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Chemical Kinetics Analysis of Alternative Reagents for the SNCR Process

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Abstract

The objective of this thesis is to investigate alternative reagents for Selective Non-Catalytic Reduction (SNCR) of nitrogen oxides (NO_x) for coal-fired power plants.

This thesis first reviews reported studies about available alternative reagents for SNCR NO_x reduction processes. Monomethylamine is then selected as a major subject of study, because of its superior nitrogen oxides reduction performance at temperatures under 800 K. Additionally, available chemical kinetics mechanisms for monomethylamine suited for the SNCR NO_x reduction process were modeled using the CHEMKIN software. From the chemical kinetics modeling, the detailed mechanism by Kantak et al. was selected to perform a sensitivity analysis. Two reduced mechanisms for monomethylamine are proposed. Finally, a monomethylamine-based SNCR NO_x removal system for a natural gas turbine plant was modeled and estimate of the usage of reagent in such system was calculated. The results of the simulations in this study show that the potential of monomethylamine-based SNCR NO_x reduction systems for full-scale power plants is promising and further laboratorial and field studies in this area would be valuable.

Chapter I – Introduction

1.1   Background

Nitrogen oxides (NO_x) are one of the major pollutants emitted by combustion along with other pollutants such as sulfur oxides (SO_x) and particulate matter [1]. NO_x emissions cause serious environmental problems which includes ground-level ozone, acid rain, water quality deterioration, global warming and formation of particulate matter [2]. According to 2012 data from the US Environment Protection Agency (EPA), fuel combustion was the second largest source of NO_x emissions in the US, mounting up to 33.1%. Furthermore, as shown in **Figure 1**, 16% of the NO_x emissions comes from fuel combustion for power generation. Meanwhile, despite the increasing contribution to electrical power by natural gas, due to its lower pollutant emissions and large amount of its reserves, coal is still the major fuel for power generation in the US. Coal contributed in 2013 to 1530 billion kilowatt-hour of electricity, accounting for 39% of the total electricity generation [4] (see in **Figure 2**). Coal combustion contributes to 93% of the NO_x emissions in the electricity sector [5]. Therefore, research and technology development of NO_x control technologies for coal-fired plants and other stationary sources is of great importance.
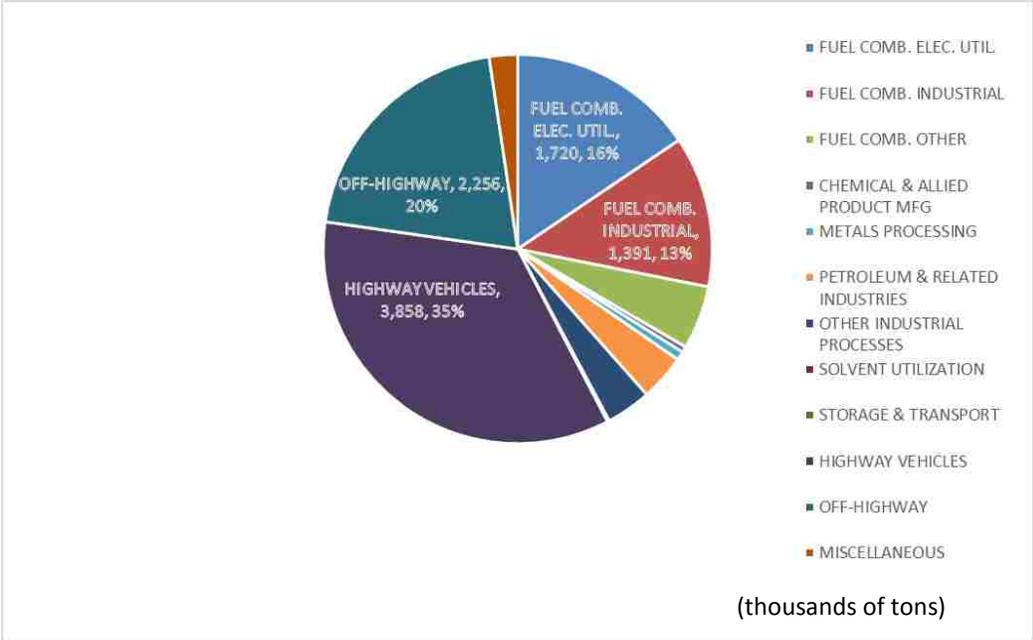
Figure 1. US sources of NO$_x$ emissions in 2012 [3].
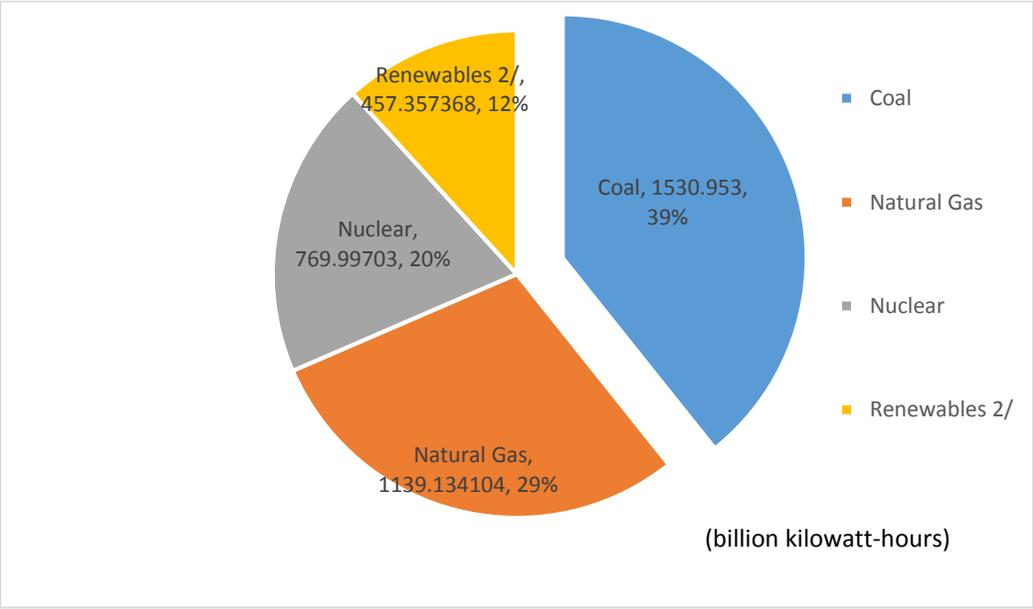
Figure 2. Electricity generation by fuel sources [4].

1.2   NO$_x$ Control Techniques for Coal-Fired Power Plants (CFPPs)

1.2.1   NO$_x$ Formation in CFPPs

NO$_x$ formation in CFPPs is relatively complex and understanding the mechanisms of NO$_x$ formation has led to effective development of NO$_x$ control technologies for CFPPs. NO$_x$ formed in fuel combustion processes is generally due to three different chemical mechanisms: (1) thermal fixation of nitrogen in the combustion air, which is termed "thermal NO$_x$" [6], (2) reaction between hydrocarbon radicals and atmospheric nitrogen, which is termed "prompt NO$_x$" [7], (3) and conversion of fuel bound nitrogen to NO$_x$ during combustion, which is referred to as "fuel NO$_x$" [8]. Thermal NO$_x$ can mount up to 20% of the NO$_x$ emissions while the fuel NO$_x$ can contribute up to 80% [9] of the total NO$_x$ formation in CFPPs. Prompt NO$_x$ is a minor contributor to NO$_x$ production in coal-fired units. Thermal NO$_x$ can be controlled by lowering peak flame temperatures and the amount of excess air in the combustion process; meanwhile fuel NO$_x$ can be generally controlled by limiting the supply of oxygen during the initial combustion stages [1].

1.2.2   NO$_x$ Control Techniques for CFPPs

There are three primary categories of NO$_x$ technologies available for NO$_x$ emissions control for CPPPs: pre-combustion control, combustion control and post-combustion control.

Pre-combustion NO$_x$ control refers to the technique that reduces the nitrogen content in the fuel or to switch to other fuels that contain lower nitrogen level. However, unlike sulfur in the coal, eliminate or reduce nitrogen species in the coal is difficult. Additionally, nitrogen is not the only parameter that has an impact on NO$_x$ formation. Other factors such

as fixed carbon, volatile matter, oxygen and moisture content also play a role in the formation of NO_x in the coal combustion process [1].

Combustion control generally includes techniques that reduce combustion temperature, oxygen availability in the primary combustion stage and modify the residence time of the combustion zone in the high temperature zones. Available technologies for combustion control of NO_x include, burner tuning, boiler optimization, excess air control, low-NO_x burners, oxygen-enriched combustion, flue gas recirculation and gas reburning. These technologies are effective in reducing NO_x and used nowadays by most of the existing CFPPs. However, there are issues with them such as boiler efficiency losses, increasing the unburned carbon content in the fly ash and accelerating the rates of corrosion in the lower furnace, due to operation under a reducing atmosphere in the furnace.

Post-combustion NO_x control, also called flue gas treatment, refers to technologies that focus on removing or reducing pollutant emissions in the post-combustion gases. Most widely used post-combustion NO_x technologies are Selective Catalytic Reduction (SCR) and Selective Non-Catalytic Reduction (SNCR). SCR is one of the most common post-combustion NO_x reduction technologies employed in CFPPs, due to its high NO_x removal efficiency. SCR is associated with relatively higher retrofit costs, potential sulfur dioxide (SO_2) to sulfur trioxide (SO_3) conversion, catalyst deactivation and ammonia (NH_3) slip. NH_3 slip can lead to fouling of the air preheaters in CFPPS, which impacts unit availability and increase the operating and maintenance cost of the unit.

1.3   Selective Non-Catalytic Reduction (SNCR) Technology

1.3.1   SNCR Overview

NO_x reduction by SNCR, or SNCR De-NO_x, is a technology that consists of injecting chemical reagents (usually at a location where the temperature is in the active reagent reaction temperature range), which mix thoroughly with the flue gases containing NO_x. The NO_x is removed by chemical reactions between the reagent and the NO_x in the flue gas. A schematic of the general SNCR concept is shown in **Figure 3**.
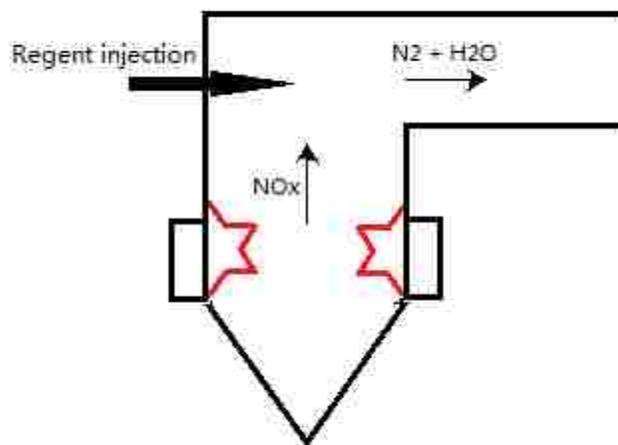
Figure 3. Schematic of SNCR concept.

Most commonly used reducing SNCR reagents for full-scale applications include ammonia, (NH_3), (introduced by Exxon Research & Engineering Co. [10] in 1975) and urea, ($CO(NH_2)_2$), (patented by Arand et al. [11] in 1980). These reagents require a reaction

temperature window between 1125 K and 1450 K [12]. The assumed global NH_3 and urea SNCR chemical reactions are presented below [1]:

Ammonia: $4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$

Urea: $2NO + (NH_2)_2CO + \frac{1}{2}O_2 \rightarrow 2N_2 + 2H_2O + CO_2$
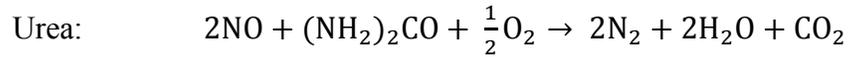
Reported studies show that the performance of SNCR system can theoretically be affected by the following factors: injection point temperature and cumulative residence time, oxygen content of the flue gas, sulfur content in the fuel, untreated NO concentration in the flue gas, and moisture concentration and carbon monoxide (CO) content of the flue gas. Additionally, due to the sensitivity of the SNCR process to the boiler process conditions, to achieve greatest NO_x removal effectiveness, the SNCR is also highly dependent on the flue gas temperature window at the regent injection zone, flue gas residence time in the active temperature range, the normalized stoichiometric ratio between the reagent and NO_x, and mixing between the reagent and the flue gas. These factors are important to maximize the NO_x reduction performance of SNCR systems in full-scale applications [13].

1.3.2   Issues with SNCR Systems

Most critical issues with current SNCR systems are related to the narrow active temperature window and potential NH_3 slip. Theoretically, NH_3-based and urea-based SNCR systems can achieve as high as 70-80% of NO_x reduction under ideal process conditions; however, 35% to 50% abatement is typically achieved in large full-scale power plants.

The optimal reduction temperature for the SNCR technology is around 1235 K for NH_3, with an effective temperature window between 1175 K – 1275 K (Poole and Graven [14] and Wise and Frech [15]), as shown in **Figure 4**. Below the optimal temperature, the NO_x reduction rate is limited by insufficient hydroxide ([OH]) and oxygen ([O]) radical concentrations and slows down the kinetics rates [14]. At temperatures below the optimal level, the amount of unreacted NH_3 increases. At temperatures higher than the optimal level, the NH_3 starts to react with O_2 rather than with NO leading to increased NO_x formation. Many studies have been carried out on shifting the optimal reduction temperature to lower levels and widening the reduction temperature window. By adding additives, the NO_x reduction rate by NH_3 and urea SNCR system can be improved. For example, Lee et al. [16] reported that by adding alkalines as additives to an urea-based SNCR system, more than 30% additional NO_x reduction improvement can be achieved.

Muzio et al. [17] reported a study on monomethylamine (CH_3NH_2), dimethylamine ((CH_3)$_2NH$) and trimethylamine ((CH_3)$_3N$) as substitutes for NH_3 injection. Research with hydrazine (N_2H_4) was carried out by Azuhata et al. [18] and the result showed that a lower optimal temperature (from 775 K to 875 K) was achieved by injecting N_2H_4 at low oxygen conditions. Wenli et al. [19] studied widening the temperature window of the SNCR and their experiments showed that several additives, including monomethylamine (CH_3NH_2), can greatly lower the temperature window, achieving an 800 K optimal temperature window. Bae et al. [20] also found that adding CO or CH_4 can successfully lower the optimal SNCR temperatures and widen the effective temperature window. These mentioned researches indicate that there is a major interest and there are opportunities to

improve the SNCR temperature situation by using additives. This is also true for alternative reagents, which can be used as substitutes to NH_3 and urea.
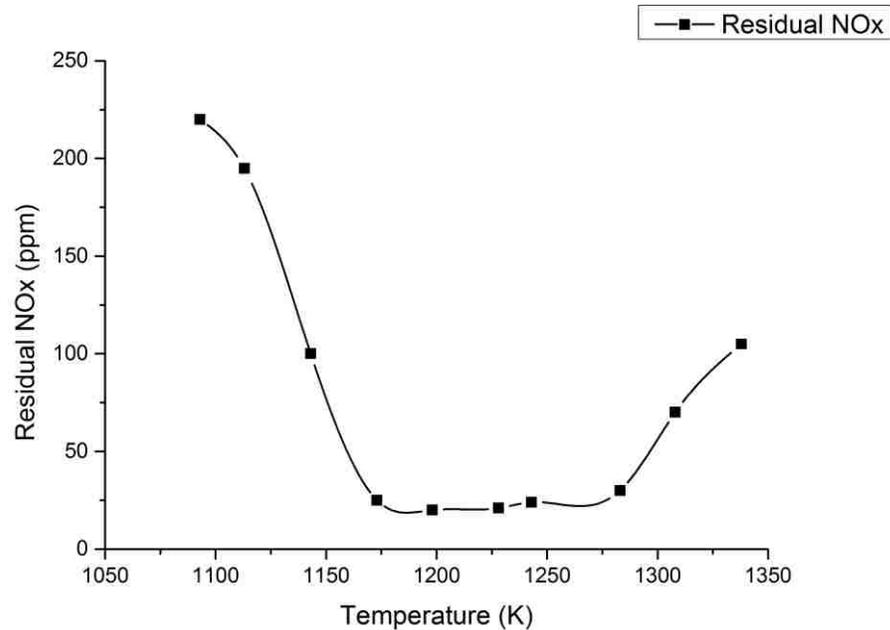
Figure 4. Temperature Window of SNCR Process using ammonia at a molar ratio (NO_2/NO_i) = 1.5 [21].

The resulting NH_3 from SNCRs is also considered an air pollutant in industrial applications. Unreacted NH_3 emissions, which is also termed ammonia slip, is a key factor that reflects the performance of the NO_x reduction system along with the regent consumption and NO_x reduction rate. The unreacted NH_3 can lead to: (1) ammonium salts formation which usually include ammonia bisulfate (NH_4HSO_4), a salt that causes fouling of air preheaters and other downstream surfaces in boilers; (2) ammonium chloride plume from the stack; (3) ammonia odor from the fly ash; and (4) gaseous ammonia emission, if the level of the slip is high because of poorly SNCR control. Since ammonium bisulfate is extremely sticky and corrosive, the formation of it causes serious problems to the boiler back-end combustion equipment and contribute to fouling and plugging [22]. As stated

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previously, high levels of NH_3 slip can occur when the reaction temperature is on the left side of the SNCR temperature window and such situation is usually aggravated by improper reagent injection, poor mixing between reagent and flue gas and insufficient residence time for regent and flue gas staying at the desired temperature range. Moreover, unsteady boiler operating conditions can also contribute to the regent and flue gas reacting outside the temperature window even if the SNCR system is well-designed, resulting in high levels of NH_3 slip. All this indicates again the need of additives and alternative SNCR reagents, which would not suffer from the NH_3 slip problems associated with conventional SNCR systems.

Despite the mentioned issues of the SNCR technology, it is still considered a cost-effective post-combustion NO_x reduction technique, because of its relatively simple retrofit, and low capital and operating cost, as compared to other NO_x reduction technologies for existing coal-fired utility boilers.

1.4   Purpose of the Thesis

The main purpose of the research performed for this thesis was to study alternative reducing regents for the SNCR De-NO_x system, which are capable of being effective at lower flue gas temperatures, with a wider temperature window and lower or negligible NH_3 slip. The research focused particularly on studying the chemical kinetics mechanism of an alternative reagent, monomethylamine (MMA) or also known as methylamine, for NO_x reduction by SNCR systems. MMA was chosen due to its indicated performance at comparatively low temperatures. An additional goal of this study is to propose a reduced MMA-based SNCR NO_x reduction kinetics mechanism for modeling of SNCR systems,

which has a good agreement with available experimental data. A reduced mechanism could then be used to simulate the performance of a MMA-based SNCR system, which would justify the benefit from alternative reagents. Research on chemical kinetics modeling of alternative reagents for the SNCR NO_x removal process provides a good tool for SNCR systems analysis and it also broadens the application of the SNCR technology to other industrial applications that can possibly lead to new markets.

