.2}$$
Oxygen pairs are easily separated to eagerly combine with single nitrogen atoms.

$$N + OH \rightarrow NO + H \hspace{4cm} \text{Equation 2.3}$$
Hydroxide will also separate, and the radical oxygen will bond easily bond with the available nitrogen atom.

2.1.2 Prompt NO$_x$

The second NO$_x$ formation process in combustion is known as Prompt NO$_x$. This process of NO$_x$ formation was first discovered by Fenimore in 1971 [8]. This is when N$_2$ rapidly reacts in the first stages of combustion with O$_2$ and radical HC, typically carbon (C), methylidyne radicals (CH) and methylene (CH$_2$) to eventually form NO, NO$_2$, CO, and H$_2$O [1]. There are various intermediate molecules such as imidogen (NH), hydrogen cyanide (HCN), methyleneaminyl radical (H$_2$CN) and cyanide (CN-) that form and continue to react to eventually form NO$_x$ through numerous and complex chemical reactions [7]. This process typically takes place in the initial stages of combustion in fuel-rich regions near the flame front(s) [6]. The main reactions for the initial intermediate species are shown in equations 2.4 through 2.8.

$$CH + N_2 \rightarrow HCN + N \qquad \qquad \text{Equation 2.4}$$
Methylidyne radicals will combine with broken nitrogen pairs to form hydrogen cyanide.

$$CH_2 + N_2 \rightarrow HCN + NH \qquad \qquad \text{Equation 2.5}$$
Methylene will combine with broken nitrogen pairs to form hydrogen cyanide and imidogen.

$$CH_2 + N_2 \rightarrow H_2CN + N \qquad \qquad \text{Equation 2.6}$$
Methylene will combine with broken nitrogen pairs to form amidogen.

$$C + N_2 \rightarrow CN + N \qquad \qquad \text{Equation 2.7}$$
Carbon will combine with broken nitrogen pairs to form cyanide.

$$C_2 + N_2 \rightarrow CN + CN \qquad \qquad \text{Equation 2.8}$$
Broken carbon pairs will combine with broken nitrogen pairs to form cyanide.

Figure 2.1 from Miller and Bowman shows the different paths of NO$_x$ formation from the intermediate species in Prompt NO$_x$ [6].

Miller and Bowman - 1989
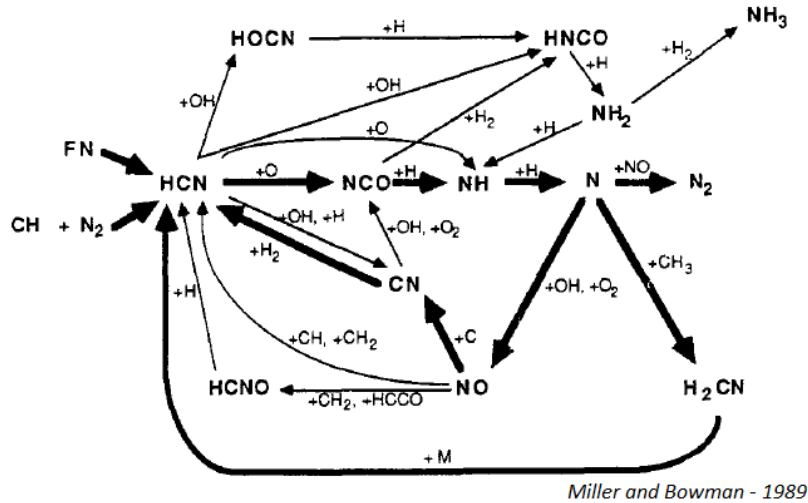
Figure 2.1 – Illustration of Prompt NO_x and Fuel NO_x paths of formation by Miller and Bowman, 1989 [6]

2.1.3 Fuel NO_x

The third mechanism of NO_x formation is known as Fuel NO_x. This process takes place when bounded nitrogen in certain fuels such as coal and petroleum bases directly oxidizes during combustion. This mechanism occurs due to the formation of HCN and NH_3 from the bounded fuel nitrogen [6]. These intermediate compounds are then oxidized in the early stages of combustion through a multitude of reactions. Again, these newly formed compounds complete hundreds of various reactions to eventually form NO_x. This mechanism is also illustrated in Figure 2.1 [6].

2.2 NO_x Reduction Strategies

For the last seven decades, since the discovery by Haagen-Smit that automobile exhaust was a major contributor to ground level ozone, scientists and manufacturers have been researching and developing methods to control harmful combustion emissions such as NO_x [9]. As regulations on combustion emissions have become more stringent over the years, a number of NO_x reduction strategies have been developed. This is especially true for diesel engine emissions, considering their vast consumer and commercial use. All methods of reducing NO_x in

diesel combustion can be placed in one of two categories: in-cylinder and after treatment. In-cylinder reduction usually refers to modification to the combustion process itself, including the use of fuel additives. After treatments are additional processes that occur downstream in the exhaust system, or post combustion.

2.3   In-Cylinder Reduction

One in-cylinder method to reduce NO_x in diesel engine exhaust is by reducing the combustion temperature. As previously stated, Thermal NO_x in emissions are the largest contributors of Diesel NO_x emissions. Different strategies to lower combustion temperature inherently produce different performance levels of NO_x reduction. As previously stated, significant NO_x formation in combustion typically starts to occur at 1873 K [7]. Though at lower temperatures, NO_x formation may be reduced, but an increase in PM will occur. This is because at lower temperatures and equivalency ratios unburned radical HC can form PM [10].

2.3.1   EGR

One temperature reducing NO_x reduction technique, and perhaps the most widely implemented in diesel engines, is exhaust gas recirculation (EGR). NO_x formation is greatest when combustion flame temperatures are high, so by lowering these temperatures increases the potential for unburned HC and PM formation. The EGR strategy redirects exhaust gases from the exhaust stream into the intake, ultimately reducing in-cylinder temperatures, as well as burning some of the unburned HC and PM [10]. In 1995, Pierpoint, et al. showed that with the triple injection strategy and 125 degree spray angle with 6% EGR, an approximate 40% reduction of NO_x and a 50% reduction in PM could be achieved at 75% load at 1600 rpm [11]. In these tests, it was shown that PM formation was reduced by modified injection strategies due to the improved mixing of air and fuel or an increase in homogeneity. Unfortunately, the reduction

technique in the aforementioned study greatly increased brake specific fuel consumption,

(BSFC) due mainly from the retardation of injection timing needed. More recently, however, a

low temperature EGR study by Mehrotra et al. in 2014 showed that with a combustion

temperature reduction of 275 to 323 K, a cumulative reduction of 16.14% in NO_x emissions and

23.33% reduction in PM emissions could be achieved while not affecting fuel economy [12].

2.3.2   Water Injection / Emulsification

Another in-cylinder temperature lowering technique for NO_x reduction is the use of water

injection or water emulsification of the diesel fuel. By adding liquid water to the combustion

process, an evaporative effect takes place, lowering the combustion temperature and in turn

reducing the amount of NO_x formed. This can be done by directly injecting the water into the

cylinder or into the intake manifold to mix with the intake air. A study by Ishida, et al. in 1997,

used gasoline injectors to port inject water into the intake manifold, reducing NO_x by 50% under

all operating conditions by maintaining a proper water-to-air ratio [13].

Another way of introducing water into the combustion process is stratified direct water-

diesel injection. This type of injection utilizes a single injector that introduces the diesel fuel and

water together instead of using separate injectors. Belford et al. in 2000 conducted a study using

KIVA-3V computational fluid dynamics (CFD) models and experimental test engine data on the

stratified water-diesel strategy [14]. In this study, two different levels of load, 44% and 86%,

were examined. Simulations and engine test data correlated to show an average reduction in NO_x

of 50.8% and 39.4%, respectively, while BSFC remained approximately the same at the 44%

load level. At the 86% load level, NO_x reductions of 85.6% in models and 71.1% in engine tests

where observed. Unfortunately, at the higher load, other emissions such as PM were higher with

an increase in BSFC of 9.1% in models and 15.6% in engine tests.

Much like water injection, water emulsification of diesel fuel, or mixture, introduces water into the combustion chamber to achieve lower temperatures. In a 2011 study by Mailboom and Tauzia, 25.6% water emulsified diesel fuel was injected into a 1.5L high speed direct injection (HSDI) automotive engine using four different injection strategies [15]. In this study, a maximum reduction in NO_x emissions of 50% was observed which varied depending on injection timing.

2.3.3 Fuel Additives

The use of additives to diesel fuel is another in-cylinder technique of reducing diesel emissions. Additives such as ethanol, biodiesel and cetane booster have been the subject of numerous emission reducing experiments. The results from the use of these additives to reduce NO_x emissions have been mixed depending on variables such as engine capability and fuel blend composition. A study by Li et al. in 2004, compared ethanol-diesel blends and the effects on engine performance and emissions [16]. The analysis concluded that NO_x emissions of the 10% ethanol-diesel (E10) and 15% ethanol-diesel (E15) blends were reduced by 2.2% and 4.2%, respectively, while also decreasing other emissions such as CO and an increase in brake thermal efficiency (BTE) from the addition of the oxygenated ethanol fuel. Unfortunately, the ethanol-diesel blends also showed an increase hydrocarbon emissions of up to 40%, as well as an increase of BSFC due to the reduced heating value of ethanol compared to diesel. In another study by Xing-cai et al. in 2004, ethanol-diesel blends were tested with the addition of cetane booster [17]. In this study, for an ethanol / diesel / cetane booster blend of 15% ethanol, 0.4% cetane booster (E15-D+0.4%), resulted in higher CO emissions but reduced NO_x by approximately 20% at 0.6 MPa brake mean effective pressure (BMEP). For bio-diesel / diesel blends, a 2009 study conducted by Thompson and Nuszkowski tested 10% (B10) and 20% (B20)

bio-diesel / diesel fuel blends on a 1992 Detroit Diesel Series 60 engine [18]. That study showed that while decreasing fuel consumption and other emissions, there was an increase of NO_x emissions of 3% and 5% in the B10 and B20 blends, respectively.

2.3.4 Alternate Combustion Strategies

Recently, in the push in efficiency and performance, alternative combustion strategies have been explored. Strategies such as dual fuel and Homogeneous Charge Compression Ignition (HCCI) utilize multiple fuels, typically a spark ignited (SI) fuel with a compression ignition (CI) fuel for initial detonation. Common SI fuels in these applications often include non-Nitrogen bound fuels such as natural gas (CH_4). Naturally, by implementing these non-Nitrogen bound fuels, a reduction in the production of NO_x in emissions by the Fuel NO_x mechanism of formation is achieved. In addition, this method makes it possible to achieve better homogeneous fuel mixing, reducing the likelihood of fuel rich areas in the combustion cylinder and thus the likelihood of forming Prompt NO_x. Initial attempts of diesel-natural gas HCCI engines were retro-fitted diesel engines that produced poor performance, reliability and emissions [19]. More recently, however, studies such as that conducted by Stanglmaier, et al. in 2001, have shown that a natural gas-diesel HCCI engine can decrease NO_x emissions by up to 90% while maintaining high load fuel efficiency and a 10 to 15% increase in low load fuel efficiency when compared to traditional spark ignited natural gas engines [20]. Other benefits to this strategy include the possibility to operate solely on diesel fuel if natural gas, or whichever SI fuel, may become scarce or unavailable [19]. Obvious downfalls of this strategy would be the initial cost of conversion of the vehicle as well as the current limited availability of natural gas in most markets, especially the consumer market.

2.4   After Treatments

After treatment strategies for emission reduction take place in the post-combustion exhaust stream. Such strategies almost always involve the addition of extra, and in most cases, costly equipment. Examples of such equipment may include precious metal catalysts, filters, injection systems, etc.

An example of an after treatment device for reducing NO_x are NO_x absorber catalyst (NAC) or lean NO_x traps (LNT). These catalysts are often constructed of multiple specific elements in order to achieve the desired NO_x control; for example, the use of platinum for oxidation of the NO_x, barium to store the NO_x and rhodium for NO_x reduction [21]. NAC absorb NO_x in lean burning conditions and then sequentially release the converted N_2 in rich burning purges [10]. This rich burning, or regeneration, is often done by the addition of flame igniter [10]. Also, since the use of these devices increases PM, many applications include the use of a PM filter to reduce PM emissions. In a study by West and Sluder in 2000, a Mercedes A170 was fitted with an aftermarket "light off" catalyst and NO_x absorber [22]. In this study NO_x reductions of up to 90% were achieved. In 2001, Schenk, et al. achieved reduction of NO_x in excess of 90% in testing of 1999 emission specification 5.9L medium-duty diesel engine over multiple steady-state operating conditions utilizing a dual path alternating flow restriction with catalyzed PM filters and NAC [23]. In a 2005 study by Hinz et al., a heavy-duty diesel, single leg strategy was tested [24]. The absorber catalyst system in this study incorporated a bypass during rich generation. A result of a 67% and 79% NO_x reduction was observed with the Federal Test Procedure (FTP) and the Supplemental Emissions Test (SET), respectively.

2.5   Selective Reduction

Another method of after treatment is the selective reduction of NO_x, a process in which NO_x is reduced by a specific chemical reaction by means of a reducing agent. Selective reduction of NO_x in combustion gasses was first discovered in 1972 by Lyon and the Exxon Research and Engineering Group and was patented in 1975 [25]. Lyon's method utilized the injection of Ammonia (NH_3) directly into combustion flue gas in the presence of excess O_2. Lyons original process, using NH_3 as the reducing agent, is called Thermal DeNO$_x$. Different reducing agents and the addition of a catalyst have also been adapted to the selective reduction strategy. Lyon's original reduction process is now known as SNCR while the addition of said catalyst has become known as SCR.

The chemical reaction mechanism behind the selective reduction of NO_x is centered on one main compound, amidogen (NH_2) [26]. In the Thermal DeNO$_x$ process, NH_3 reacts with OH, O, and H radicals that are available in the high exhaust gas temperatures (>1073 K) to form NH_2. These radicals are what are believed to "drive" the selective reduction process [27]. Lyon also showed that NH_3 for use in selective reduction assists in the reduction of sulfur trioxide (SO_3) and HC in combustion exhaust gasses [28]. Though there have been numerous reactions studied over the years for the Thermal DeNO$_x$ process, the main reactions are shown below in equations 2.9 through 2.13, as well as an illustration of further reaction processes from Kimball-Linne and Hanson, 1986 (Figure 2.2), showing diazenylium (N_2H) and other interstitial compounds [26]. Additional combustion products not including compounds of N_2 and O_2 are represented as the symbol M:
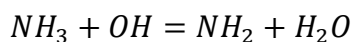
$$NH_3 + OH = NH_2 + H_2O \hspace{4cm} \text{Equation 2.9}$$
Ammonia will combine with hydroxide to form amidogen and water.
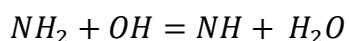
$$NH_2 + OH = NH + H_2O \hspace{4cm} \text{Equation 2.10}$$

Amidogen will combine with hydroxide to further breakdown into imidogen and water.

$$NH_2 + NO = N_2H + OH$$ Equation 2.11

Amidogen will combine will nitric oxide to form diazenylium and hydroxide.

$$NH_2 + NO = N_2 + H_2O$$ Equation 2.12

Amidogen will combine with nitric oxide to also form nitrogen and water.

$$N_2H + M = N_2 + M$$ Equation 2.13

Diazenylium will combine with additional products (excluding nitrogen and oxygen) to nitrogen and other additional products.
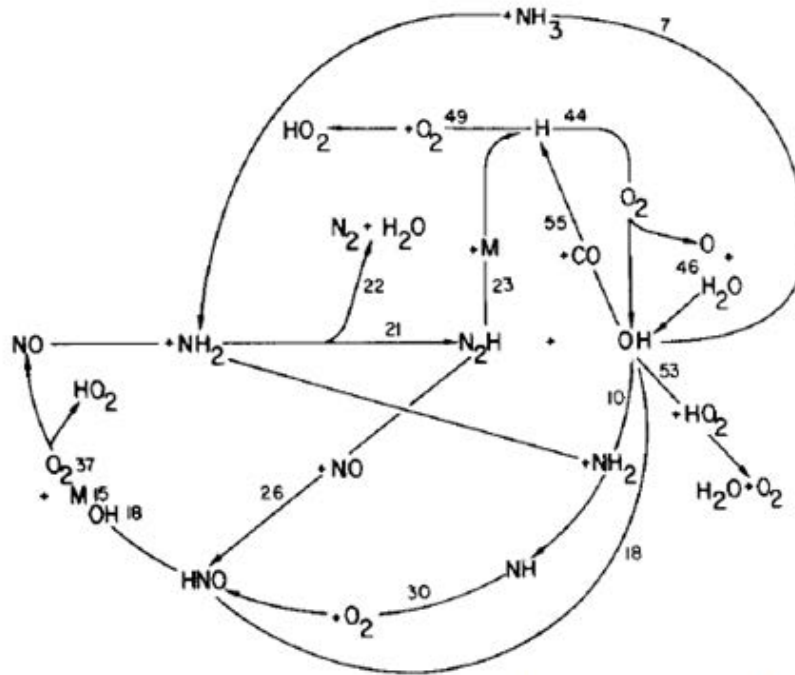
Kimball-Linne and Hanson - 1986

Figure 2.2 – Illustration of further Thermal DeNO$_x$ reactions by Kimball-Linne and Hanson, 1986 [26]

Another agent that has been studied in the selective reduction of NO$_x$ is cyanuric acid

((HOCN)$_3$), which breaks down into isocyanic acid (HNCO) when exposed to high temperatures.

This selective reduction process using HCNO as the reducing agent has become known as

REPRENO$_x$ which is an abbreviation for rapid reduction of NO$_x$ [29]. This process is said to be

rapid due to the speed at which the reduction reaction takes place. One drawback to this

reduction process is the excess of N$_2$O byproducts from NO$_x$ reduction due to the interstitial

formation of the compound cyanate (NCO) [6]. The primary selective reduction reactions for this process are shown below in equations 2.14 and 2.15 [29]:

$$HNCO + OH = NCO + H_2O$$

Equation 2.14

Isocyanic acid combines with hydroxide to form cyanate and water.

$$NCO + NO = N_2O + CO$$

Equation 2.15

Cyanate will react with nitric oxide to form nitrous oxide and carbon monoxide.
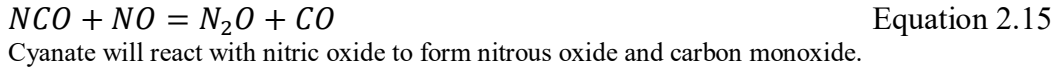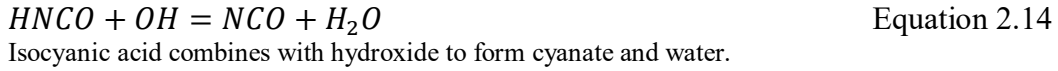
An alternative reducing agent for the selective reduction of NO_x is urea ($CO(NH_2)_2$), and was first patented in 1980 by Arand et al. [30]. This process of using urea as the reducing agent has become known as the NO_xOUT process [4]. Unlike NH_3, urea is nontoxic and easily transported, especially when in an aqueous solution, making it more practical for use in mobile applications [31]. In addition, urea is an ideal agent for selective NO_x reduction for it is a carrier of NH_3 and HNCO and thus combining the Thermal $DeNO_x$ and $REPRENO_x$ reduction processes. It has been shown decomposition of urea produces equal parts of NH_3 and HNCO [29]. The decomposition reaction of urea is shown in Equation 2.16:

$$CO(NH_2)_2 = NH_3 + HNCO$$

Equation 2.16

Urea will decompose into ammonia and isocyanic acid.
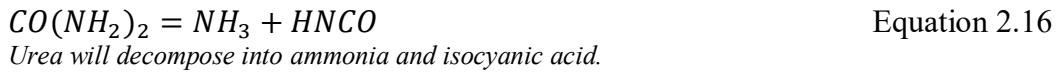
An illustration of urea decomposition and NO_x reduction mechanism by Caton and Siebers, 1989 can also be seen below in Figure 2.3 [29]:

Caton and Siebers - 1989
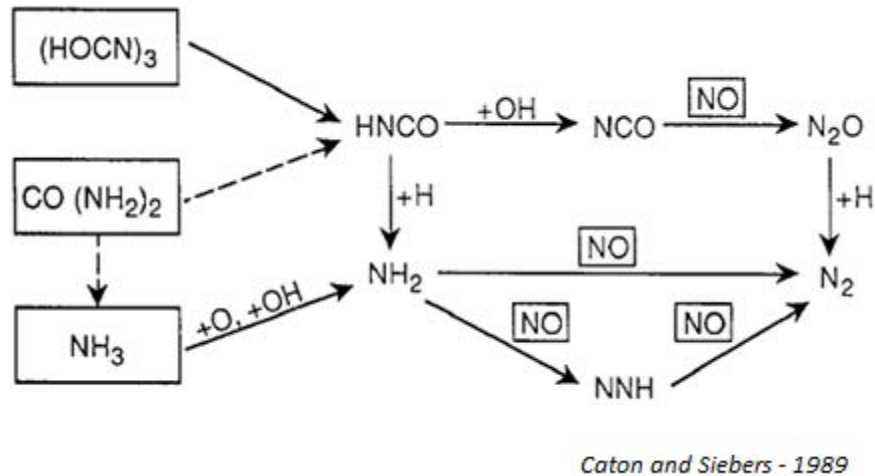
Figure 2.3 – Illustration of urea decomposition and NO_x reduction mechanism by Caton and Siebers, 1989 [29]

More recently, the reducing agent Methylamine (CH_3NH_2) has been studied as an alternative to the ammonium species. This agent has a NH_2 molecule as part of its main composition. CH_3NH_2 is desirable in NO_x reduction primarily due to its low reaction temperature for the selective reduction process. CH_3NH_2 reacts with NO closer to the diesel exhaust stream temperatures at around 573 K, compared to NH_3 and HNCO that begins to react with NO at around 1023 K [32]. Average diesel exhaust system temperatures were measured to be approximately 633 K [33]. The main decomposition reactions for CH_3NH_2, presented by Minkoff and Tipper, 1962, are shown below in equations 2.17 through 2.21 [34]:

$$CH_3NH_2 + O_2 = CH_2NH_2 + HO_2 \qquad \text{Equation 2.17}$$
Methylamine combines with oxygen to form methenamine radicals and water.

$$CH_2NH_2 + O_2 = CH_2NH_2OO \qquad \text{Equation 2.18}$$
Methanamine radicals will further combine with oxygen to form oxygenated methenamine radicals.

$$CH_2NH_2OO = NH_3 + CO + OH \qquad \text{Equation 2.19}$$
Oxygenated methenamine radicals will then break down into ammonia, carbon monoxide and hydroxide.

$$CH_2NH_2OO + CH_3NH_2 = NH_2CH_2OOH + CH_2NH_2 \qquad \text{Equation 2.20}$$
Oxygenated methenamine radicals will also combine with Methylamine to form aminomethanol and methenamine radicals.

14

$$NH_2CH_2OOH = NH_2 + CH_2O + OH \qquad\qquad \text{Equation 2.21}$$
Aminomethanol will also break down in amidogen, formaldehyde and hydroxide.

From these species, the NO_x reduction follows the NH_2 reactions from the Thermal DeNO$_x$ process mentioned above.

2.5.1 SCR

In recent implementations of selective reduction of NO_x in diesel exhaust emissions on heavy duty engines, the addition of a reduction catalyst to the exhaust system has been common, specifically with aqueous urea as a reduction agent. The use of catalysts in selective reduction has dated back more than 50 years in stationary power systems, as reported by Mitsubishi Chemicals [35]. In SCR, the catalyst aids in the reduction in multiple ways. One way the catalyst aids selective reduction is in the decomposition of urea into NH_3 and HNCO. The typical temperature necessary for urea decomposition, as reported by Alzueta et al., is just below 1300 K, while complete decomposition of urea can occur with a catalyst at around 623 K [31]. With typical composition of a copper exchanged Zeolite Socony Mobil–5 (CuZSM5) catalyst, which is a common catalyst for SCR, the hydrolysis of HNCO can be as high as 95% conversion into NH_3 at a rapid rate at temperatures as low as 423 K [31].

In addition to aiding urea decomposition, SCR can theoretically remove NO_x with 100% efficiency, or complete NO_x reduction [36]. Studies completed on SCR have shown up to 80% NO_x reduction at exhaust temperatures as low as 673 K without any additional emissions control, as reported in a numerical study by Hui, Boyan and Wang in 2014 [36]. In a 1993 study by Hug et al., up to 95% NO_x, as well as over 50% CO and over 89% HC reduction is achievable through Urea-SCR when used in conjunction with additional emissions reducing devices such as oxidation catalysts and traps [35].