Chapter II – Alternative Reagents for NO_x Reduction in SNCR Systems

2.1 Introduction

There are different reagents for SNCR systems, which have a range of performances and different impact on the NO_x reduction process. The most currently used reagents for coal-fired power plant applications are NH_3 and urea. However, other alternative SNCR reagents have been studied and experimented in either laboratory or small-scale units. This chapter provides a literature review of reagents that have been studied and their indicated industrial applications.

2.2 Ammonia

As a NO_x reduction reagent for SNCR systems in CFPPs, NH_3 was first introduced and studied in 1975 by Exxon Research & Engineering Co. [10]. Since then, many studies have been carried out in order to improve the performance of NH_3-based SNCR systems. Generally, improvements are obtained by adding other chemicals as additives, mixed with NH_3. In 1975, Lyon [10] stated that the addition of hydrogen can effectively reduce the optimal temperature at which NH_3 and flue gas react, NO_x reduction is enhanced and NH_3 slip is reduced at temperatures lower than the typical optimal temperatures. Data collected by Muzio et al. [23, 24] confirmed that even small quantities of hydrogen addition can provide significant improvement over the solely NH_3-based SNCR. In another study, Azuhata et al. [25] reported 90% NO_x reduction in experiments in a Pyrex flow reactor at 825 K at different O_2 levels by injecting hydrogen peroxide (H_2O_2). **Figure 5** shows result

from that research where H_2O_2/NO ratios as low as 1.0 were enough to shift the SNCR

temperature window by approximately 300 K.
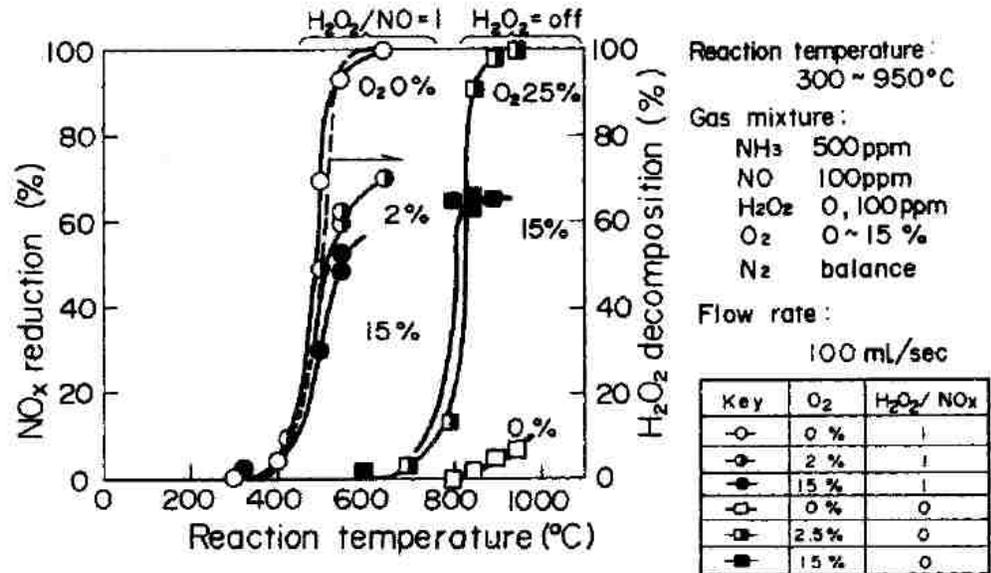
Figure 5. Relationship of NO_x reduction rate and temperature by Azuhata et al. [25]. Gas mixture: 100 ppm NO, 500 ppm NH_3, 0 or 100 ppm H_2O_2, 0 ~ 15% O_2.

Lodder and Lefers [26] reported that by injecting natural gas, ethane (C_2H_6) and carbon

monoxide along with NH_3 can decrease the optimal reaction temperature by 150 K – 200

K while achieving up to 75% NO_x removal efficiency, see **Figure 6**.
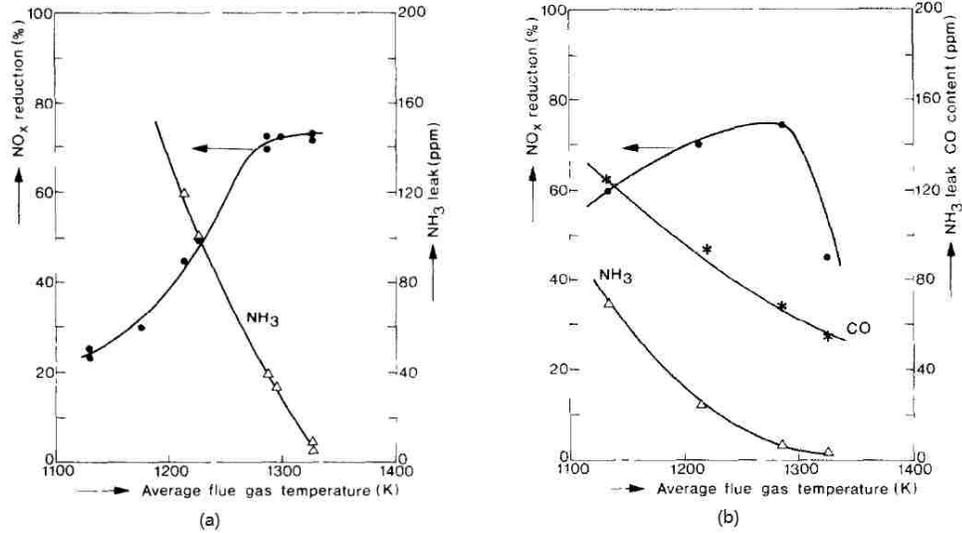
Figure 6. NO_x reduction rate vs. average flue gas temperature by Lodder and Lefers [26]. $[NH_3]/[NO_x]_{in}$= 1.5, O_2 = 1%. (a) - No additives injected; (b) – CO injected.

Wenli et al. [27] conducted studies on improving the NH_3-based SNCR performance by adding a hydrocarbon, such as methane (CH_4), ethane (C_2H_6), butane (C_4H_{10}) or ethylene (C_2H_4). The results showed that the temperature window can be downward shifted while achieving greater than 75% NO_x removal efficiencies. Other work by Leckner et al. [28] found very little effectiveness of hydrogen, methane, ethane and butane for SNCR enhancement under specific conditions in circulating fluidized bed boilers.

Besides the mentioned studies on additives, researches have also focused on lowering or eliminating NH_3 slip from the SNCR process. Robin et al. [29] reported that NH_3 slip can be dramatically reduced by adding CH_4 at 1120 K with minor impact on NO_x emissions reduction, with the NH_3 slip limited to below 10 ppm, at a CH_4 to NH_3 ratio of 2.4. An investigation carried out by Teixeira et al. [30-32] indicated that a decrement in NH_3 slip can result from an increment in gas CO level. NH_3 slips of less than 5 ppm, over a temperature range from 1025 K to 1350 K, was achieved when the initial CO concentration was 2000 ppm. Hemberger et al. [33] experimentally and numerically

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studied the effect of hydrocarbon additives on NH_3 slip, the results showed that in the presence of additives, NH_3 emissions are much less than without additives. The NH_3 slip was below the 5 ppm detection limit with a 200 ppm hydrocarbon level and $NH_3/NO_i =$ 1.5. However, these researchers also reported that when additives were added, large amounts of HCN were produced, which was up to 300 ppm, as shown in **Figure 7**.
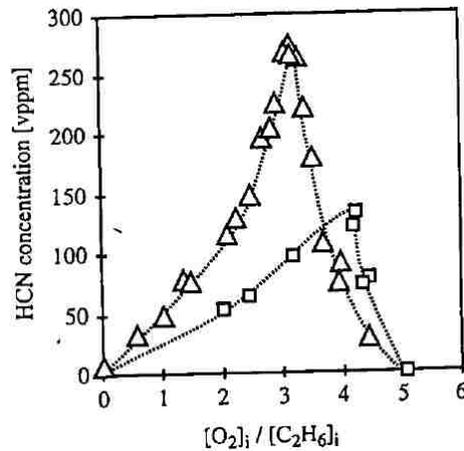
Figure 7. Formation of HCN from NH_3 and C_2H_6 in the presence of oxygen [33]. Conditions: 1000 vppm NH_3, residual N_2, $\tau = 0.45$ sec, T = 1073 K, p = 1 bar, O_2 varied. $\triangle$, 300 vppm C_2H_6; $\square$, 1500 vppm C_2H_5; the dotted line is to guide the eye.

The major advantages of using ammonia as a regent in SNCR systems are that it is a highly-mature technology and its relatively cost-effective. However, it has many associated drawbacks, such as low NO_x reduction rate at low temperatures, higher NH_3 slip at required NO_x reduction rates, handling difficulty and high toxicity.

2.3   Urea

Urea was first studied as an alternative regent to NH_3 in 1980 by Salimian and Hanson [34]. They found that the maximum NO removal rate by urea was comparable to that of NH_3 injection while the temperature window for urea was lower than that for NH_3. Arand

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et al. [11] reported that the urea-based SNCR could achieve as high as 70% NO_x reduction at temperatures in the range form 1290 K to1330 K in a natural gas fired furnace. Chen et al. [35] conducted experimental studies in a tunnel furnace simulating the thermal environment of pulverized coal boilers and the results showed that around 45%-50% of NO was removed at optimal temperatures around 1273 K. Jodal et al. [36] carried out experiments with NH_3 and urea in a pilot-scale reactor. Their results included in **Figure 8** indicate that the temperature window for urea and NH_3 is similar; however, the peak NO_x reduction was larger with urea than that with NH_3, and the temperature for maximum NO_x removal was shifted upward by 50K.
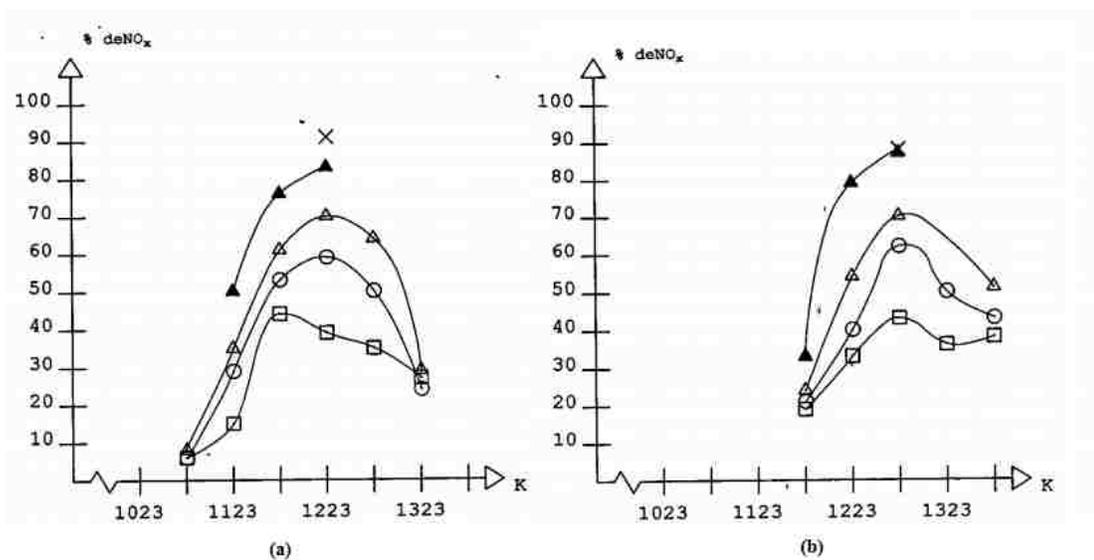
Figure 8. NO_x reduction rate vs. temperature under different molar ratio by Jodal et al. [36]. (a) Using ammonia as primary reductant; (b) Using urea as primary reductant. Molar ratio: □ = 0.7; ○ = 1.0; △ = 1.3; ▲ = 1.6; X = 2.2.

A test of NO_x removal using urea injection at the KVA Bessel Municipal Incineration Solid Waste Plant was performed by Jones et al. [37]. A 65% NO reduction was achieved at temperatures between 1220 K and 1270 K, while the NH_3 slip was less than 5 ppm. The effect of urea molar ratio and reaction temperature on NO abatement in a pilot-scale flow

reactor was studied by Lee and Kim [38] with good success. Similar to NH₃ injection, the performance of the urea-based SNCR NOₓ reduction can be affected by additives. Teixeira et al. [32] investigated the impact of several additives, which include methane, different combinations of hydrocarbons, carbon monoxide, ethylene glycol, hexa-methyl tetra-amine and furfural, on urea-based NOₓ reduction efficiency. The results indicate that the NOₓ reduction efficiency is very sensitive to the additive injection rates, mainly resulting in a noticeable downward reaction temperature window shift. The effect of oxygenated additives such as easters, phenols, carboxylic acids, aldehydes, ethers and alcohols on the urea-based SNCR NOₓ process was studied by Rota and Zanoelo [39] in 2003 (see **Figure 9**). According to the results from an experimental reactor, all the species studied in the reactor were capable of widening the urea reaction temperature window while maintaining peak NOₓ removal efficiencies.
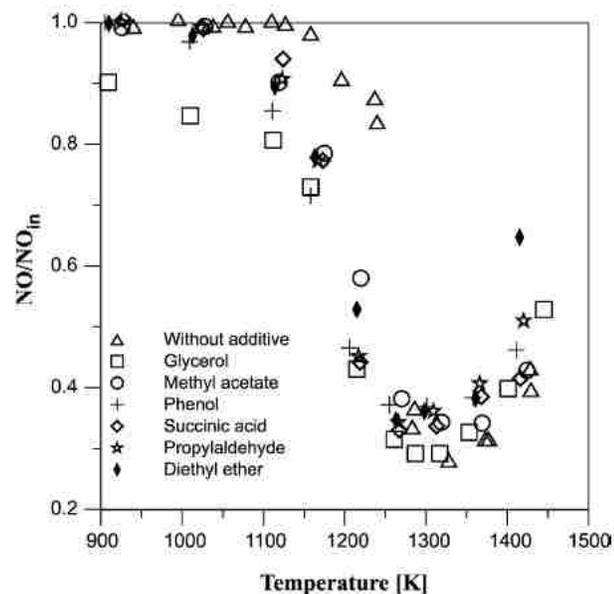
Figure 9. NO abatement with urea and urea + additives by Rota et al. [39]. Inlet conditions: NO = 500ppm; urea = 600 ppm; H₂O = 19%; O₂ = 1.7%; additive = 60 ppm; nitrogen = balance; residence time = 200/T s; P = 1 bar.

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Known problems of using urea in SNCR systems include formation of additional nitrous oxide (N_2O) and carbon monoxide emissions [37]. Additionally, the risk of fouling and corrosion at the boiler back-end is greater when using urea as a regent in SNCR systems. It should be noticed that urea as a reductant in SNCR systems has some advantages, such as ease of regent handling, since urea is a non-hazardous, stable, non-explosive and non-flammable chemical.

2.4 Cyanuric Acid

Cyanuric acid ($(CNOH)_3$) was initially studied as a NO_x reduction regent in 1986 by Perry and Siebers [40]. They experimentally investigated the cyanuric acid (CYA) reduction process in a flow reactor with simulated exhaust gas and the exhaust gas from a diesel engine. The results showed CYA has a better performance in NO_x reduction than NH_3 at high O_2 and CO concentrations in the exhaust gas. The commercial process that uses CYA as a regent to reduce NO_x in flue gases is termed RAPRENO$_x$ and it was patented in 1988 by Perry [41]. Caton and Siebers [42] compared the NO removal by CYA with that by NH_3 and suggested that CYA and NH_3 have different reduction processes according to the experimental results. Miller and Bowman [43] performed modeling studies on the chemical mechanism of the CYA-based NO_x reduction process. The proposed chemical mechanism of the process is shown in **Figure 10**. Streichsbier et al. [44] investigated a technique which uses CYA as a NO_x reduction regent and was able to obtain up to 85% NO_x reduction at temperatures between 970 K and 1070 K (see **Figure 11**).
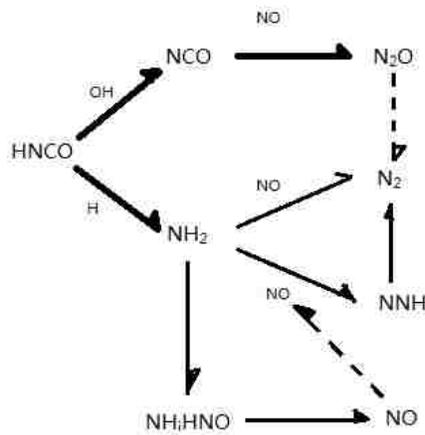
Figure 10. Reaction path diagram illustrating the primary steps for nitrogen species in current RAPRENOx mechanism by Miller and Bowman [44].
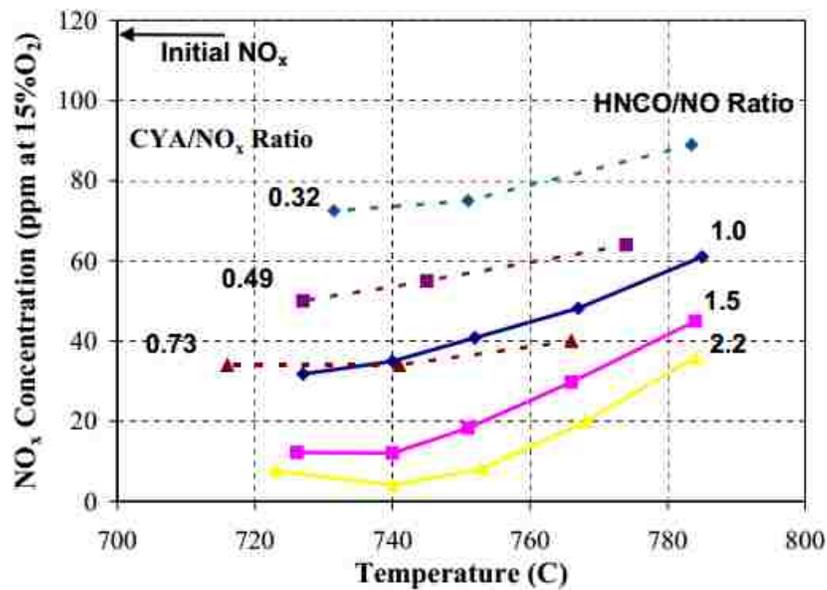
Figure 11. Experimental and numerical NO_x reduction with CYA by Streichsbier et al. [44]. The solid lines are numerical results while the dash lines represent the experimental values.

The major advantages of using CYA as a NO_x reduction regent are the absence of unreacted ammonia in the flue gases, high efficiency and its relatively low cost. However, the CYA-based process does suffer of problem of potential N_2O emissions.