2.5.2 SNCR

Despite the recent implementation of SCR in automotive diesel exhaust, research and development of SNCR is still a popular topic among engineers. This continued push in SNCR technology is primarily due to the excessive costs and complexity of the SCR strategy. A noteworthy example is presented by Lyon in his 1987 report on Thermal $DeNO_x$, where it points out the obvious cost difference in the two selective reduction techniques, showed then to be over \$1/lb NO_x removed [28]. This main cost of SCR Lyon refers to comes with the metal catalysts such as CuZSM5, Vanadium Pentoxide (V_2O_5), or Tungsten Trioxide (WO_3) / Titanium Dioxide (TiO_2) used in stationary power production plants at the time.

In a flow reactor study conducted by Bowman and Hanson in 1997, NO_x reduction of up to 80% was achieved with the injection of NH_3 into the chamber after the burner [27]. A flow reactor is a type of laboratory furnace in which gases can be introduced and temperature controlled precisely. Nam and Gibbs in 2012 conducted an experimental and kinetic model study of NH_3 reduction of NO_x in a stainless steel flow reactor to simulate in-cylinder and exhaust pipe conditions [37]. That study showed a 34% reduction of NO_x was achieved with a 1.5 molar ratio of reducing agent to NO_x and an optimum temperate of 1240 K.

Miyamoto et al., in 1994, obtained up to 60% NO_x reduction without an increase in smoke (PM and unburned HC) or BSFC by injecting aqueous urea while testing different ammonium compounds [38]. This was done by injecting the reducing agent directly into the cylinder of a single cylinder swirl chamber engine under a single load BMEP of 0.4 and at 500 rpm injected at multiple NH_3/NO_x ratios and injection timings. In 1998, Willand et al. conducted numerical simulation of aqueous urea injection into cylinder, as well as experimental injection into the immediate exhaust exit (top of the exhaust valve) at different NH_3/NO_x ratios and

injection timings [39]. This study showed that a 65% NO_x reduction is obtainable when aqueous urea was injected into the combustion chamber when exhaust temperatures were increased to 923 K by increasing backpressure. Hossain et al, in 2004 experimented with a pilot-scale diesel reactor to test injection of aqueous urea with a commercial grade sodium carbonate (Na_2CO_3) additive [40]. The best results in that study showed that with a 5% addition of Na_2CO_3 to aqueous urea solution, a reduction in NO_x of 69% was obtainable. This is due primarily from the effect of larger droplet size and respective "survivability" in high exhaust temperature allowing further NO_x reduction to take place. In 2006, Nam, et al. tested aqueous urea injection into a simulated diesel flow reactor, achieving NO_x reduction of 40-60% depending on normalized stoichiometric ratios (NSR) of reducing agent to NO_x [41]. A 2007 numerical evaluation using KIVA-3V code by Golovitchev, et al. was conducted on the reduction of NO_x from in-cylinder direct injection of aqueous urea [42]. In this simulation study, a Direct Water Injection (DWI) duel fuel injector was used to inject the aqueous urea directly into the flame plume during combustion. It was shown that NO_x was able to be reduced, hypothetically, by 80% with proper injection timing and optimized urea content of the solution.

In a 2003 study by Nakanishi et al., the injection of CH_3NH_2 into a flow reactor attached to the exhaust of a single cylinder four-stroke, water cooled diesel engine was reported [34]. The reaction chamber incorporated an electric heater to sustain adequate temperatures for the reduction process. Results showed a 64% reduction in NO_x at a temperature range of 673-813 K and molar ratio of 1 without any additional reducing device and up to 80% with the addition of a pre-SNCR inline particulate filter. In another Methylamine study conducted by Xu et al. in 2011, an 80% reduction in NO_x at a 1.2 CH_3NH_2 to NO_x ratio at 693 K was obtained [32].

2.6 Important Factors

In the selective reduction of NO_x, especially in SNCR, there are a number of important reaction conditions that must be met in order to achieve optimal reduction, as well as characteristics of particular importance in the reduction processes. These factors, are: temperature and pressure; reducing agent-NO_x ratio; oxygen and radical content; residence time; and NH_3 slip.

2.6.1 Temperature

Perhaps the most critical reaction condition for SNCR to be effective is the temperature window at which it occurs. This becomes particularly important when addressing such factors as reducing agent, method in which the agent is introduced, and location in the combustion process where the agent is introduced. In Lyon's initial NO_x reduction strategy, it is indicated that the NO and NH_3 reduction reactions takes place at 1123-1423 K [25]. The formation of NH_2 from NH_3 occurs at a "narrow temperature range around 1300 K" [38]. One factor in the temperature window is exhaust composition, specifically O_2 content [43]. This window becomes increasingly important in NO_x reduction due to undesirable effects of too low or too high of a temperature. At low temperatures, NH_3 doesn't react and passes through to the atmosphere. As temperatures approach and exceed the typical window, the reduction of NO_x decreased and may increase NO_x emissions from non-treated exhaust levels due to the oxidation of the NH_3 [43]. According to most of the studies examined, the peak reaction occurs at around 1250 K [25, 38, 43].

2.6.2 Pressure

Some studies on SNCR refer to the effect of pressure on the reduction reaction of NO_x. These studies seem to be contradictive. Kasuya et al. with a flow reactor experiment, concluded that higher pressures adversely effected the reduction NO_x due to excessive molar concentrations

of O_2 [43]. While Bowman and Henson showed that in jet turbine exhaust elevated to 20 atm the NO_x reduction was about the same as 1 atm, and a widening of the reduction temperature window to 1200-1500 K with a peak reduction at around 1325 K at the higher pressure [27].

2.6.3 Reducing Agent/NO$_x$ Ratio

Ratio of reducing agent added to NO_x content in the exhaust in the selective reduction process are typically described as NSR or molar ratios. It has been shown that the ratio of reducing agent to NO_x and proper mixing plays an important role in reduction especially at different temperature levels and residence times [32, 34, 38, 39, 41]. In all studies examined, the average reducing agent / NO_x ratio that was most effective was between 1 and 4, with most finding the optimal ratio at around 1.5.

2.6.4 Oxygen and Radical Content

Oxygen and radical content refer to the amount of O_2, O, H and OH available during the reduction process. In the prior discussion of NO_x formation and reduction mechanisms, these radical elements play a substantial role [4] [25, 27, 34, 43]. Specifically, the availability of excess oxygen and the role it plays on NO_x reduction as a function of O_2. A minimum of 2% available excess O_2 is needed for reduction to occur [4]. Radicals of O, H, and OH begin to generate at temperatures over 923 K [34]. It is these radicals that combine and break down NO_x into N_2 and N_2O [27].

2.6.5 Residence Time

Residence time refers to the amount of time available for the reduction reactions to take place. Temperature effects the residence time requires as shown by Willand et al. [39]. The residence time usually depends on the speed of the exhaust gas. That is why, in most studies

examined, high rates of NO_x reduction are obtainable at lower engine speeds as seen in Miyamoto et al., 1995 [38].

2.6.6 NH₃ Slip

Another important factor in both SCR and SNCR is NH_3 slip. This is when NH_3 passed through unreacted. This is critical from an environmental stand point as NH_3 emissions, though not regulated in the United States, are regulated in many other countries [44]. In addition, as a regulated emission, NH_3 is considered hazardous to living creatures. NH_3 slip is directly dependent on many factors in the reduction of NO_x emissions such as injection method and location, as well as configuration of the reducing process [44].

3   EXPERIMENTAL SETUP AND PROCEDURE

This experiment explored the in-cylinder SNCR of NO_x emissions of a single cylinder diesel test engine while operating under two loads at low engine speed with the varying secondary injection timing and duration. This study focused on the testing of direct injection of secondary reducing agents being compared to baseline, diesel-only operation. NO_x emissions from these tests will be compared in order to observe maximum reduction. In addition to the NO_x emissions, maximum in-cylinder temperature and O_2 percentage of the emissions were observed. For the study, testing was carried out at the University of North Florida's Vehicles, Engines, Fuels, and Emissions Laboratory (VEFEL). A picture of the testing equipment and the overall testing configuration is shown in Figure 3.1. A complete table of all sensors and measuring equipment can be found in Appendix 1.
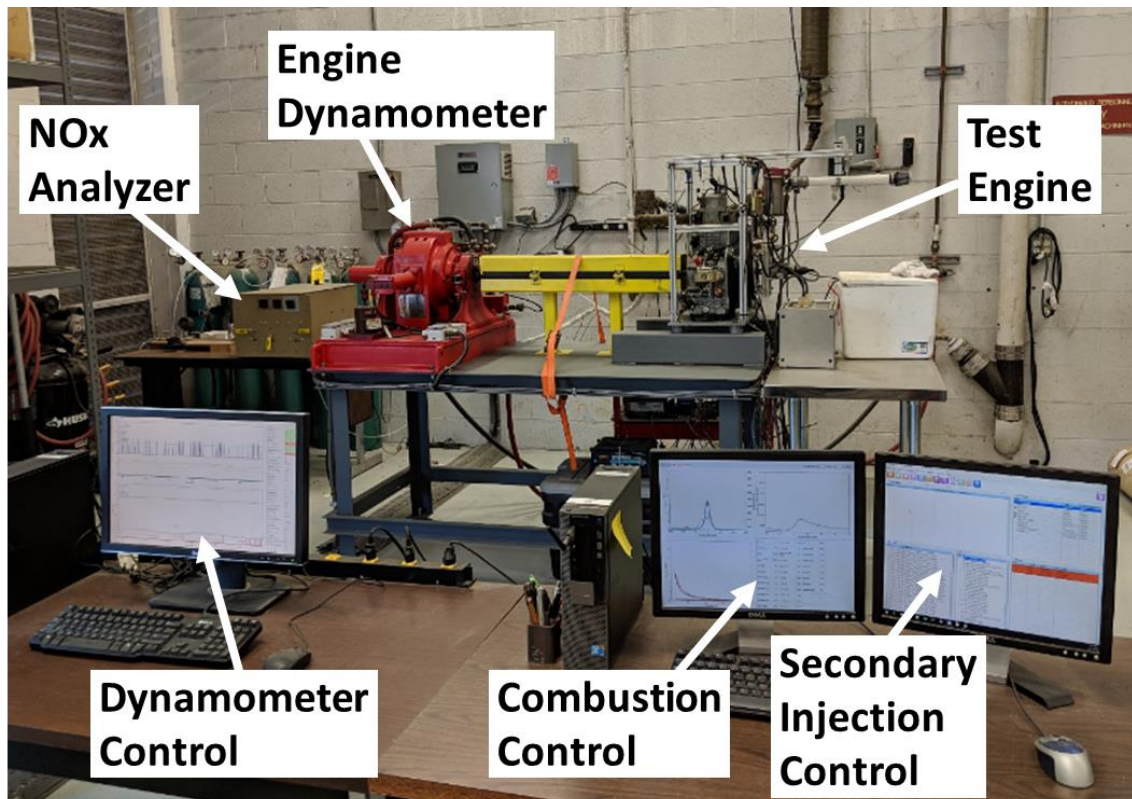
Figure 3.1 – Testing equipment at the University of North Florida's Vehicles, Engines, Fuels, and Emissions Laboratory
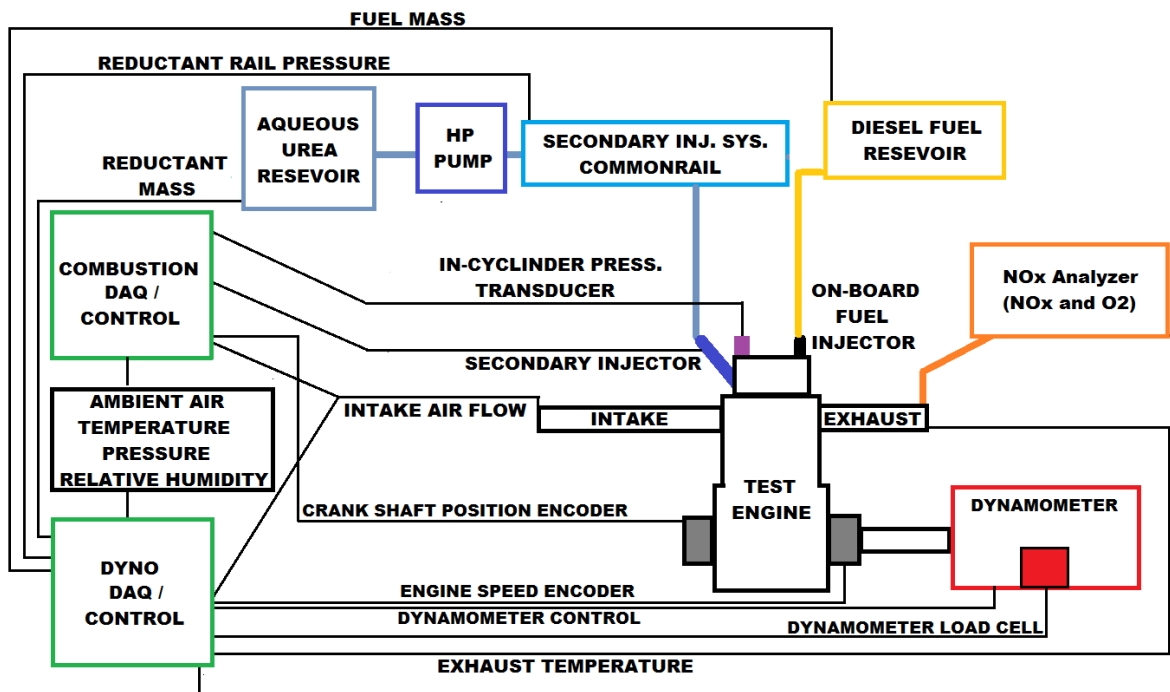
Figure 3.2 – Test Schematic

3.1 Test Fuels and Reducing Agent

3.1.1 Diesel Fuel

For the diesel fuel, standard highway low-sulfur diesel provided from the University of North Florida on-site fuel station was utilized. All fuel used in the experiments were from the same single fill fuel storage container in order to maintain consistency of fuel properties between re-fueling. The main diesel fuel for engine operation was supplied by the stock mechanical primary fuel pump on the engine.

3.1.2 Primary Reducing Agent / Aqueous Urea

The aqueous urea reducing agent was Peak[©] Blue[®] diesel exhaust fluid (DEF). DEF is 32.5% urea and 67.5% deionized water, by mass. This concentration of urea in water is standardized as aqueous urea solution 32 (AUS 32) in ISO 22241 [45].

3.1.3   Secondary Injection Testing Blends

When implementing the secondary injection of aqueous urea, in order overcome lubricity issues with the repurposed VW diesel injectors, the primary reducing agent tested was an 80-20 blend by mass of aqueous urea and glycerol ($C_3H_8O_3$). Due to the addition of glycerol to the aqueous urea, the test sequence for SNCR was repeated with an 80-20 water-glycerol blend, by mass, to determine the effects of the glycerol. Additionally, since the urea was in an aqueous solution, the effects of evaporative cooling and added energy capacity of the water on the reduction process were considered with a third reducing agent of neat water was also tested. This means, that in total, there were three different reducing agent blends (by mass) tested via the direct injection by the secondary injection system were:

1. 80-20 Aqueous Urea – Glycerol

2. 80-20 Water – Glycerol

3. Neat Water

3.2   Test Engine

A Changfa Apollo CF186 air cooled four stroke CI engine (Figure 3.2) was used for this experiment. This engine is mechanically controlled by an on-board diesel fuel pump. The cylinder head of the engine was modified by machining additional ports which were added to equip the secondary injector as well as the in-cylinder pressure transducer. The test engine specifications are shown in Table 3.1. The test engine was also equipped with a custom exhaust that has been fitted with a heated sample probe for the NO_x analyzer. Attached in line with the engine shaft and dynamometer, a BEI Sensors, Express® displacement encoder, model H20 with 1440 pulses per revolution (PPR) resolution was used for engine crank shaft position.
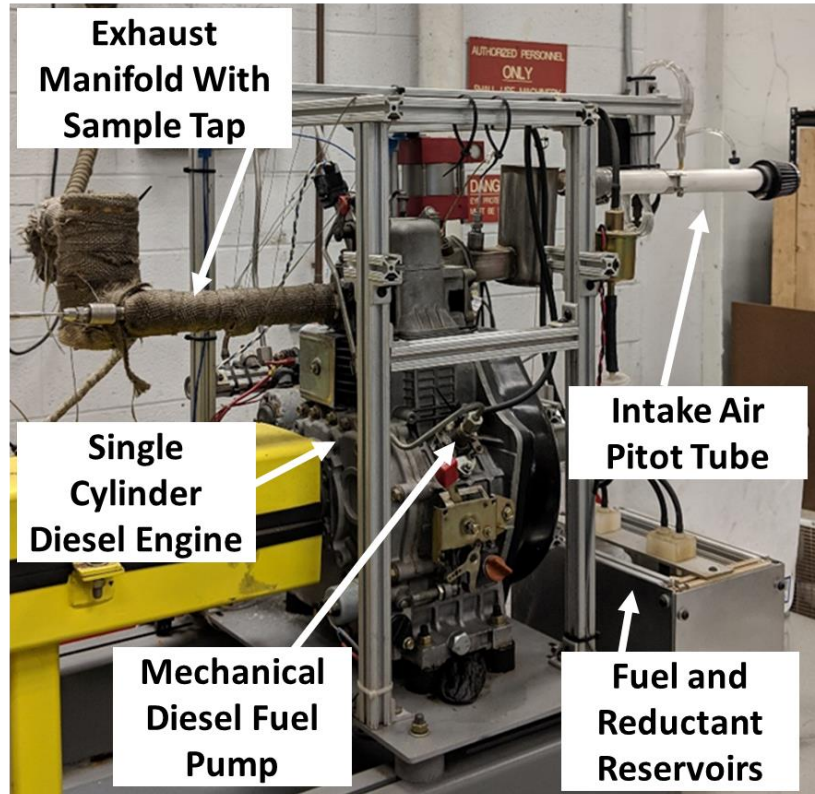
Figure 3.3 – Changfa Apollo CF186 single cylinder diesel engine

Table 3.1 – Test Engine Specifications

Engine Model	Changfa Apollo CF186
Engine Type	Air Cooled, Four Stroke
Bore and Stroke (mm)	86x72
Compression Ratio	19:1
Total Displacement (cm^3)	418
Rated Speed (rpm)	3600
Rate Power (kW)	9.1
Intake	Natural Aspiration
Ignition Type	Compression Ignition
Primary Fuel Injection System	Pump Line Nozzle
Primary Fuel Injection Pressure	200 MPa
Secondary Injection System	Common Rail
Secondary Fuel Injection Pressure	500 MPa

3.3   Secondary Common Rail Injection System

A VW electrically controlled common rail diesel fuel injection system from a 2012 Jetta

TDI was used for the secondary injection system, as shown in Figure 3.3. This system was used

to inject the reducing agent directly into the combustion cylinder for SNCR testing. This VW common rail injection system included the fuel common rail with pressure regulator valve and rail pressure transducer, as well as the fuel lines and diesel fuel injector. The stock injector supply line was replaced with a custom supply line to accommodate the changes in mounting location and geometry. Since the system is designed to deliver fuel for a turbocharged diesel engine, it was well suited for the secondary in-cylinder injection of aqueous urea into the test engine, and able to overcome the high in-cylinder pressures.
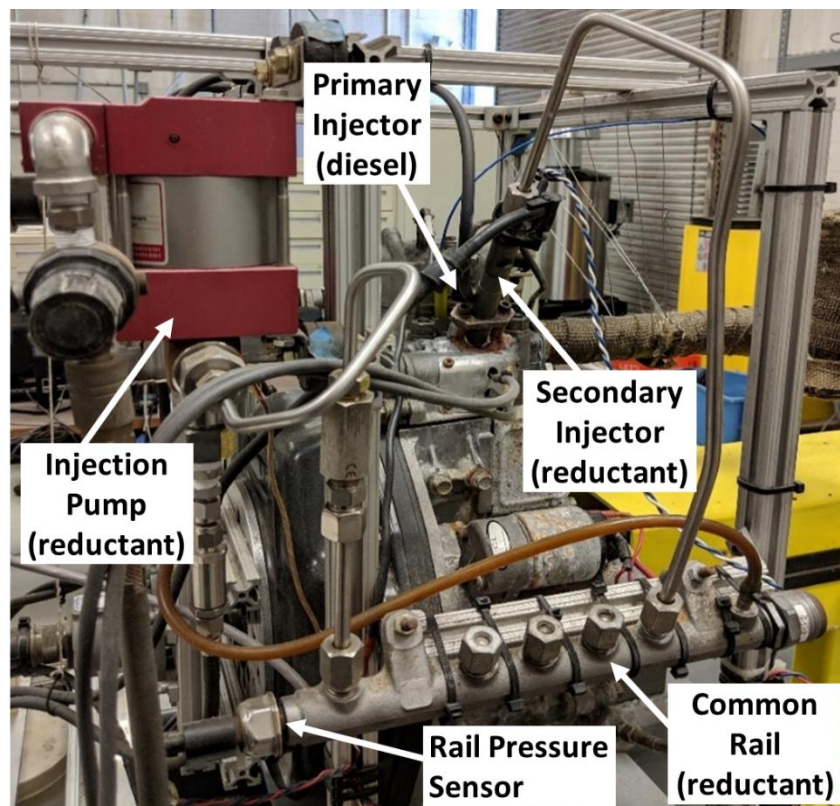
Figure 3.4 – VW common rail injection system used for secondary in-cylinder injection

The high-pressure pump used for supplying the aqueous urea to the common rail system is a Maxpro Technologies, Inc. MAXIMATOR® PP-189 VP air driven liquid pump. This pump has a maximum outlet pressure of 220 MPa, which worked suitably with the aqueous urea in-cylinder injection [46]. This high injection pressure was necessary to overcome in-cylinder

pressures at time of injection. Prior to the experiments, all the injectors were test benched with the aqueous urea-glycerol blend, the water-glycerol blend, and neat water in order to calibrate the mass injected as a function of injector pulse width.

3.4   Engine Dynamometer

To simulate engine loads and measure engine torque output, an eddy current dynamometer was installed in line with the test engine output shaft. The dynamometer that was used is a wet gap Dynamatic Absorbing Dynamometer Model 758 DG (Figure 3.4). This engine dynamometer has a maximum power rating of 50 hp, which will accommodate the 10 hp Changfa test engine. An additional encoder was installed on the dynamometer's opposing shaft to record engine speed.
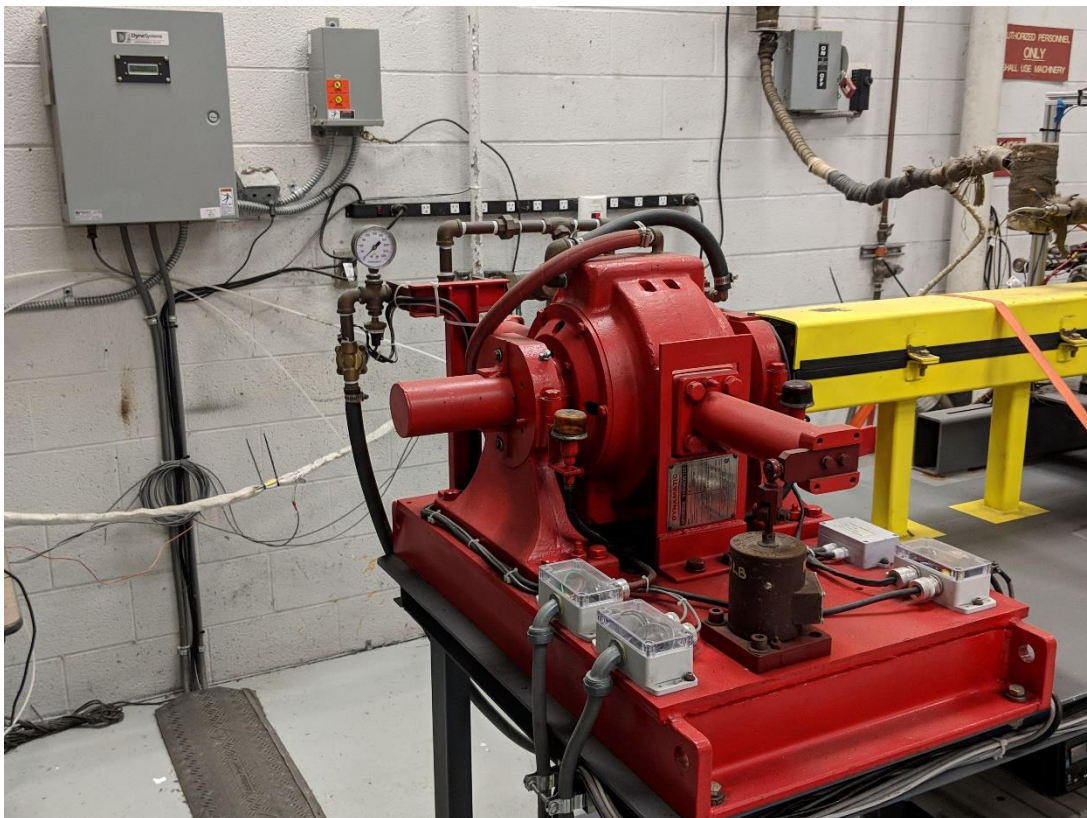
Figure 3.5 – Dynamatic Absorbing Dynamometer Model 758 DG

3.5   NO$_x$ Analyzer

The NO$_x$ analyzer used in this study is a custom-made in-house device using a Ford NO$_x$ sensor and control module, as shown in Figure 3.5. These sensors are common to multiple existing automotive emissions applications available on the market today, such as automotive diesel SCR exhaust systems. The analyzer included two valve selectable flow paths with catalysts for the measurement of NO$_x$ and NO$_x$ + NH$_3$ and by subtraction, a measurement of NH$_3$ was obtained. This sensor can identify said gas composition to 1 ppm and has been tested in-house to have an accuracy of within 2% when measuring NO compared to calibration gases [47].