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2.5   Monomethylamine

Early studies on methylamine or monomethylamine (MMA) by Jolley [45] and Emeleus [46] indicated that MMA can be thermally decomposed to H_2, hydrogen cyanide (HCN), CH_4 and NH_3 at temperatures in the range between 830 K and 950 K. Later, Dorko et al. [47] studied the thermal decomposition of MMA in a shock tube at temperatures ranging from 1275 K to 2400 K and a decomposition mechanism was proposed as below:

$$CH_3NH_2 \rightarrow CH_3 + NH_2$$
$$CH_3 + CH_3NH_2 \rightarrow CH_4 + CH_2NH_2$$
$$CH_3 + CH_2NH_2 \rightarrow CH_4 + CH_2NH$$
$$NH_2 + CH_3NH_2 \rightarrow NH_3 + CH_2NH_2$$
$$NH_2 + CH_2NH_2 \rightarrow NH_3 + CH_2NH$$
$$CH_2NH \rightarrow H_2 + HCN$$
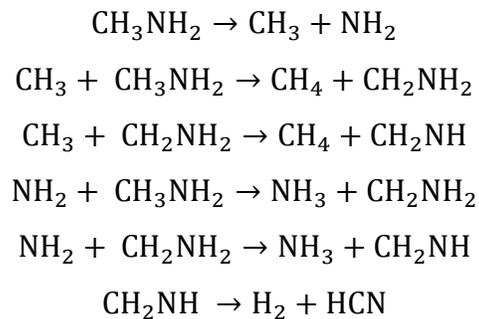
Wenli et al. [19] conducted an experimental investigation aiming at widening the temperature window of the SNCR NO_x removal process and studied the behavior of MMA, both as a reagent and an additive. The data from their laboratory experiments indicate that MMA is capable of achieving significant NO reductions at temperatures as low as 800 K, with a comparatively wide reaction temperature window. The use of MMA as regent in SNCR NO_x reduction systems was also studied by Yoshihara et al. [48] and Nakanishi et al. [49]. They applied MMA to a proposed SNCR system for diesel engines [50]. The experimental results showed that up to 80% of NO_x removal can be obtained at system temperatures in the range between 690 K and 715 K. The results were confirmed by Xu et al. [51] using an actual engine equipped with an experimental SNCR system, with 40% MMA aqueous solution injection. Additionally, Milewska et al. [52] tested a laboratory scale MMA-based SNCR NO_x reduction setup, with highest NO_x removal efficiencies

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obtained at temperatures between 735 K and 750 K, with relatively long residence times, above 3 seconds. However, high HCN emissions were detected in the tests which could be considered as a major drawback of a MMA-based SNCR NO_x control system. Available literature and experimental results on the potential application of MMA for NO_x emissions reduction in coal-fired boilers are still lacking. However, bench-scale studies and the experiments on diesel engines do provide a promising possibility of using MMA as a regent in SNCR NO_x reduction systems for coal-fired boilers. Furthermore, an appropriate, validated, detailed chemical kinetics model that would provide reasonable predicting capabilities is of great interest.

2.6   Other Reagents

Some other novel reagents for the SNCR NO_x reduction process have been studied by many researchers. Chen et al. [35] conducted both experimental and kinetic modeling studies on NO_x reduction by –NH and –CN compounds, which included $(HOCN)_3$, $CO(NH_2)_2$ and ammonium sulfate. Among the reagents studied, ammonium sulfate showed superior performance as a NO reducing reagent, compared to traditional reagents such as urea and CYA; however, the extra SO_2 production might be a drawback for actual industrial application. Mahmood et al. [53] performed experiments on the performance of ammonium carbonate for NO_x removal and achieved a 32% NO_x reduction efficiency at about 1150 K. Wenli et al. [19] investigated the use of ethylenediamine $(CH_2NH_2)_2$ as a reagent for the SNCR NO_x reduction processes and reported that $(CH_2NH_2)_2$ starts to react with NO at temperature around 925 K and gets a wider temperature window at about 1110 K.

Table 1 shows a comparisons between different reagents regarding their NO_x reduction performance. Although, researches have succeeded in widening the SNCR active temperature window or enhancing the removal efficiency of commercial SNCR systems by using alternative reagents, one alternative reagent, MMA seems to provide an interesting option to the traditional NH_3- and urea-based SNCR systems. The NO removal efficiency and the low optimal reaction temperatures of MMA are the main advantages seen from a MMA-based process which can perform at temperatures below 900 K. This warrant a further study of MMA for SNCR applications.

Table 1. Comparisons of different regents of SNCR systems in non-experimental reactor units.

Regent	Optimal Temperature Range	Typical/ Reported peak NO_x Reduction Rate	NH_3 Slip	Disadvantages
NH_3	1000 K – 1200 K	50% – 70%	≤5 ppm	• Not active at temperatures below 800 K; • Toxic
Urea	1220 K – 1330 K	45% – 67%	≤5 ppm	• Additional nitrous oxide and carbon monoxide emissions; • Greater chances of fouling and corrosion; • Not active at temperatures below 800 K
CYA	970 K – 1340 K	60% – 80%	≤5 ppm	• Additional nitrous oxide emissions; • Not active at temperatures below 800 K
MMA	690 K – 800 K	Up to 80%	≤5 ppm	• HCN emissions

Chapter III – Chemical Kinetics Modeling of Monomethylamine for SNCRs

3.1 Introduction

Monomethylamine is a colorless, flammable, corrosive and toxic gas with strong odor. It is usually used as an aqueous solution and stored in well-ventilated systems [54]. The physical properties of aqueous methylamine are listed in **Table 2**.

Table 2. Physical properties of aqueous monomethylamine [55].

Aqueous Monomethylamine		
Property	40% MMA	50% MMA
Boiling point (K)	316	304
Freezing Point (K)	235	227
Density (liquid) at 298 K (g/ml)	0.897	0.880
Vapor pressure at 298 K (kPa)	50	76
Flash point, Closed cup (ASTM D-92) (K)	261	239

MMA has shown the promise of better performance as an SNCR NO_x reduction reagent than traditional chemicals like NH_3, urea and CYA, due to its low optimal temperature range (below 950 K) and comparatively low NH_3 slip [50]. This chapter focuses on reviewing available kinetics models of MMA – NO_x reactions and reports a reduced chemical kinetics scheme for the MMA SNCR NO_x reduction process. It also reports comparisons with other alternative reagents in order to evaluate the advantages of using MMA for the SNCR process over other chemicals. Chemical kinetic simulations were performed using the CHEMKIN software, under plug flow reactor conditions.

3.2   Existing Monomethylamine Chemical Kinetics Models

Early studies of MMA kinetics mainly focused on the reactions that take place at high temperatures. Higashihara et al. [56] in 1987 proposed a chemical kinetics mechanism of MMA thermal decomposition valid in a temperature range from 1436 K to 1820 K. The mechanism consists of 18 species and 28 reactions and satisfactorily agrees with experimental results obtained by using laser kinetic absorption spectroscopy behind reflected shock waves in a shock tube. The Higashihara's mechanism is listed in **Table 3**.

Table 3. Higashihara et al. [56] chemical kinetics mechanism. Units are cm3/(mol·s) for A and cal/mol for E. Rate constants were expressed as $k = AT^m \exp(-E/RT)$.

Reaction		A	m	E
1.	CH3NH2+M=CH3+NH2+M	4.80E+17	0	62618
2.	CH3NH2+M=CH2NH2+H+M	2.00E+17	0	88430
3.	CH3+CH3NH2=CH4+CH2NH2	5.50E-01	4	8365
4.	NH2+CH3NH2=NH3+CH2NH2	1.30E+14	0	20076
5.	H+CH3NH2=H2+CH2NH2	5.50E+12	0	3107
6.	CH2NH2=H+H2CNH	1.50E+11	0	39913
7.	H+CH2NH2=H2+H2CNH	1.00E+13	0	0
8.	H+CH2NH2=CH3+NH2	1.00E+13	0	0
9.	H+H2CNH=H2+HCNH	1.50E+14	0	10038
10.	H+HCNH=H2+HCN	2.00E+13	0	0
11.	HCNH+M=H+HCN+M	3.00E+15	0	32026
12.	H2CNH+M=H2+HCN+M	1.00E+09	0	0
13.	H2+CN=H+HCN	7.50E+13	0	0
14.	NH3+M=NH2+H+M	2.50E+16	0	93688
15.	NH3+H=NH2+H2	1.30E+14	0	21510
16.	N2H4+M=NH2+NH2+M	4.00E+15	0	41108
17.	CH4+M=CH3+H+M	2.00E+17	0	88430
18.	CH3+H2=CH4+H	6.50E+02	3	7648
19.	C2H6+M=CH3+CH3+M	6.30E+19	0	82455
20.	C2H6+H=C2H5+H2	1.30E+14	0	9321
21.	C2H5+M=C2H4+H+M	1.00E+17	0	34894
22.	C2H6+CH3=C2H5+CH4	5.50E-01	4	8365
23.	H+C2H5=CH3+CH3	3.00E+13	0	0
24.	H+C2H5=C2H4+H2	1.70E+12	0	0
25.	H+C2H4=H2+C2H3	1.50E+14	0	10277

26.	C2H3+M=C2H2+H+M	3.00E+15	0	32026
27.	H+C2H3=H2+C2H2	2.00E+13	0	0
28.	CH3+CH3=C2H4+H2	1.00E+16	0	32026

Hwang et al. [57] used a similar approach for modeling MMA oxidation at a temperature range from 1260 K to 1600 K, the kinetics model simulation results were consistent with experiment results. The Hwang mechanism contains 141 reactions and 44 species as shown in **Table 4**.

Table 4. Hwang et al. [57] chemical kinetics mechanism. Units are cm3/(mol·s) for A and cal/mol for E. Rate constants were expressed as $k = AT^m \exp(-E/RT)$.

Reaction		*A*	*m*	*E*
1.	CH3+NH2=CH3NH2	2.50E+13	0	0
2.	CH3+NH2=CH2NH2+H	5.50E+13	0	11711
3.	CH3+NH2=CH2NH+H2	6.00E+12	0	16491
4.	CH3NH2=CH2NH2+H	1.00E+15	0	84128
5.	CH3NH2+CH3=CH2NH2+CH4	6.50E+15	0	27724
6.	CH3NH2+NH2=CH2NH2+NH3	3.30E+15	0	22227
7.	CH3NH2+H=CH2NH2+H2	1.80E+13	0	5258
8.	CH3NH2+H=CH3+NH3	3.90E+14	0	11472
9.	CH2NH2=CH2NH+H	1.00E+13	0	43020
10..	CH2NH2+H=CH2NH+H2	1.00E+13	0	0
11.	CH2NH+M=CHNH+H+M	1.30E+17	0	65725
12.	CH2NH+M=HCN+H2+M	3.30E+15	0	38240
13.	CH2NH+H=CHNH+H2	5.30E+14	0	10038
14.	CHNH+M=HCN+H+M	1.60E+15	0	24856
15.	CHNH+H=HCN+H2	2.00E+13	0	0
16.	CH3NH2+O2=CH2NH2+HO2	4.00E+12	0	42064
17.	CH3NH2+O=CH2NH2+OH	5.40E+12	0	1673
18.	CH3NH2+OH=CH2NH2+H2O	1.20E+07	2	1195
19.	CH3NH2+HO2=CH2NH2+H2O2	1.60E+12	0	6453
20.	CH2NH2+O2=CH2NH+HO2	9.10E+13	0	9799
21.	CH2NH2+O=CH2NH+OH	5.00E+13	0	0
22.	CH2NH2+OH=CH2NH+H2O	5.00E+13	0	0
23.	CH2NH+O=CHNH+OH	1.60E+09	1.2	717
24.	CH2NH+OH=CHNH+H2O	6.00E+13	0	3107
25.	CHNH+O=HCN+OH	3.00E+13	0	0
26.	CHNH+OH=HCN+H2O	3.00E+13	0	0

27.	CH3+CH3=C2H6	9.00E+16	-1.2	717
28.	CH3+CH3=C2H4+H2	6.00E+12	0	16791
29.	C2H6+CH3=C2H5+CH4	5.50E-01	4	8365
30.	C2H6+H=C2H5+H2	1.30E+14	0	9321
31.	C2H5=C2H4+H	2.00E+13	0	39674
32.	C2H5+H=CH3+CH3	3.70E+13	0	0
33.	C2H5+H=C2H4+H2	1.70E+12	0	0
34.	C2H4+M=C2H2+H2+M	2.60E+17	0	79348
35.	C2H4+M=C2H3+H+M	2.60E+17	0	96556
36.	C2H4+H=C2H3+H2	1.50E+14	0	10277
37.	C2H3+H=C2H2+H2	2.00E+13	0	0
38.	C2H2+H=C2H3	5.50E+12	0	2151
39.	CH4=CH3+H	1.00E+15	0	99902
40.	CH4+H=CH3+H2	2.20E+04	3	8843
41.	CH4+O=CH3+OH	1.20E+07	2.1	7648
42.	CH4+OH=CH3+H2O	1.60E+06	2.1	2390
43.	CH3+H=CH2+H2	7.20E+14	0	15057
44.	CH3+O2=CH3O+O	2.20E+14	0	33699
45.	CH3+O2=CH2O+OH	3.20E+11	0	9082
46.	CH3+O=CH2O+H	7.00E+13	0	0
47.	CH3+OH=CH2+H2O	2.00E+13	0	0
48.	CH2+H=CH+H2	3.00E+13	0	0
49.	CH2+O2=CO+OH+H	1.30E+13	0	1434
50.	CH2+O=CH+OH	8.00E+13	0	0
51.	CH2+OH=CH+H2O	3.00E+13	0	0
52.	CH+O2=CO+OH	2.00E+13	0	0
53.	CH3O+M=CH2O+H+M	1.00E+14	0	25095
54.	CH2O+M=CHO+H+M	5.00E+16	0	76480
55.	CH2O+H=CHO+H2	2.50E+13	0	4063
56.	CH2O+O=CHO+OH	3.50E+13	0	3585
57.	CH2O+OH=CHO+H2O	3.00E+13	0	1195
58.	CHO+M=CO+H+M	2.50E+14	0	16730
59.	CHO+H=CO+H2	2.00E+14	0	0
60.	CHO+O2=CO+HO2	3.00E+12	0	0
61.	CHO+O=CO+OH	3.00E+13	0	0
62.	CHO+OH=CO+H2O	5.00E+13	0	0
63.	C2H6+O=C2H5+OH	3.00E+07	2	5019
64.	C2H6+OH=C2H5+H2O	6.30E+06	2	717
65.	C2H4+O=CH3+CHO	1.60E+09	1.2	717
66.	C2H4+OH=C2H3+H2O	5.00E+13	0	6692
67.	C2H3+O2=CH2O+CHO	4.00E+12	0	-239
68.	C2H2+O=CH2+CO	4.10E+08	1.5	1673
69.	C2H2+O=CHCO+H	4.30E+14	0	12189

70.	C2H2+OH=CH2CO+H	1.00E+14	0	11472
71.	CH2CO+M=CH2+CO+M	3.60E+15	0	59272
72.	CHCO+H=CH2+CO	3.00E+13	0	0
73.	NH2+NH2=N2H2+H2	4.00E+13	0	11711
74.	NH2+NH=N2H2+H	3.20E+13	0	956
75.	N2H2+M=N2H+H+M	1.00E+16	0	49951
76.	N2H2+H=N2H+H2	5.00E+13	0	956
77.	NH3+M=NH2+H+M	2.50E+16	0	93688
78.	NH3+H=NH2+H2	1.30E+14	0	21510
79.	NH3+O=NH2+OH	2.20E+13	0	8843
80.	NH3+OH=NH2+H2O	5.80E+13	0	8126
81.	NH2+H=NH+H2	1.90E+13	0	0
82.	NH2+O2=HNO+OH	1.50E+12	-0.4	36089
83.	NH2+HO2=NH2O+OH	3.00E+13	0	21988
84.	NH2+NO=N2H+OH	8.80E+15	-1.25	0
85.	NH2+NO=N2+H2O	6.30E+19	-2.5	1912
86.	NH2+O=HNO+H	8.90E+14	-0.5	239
87.	NH2+O=NH+OH	6.90E+11	0.4	-239
88.	NH2+OH=NH+H2O	5.00E+11	0.5	1912
89.	NH+H=N+H2	1.00E+14	0	0
90.	NH+O2=NO+OH	1.40E+11	0	1912
91.	NH+O2=HNO+O	1.00E+13	0	11950
92.	NH+NO=N2O+H	1.70E+14	-0.5	0
93.	NH+O=NO+H	6.30E+11	0.5	0
94.	NH+OH=HNO+H	1.50E+12	0.5	1912
95.	NH+OH=N+H2O	5.00E+11	0.5	1912
96.	NH2O+M=HNO+H+M	3.60E+13	0	25095
97.	N+O2=NO+O	6.00E+09	1	6214
98.	N2+O=N+NO	1.80E+14	0	76241
99.	NO+H=N+OH	1.70E+14	0	48756
100.	HNO+M=H+NO+M	1.90E+16	0	48756
101.	HNO+H=NO+H2	1.30E+13	0	4063
102.	HNO+OH=NO+H2O	3.60E+13	0	0
103.	N2H+M=N2+H+M	2.00E+14	0	5975
104.	N2H+NO=N2+HNO	2.50E+12	0	0
105.	N2O+M=N2+O+M	6.90E+23	-2.5	65008
106.	N2O+H=N2+OH	7.60E+13	0	15057
107.	N2O+O=NO+NO	1.00E+14	0	27963
108.	HCN+O=CN+OH	5.00E+13	0	21988
109.	HCN+O=NCO+H	1.70E+08	1.5	7409
110.	HCN+O=NH+CO	2.20E+13	0	15296
111.	HCN+OH=CN+H2O	4.40E+12	0	9082
112.	CN+H2=HCN+H	2.50E+02	3.62	912

113.	CN+O2=NCO+O	5.60E+12	0	0
114.	CN+O=CO+N	2.00E+13	0	478
115.	CN+OH=NCO+H	5.60E+13	0	0
116.	NCO+M=CO+N+M	6.30E+16	-0.5	47800
117.	NCO+H2=HNCO+H	3.00E+13	0	5258
118.	NCO+H=NH+CO	4.00E+13	0	0
119.	NCO+NO=N2O+CO	1.00E+13	0	-478
120.	NCO+O=NO+CO	5.80E+13	0	0
121.	HNCO+M=NH+CO+M	5.00E+13	0	70027
122.	HNCO+H=NH2+CO	2.00E+13	0	3107
123.	HNCO+O2=NCO+HO2	1.00E+13	0	70027
124.	H2+M=H+H+M	2.20E+14	0	96078
125.	H+O2=OH+O	2.20E+14	0	16730
126.	O+H2=OH+H	1.50E+07	2	7648
127.	OH+H2=H2O+H	1.00E+08	1.6	3346
128.	OH+OH=H2O+O	1.50E+09	1.14	0
129.	H+O2+M=HO2+M	2.50E+15	0	0
130.	H+OH+M=H2O+M	7.50E+23	-2.6	0
131.	HO2+H=OH+OH	2.50E+14	0	1912
132.	HO2+H=H2+O2	2.50E+13	0	717
133.	HO2+OH=H2O+O2	2.00E+13	0	0
134.	HO2+O=OH+O2	2.00E+13	0	0
135.	HO2+HO2=H2O2+O2	2.00E+12	0	0
136.	H2O2+M=OH+OH+M	1.20E+17	0	45410
137.	CO+OH=CO2+H	4.40E+06	1.5	-717
138.	CH3+NO=HCN+H2O	4.30E+12	0	20315
139.	CH2+NO=HCN+OH	1.40E+12	0	-1195
140.	CH+NO=HCN+O	1.20E+14	0	0
141.	CH+N2=HCN+N	2.10E+12	0	16730

The previously reported chemical kinetics mechanisms were proposed for reaction temperatures in excess of 1225 K. Additionally, the mechanism by Higashihara et al. [57] contains no reactions that include the species NO and NO₂.