Figure 3.6 – In-house NO$_x$ analyzer

The in-house NO$_x$ analyzer was calibrated for accuracy prior to connection to the test engine exhaust stream was made. The calibration was done using laboratory grade samples of N$_2$, O$_2$, NO, NO$_2$, and NH$_3$. Each bottle of these calibration gases were certified Primary Standard grade and were to +/- 2% accuracy of composition. In addition to initial calibration,

zero and span tests were performed in between each trial in order ensure NO_x measurement accuracy.

3.6   Data Acquisition and Monitoring

The testing apparatus was split into two separate control and data acquisition (DAQ) systems: Dynamometer and Combustion. Each system utilizes a custom written Python control and data collection program.

3.6.1   Dynamometer DAQ System

The dynamometer DAQ system controlled both engine and dynamometer operation, as well as recording input data from the engine and dynamometer. Additionally, for this experiment the Dynamometer DAQ system was utilized in the monitoring of NO_x emissions and O_2 percentage in the exhaust stream, as well as intake and exhaust flow rates. Table 3.2 shows the control functions, data acquired and data calculated of the dynamometer DAQ system.

Table 3.2 – Dynamometer DAQ system data acquired and control function

Function Control	Data Monitored	Data Calculated
Dynamometer Load Control (variable control)	Time (s)	Engine Power (W)
Diesel Fuel Supply Pump (on/off)	Dynamometer System Status (disabled/enabled)	BMEP (kPa)
Engine Starter (on/off)	Engine Speed (rpm)	Intake Air Flowrate (g/s)
Exhaust Blower (on/off)	Engine Torque (N-m)	Diesel Fuel Flowrate (g/s)
	Engine Oil Pressure (kPa)	Air to Fuel Ratio (-)
	Engine Oil Temperature (°C)	Exhaust Mass Flowrate (g/s)
	Ambient Air Pressure (kPa)	Exhaust Molar Flowrate (mol/s)
	Ambient Air Temperature (°C)	NO_x Exhaust Mass Flowrate (g/s)
	Intake Air Pressure (kPa)	CO_2 Exhaust Mass Flowrate (g/s)
	Intake Air Flow Pitot Tube (ΔPa)	
	Intake Air Temperature (°C)	
	Secondary Injection Rail Pressure (bar)	
	Reductant Reservoir Mass (g)	
	Diesel Fuel Reservoir Mass (g)	
	NO_x Exhaust Concentration (ppm)	
	O_2 Exhaust Concentration (%)	
	CO_2 Concentration (%)	
	Relative Humidity (%)	

3.6.2 NO_x Emission Mass Flow Rate

Part of the dynamometer DAQ system was the calculation of NO_x mass flow rate (g/s) which comes from the conversion of NO_x concentration measured by the NO_x analyzer as per the Code of Federal Regulations (CFR), section 40, part 1065 shown in Equation 3.1 [48]. In order to calculate NO_x mass flow rate, the molar mass (M) of NO_x, corrected concentration and the exhaust molar flow rate were required. From the CFR, the NO_x concentration was corrected for intake air temperature and humidity (40 CFR equation 1065.670-1). This correction aids in

taking into account the ambient conditions effect on NO_x formation and reduction. The exhaust molar flow rate was found using a chemical balance (40 CFR equation 1065.655-20) based on the intake air flow from an averaging pitot tube and on the fuel flow from a scale. It should be noted that UNF's VEFEL used the CFR 1065 as a guidance but was not a CFR 1065 compliant laboratory.

$$\dot{m}_{NOx} = M_{NOx} x_{NOx,cor} \dot{n}_{exh}$$ Equation 3.1

Mass flow rate of NO_x is found by multiplying the molar weight by the corrected NO_x concentration and exhaust molar flow rate, as per the CFR Section 40 Part 1065

3.6.3 Combustion DAQ System

The combustion DAQ system's primary function was to monitor combustion while controlling the secondary injection system. Table 3.3 shows the functions controlled, data collected, and data calculated by the combustion DAQ system.

Table 3.3 – Combustion DAQ system data acquired and control function

Function Control	Data Monitored	Data Calculated
Injection Start Time (°ATDC)	Crank Angle (° ATDC)	Intake Air Flow (kg/min)
Length of Injection (°)	Exhaust Temperature (K)	Exhaust Flow (kg/min)
	Maximum In-Cylinder Pressure (kPa)	Air to Fuel Ratio (-)
	Ambient Air Pressure (kPa)	IMEP (kPa)
	Ambient Air Temperature (°C)	Average In-Cylinder Temperature (K)

3.6.4 Single Zone In-Cylinder Combustion Model

To observe the average in-cylinder temperature (T_{cyl}), a single zone model calculation was used based on the ideal gas law, shown in Equation 3.2, and then rearranged to find the average in-cylinder temperature in Equation 3.3. The mass and the gas constant were found by assuming that the in-cylinder pressure and temperature were the same as the intake pressure and temperature at inlet valve closing. In addition, the continuously measured in-cylinder pressure and the calculated cylinder volume based on crank angle were used to find the average in-

cylinder temperature. This single zone model provides a way to monitor theoretic average in-cylinder temperature based on the cylinder pressure during combustion. This temperature was used to observe and gage the appropriate temperature window for the SNCR reactions.

$$P_{cyl}V_{cyl} = m_{cyl}RT_{cyl}$$
Ideal gas law.

Equation 3.2

$$T_{cyl} = \frac{(PV)_{in-cyl}}{(mR)_{inlet}}$$
Ideal gas law rearranged to solve for in-cylinder temperature.

Equation 3.3

3.7 Test Sequence and Method

3.7.1 Scoping

Prior to carrying out the experiments, preliminary baseline scoping tests were operated at both engine loads to determine the baseline NO_x concentration in order to calculate the amounts of reducing agent to NO_x emissions (NH_3/NO_x) molar ratios.

3.7.2 Baseline Testing

In order to establish proper baseline data for the percent reduction of NO_x comparison, multiple baseline (BL) tests were performed. These baselines tests were carried out at the start of each set of tests, as well as in between and after each change in the length of injection (LOI) or NH_3/NO_x molar ratio test sets. This means that for the four molar ratios tested, a before and after baseline test was performed. This was repeated for each reducing agent and for both loads tested. The purpose of the interstitial or "in-between" baseline tests was to reduce the influence of the varying engine and environmental conditions and give a precise percent reduction of NO_x.

Additionally, the complete set of baselines for each load were compiled for each load and analyzed for variation and repeatability. For each load tested, the average, standard deviation, maximum, minimum, range, as well as the 95% confidence intervals were found. From the

maximum and minimum, the baseline NO_x levels significance for the reduction results were determined.

3.7.3 SNCR Engine Operation

Based on the baseline engine test data, such as in-cylinder temperature, pressure, residence time, and NO_x concentration, a secondary aqueous urea injection strategy was implemented for the SNCR operation tests. The SNCR operation tests included testing of the two different variables: start of secondary injection and secondary injection duration (molar ratio of NH_3/NO_x). For all tests, secondary injection pressure was held constant at 500 bar.

3.7.4 Test Modes

Each set of tests, for baseline and SNCR operation consisted of the following engine loads and speeds:

1. 40% Load / 1500 rpm

2. 80% Load / 1500 rpm

These engine loads were chosen to provide a spectrum of typical diesel engine load ranges, low and high.

For SCNR operation, the control variables for the secondary reducing agent injection were the start of injection (SOI) and the LOI. For each secondary reducing agent tested, an assortment of SOI timings were chosen to create a range over the combustion stroke. The chosen SOI timings were -30°, 0°, 10°, 20° and 60° after top dead center (ATDC). For NH_3/NO_x molar ratio, the molar ratios of 0.5, 1.0 and 4.0 were tested by means of changing the LOI. In total 75 tests were performed (Table 3.4), for each load tested. A daily engine warm up period was performed prior to the start of each testing day. Each test was operated for five minutes in order to allow steady state operation. From each test, the last two minutes of data was analyzed. The

baseline tests were performed before and after each set of five molar ratio tests in order to

observe relative baseline characteristics for each subset of tests.

Table 3.4 – The testing variables of NH_3/NO_x molar ratio and start of injection for each secondary injection blend

Urea / Glycerol (80/20)			Water / Glycerol (80/20)			Water Only		
Test #	NH3/NOx	SOI (ATDC)	Test #	NH3/NOx	SOI (ATDC)	Test #	NH3/NOx	SOI (ATDC)
1	BL		26	BL		51	BL	
2	4	60	27	4	60	52	4	60
3	4	20	28	4	20	53	4	20
4	4	10	29	4	10	54	4	10
5	4	0	30	4	0	55	4	0
6	4	-30	31	4	-30	56	4	-30
7	BL		32	BL		57	BL	
8	2	60	33	2	60	58	2	60
9	2	20	34	2	20	59	2	20
10	2	10	35	2	10	60	2	10
11	2	0	36	2	0	61	2	0
12	2	-30	37	2	-30	62	2	-30
13	BL		38	BL		63	BL	
14	1	60	39	1	60	64	1	60
15	1	20	40	1	20	65	1	20
16	1	10	41	1	10	66	1	10
17	1	0	42	1	0	67	1	0
18	1	-30	43	1	-30	68	1	-30
19	BL		44	BL		69	BL	
20	0.5	60	45	0.5	60	70	0.5	60
21	0.5	20	46	0.5	20	71	0.5	20
22	0.5	10	47	0.5	10	72	0.5	10
23	0.5	0	48	0.5	0	73	0.5	0
24	0.5	-30	49	0.5	-30	74	0.5	-30
25	BL		50	BL		75	BL	

4   RESULTS AND DISCUSSION

4.1   Preliminary Baseline Scoping

From the preliminary scoping, two NO_x measurements were observed. The 40% engine load (5 N-m) baseline series produced an approximate 250 ppm or 0.00434 g/s NO_x, and the 80% engine load (10 N-m) baseline series produced an approximate 500 ppm or 0.0114 g/s NO_x. From these values the LOI or amount of the SNCR (Aqueous Urea-Glycerol) reducing agent was determined for each of the four molar ratios tested.

4.2   Baseline Tests

From the collective of baseline tests performed statistical data was found as shown in Table 4.1. A 95% confidence interval, as well as a maximum and minimum values in order to assess engine repeatability and NO_x level significance, respectfully. The percent difference of the 95% confidence interval from the average was used to access whether an increase or decrease in the NO_x was a significant change.

Table 4.1 – Baseline test average, standard deviation, maximum, minimum, 95% confidence interval, and the percent difference of the 95% confidence interval from the average

Load	Average (g/s)	Standard Deviation (g/s)	Maximum (g/s)	Minimum (g/s)	95% Confidence Interval	Percent Difference
40%	0.0042	0.0004	0.0049	0.0034	± 0.0002	5%
80%	0.0118	0.0030	0.0123	0.0113	± 0.0015	13%

4.3   SNCR 40% Load (5 N-m) Results

The following results are for the three reducing agents tested at 40% engine load (5 N-m) and 1500 rpm. As previously stated, each reducing agent test sequence was broken into four sub-series for each of the four molar ratios tested. The NO_x level results of each test was compared to the average of the before and after interstitial sub-series baseline tests NO_x levels.