Other available mechanisms for MMA, such as by Coda et al. [58], and Dean and Bozzelli [59], were also proposed for high temperature MMA oxidation and might not be

able to predict the chemistry of an MMA-based SNCR NO_x process with a good degree of accuracy.

Kantak et al. [60] conducted studies on MMA oxidation modeling at temperatures from 600 K to 1400 K. Chemical reaction predictions from the Kantak et al.'s [60] mechanism, which has 350 reactions and 65 species, showed good agreement with experimental data from Hjuler et al. [61] in the temperature range from 600 K to 1400 K, thereby becoming a good candidate to be used for MMA-based SNCR NO_x reduction simulations.

3.3   Plug Flow Reactor Modeling

A plug flow reactor (PFR) modeling approach was used in this study to investigate the progress of the chemistry of MMA for SNCR applications. Plug flow reactor modeling is a chemical numerical model that describes an ideal plug flow with the following assumption:

(1) No temperature or species concentration gradient in the radial direction, that is, on each cross-section plane in the flow direction, the temperature is constant and every chemical species on the cross-section is evenly distributed;

(2) No back-mixing, that is, the species are perfectly mixed in the radial direction but not in the axial direction.

A schematic of the PFR concept is shown **Figure 12**.
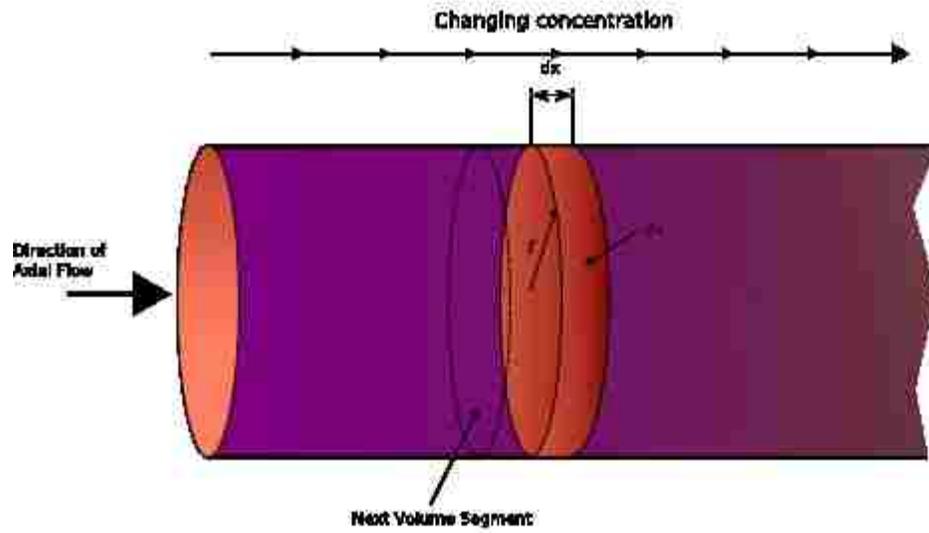
Figure 12. Schematic diagram of a plug flow reactor.

The species concentration part of the PFR model is governed by ordinary differential equations and the problem can be defined by the mass balance equation:

$$[accumulation] = [in] - [out] + [generation] - [consumption] \qquad \text{Eq. 1}$$

Assuming the system is at steady state, then accumulation is 0, hence Eq. 1 can be re-written as:

$$F(x) - F(x + dx) + A \cdot v \cdot r \cdot dx = 0 \qquad \text{Eq. 2}$$

Where: x is the axial position is the reactor

dx is the differential thickness of the fluid plug

$F(x)$ is the molar flow rate of species

A is the cross sectional area

v is the stoichiometric coefficient

r is the volumetric reaction rate

Considering a flow linear velocity of u, concentration of species C and the assumption that $dx \to 0$, the above equation can be re-written as:

$$u\frac{dC}{dx} = vr$$

Eq. 3

or,

$$\frac{dC}{dt} = vr$$

Eq. 4

Where : t is time

r can be calculated by the equation:

$$r = k(T)[reactant\ A]^n[reactant\ B]^m$$

Eq. 5

Where: m and n are the partial orders of the reactions and depend on the reaction mechanism.

$k(T)$ is defined by the modified Arrhenius expression:

$$k(T) = AT^m e^{(-E/RT)}$$

Eq. 6

Where: A is the pre-exponential constant

m is the temperature exponent

E is the activation energy

R is the universal gas constant

T is the temperature

Solving the Equations 1 to 6 with initial conditions, which are the PFR inlet conditions; and the parameters from the kinetics mechanism list, the results of the simulation can be obtained.

Despite the limitation that the PFR model is one-dimensional, thereby it does not handle spatial variations in temperature and velocity at a given multiple-dimensional space,

it can still provide reliable results for the study of the potential of the NO_x reduction performance of different alternative reagents for the SNCR process.

3.4   Model Validation

The model validations were performed using the CHEMKIN package and the SENKIN subroutine.

The CHEMKIN package is an interpreter program that reads the symbolic description of a given chemical reaction mechanism and the thermodynamic database which includes the thermodynamic properties of the relevant species. The output of the program is a data file which links to the CHEMKIN subroutine library and it can return the information on species and reactions and their production rates. The linking file can be considered as part of the input to the SENKIN code.

The SENKIN code is a plug flow model subroutine which can be coded as a program that reads in several parameters such as initial temperature, temperature slope (along the plug flow reactor), reaction pressure, residence time, input species and their concentrations and it conducts calculations based on the mentioned linking file to simulate the rate of progress of chemical mechanism under certain conditions. The CHEMKIN and SENKIN model structure is shown in **Figure 13**.
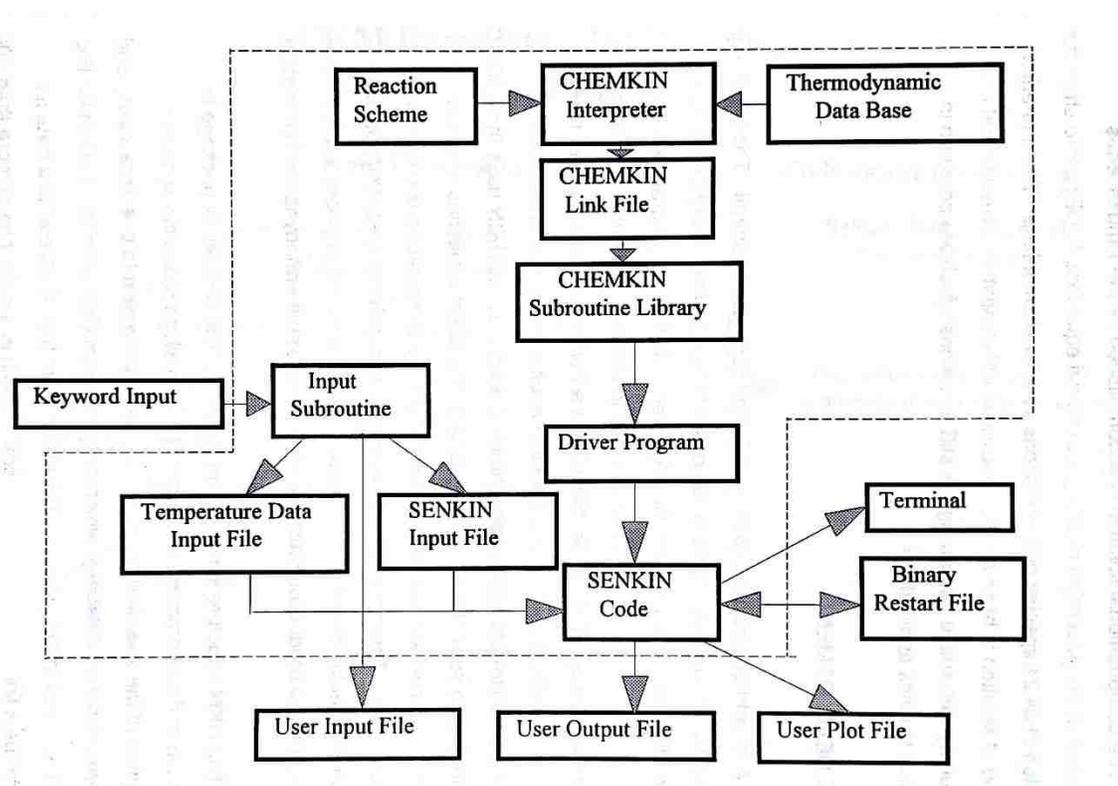
Figure 13. Chemical kinetics modeling by implementing CHEMKIN and SENKIN [63].

PFR modeling with CHEMKIN and SENKIN was executed with the kinetics mechanisms listed in Section 3.2 to validate their chemical kinetics scheme capabilities for simulating the MMA-based SNCR NO_x reduction process. A first validation was done by comparing the simulation data (Simul. Data) from the MMA kinetics mechanisms by Hwang et al. [57], Coda et al. [58] and Kantak et al. [60] with experimental data (Exp. Data) by Hjuler et al. [61]. The results of the simulations are presented below (**Figures 14 to 16**).

As previously discussed, **Figure 14** clearly illustrates that the mechanism by Hwang et al. [57] is not able to follow the MMA – NO/NO_2 experimental results, with a very poor agreement with the experimental data. Similarly, results obtained from simulations using the chemical kinetics scheme by Coda et al. [58] (**Figure 15)** are also in poor agreement.

Both mechanisms by Hwang et al. [57] and Coda et al. [58] are not capable of predicting formation of NO_2. Therefore, the mechanisms that were developed for a high temperature environment are not a proper choice for low-temperature SNCR NO_x reduction process simulation.
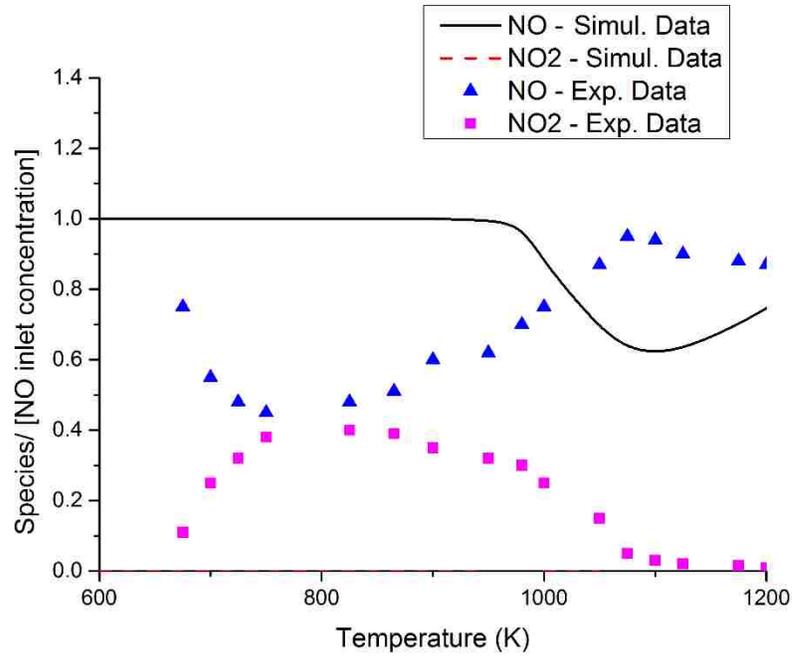
Figure 14. Comparison between experimental data by Hjuler et al. [61] and the simulation predictions by using the mechanism by Hwang et al. [57] for species NO and NO_2. Inlet conditions: 1.0 atm; 600 K – 1200 K; residence time = 0.2 s; (in mole %) $[CH_3NH_2] = 0.026$, $[NO] = 0.0471$, $[O_2] = 4.0$, $[H_2O] = 0.1$, balance nitrogen.
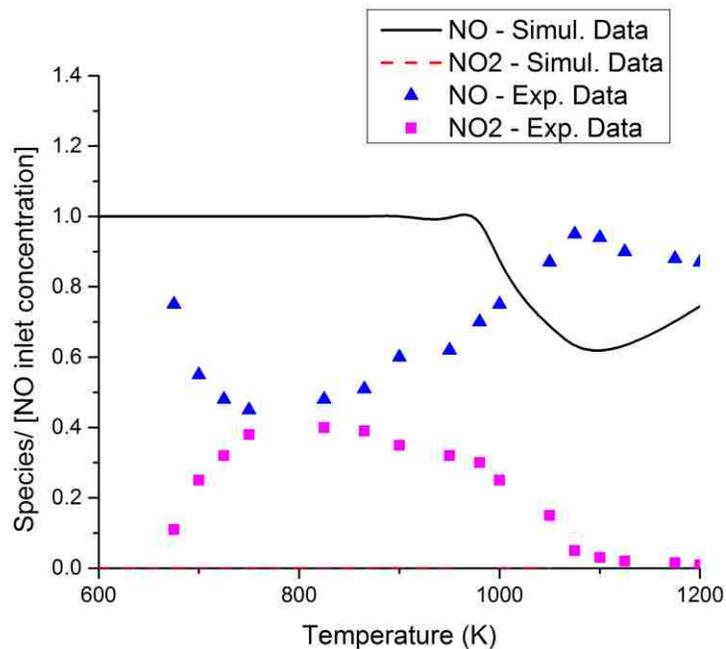
Figure 15. Comparison between experimental data by Hjuler et al. [61] and the simulation predictions by using the mechanism by Coda et al. [58] for species NO and NO_2. Inlet conditions: 1.0 atm; 600 K – 1200 K; residence time = 0.2 s; (in mole %) $[CH_3NH_2]$ = 0.026, [NO] = 0.0471, $[O_2]$ = 4.0, $[H_2O]$ = 0.1, balance nitrogen.

In **Figure 16**, the simulation results from the mechanism by Kantak et al. [60] are relatively consistent with the experimental data by Hjuler et al. [61] especially at the points around the peak NO reduction. However, at temperatures below 800 K, the differences between the simulation data and the experimental data become significant. The mechanism by Kantak et al. [60] also provides NO_2 predictions that are in line with the experimental data.

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Figure 16. Comparison between experimental data by Hjuler et al. [61] and the simulation predictions by using mechanism by Kantak et al. [60] for species NO and NO_2. Inlet conditions: 1.0 atm; 600 K – 1200 K; residence time = 0.2 s; (in mole %) $[CH_3NH_2] = 0.026$, $[NO] = 0.0471$, $[O_2] = 4.0$, $[H_2O] = 0.1$, balance nitrogen.

Figure 17 presents another validation for the mechanism by Kantak et al. [60] with reference from experimental data by Milewska [64]. These data were produced by the Institute of Power Engineering in Poland to evaluate the NO reduction capability of MMA in the laboratory data. The comparison shows not a perfect agreement with the data; however, for same conditions, the model provides a good level of prediction accuracy.

It can be seen in **Figure 17** that there are three groups of data (data that falls on the 45 degree line, and two other groups of data above and below this line). The predicted trend for all three groups are correct, indicating that there may have been a drift in the laboratory measurements reported by the Institute of Power Engineering in Poland.
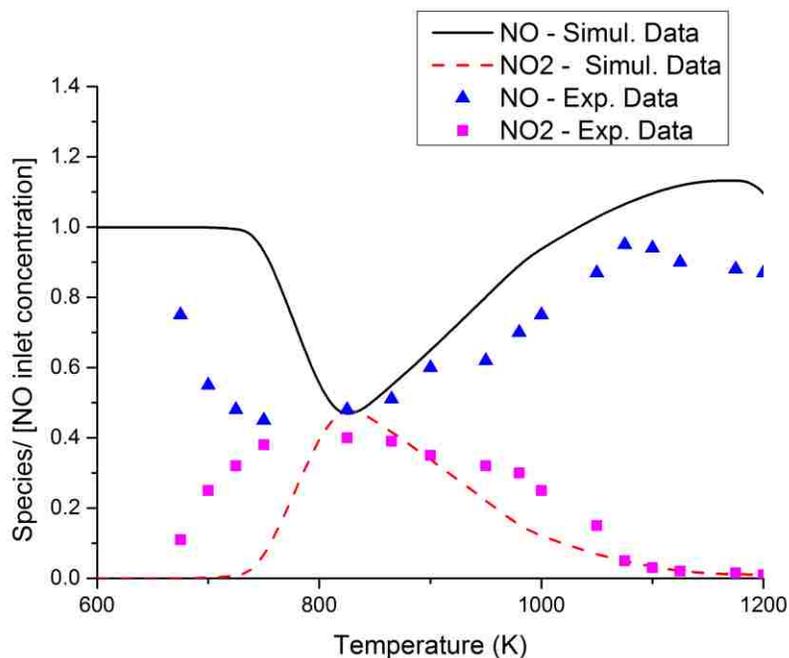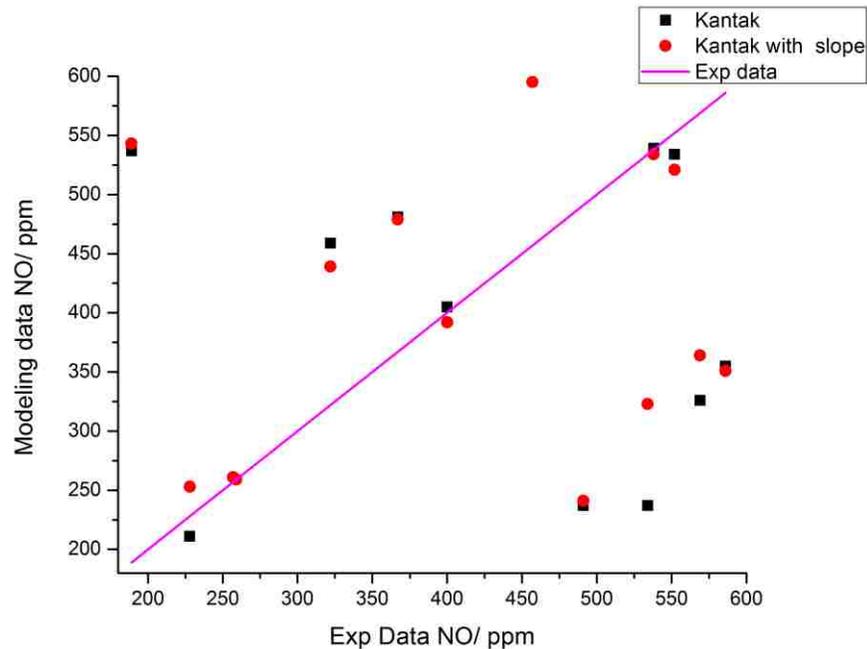
Figure 17. Comparison between experimental data by Milewska [64] and the simulation predictions by using mechanism by Kantak et al. [60] for outlet NO concentration. The inlet condition is varied and corresponding to different cases. The temperature slope for the simulation that is with slope is 100 K/s.

In summary, the mechanism by Kantak et al. [60] is arguably the most promising MMA-NO reaction mechanism for modeling the MMA-based SNCR NO_x reduction process, despite its limitation in accurately matching experimental data at lower temperatures. A sensitive analysis was performed and reported in Section 3.5. This was done to obtain a better understanding of the features related to the MMA NO_x reduction process.

3.5   Sensitive Analysis

Sensitive analysis helps understand the impact of different parameters on the output of the simulation under specified inlet conditions. This section discusses the influence of the following parameters: normalized stoichiometric ratio (NSR, defined as the actual mole

ratio of the reagent, MMA in this case, to NO), initial CO and NO concentration, residence time and temperature. In **Table 5**, simulation baseline conditions are underlined. Sensitivity results are provided in terms of outlet NO, NO_2, NH_3 and HCN. The range of the parameters for the simulations of the sensitivity analysis are listed in **Table 5**.

Table 5. Inlet conditions for sensitive analysis. *The underline values are the baseline conditions.

Temp /K	600-1400
Residence time /s	0.1, <u>0.3</u>, 0.5
NO /ppm	50, <u>500</u>, 800
O_2 /%	<u>4</u>
CO_2 /%	<u>10</u>
CO /ppm	<u>0</u>, 10, 100
NSR	0.25, <u>0.5</u>, 1
H_2O /%	<u>5</u>
N_2 /%	Balance

3.5.1   NSR Simulations

Figure 18 shows an optimal temperature window for the reaction of NO by MMA. This window is from approximately 750 K to 1000 K. There temperature levels are relatively lower than those of the NH_3 and urea processes. NO reductions up to 90% can be theoretically achieved with a NSR of 1.0 and at about 800 K. NO_2 production as high as 380 ppm can be achieved at that 1.0 NSR. HCN emissions as high as 90 ppm can result from injection of MMA at the NSR of 1.0.

Simulations with different NSRs show that NSR has a great impact on NO, NO_2 and HCN reduction/production, while the influence is relatively small on NH_3 formation (see **Figures 18** to **20**). Note that predicted HCN emissions is of a concern, while NH_3 slip from the process is rather negligible, at less than 3 ppm (see **Figures 19** and **20**).
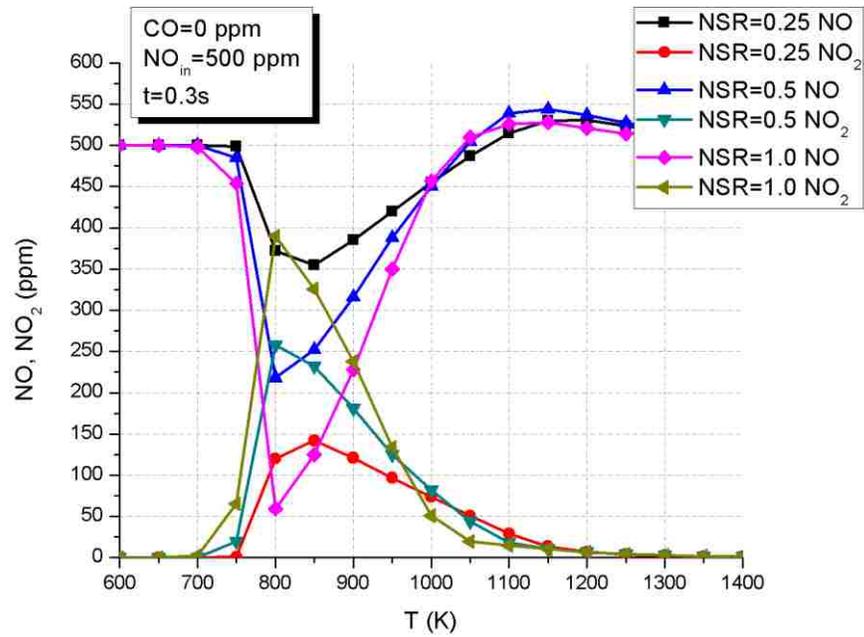
Figure 18. Predicted outlet NO and NO_2 concentrations vs. temperature under various NSRs.

Figure 19. Predicted outlet NH_3 concentrations vs. temperature under various NSRs.

Figure 20. Predicted outlet HCN concentrations vs. temperature under various NSRs.

3.5.2   Initial CO Concentration Simulations

Figures 21 to **23** show simulations including different initial CO concentrations and indicate that the inlet CO level has a negligible impact particularly at low temperatures on NH_3 and HCN emissions, but a greater impact on NO and NO_2 reduction/production. At high CO levels, the temperature window for MMA to react with NO seems to significantly widen and the reactions starts to take place below 700 K. NO_2 production also increases at high CO levels. These results are in line with the report by Lodder and Lefers [26] that CO addition can accelerate the reduction process of NO_x by NH_3, considerably shifting downward the optimal reaction temperature of MMA.
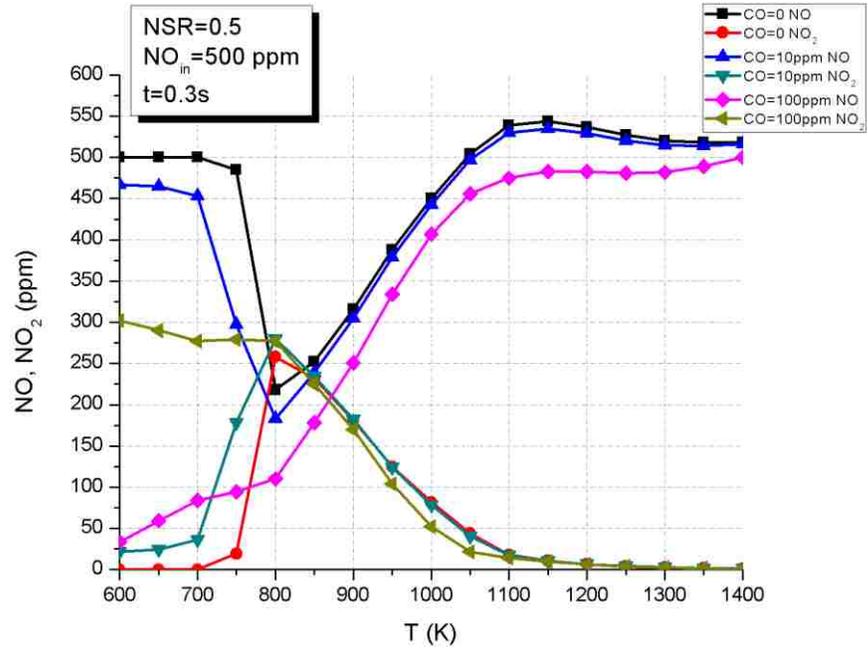
Figure 21. Predicted outlet NO and NO_2 concentrations vs. temperature under various initial CO concentrations.
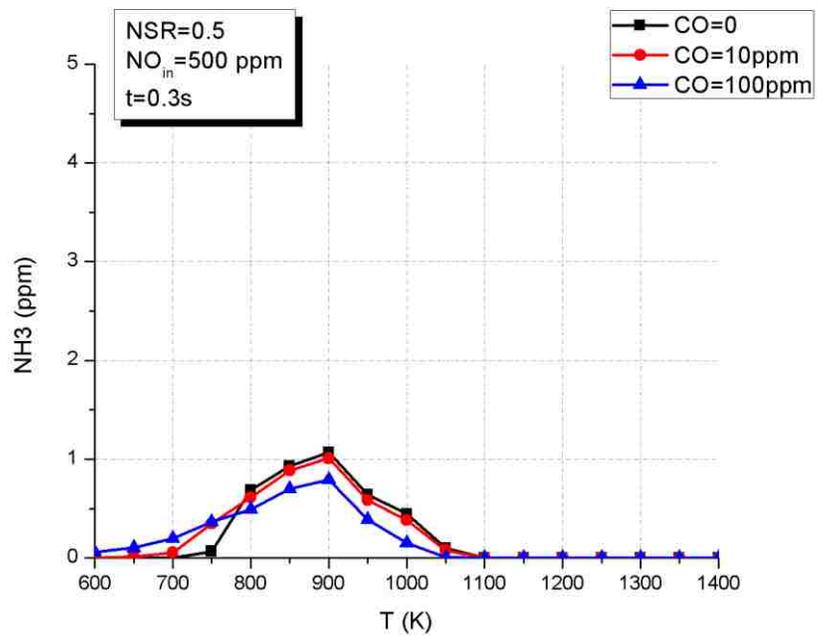
Figure 22. Predicted outlet NH_3 concentrations vs. temperature under various initial CO concentrations.
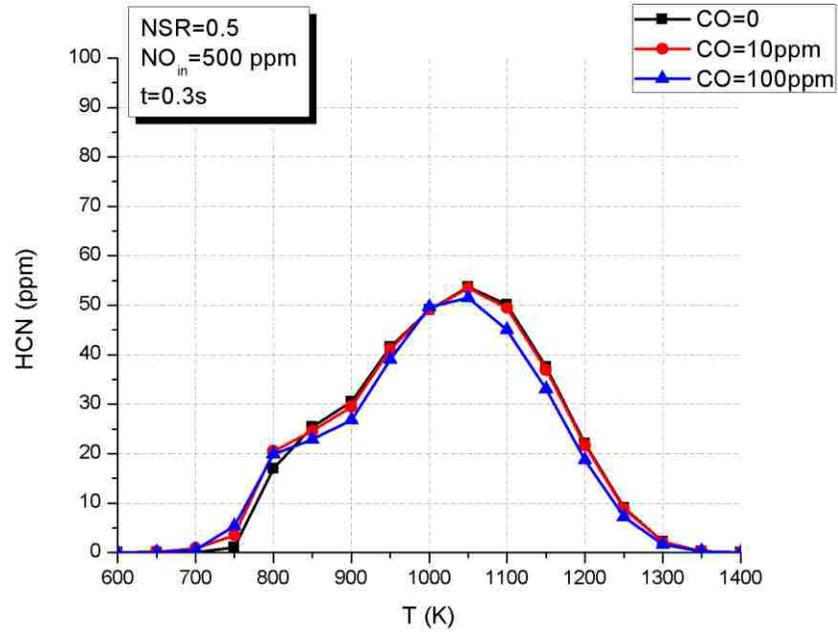
Figure 23. Predicted outlet HCN concentrations vs. temperature under various initial CO concentrations.

3.5.3   Initial NO Concentration Simulations

The results at different inlet NO levels (**Figures 24** to **26**) are consistent with results previously obtained in this study. The percentage of NO reduction for the different initial levels are 50%, 55% and 52.5%, for NO = 50 ppm, 500 ppm and 800 ppm, respectively. The HCN and NH_3 slip result at different initial NO levels are consistent with the MMA increased injection level to maintain a NSR of 0.5 for the simulations.
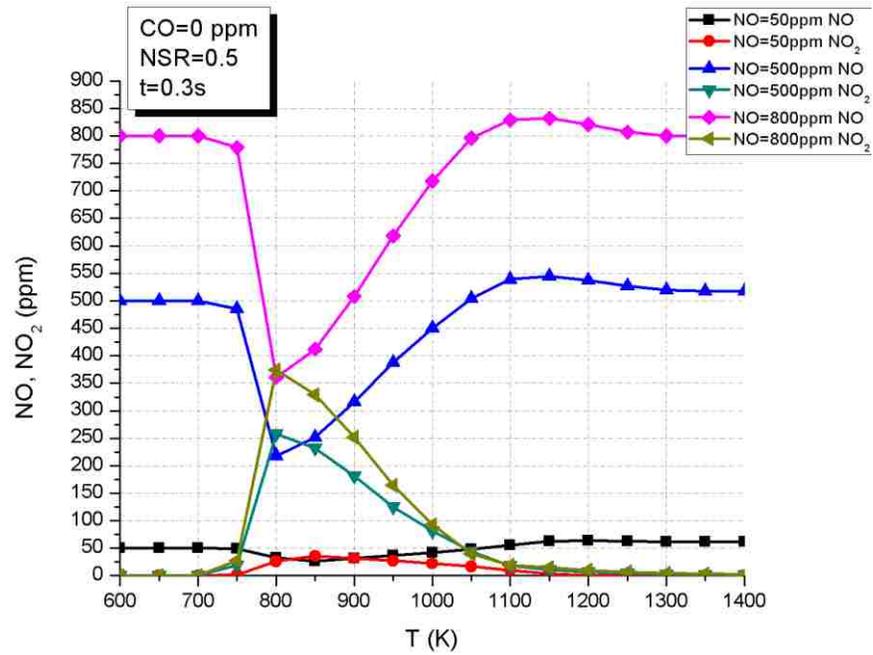
Figure 24. Predicted outlet NO and NO_2 concentrations vs. temperature under various initial NO concentrations.
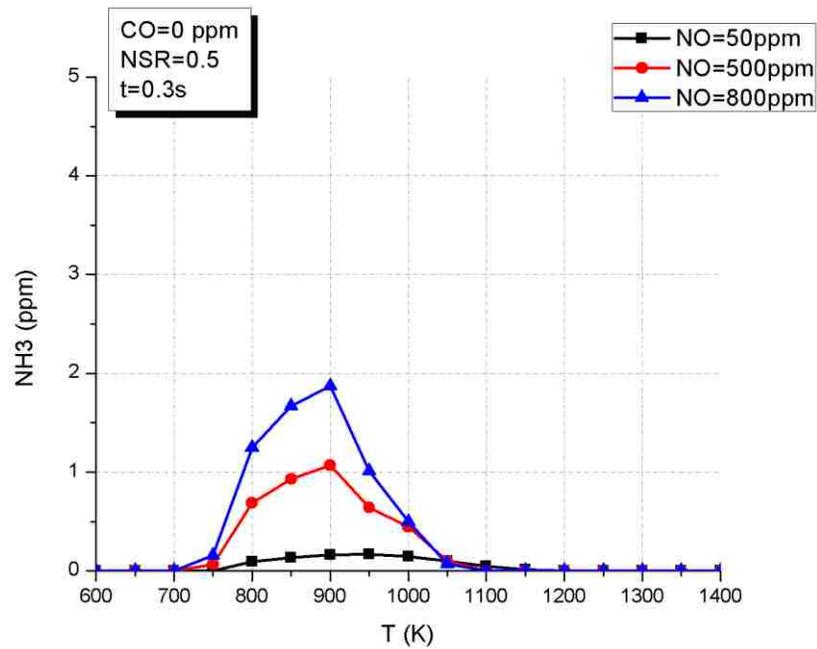
Figure 25. Predicted outlet NH_3 concentrations vs. temperature under various initial NO concentrations.
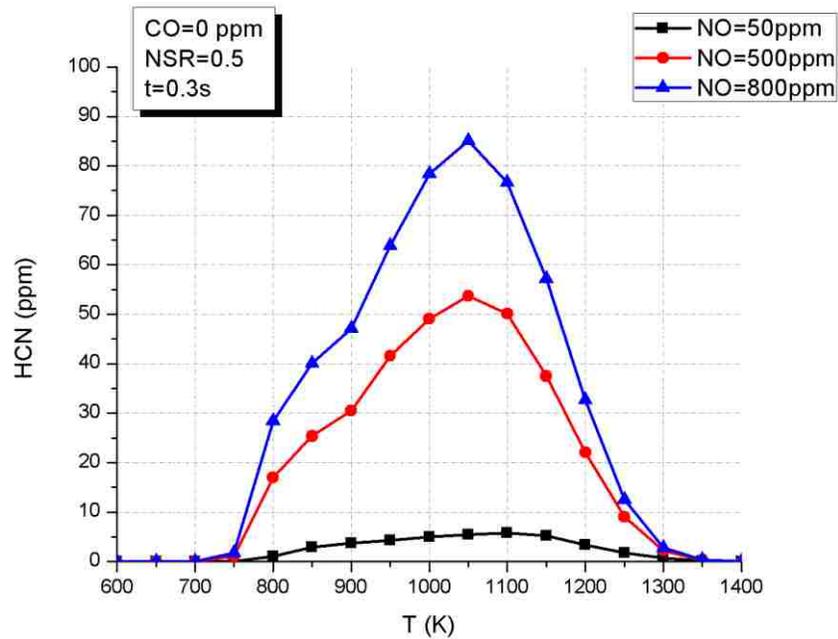
Figure 26. Predicted outlet NH_3 concentrations vs. temperature under various initial NO concentrations.

3.5.4 Residence Time Simulations

The residence time simulations suggest that the residence time tends to shift the temperature window to the left for all the parameters of interest (see **Figures 27** to **29**). This is because the NO_x reduction process by MMA requires longer than 0.3 sec to complete the reaction.