4.3.1 80-20 Aqueous Urea-Glycerol Injection (40% Load)
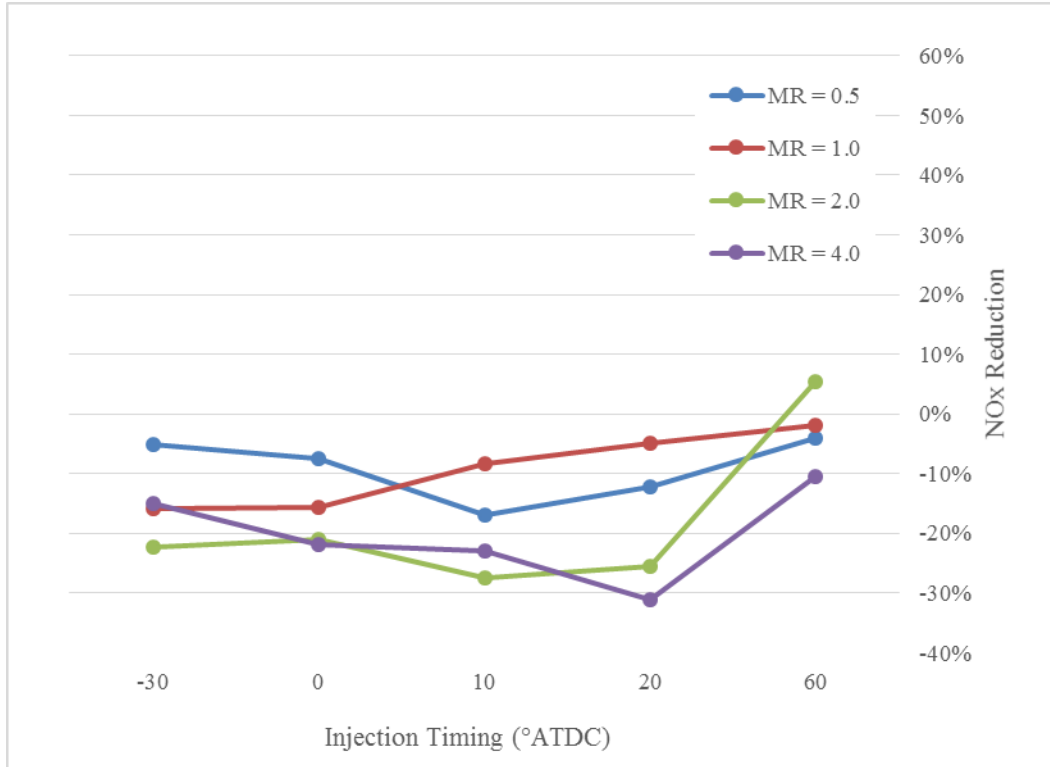
Figure 4.1 – 40% load 80-20 aqueous urea-glycerol SNCR NO_x reduction results for the different molar ratios tested

Figure 4.1 shows the percentage of NO_x reduction percentage for each NH_3/NO_x molar ratio tested (0.5, 1.0, 2.0 and 4.0) plotted against each injection timing tested (-30°, 0°, 10°, 20° and 60° ATDC). Each colored line on the graph is one of the four molar ratios tested. It was observed from this trial that under the test conditions, a maximum NO_x reduction of 5% was observed for the 2.0 ratio test at the 60° ATDC injection timing. Unfortunately, this reduction is within the 95% confidence baseline level threshold and thus deemed insignificant. For all of the other tests for this reductant series showed an increase in NO_x emissions that ranged from 2% to 31%. Though no significant reduction was observed in this series, it was noted that the 2.0 and 4.0 molar ratio series showed a higher increase in NO_x production versus the 0.5 and 1.0 molar ratio series, overall. Additionally, of all the molar ratios tested, that the best reduction, or in this case, least in increase came from SOI of 60 degrees ATDC.

4.3.2 80-20 Water-Glycerol Injection (40% Load)
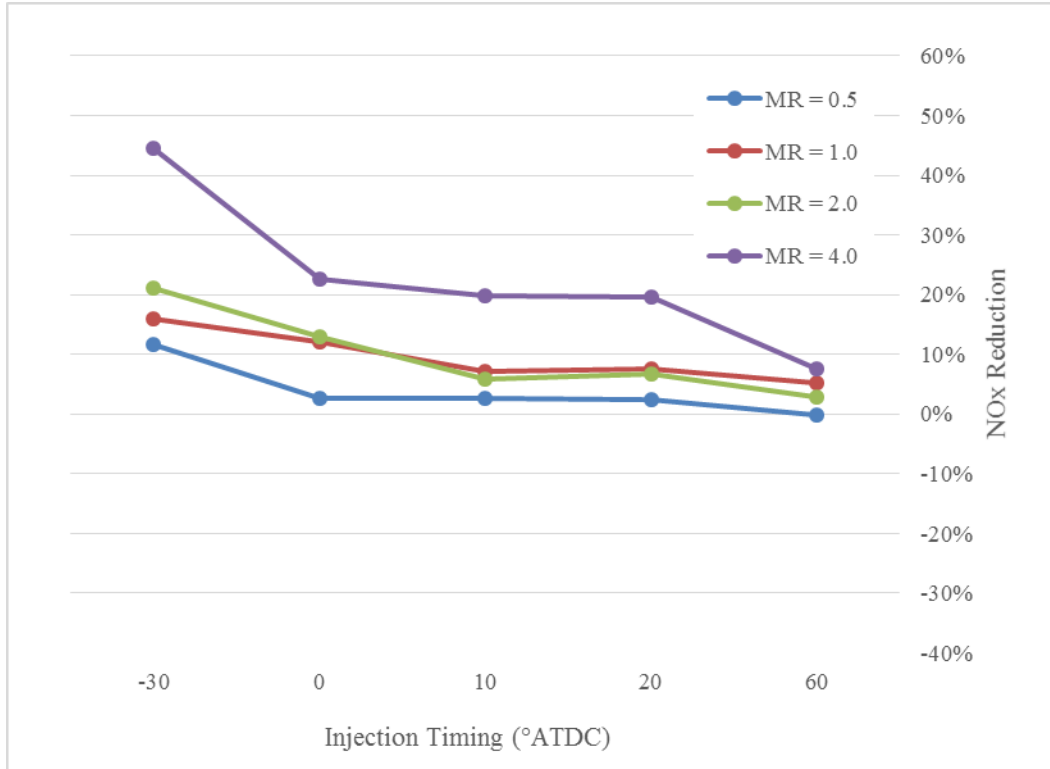
Figure 4.2 – 40% load 80-20 water-glycerol NO_x reduction results for the different molar ratios tested

In order to determine the effects of the mixing of the aqueous urea with glycerol, the tests were repeated with the 80-20 water-glycerol mixture. Figure 4.2 shows these 80-20 water-glycerol tests under 40% load. For these 40% load experiments, a maximum reduction of NO_x by 44% was achieved with the 4.0 molar ratio at -30° ATDC, when compared to the interstitial baseline average. Additionally, the 4.0 molar ratio sub-series produced the best overall reduction of all the molar ratios tested in this series. Subsequently, the reduction of NO_x increased as the reductant molar ratio was increased. This is consistent with the increase in evaporative cooling effect and increased heat capacity available from the water and glycerol. Of all the molar ratios tested in the series, the reduction decreased as injection timing was progressed (earlier to later). This indicates that the evaporative cooling effect of the water and glycerol was more effective

prior to the combustion of the primary fuel. As a result, it was clear that the mixing with glycerol was not solely responsible for the lack of reduction from the aqueous urea.

4.3.3   Neat Water Injection (40% Load)
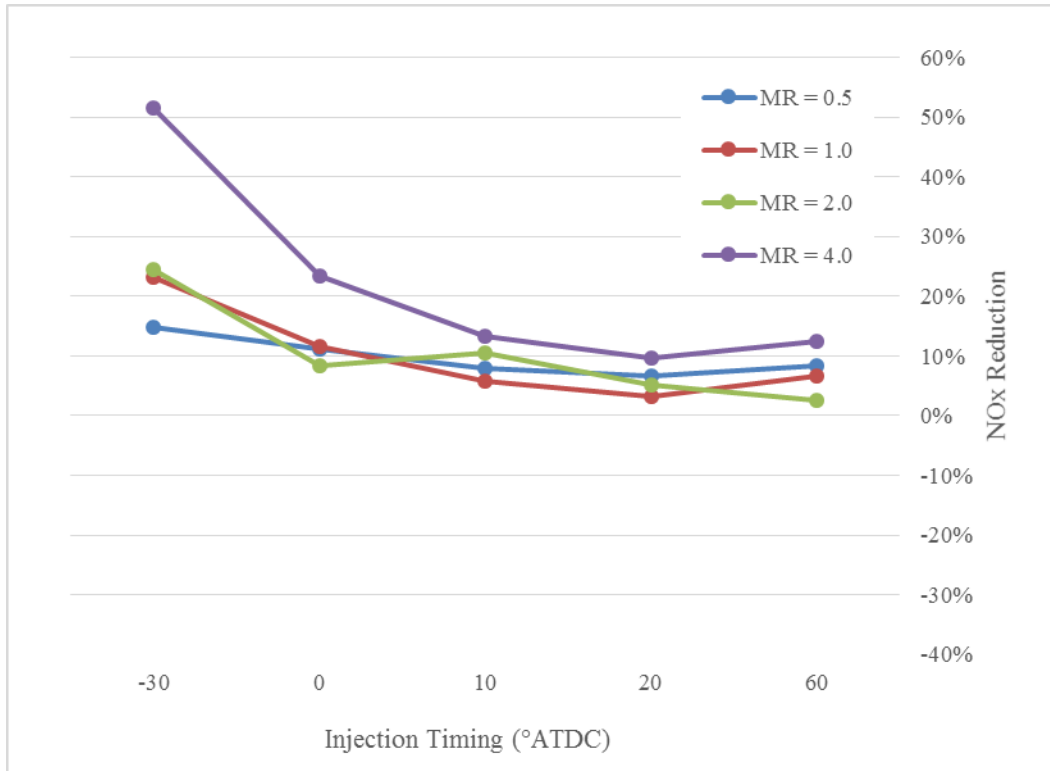
Figure 4.3 – 40% load neat water NO_x reduction results for the different molar ratios tested

Like the water-glycerol tests, neat water was also tested in place of the reducing agent in order to determine the effects of reduction by evaporative cooling and increased heat capacity made available from the secondary injection of water alone. Figure 4.3 shows the results of the 40% load experiment repeated with neat water. The data shows a maximum decrease of NO_x occurring at the 4.0 molar ratio and at the -30° ATDC injection timing with a 51% reduction when compared to interstitial baseline NO_x levels. Similar to the 40% load water-glycerol test series, this occurred when injecting the most reductant, and at earliest injection timing. Similarly, the reduction of NO_x increased as molar ratio was increased, except at the 0° ATDC, where the

1.0 and 0.5 molar ratio outperformed the 2.0 molar ratio; however, these results fell within the 95% confidence interval for the baseline and were thus deemed insignificant. In fact the trends of the sub-series tests for the neat water follow closely to the water-glycerol, all but the 2.0 molar ratio, but again these results were found to be insignificant due to the 5% baseline variation.

4.4   SNCR 80% Load (10 N-m) Results

The following results are for the three reducing agent performed at 80% engine load (10 N-m) and 1500 rpm at their respective molar ratios. These 80% load experiments followed the same format as the 40% load experiment in the previous subsection.