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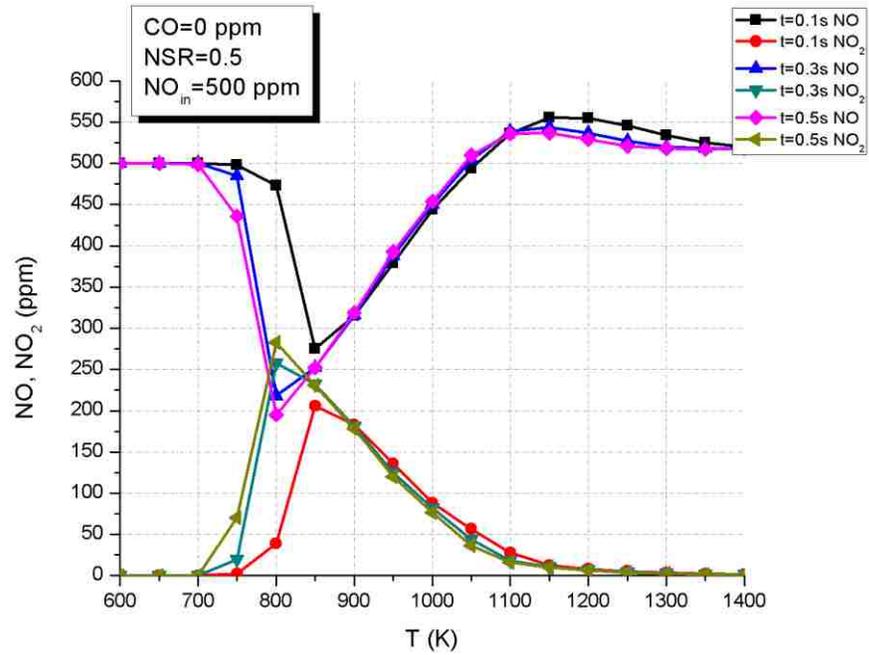
Figure 27. Predicted outlet NO and NO_2 concentrations vs. temperature under various residence times.
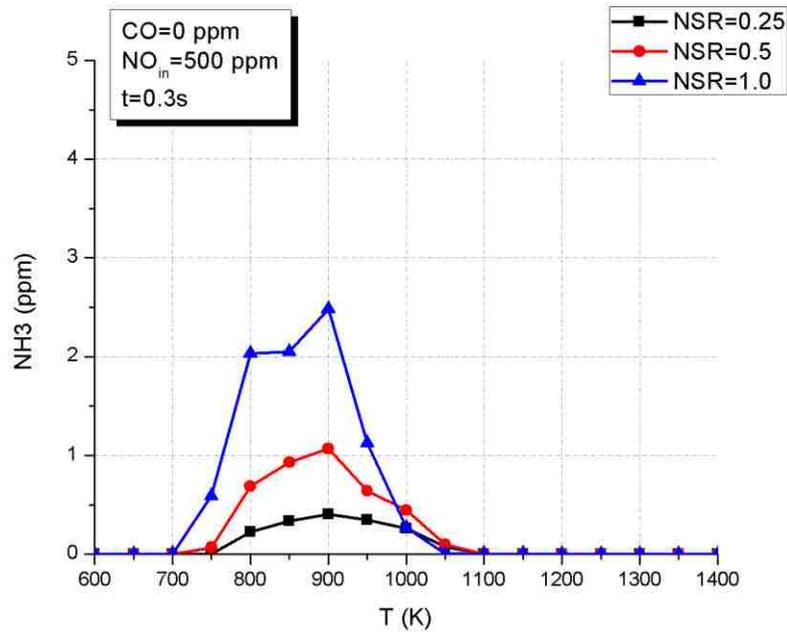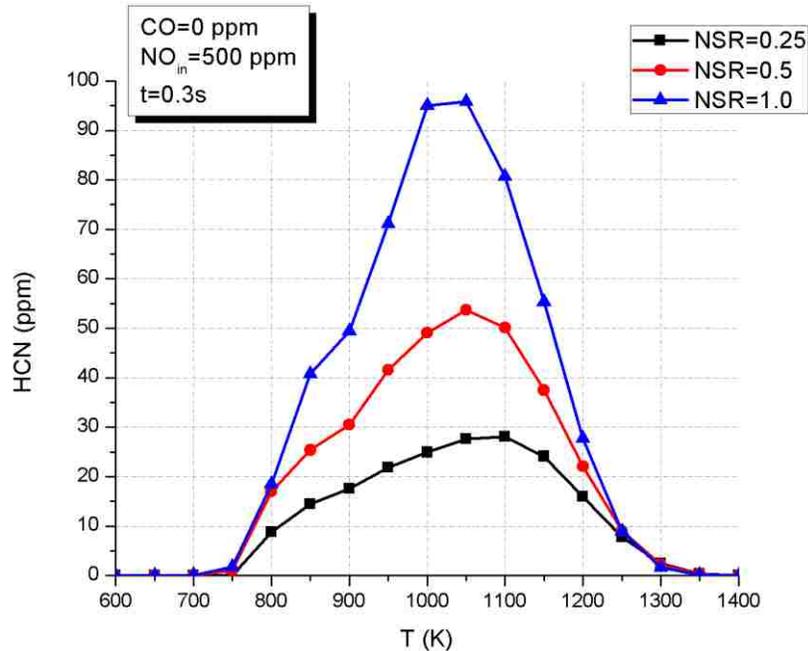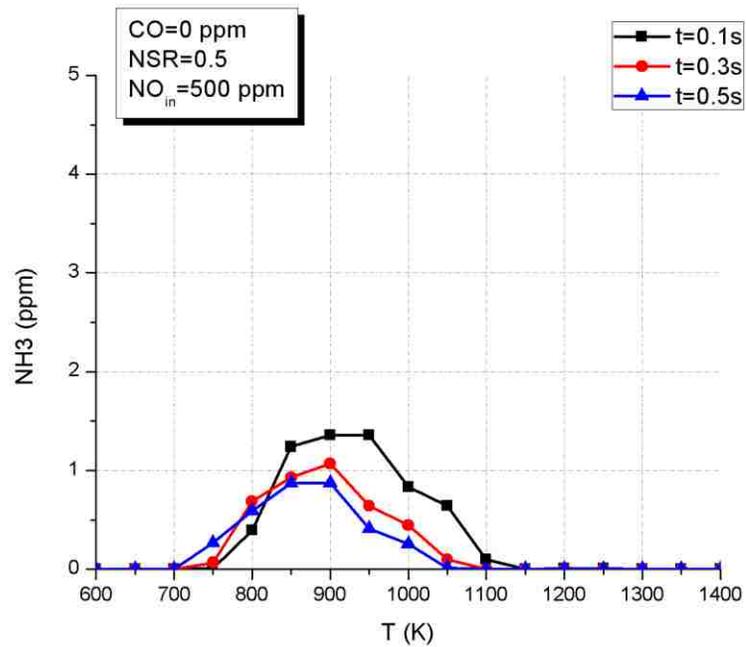

Figure 28. Predicted outlet NH_3 concentrations vs. temperature under various residence times.
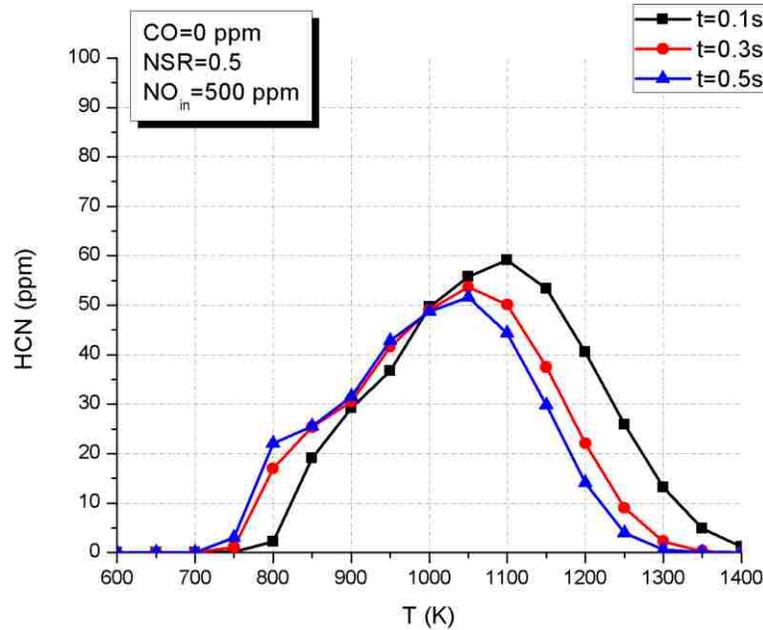
Figure 29. Predicted outlet HCN concentrations vs. temperature under various residence times.

According to the sensitivity simulation results, NSR and initial NO concentration are identified to be the most critical parameters that significantly affect the outcome of the kinetics of MMA under SNCR conditions. The results are also in line with the results reported in the literature, that CO addition to the NO reduction process can shift the optimal reaction temperature of the reducing process.

3.6   Monomethylamine Kinetics Mechanism Reduction

The goal of chemical kinetics mechanism reduction is to introduce a reduced mechanism model which has relatively less species and reactions than the detailed one does, helping in that it can be easily fitted into full computational fluid mechanics (CFD) simulations.

Typical approaches for the mechanism reduction include a combination of rate of production and rate of reaction analysis. In this study, a rate of production analysis was

used to evaluate the contribution to the molar rate of production of each species in the

MMA chemical kinetics mechanism from each reaction. A temperature range from 200 K

to 900 K was used in the analysis. Reactions that showed negligible effect to the evaluation

of major chemical species, MMA (CH_3NH_2), NO, NO_2, N_2O, CO, NH_3 and HCN, were

temporally eliminated. Then the modified mechanism was tested with SENKIN code under

the baseline conditions presented in the caption of **Table 6**, and the simulation results were

compared with the results from the original detailed mechanism by Kantak et al. [60],

under the same initial conditions. Once the comparison results showed acceptable

differences (less than 10% of the concentrations) for most cases, the temporally eliminated

reactions were considered not critical to the entire mechanism and removed permanently.

Following the above procedure, the comparison of simulation results between the full

mechanism by Kantak et al. [60] and the reduce mechanism is listed in **Table 6**. According

to the data in **Table 6**, the reduced mechanism shows decent agreement with the original

mechanism by Kantak et al. [60] despite the fact that relative errors at some temperatures

for several species exceed 10%. However, since that the actual value of the concentration

of the species whose relative error is larger than 10% is sufficiently small, the mentioned

data pair can be still considered as in good agreement. For example at 775 K, $[NO]_{ORG} =$

2.1 ppm and $[NO]_{RED} = 1.59$ ppm and the difference between the two result is just 0.51

ppm.

Table 6. Simulation result comparison between reduced mechanism and original mechanism by Kantak et al. [60]. Inlet condition: 1.0 atm; 700 K – 900 K; residence time = 1.0s; (in mole %) [CH$_3$NH$_2$] = 0.01, [NO] = 0.01, [O$_2$] = 11.75, [H$_2$O] = 9.95, [CO$_2$] = 4.12, balance nitrogen. ORG – original Kantak et al.'s, RED – reduced Kantak et al.'s, ∆% - the relative error = $\frac{|[\text{ORG species}]-[\text{RED species}]|}{[\text{ORG species}]} \times 100\%$.

	NO			NO2		
TEMP/ K	ORG/ppm	RED/ppm	∆%	ORG/ppm	RED/ppm	∆%
700	82.8	82.7	0.10%	24	24.1	0.40%
725	42.7	42.9	0.50%	90.8	90.7	0.10%
750	6.48	6.01	7.30%	156	157	0.60%
775	2.1	1.59	24.30%	166	166	0.00%
800	7.1	6.3	11.30%	162	162	0.00%
825	14.7	13.8	6.10%	154	155	0.60%
850	22.9	21.8	4.80%	147	148	0.70%
875	30.9	29.6	4.20%	139	140	0.70%
900	38.7	37	4.40%	131	132	0.80%
	NH3			N2O		
TEMP/ K	ORG/ppm	RED/ppm	∆%	ORG/ppm	RED/ppm	∆%
700	0.00565	0.00514	9.00%	1.29	1.14	11.60%
725	0.0473	0.0479	1.30%	6.41	6.4	0.20%
750	0.0891	0.09	1.00%	9.6	9.61	0.10%
775	0.131	0.134	2.30%	9.39	9.4	0.10%
800	0.184	0.191	3.80%	8.67	8.69	0.20%
825	0.245	0.265	8.20%	7.87	7.91	0.50%
850	0.307	0.349	13.70%	7.08	7.16	1.10%
875	0.355	0.429	20.80%	6.37	6.48	1.70%
900	0.387	0.485	25.30%	5.73	5.89	2.80%
	CH3NH2			HCN		
TEMP/ K	ORG/ppm	RED/ppm	∆%	ORG/ppm	RED/ppm	∆%
700	71.3	71.2	0.10%	1.13	1.14	0.90%
725	24.8	24.9	0.40%	3.84	3.89	1.30%
750	3.07	3.04	1.00%	7.04	7.2	2.30%
775	0.448	0.477	6.50%	8.91	9.26	3.90%
800	0.117	0.136	16.20%	9.94	10.3	3.60%
825	0.0425	0.0551	29.60%	11.1	11.4	2.70%
850	0.0147	0.0228	55.10%	12.3	12.5	1.60%
875	0.00368	0.00723	96.50%	13.6	13.7	0.70%
900	0.000704	0.00128	81.80%	14.7	14.8	0.70%
	CO					
TEMP/ K	ORG/ppm	RED/ppm	∆%			
700	1.21	1.21	0.00%			
725	15.7	15.5	1.30%			
750	47.3	47.4	0.20%			
775	58	58	0.00%			
800	60.3	60.4	0.20%			
825	60.9	61.2	0.50%			
850	60.9	61.4	0.80%			
875	59.9	60.8	1.50%			
900	58.2	59	1.40%			

Using the mentioned approach, a reduced kinetic mechanism that contains 36 species and 67 reactions (derived from 65 species and 350 reactions by Kantak et al. [60]) is proposed. The reduced mechanism (RM) is shown in **Table 7**.

Table 7. Reduced mechanism. Units are $cm^3/(mol \cdot s)$ for A and cal/mol for E. Rate constants were expressed as $k = AT^m \exp(-E/RT)$.

Reactions		A	m	E
1.	CH3NH2(+M)=CH3+NH2(+M)	3.16E+15	0	85800
Low pressure limit: .48000E+18 .00000E+00 .62618E+02				
2.	CH3NH2+O=CH2NH2+OH	3.26E+12	0	1700
3.	CH3NH2+OH=CH2NH2+H2O	3.68E+12	0	-500
4.	CH3NH2+OH=CH3NH+H2O	2.46E+12	0	-500
5.	CH3NH2+O2=CH3NH+HO2	8E+12	0	39000
6.	CH2NH2+O2=H2CNH+HO2	10000000	2	9200
7.	CH2NH2+HO2=CH3NH2+O2	10000000	2	1200
8.	CH2NH2+O2=CH3O+HNO	6.00E+12	0	4000
9.	CH3NH+O2=H2CNH+HO2	10000000	2	6300
10.	CH3NH+O2=CH3O+HNO	6E+12	0	4000
11.	H2CNH+O2=HCNH+HO2	3.16E+08	2	4800
12.	HCNH+O2=HCN+HO2	3.16E+08	2	4800
13.	H2CNNCH2=H2CN+H2CN	3.16E+15	0	-400
14.	OH+CO=H+CO2	15000000	1.3	-800
Reverse Arrhenius coefficients: 1.68E+09 1.3 21600.0				
15.	HO2+M=H+O2+M	2.31E+15	0	45900
Reverse Arrhenius coefficients: 1.65E+15 .0 -1000.0				
N2	Enhanced	by	0	
H2O	Enhanced	by	21	
CO2	Enhanced	by	5	
CO	Enhanced	by	2	
H2	Enhanced	by	3.3	
16.	CH2O+OH=HCO+H2O	7.5E+12	0	200
Reverse Arrhenius coefficients: 2.59E+12 .0 30000.0				
17.	CH3+O2=CH3O+O	4.8E+13	0	29000
Reverse Arrhenius coefficients: 3.04E+14 .0 700.0				
18.	CH3O+M=CH2O+H+M	3.89E+37	-6.7	33300
Reverse Arrhenius coefficients: 7.71E+32 -6.7 9700.0				
19.	CH3O+O2=CH2O+HO2	7.6E+10	0	2700
Reverse Arrhenius coefficients: 1.28E+11 .0 32200.0				
20.	CH3+HO2=CH4+O2	3.61E+12	0	0
Reverse Arrhenius coefficients: 4.00E+13 .0 56900.0				
21.	HCO+O2=CO+HO2	4.2E+12	0	0

Reverse Arrhenius coefficients: 7.38E+12   .0   34300.0

22.	HO2+NO=NO2+OH	2.11E+12	0	-500
23.	NO2+H=NO+OH	3.5E+14	0	1500
24.	NO2+O=NO+O2	1E+13	0	600
25.	HNO+OH=NO+H2O	3.6E+13	0	0
26.	NH+CO2=HNO+CO	10000000	2	1700
27.	NH+O2=NO+OH	1300000	1.5	100
28.	NH+NO=N2O+H	2.9E+14	-0.4	0
29.	NH+NO2=N2O+OH	1E+13	0	0
30.	NO+OH(+M)=HONO(+M)	2E+12	0	-700

Low pressure limit: .50000E+24 -.25100E+01 -.68000E-01

N2	Enhanced	by	1	
H2O	Enhanced	by	5	
31.	HNO+O2=NO+HO2	1.00E+13	0	25000
32.	HNO+NO=N2O+OH	2E+12	0	26000
33.	HNO+NO2=HONO+NO	6E+11	0	2000
34.	HNO+HNO=N2O+H2O	4E+12	0	5000
35.	H2NO+H=NH2+OH	5E+13	0	0
36.	H2NO+OH=HNO+H2O	20000000	2	1000
37.	H2NO+NO=HNO+HNO	2.00E+07	2	13000
38.	H2NO+NH2=HNO+NH3	3E+12	0.00E+00	1000
39.	HONO+OH=NO2+H2O	1.3E+10	1	100
40.	H+O2+N2=HO2+N2	6.70E+19	-1.4	0
41.	HCO+M=H+CO+M	5.12E+21	-2.1	20400

Reverse Arrhenius coefficients: 1.78E+18   -1.1   3000.0

42.	H2O2+OH=H2O+HO2	1.00E+13	0	1800

Reverse Arrhenius coefficients: 2.80E+13   .0   32800.0

43.	HCO+HO2=CH2O+O2	1E+14	0	3000

Reverse Arrhenius coefficients: 3.66E+15   .0   46000.0

44.	H+HO2=OH+OH	2.50E+14	0	1900

Reverse Arrhenius coefficients: 1.20E+13   .0   40100.0

45.	H2O2+O2=HO2+HO2	4.46E+12	0	39500

Reverse Arrhenius coefficients: 3.02E+12   .0   1400.0

46.	H2O2+M=OH+OH+M	6.00E+16	0	45500

Reverse Arrhenius coefficients: 4.55E+14   .0   -5100.0

N2	Enhanced	by	1	
H2O	Enhanced	by	7	
47.	H2CN+M=HCN+H+M	3E+14	0.00E+00	22000
48.	HCO+NO2=H+CO2+NO	8.40E+15	-0.8	1900
49.	CH3NH2+O=CH3NH+OH	2.17E+12	0	1700
50.	CH3NH2+M=CH2NH2+H+M	2.00E+17	0	88400
51.	CH3NHOH=CH4+HNO	6E+12	0	0
52.	H+O2=OH+O	5.13E+16	-0.8	16500

Reverse Arrhenius coefficients:	1.31E+13	.0	700.0	
53.	O+H2O=OH+OH	6.8E+13	0	18400
Reverse Arrhenius coefficients:	6.30E+12	.0	1100.0	
54.	H+H2O=OH+H2	9.50E+13	0	20300
Reverse Arrhenius coefficients:	2.20E+13	.0	5100.0	
55.	OH+HO2=H2O+O2	5E+13	0	1000
Reverse Arrhenius coefficients:	6.33E+14	.0	73900.0	
56.	NH3+OH=NH2+H2O	2040000	2	600
57.	NH3+H=NH2+H2	636000	2.40E+00	10200
58.	CN+H2O=HCN+OH	8E+12	0	7500
59.	CN+O2=NCO+O	7.5E+12	0	-400
60.	NCO+NO2=CO+NO+NO	1.3E+13	0	0
61.	NCO+NO2=CO2+N2O	5.4E+12	0	0
62.	H2NO+O=NH2+O2	4E+13	0	0
63.	NH2+NO2=N2O+H2O	3.20E+18	-2.2	0
64.	NH2+NO=N2+H2O	1.30E+16	-1.3	0
65.	NH+O2=HNO+O	460000	2	6500
66.	NH+NO=N2+OH	2.2E+13	-0.2	0
67.	HNO+H=H2+NO	4.4E+11	0.7	700
Reverse Arrhenius coefficients:	1.50E+13	.0	52000.0	

A similar rate of production analysis was performed, but only considering the most important outlet species (HCN, NO, NO_2, NH_3 and N_2O). A further reduction of the mechanism was achieved. The reaction tree of the further reduced mechanism (FRM) is shown in **Figure 30**. The FRM consists of only 18 reactions and 21 species as shown in **Table 8**, which presents a significant reduction in comparison to the detailed mechanism. A further analysis with adjustment of the reaction rate constant (where *A*, *m* and *E* are adjusted) was not attempted, since that it would produce a mechanism with empirical reaction rate constants.

Figure 30. Further reduced mechanism tree.

Table 8. Further reduced mechanism. Units are $cm^3/(mol \cdot s)$ for A and cal/mol for E. Rate constants were expressed as $k = AT^m \exp(-E/RT)$.

Reactions		A	m	E
1.	CH3NH2+OH=CH2NH2+H2O	3.68E+12	0	-500
2.	CH3NH2+OH=CH3NH+H2O	2.46E+12	0	-500
3.	CH2NH2+O2=H2CNH+HO2	10000000	2	9200
4.	CH2NH2+O2=CH3O+HNO	6.00E+12	0	4000
5.	CH3NH+O2=H2CNH+HO2	10000000	2	6300
6.	CH3NH+O2=CH3O+HNO	6E+12	0	4000
7.	H2CNH+O2=HCNH+HO2	3.16E+08	2	4800
8.	HCNH+O2=HCN+HO2	3.16E+08	2	4800
9.	CH2O+OH=HCO+H2O	7.5E+12	0	200
10.	CH3O+M=CH2O+H+M	3.89E+37	-6.7	33300
Reverse Arrhenius coefficients:	7.71E+32 -6.7 9700.0			
11.	CH3O+O2=CH2O+HO2	7.6E+10	0	2700
Reverse Arrhenius coefficients:	1.28E+11 .0 32200.0			
12.	HCO+O2=CO+HO2	4.2E+12	0	0
Reverse Arrhenius coefficients:	7.38E+12 .0 34300.0			
13.	HO2+NO=NO2+OH	2.11E+12	0	-500
14.	NH+CO2=HNO+CO	10000000	2	1700
15.	NH+NO2=N2O+OH	1E+13	0	0
16.	H2NO+NO=HNO+HNO	2.00E+07	2	13000
17.	H2NO+NH2=HNO+NH3	3E+12	0.00E+00	1000
18.	NH2+NO2=N2O+H2O	3.20E+18	-2.2	0

3.7 Simulation Comparison of Alternative Reagents for NO_x Reduction

A comparison was performed in terms of NO_x reduction performance for MMA, urea, CYA and ammonium sulfate. The RM for MMA, a chemical kinetics scheme developed by the Lehigh University Energy Research Center (ERC) for urea and CYA, and Chen et al.'s [35] mechanism for ammonium sulfate, were used in the simulation comparison. The inlet conditions used for the simulation were: 1.0 atm, temperature from 600 K to 1400K, molar concentrations for: $[CO] = 0.001$, $[CO_2] = 4.12$, $[NO] = 0.01$, $[O_2] = 11.75$, $[H_2O] = 9.95$; and NSR = 1. The results of the simulation are included in **Figures 31** to **33**.

The comparison results in **Figure 31** show that an MMA-based SNCR NO_x reduction process has the great advantage of reducing NO at much lower temperatures than the other reagents. MMA works best at injection temperatures around 700 K, as compared to the other reagents that work at around 1100 K. This implies that MMA could be injected after the convective tube bank sections in utility boilers, where flow is more homogenous and there is easier access for the injection lances. Additionally, the temperature window of MMA is comparatively wider than the windows for the other tested regents. However, the production of NO_2 from MMA model is significantly larger, while the other reagents have only relatively negligible NO_2 formation. This can possibly result from the following reaction:

$$HO_2 + NO \rightleftharpoons OH + NO_2$$
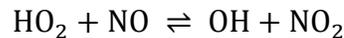
Excess HO_2 is generated by the below pathway of CH_3NH_2 decomposition:

$$CH_3NH_2 \rightarrow CH_2NH_2, CH_3NH \longrightarrow CH_3O \longrightarrow HO_2$$

This is supported from studies by Miller and Bowman [43] that report that the primary product of the H_2O_2 + NH_3 (note that H_2O_2 becomes HO_2 during the reaction process) reaction would be NO_2 rather than N_2 at lower temperatures. The overall NO_x reduction efficiency of MMA seems to be hampered by the production of NO_2. Nevertheless, additional studies are needed on NO_2 production and how to tune its production down, because experimental studies by Nakanishi et al. [49] for example, indicate that high NO reduction can be obtained at low temperatures (around 695 K) avoiding that the reaction which generates NO_2 from NO influence the chemical reduction process. In regard to NH_3 slip, the slips for all four investigated reagents were acceptable since that they all fall below the 5 ppm level, at maximum reduction conditions. However, for MMA, the NH_3 level is below 5 ppm for the entire temperature range, which indicates that NH_3 slip is not an issue when using MMA as a reagent in the SNCR NO_x reduction process. HCN can become an issue with MMA systems and a mitigation method for HCN needs to be further explored.
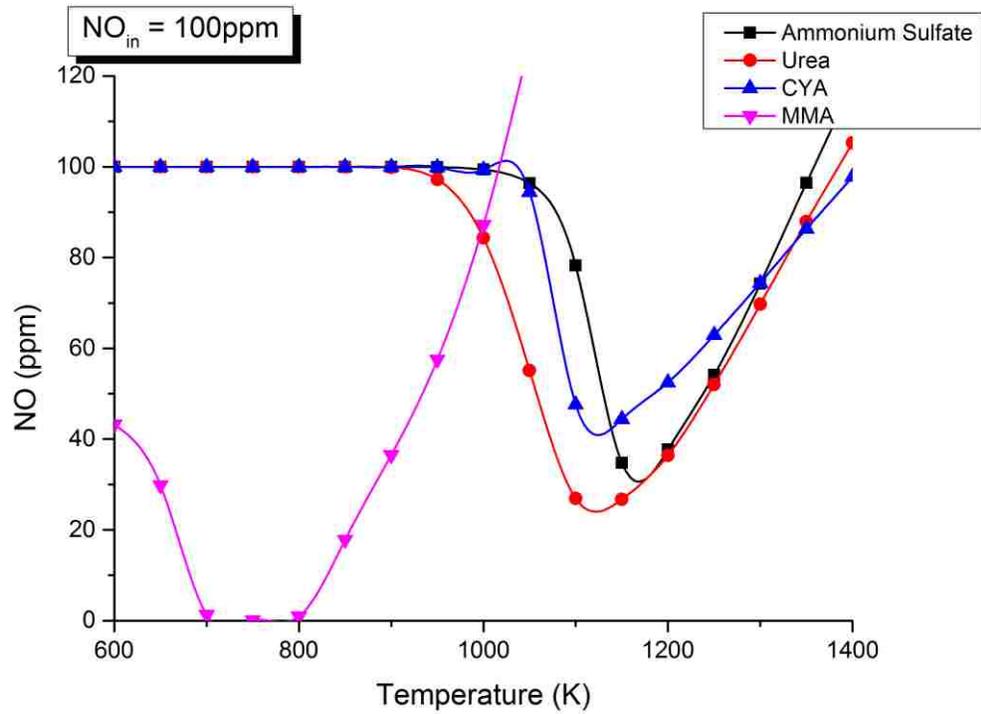
Figure 31. Predictions of outlet NO concentration using different reagents predicted by corresponding kinetics model.
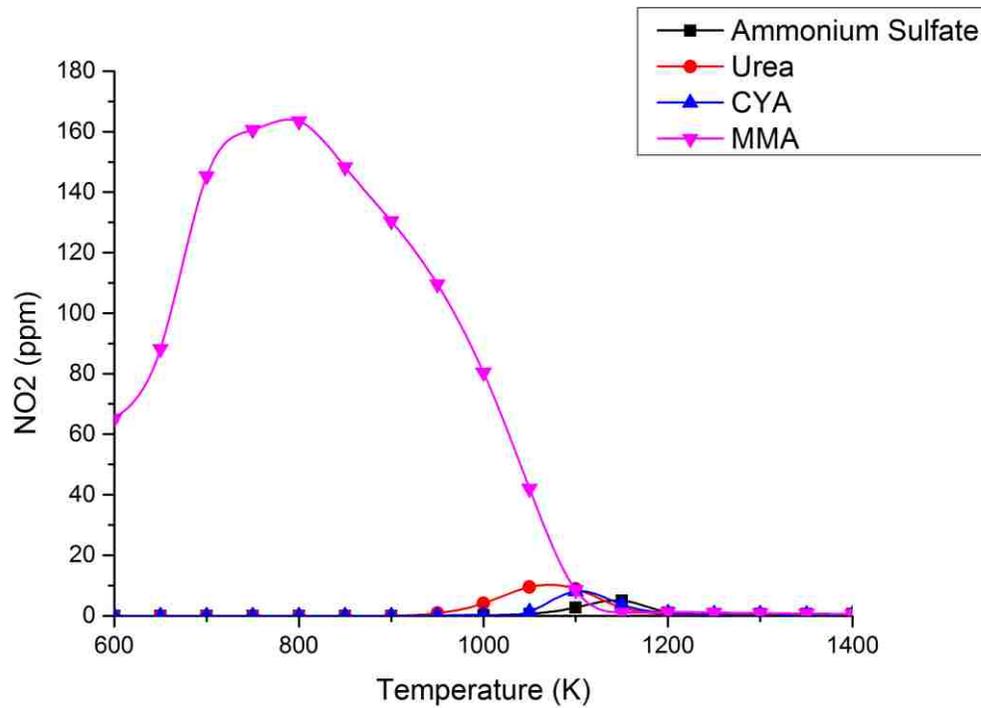
Figure 32. Predictions of outlet NO_2 concentration using different reagents predicted by corresponding kinetics model.
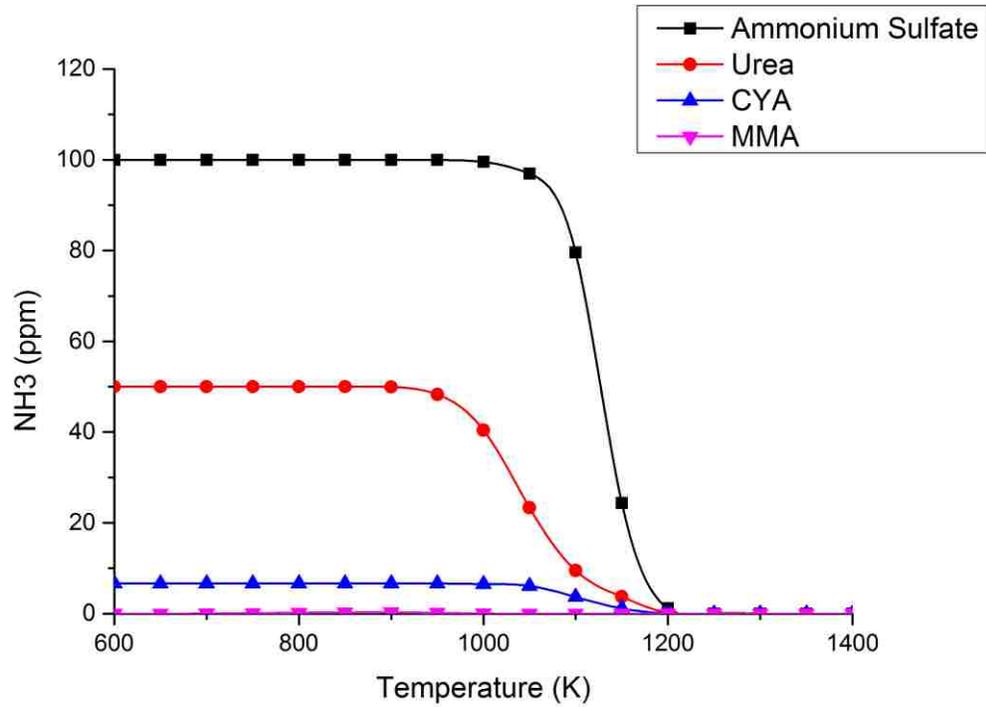
Figure 33. Predictions of Outlet NH$_3$ concentration using different reagents predicted by corresponding kinetics model.

According to the above comparisons and the previous discussions, the design of an MMA-based SNCR system would be similar to a conventional SNCR system, except for the injection location, due to the different optimal reaction temperatures of a MMA-based SNCR process. The form of MMA is expected to be aqueous. As previously mentioned, the injection points of MMA-based SNCR should be placed at areas where the temperatures are around 700 K – 800 K, which are most likely locations near the economizer in most CFPPs.

Chapter IV – Opportunities for Monomethylamine-Based SNCR in Other Industrial Applications

4.1　Introduction

The chemical kinetics simulation results of this study illustrate that MMA has great advantages as a reagent for SNCR systems, working at relatively low temperatures in the range from 700 K to 850 K. This provides additional opportunities for the potential of applying the MMA process to other industrial applications. Modeling of a gas turbine was performed, using the reduced MMA kinetics mechanism model developed in this study. This application is associated with relatively lower flue gas temperatures than are experiencing in coal-fired units.

4.2　Gas Turbine Simulation

The objective of this simulation is to predict NO reduction performance and reagent consumption of a MMA-based SNCR NO_x reduction system for a 42 MW natural gas turbine plant. One major reason for estimating the reagent consumption of the MMA-based SNCR system is that, in general, the price of MMA is higher than that of conventional reagents like NH_3 and urea, the estimation of MMA usage is then valuable for analyzing the cost-effectiveness of MMA-based SNCR systems in comparison to other conventional SNCR systems. Another reason for doing such modeling is that the temperatures of exhaust gases in the gas turbine outlet duct are usually below 850 K, which means that conventional reagent-based SNCR NO_x control systems have difficulties to perform as required under such temperature conditions. Typically, catalysis systems (selective catalytic reduction)

are retrofit in gas turbine plants, which results in increased operating and maintenance costs. Using a novel MMA SNCR system in gas turbines seems to have merit, and motivates the an expansion of the present study to explore this option theoretically.

The dimensions of a typical facility are attached in **Figure 34**. Assuming a flue gas flow velocity and a linear temperature distribution along the flow path, a PFR model was used to treat the physical problem. A target for NO_x removal of 25% was set for the simulations. Simulations where performed with the gas turbine working on an open cycle (no combined cycle). The inlet temperature of the flue gases into the PFR model was set at 823 K. The outlet temperature was set at 623 K. The gas flow rate for this typical unit is 217 m^3/s. The suggested flow gas path way is shown in **Figure 35**. Following the above conditions and assumptions, the following calculations were performed:

The length of AB:

$$h = 51.857 - 32.639 = 19.218 \ m \quad\quad\quad \text{Eq. 7}$$

The length of BC:

$$l = 5.105 + 2.873 + 3.010 = 10.988 \ m \quad\quad\quad \text{Eq. 8}$$

Total approximate flow path way length:

$$L = l + h = 30.206 \ m \quad\quad\quad \text{Eq. 9}$$

Average radius of the path way:

$$r = 3.010 \times \frac{19.218}{30.200} + 2.24 \times \frac{10.988}{30.200} = 2.730 \ m \quad\quad\quad \text{Eq. 10}$$

Maximum residence time:

$$t_{max} = \frac{(2.730m)^2 \times \pi \times 30.206}{217 \ ^{m^3}/_s} = 3.20 \ s \quad\quad\quad \text{Eq. 11}$$

Estimated temperature slope along the path way:

$$\Delta T = \frac{550°\text{C} - 350°\text{C}}{3.20s} = 62.5 \; °\text{C}/s = 62.5 \; K/s \qquad \text{Eq. 12}$$
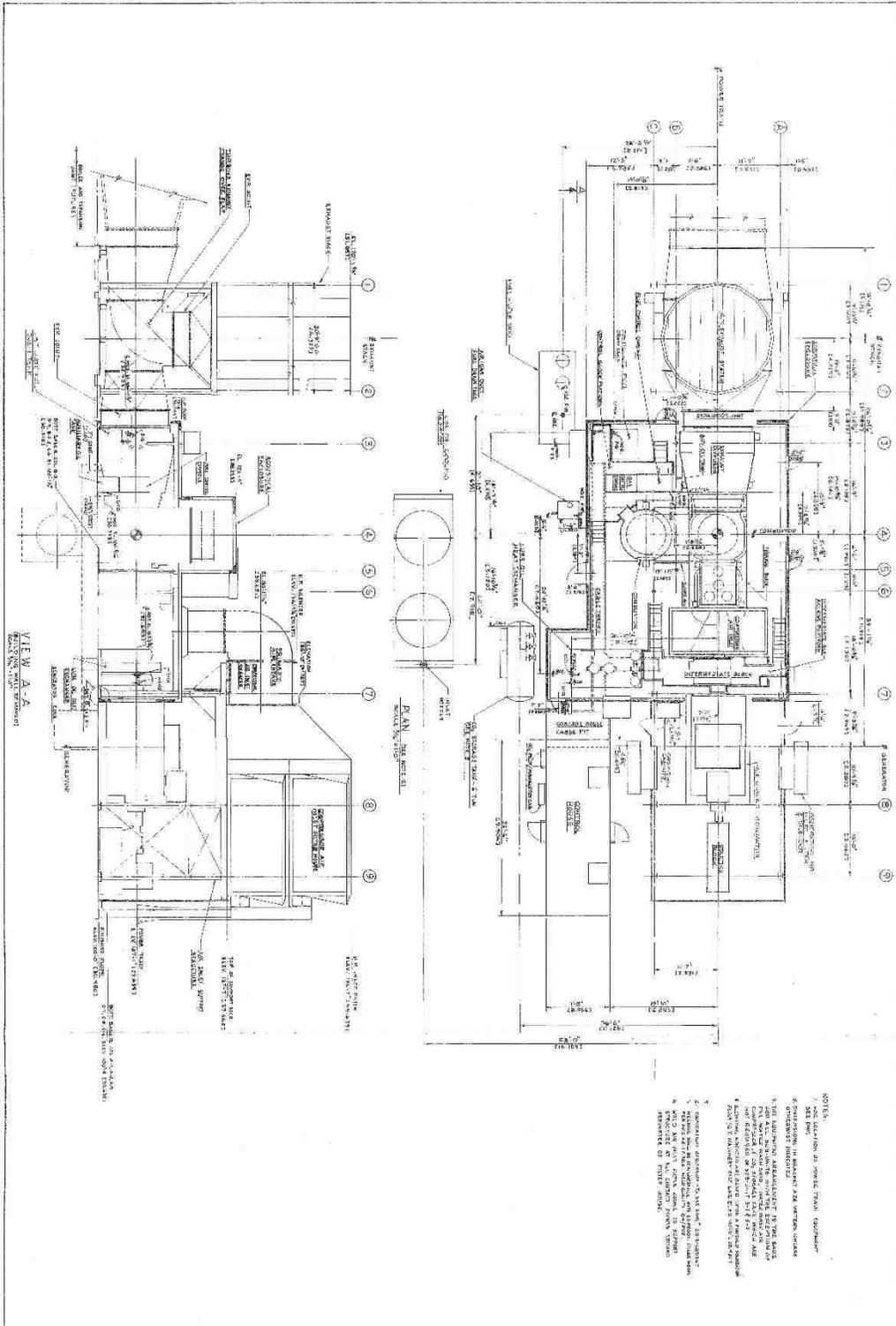
Figure 34. Combined cycle unit diagram.