4.4.1   80-20 Aqueous Urea-Glycerol Injection (80% Load)
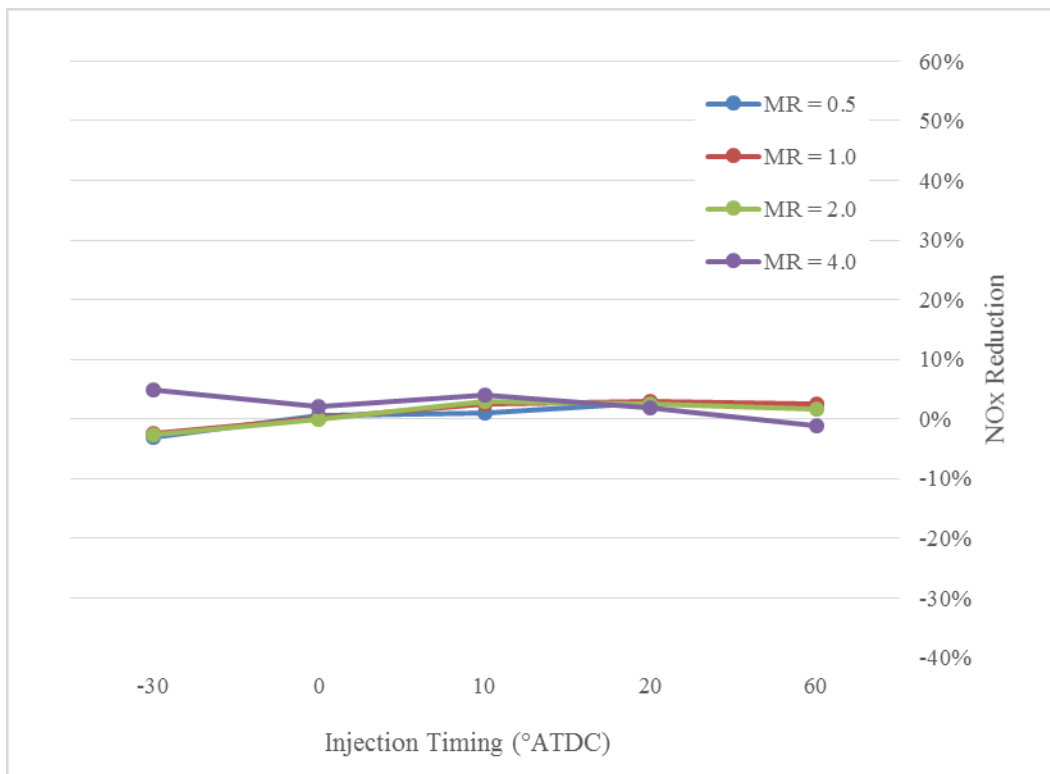
Figure 4.4 – 80% load 80-20 aqueous urea-glycerol SNCR NO_x reduction results for the different molar ratios tested

The results of the 80-20 aqueous urea-glycerol 80% load tests are shown in Figure 4.4. Similar to 40% load tests, the 80% load tests with the 80-20 aqueous urea-glycerol mixture failed to show any significant reduction in NO_x levels. Similarly a maximum of 5% reduction was

achieved at the 4.0 molar ratio and at early injection (-30° ATDC). The increased load did produce more consistent results, all within the ±13% from the 95% confidence interval baseline NO_x levels versus the like 40% load test, but again were well within the 95% confidence interval baseline variance and deemed insignificant. Additionally, no noticeable trends for molar ratio or injection timing were observed.

4.4.2 80-20 Water-Glycerol Injection (80% Load)
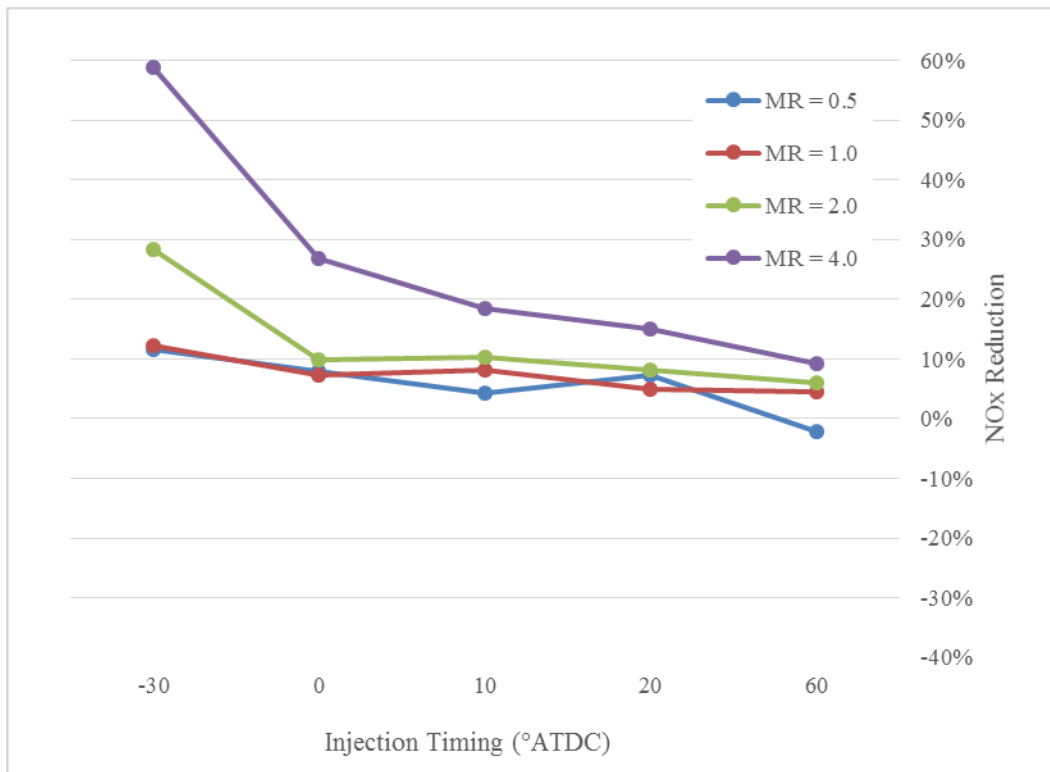
Figure 4.5 – 80% load 80-20 water-glycerol NO_x reduction results for the different molar ratios tested

Figure 4.5 shows the results of the 80% load 80-20 water-glycerol tests. The 80% load water-glycerol tests, similar to the 40% load tests, resulted in a much more significant reduction of NO_x emissions, especially in the 4.0 and 2.0 molar ratio test sub-series. Under the higher load, a maximum reduction of NO_x of 59% was achieved at the 4.0 molar ratio and early injection timing of -30 degrees ATDC. The 2.0 molar ratio early injection timing also yielded a significant maximum reduction of NO_x by 28%, followed by the 1.0 and 0.5 molar ratios both at 12% (not

significant, but close). Again, similar to the 40% load tests the reduction of NO_x decreased as

molar ratio was decreased and injection timing increased, all except the 1.0 and 0.5 molar ratio

sub-series. The 1.0 and 0.5 molar ratio sub-series had some irregularities in this trend at the 10°

and 20° ATDC injection timings, although at these instances the reduction was within the 95%

confidence interval for the baseline and therefore deemed insignificant.

4.4.3 Neat Water Injection (80% Load)
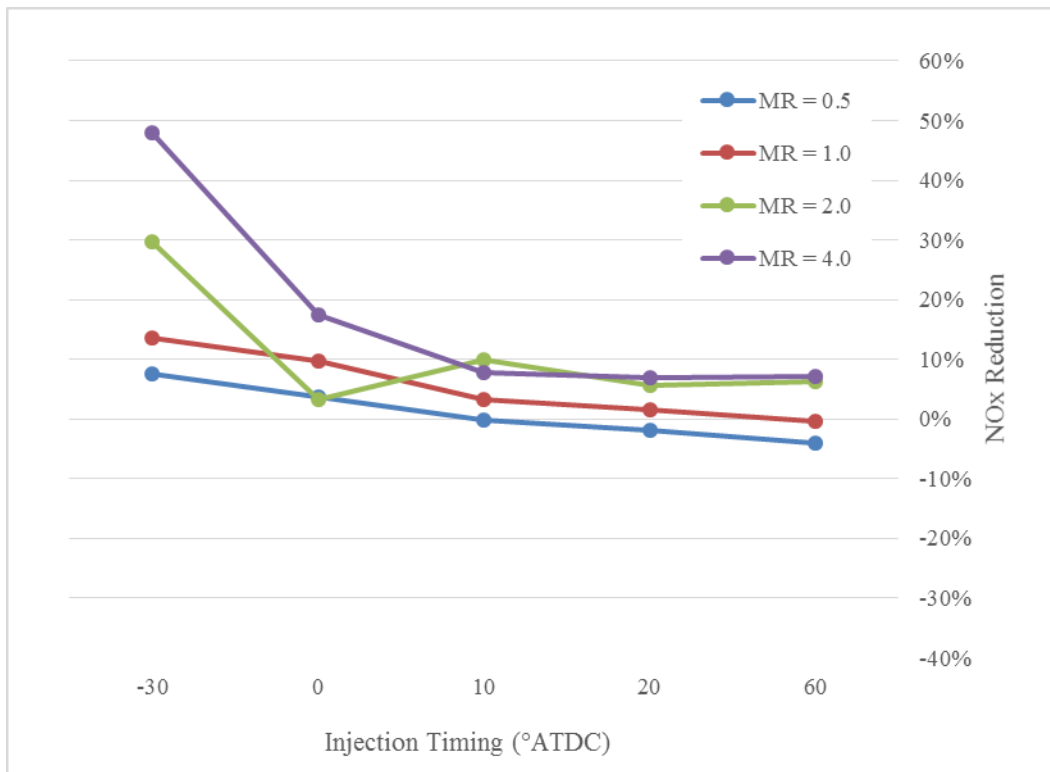
Figure 4.6 – 80% load neat water NO_x reduction results for the different molar ratios tested

Figure 4.6 shows the 80% load neat water tests. With neat water, a maximum reduction

of NO_x of 51% was achieved with the 4.0 molar ratio and at early injection (-30° ATDC). Again,

across the molar ratio sub-series tests, early injection timings yielded the highest reductions. The

2.0 molar ratio produced a maximum reduction of 28% NO_x, 13% reduction by the 1.0 molar

ratio and 8% reduction (not significant) by the 0.5 molar ratio. All the molar ratio sub-series

followed the decreasing reduction as injection timing was increased except for the 2.0 molar

ratio. The 2.0 molar ratio defied this common trend and underperformed when compared to the other molar ratios at the 0° ATDC injection timing and outperformed the group at the 10° ATDC injection timing. One additional irregularity for this neat water test set was that the 1.0 and 0.5 molar ratio sub-series showed an increase in NO_x of up to 3%, but these few results were found to be within the 95% confidence interval baseline variance and so insignificant.

4.5   Reducing Agent

From the performed tests under both 40% and 80% loads, it is clear that the desired effect of SNCR by means of aqueous urea, or in this case the 80-20 aqueous urea-glycerol mixture, was not achieved. Of the reducing agents tested in this experiment, the maximum reduction was achieved by neat water for the 40% by the 80-20 water-glycerol mixture for the 80% load with maximum NO_x reduction of 51% and 59%, respectively.

The testing of the two alternative reducing agents were to establish the effects on reduction of the glycerol used in the mixture and that of the evaporative cooling effect of the water. Based on these results, the effects of glycerol mixture was beneficial due to the increase in NO_x reduction in the 80% load tests by 9% when comparing the water and water-glycerol; however, the reduction by the evaporative cooling effect of the water was obvious in both the 40% and 80% load tests with the significant reduction in NO_x for both load's sub-series.

4.6   Molar Ratio

Based on the results of the experiments conducted, the highest NO_x reduction was achieved by the 4 to 1 molar ratio in all but one set of tests, the 40% load 80-20 aqueous urea-glycerol tests. For the others, this is consistent with evaporative the cooling effect caused by water during combustion, and thus reducing the formation of NO_x. The maximum reduction

achieved at the 4 molar ratio was found to be 59%. Unfortunately, since the desired results of SNCR was not achieved, the effect of molar ratio therein cannot be commented upon.

4.7   Injection Timing

Similar to the molar ratio, all but one set of tests yielded early injection, or -30 degrees ATDC, as the most beneficial for NO_x reduction. This is likely due to the additional time given for the evaporative cooling effect of the water to take place. The one set of tests that did not follow this trend was the 40% load 80-20 aqueous urea-glycerol tests. The maximum reduction achieved at -30 degrees ATDC was 59%.

4.8   Temperature Window

In addition to the NO_x reduction comparison of each tests, average in-cylinder temperature (T_{cyl}) by crank angle was monitored for all tests. The maximum value of T_{cyl} for the 40% and 80% load tests were determined to be 899 K and 1063 K, respectfully. It should be noted that the local temperatures inside the cylinder could be as high as the adiabatic flame temperature or as low as the cylinder wall temperature.

For the 40% load tests, the maximum T_{cyl} value of 899 K falls below the temperature needed to achieve SNCR by means of aqueous urea. This is most likely the explanation of why the 80-20 aqueous urea-glycerol tests had an adverse effect and increased NO_x rather than achieving a reduction. Figure 4.7 shows the temperature over the start of combustion where the SNCR testing took place for the 40% load baseline and the target temperature window for reduction to occur.

Figure 4.7 – Average in-cylinder temperature over the secondary injection window for the 40% load tests

The 80% load tests maximum T_{cyl} temperature of 1064 K again falls below the desired temperature window reported by Lyons of 1123-1423 K [25]. This would explain the slightly better performance when compared to the 40% load tests, but still poor SNCR NO_x reduction. Figure 4.8 shows the temperature over the start of combustion where the SNCR testing took place for the 80% load baseline and the target temperature window for reduction to occur.
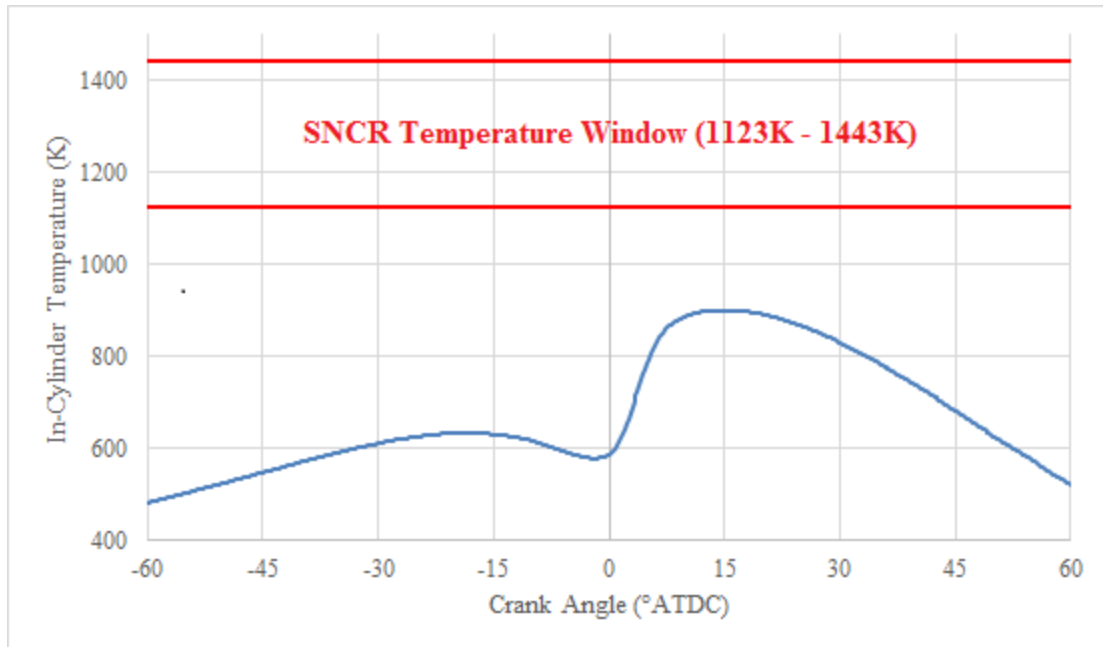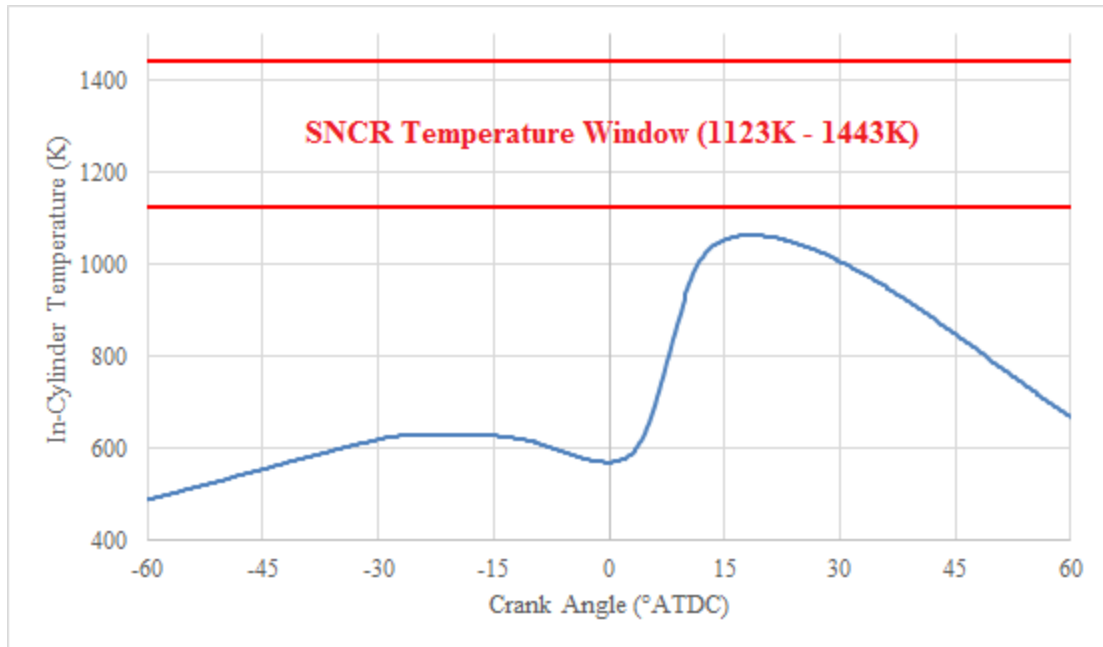
Figure 4.8 – Average in-cylinder temperature over the secondary injection window for the 80% load tests

4.9   Oxygen Content

From studies found on the effect of oxygen content effect on SNCR, a minimum of 2% is required and optimal is between 12% and 15% [4]. The lowest oxygen content found in any of the tests performed was 14% and thus sufficient for optimal SNCR NO_x reduction.

4.10   Residence Time

Studies on residence time show that based on the required temperature, residence time varies significantly. According to Willand et al., at the highest average temperatures achieved in this experiment, 1034 K or approximately 1000 K, the residence required for optimal NO_x reduction would be 1000+ msec [39]. At optimal temperatures like 1200 K to 1300 K required, the residence time would be approximately 10 msec to 100 msec. This indicates that again, reaching the desired temperature would allow for lower residence time. At 1500 rpm one stroke would be approximately 17 msec. These variances in required residence versus

44

temperature from Willand et al. show that the available residence time in this experiment require

temperatures to be 1200 and 1300 K [39].

5 CONCLUSIONS, LESSONS LEARNED AND RECOMMENDATIONS

5.1 Conclusions

The ultimate goal of this experiment was to achieve and understand the SNCR of NO_x by direct secondary injection of aqueous urea. An 80-20 aqueous urea-glycerol mixture was used, and the glycerol was added in order to provide lubrication for the injector used in the secondary injection system. In addition to the 80-20 aqueous urea-glycerol mixture, 80-20 water-glycerol mixture and neat water were tested in order to determine the any effects from the glycerol and water. In the experiment, two loads were tested, 40% (5 N-m) and 80% (10 N-m) load, at 1500 rpm. At each load, four molar ratios (0.5, 1.0, 2.0 and 4.0) of reducing agent to NO_x were tested. In addition to the molar ratio, five different injection timings (30, 0, 10, 20 and 60 degrees ATDC) were tested.

There were several important factors focused on in order to achieve SNCR of NO_x, or in this case, lack thereof. These factors were molar ratio of reducing agent, injection timing, temperature window for reduction to occur, oxygen content of the exhaust, and residence time for the reactions to take place. Of these factors, only one was found to be insufficient for SNCR to take place, and that was the temperature window. According to studies related to temperature window, the optimal reaction of selective reduction occurs at 1123 to 1423 K [25]. Other studies confirm that the optimal temperature is 1250 K [25], [38], [43]. In the experiments, the highest average cylinder gas temperatures occurred at the 80% load tests. The maximum average in-cylinder temperature (T_{cly}) based on the single zone model for the 40% load and 80% load tests were found to be 899 K and 1064 K, respectfully. These temperatures fall below the temperature window needed for SNCR to occur.

When testing for the SNCR of NO_x in diesel exhaust emissions with direct secondary injection of aqueous urea, the results for the 40% load showed no significant decrease in NO_x emissions when compared to baseline tests, but instead rather a maximum increase of 31% at the 4.0 molar ratio and 20° ATDC injection timing. In the 80% SNCR tests, no significant reduction or increase was observed. This increase in NO_x emissions and lack of reduction is believed to be from incomplete reduction reactions of the aqueous urea. The evaporative cooling and increased heat capacity from the water clearly showed a reduction in NO_x emissions, and the only explanation of the increase and lack of NO_x reduction indicates that the effect was counteracted by an increase on the NO_x formation from the addition of the urea. In the study by Kasuya et al., they discuss the effects of insufficient temperature being a failure to reduce NO_x and NH_3 slip [43]. They also found that an increase of NO_x, from the urea, only occurred when temperatures exceeded the reaction window and caused the NH_3 to oxidize to form additional NO_x. Based on the results of this experiment, the average T_{cyl} temperatures were too low and would have only allowed for NH_3 slip to have occurred. Despite this, it was believed that due to the low temperatures a failure of the urea completely breaking down must have resulted in the increase of NO_x observed.

In the trials of the 80-20 water-glycerol tests, the 40% load tests yielded a maximum reduction of 44% and in the 80% load tests a maximum reduction of 59%. The neat water tests yielded a maximum reduction of NO_x in the 40% load test and 48% in the 80% load tests. Again, these results are believed to have been achieved purely by the evaporative cooling and added heat capacity of the water injected.

5.2 Lessons Learned

In the carrying out of this experiment, a number of lessons were learned through the challenges faced. One lesson, in particular, was the issues with fouling injectors due to the injection of aqueous urea. In the experiment a number of injectors failed in the open position from what was believed to be urea crystallization and lack of lubricity. These failures continued despite the addition of glycerol, though failure occurred less frequently. The VW diesel injectors used were designed to deliver high pressure diesel fuel directly in-cylinder, not water or aqueous urea.

5.3 Recommendations

Since the main shortcoming of this experiment was insignificant in-cylinder reduction of NO_x due to the low in-cylinder temperatures for SNCR to occur, it is recommended that continued studies in future focus on methods to increase the combustion and in-cylinder gas temperature. One method recommended is the addition of a turbo charger to the engine to increase in-cylinder pressure, temperature and BMEP. Another method to attempt to increase in-cylinder and overall engine temperature may be increasing exhaust pressure by introducing baffles in the exhaust plumbing, this was utilized in the SNCR study by William et al. [39].

In addition to equipment modification, another recommendation is to consider the possibility of an existing standardized emissions test. In this study, the experimental setup and nature of the experiment did not require the use of a pre-existing emissions test.

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APPENDIX

Complete Sensor List

Sensor Type	Data	Make	Model	Accuracy
Encoder	Engine Speed (Combustion)	BEI Sensors	XH25D-SS-1440-ABZC-28V/V-EM18	100 kHz Threshold
Encoder / Hall Effect Position	Engine Speed (Dyno)	Cherry	GS100701	15 kHz Threshold
Load Cell	Dynamometer Torque	BLH Electronics	U3G1C	$\pm$ 2%
Pressure Transducer	Engine Oil Pressure	VDO	360-081-030-074C	$\pm$ 3%
Thermocouple	Engine Oil Temperature	Omega	K-Type Thermocouple	$\pm$ 0.75%
Thermocouple	Exhaust Temperature	Omega	K-Type Thermocouple	$\pm$ 0.75%
Pressure Transducer / Thermistor	Ambient Air Pressure / Temperature	SparkFun - Weatherboard V3	BMP-085	$\pm$ .01 % $\pm$ 2º C
Humidity Sensor	Relative Humidity	SparkFun - Weatherboard V3	SHT-15	$\pm$ 2%
Pitot Tube	Intake Air Mass Flow	In-House	N/A	$\pm$ 3%
Pressure Transducer	Secondary Injection Rail Pressure	VW	G247 / 06K906051	$\pm$ 2%
Fuel Scale	Primary Fuel Mass	In-House	N/A	$\pm$ 0.1%
Fuel Scale	Reductant Mass	In-House	N/A	$\pm$ 0.4%
NO$_x$ Sensor	NO$_x$ ppm / O$_2$ %	Ford	DC3A-5J299-DC	$\pm$ 2%
High Precision Pressure Transducer	In-Cylinder Pressure	PCB Piezotronics	112A05	$\pm$ 0.3%