60
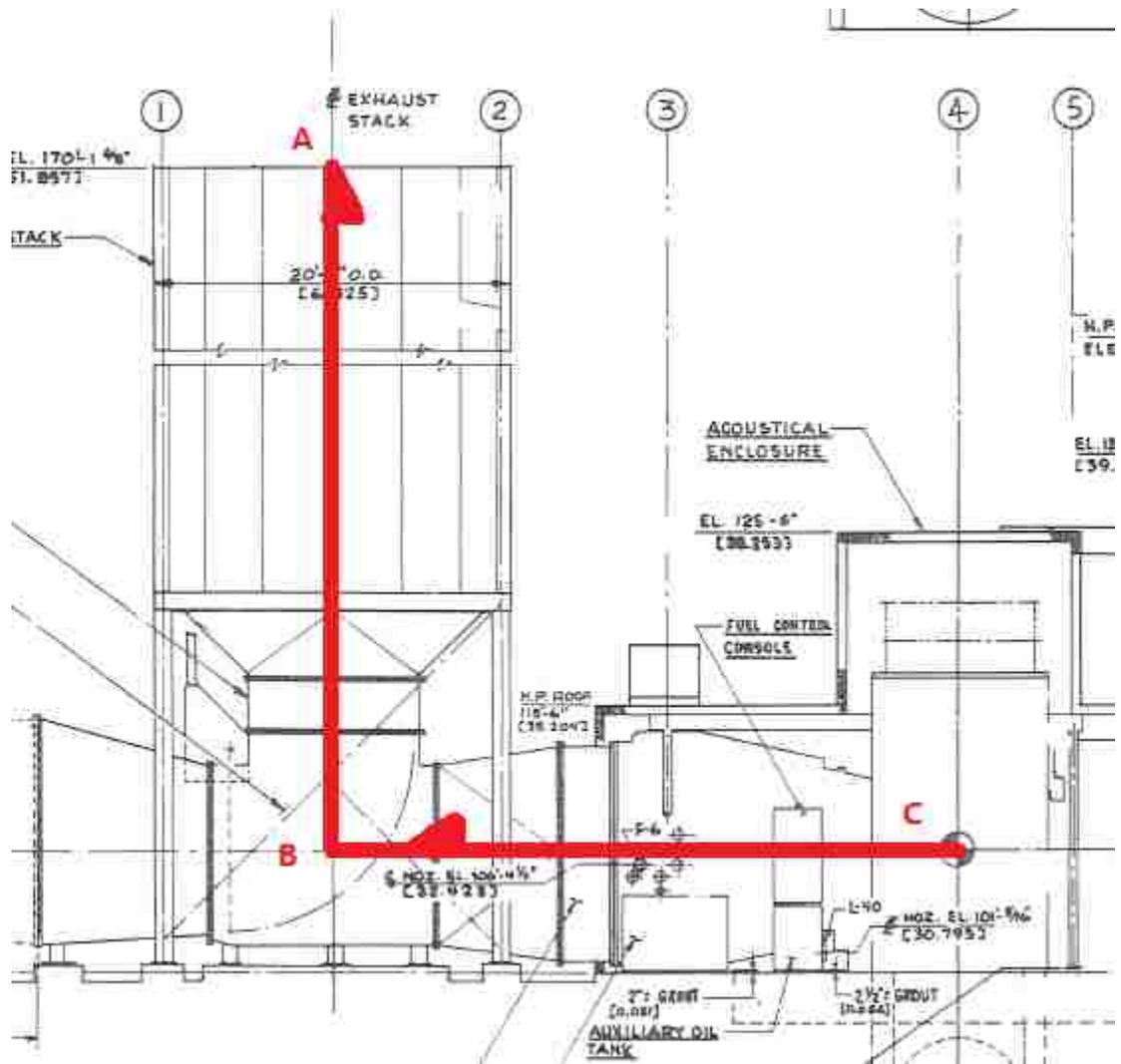
Figure 35. Modeled ideal path way of flue gases.

Initial conditions of the inlet gases used in the simulations (by volume):

$$H_2O = 9.95\ \%$$

$$O_2 = 11.75\ \%$$

$$CO = 500\ ppm$$

$$CO_2 = 4.12\ \%$$

$$NO = 800\ ppm$$

$$N_2 = balance$$

(typical from conventional natural gas turbines without low-NO$_x$ technology)

NO$_x$ reduction results at different NSRs are included in **Figure 36**. Thus to achieve NO reductions greater than the expected 25% target, NSRs in excess of 0.5 are required at inlet temperatures below 725 K. The NH$_3$ slip expected with these conditions is below 5 ppm (see **Figure 37**).

Depending on the NSR in excess of 0.5 and the temperature below 725 K chosen, the HCN emissions from the process could be as high as 5 ppm, with lower HCN values as injection occurs at lower temperatures (see **Figure 38**). To limit MMA slip at the lowest values possible, the NSRs should be at the minimum possible to achieve the required 25% NO reduction (see **Figure 39**).
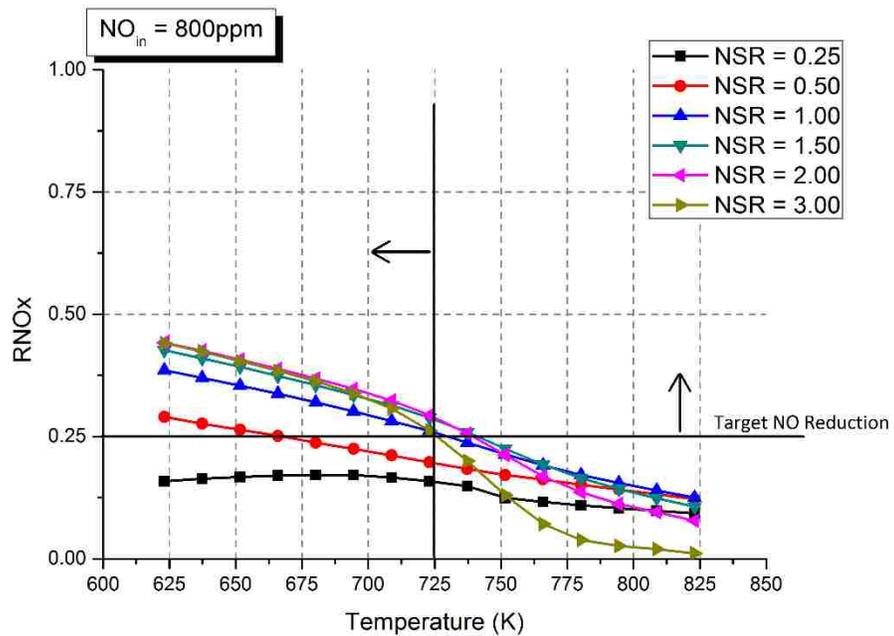
Figure 36. NO$_x$ reduction vs. temperature at various NSRs.
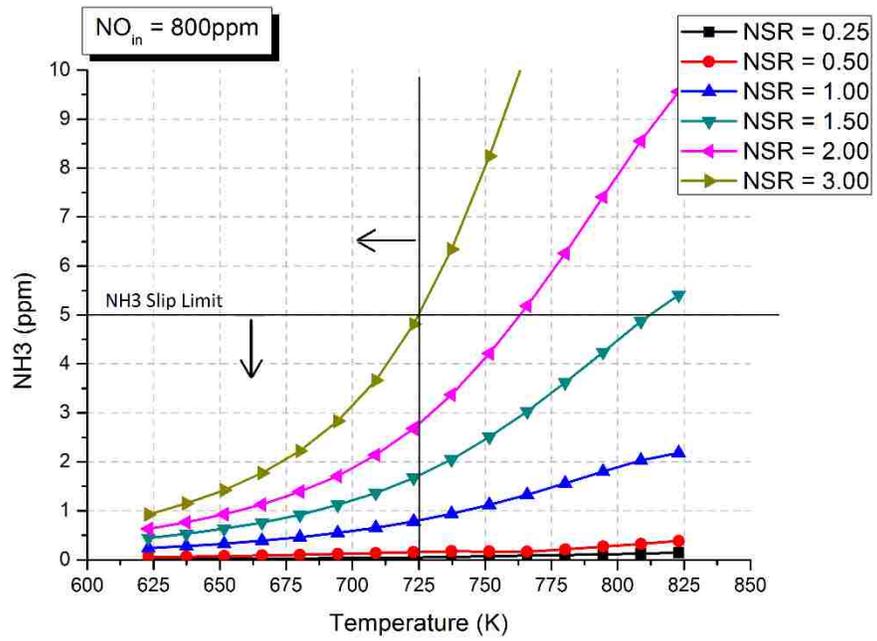
Figure 37. NH$_3$ slip vs. temperature at various NSRs.
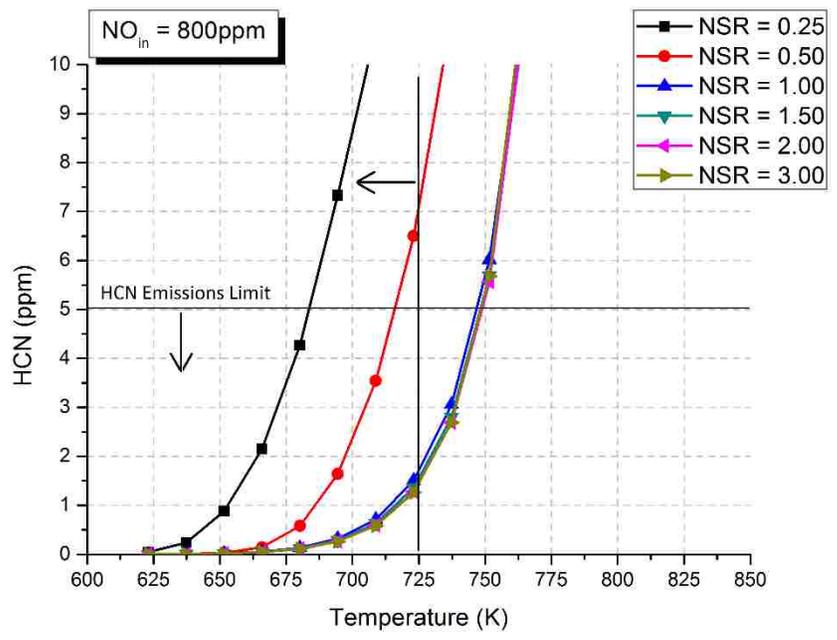
Figure 38. HCN production vs. temperature at various NSRs.
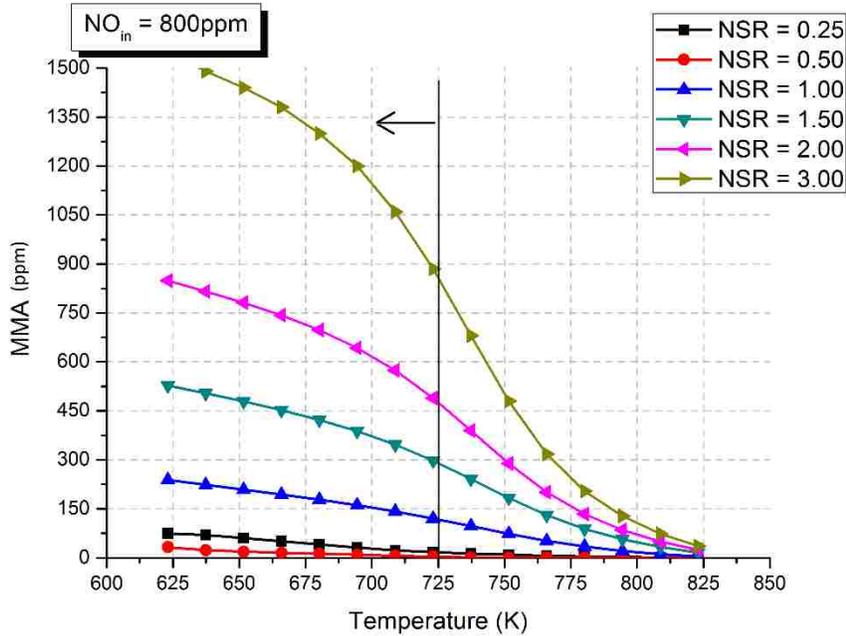
Figure 39. Unreacted MMA vs. temperature at various NSRs.

In summary, the simulation results indicate that to achieve 25% NO reduction, the MMA injection NSR should be at least around 0.5 and the injection point should be located 22.4 m away from the exhaust duct inlet (point C on **Figure 35**), where the temperature is around 675 K. To inject the MMA with a NSR = 0.5 at the point mentioned above is the best choice because it requires minimum MMA consumption while achieving the target NO removal. The overall usage of MMA at the mentioned design point is presented in **Table 9**.

Table 9. MMA consumption under best operating condition.

Description		UNITS	Single Zone NSR = 0.5
Load		**UNITS**	**42 MW**
FACILITY/BOILER			
Unit Type		-	GT
Unit Rating		MW	42
Heat Rate assumed		BTU/kW-hr	13,000
Heat Input		kW	160017
Excess Air		%	12
Gas flow assumed	wet	kg/hr	331,319
	dry	kg/hr	310,219
(1 atm, 273 K)	wet	Nm^3/hr	265,093
	dry	DNm^3/hr	238,716
NO$_x$		kg/hr	433.42
		ppmv	800.4
MMA DESIGN			
MMA consumption			
MMA solution strength		% wt	40
MMA 40 % aqueous density at 275 K		kg/m^3	909.5
MMA anhydrous density at 295 K		kg/m^3	1.3
Air density at 295 K		kg/m^3	1.2
ZONE 1			
NO$_x$ inlet		kg/hr	433.6
NO$_x$ reduction		%	25
NO$_x$ outlet		kg/hr	325.2
NO$_x$ removed		kg/hr	108.4
NSR		mol/mol	0.5
MMA consumption	anhydrous	kg/hr	223.9
aqueous (MMA + water) **40%**		kg/hr	559.8
		liters/hr	615.5

The 2005 price of anhydrous MMA is around $0.72 per pound ($1.59 per kilogram) [65]. Recent increases in MMA price has been of about $0.13 per pound ($0.28 per kilogram) [66, 67]. Assuming a list price of anhydrous MMA at $1.87 per kilogram, the

reagent cost for the example of this section is $437.4 per hour. Assuming a comparable

urea-based SNCR system can be applied to the above gas turbine example and a price of

commercial grade urea of is $0.15 per kilogram [68], using the results of reagent utilization

tests reported by Staudt et al. [69], that the urea utilization rate at 25% NO_x reduction and

0.46 NSR condition is 56%, then the usage of urea is 348.4 kg/hr and the reagent cost for

the urea-based SNCR system is $52.3 per hour. It's obvious that the reagent consumption

cost of a MMA-based SNCR system is greater than that of urea-based SNCR system.

However, utilization of a urea-based SNCR NO_x reduction system in a gas turbine is

prohibited by the relatively low temperatures of the flue gas (which would result in

excessive NH_3 slip). Hence, MMA offers an alternative to NO_x control for gas turbines,

where conventional SNCR system is not suited for and SCR is a more expensive

proposition.

Chapter V – Conclusions and Recommendations

The objective of this thesis was to study MMA as an alternative reagent for SNCR NO_x reduction systems. This was accomplished by performing a literature review, chemical kinetics mechanism research and kinetics simulations in order to find the potential advantages of using MMA over other traditional and alternative reagents. The study also attempted to propose a reduced chemical kinetics model for simulating MMA-based NO_x abatement systems. The study was also extended to discuss the possibility of MMA-based SNCR systems in full-scale fuel combustion devices, especially for units whose operating flue gas temperatures are under 850 K and require strict NH_3 emissions control.

Based on the result of the study, the following conclusions are made:

(1) Traditional SNCR NO_x systems, which use conventional reagents such as NH_3 and urea, have limitations in controlling NO_x emissions at low temperatures (below 800 K). Additionally, narrow reaction temperature windows for conventional reagents in SNCR systems result in difficulties in maintaining plant generating availability, due to NH_3 slip problems. Meanwhile, previous researches have shown that MMA could be an alternative reagent for SNCR NO_x systems, which has merit to be used at relatively low gas temperatures in SNCR systems.

(2) A chemical kinetics model was assembled, based on the kinetics scheme by Kantak et al. [60], comprising 350 reactions and 65 species. This detailed mechanism was reduced in this study to 67 reactions and 36 species, without greatly sacrificing the prediction accuracy of the model. The proposed model was validated with experimental data obtained in the temperature range from 770 K to

900 K. A further reduced kinetics mechanism, which has only 18 reactions and 21 species, was also proposed, but reaction rate adjustment would be required for this reduced scheme to provide very good agreement with results from the original mechanism. A sensitive analysis of the reduced kinetics model and a simulation comparison with other reagents under identical process conditions suggest that the MMA mechanism is very sensitive to the concentration of CO in the flue gas, which can shift the optimal temperatures downward to less than 600 K and it has superior NO reduction performance at temperatures below 900 K, when compared to other conventional SNCR reagents.

(3) An example modeling of a gas turbine was performed using the reduced MMA mechanism. The modeling results show that a MMA-based SNCR system would be capable of achieving a target NO reduction of 25% with reasonable reagent usage (NSR = 0.5), and such system would not suffer from the typical drawbacks associated with conventional SNCR systems when applied to gas turbines.

The following recommendations are provided:

(1) It is suggested to perform additional theoretically studies in order to fully understand the MMA-NO chemistry, and the mechanism of NO_2 and HCN formation in the low temperature MMA-based NO_x reduction process. It could be that the reaction, $HO_2 + NO \rightleftharpoons OH + NO_2$, plays a significant role in the MMA chemical process, or that above reaction is overrated in the kinetic model, which is supported by Nakanishi et al. [49].

(2) It is recommended to perform experimental MMA testing in laboratory and pilot-scale apparatus to better evaluate the performance and associated problems of

MMA when used in a SNCR process. The potential of using MMA in natural gas

combined cycle plant has a lot merit and needs to be fully validated in appropriate

field tests.

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Vita

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