NOX control in combustion of alternative fuels

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NO\textsubscript{X} control in combustion of alternative fuels

Kristian Krum

PhD thesis
October 2020

Supervisors

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Preface and Acknowledgments

This dissertation presents the results of three years of research from 2017 to 2020. The research was conducted at the Combustion of Harmful Emission Control (CHEC) Research Centre, Department of Chemical & Biochemical Engineering, Technical University of Denmark (DTU). The research is performed within the framework of the Sino-Danish Centre (SDC) for Education and Research, in collaboration with the Institute of Process Engineering (IPE), Chinese Academy of Sciences (CAS). The PhD project was supervised by Professor Peter Glarborg, Associate Professor Hao Wu, and Professor Songgeng Li. The work was partly funded by SDC and B&W Vølund.

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A special thanks goes to all the talented and hard-working CHEC employees, Søren P., Nikolaj, Anders, Lilian, and Malene, for their support in the construction and troubleshooting of experimental setups. I would also like to thank all of the students and fellow researchers I have had the pleasure of working with during this PhD study. I would especially like to thank my friends and colleagues, Christian, Joachim, Burak, Frederik, Jacob, And Lauge, who made every day enjoyable and memorable.

Above all, I would like to thank my parents, Sanne and Thomas, my sister Mette, and my girlfriend Stephanie, for their continued love and support. You are the foundation of my happiness, and the pillars I can always lean on, and for that I am forever grateful.

October 2020

Kristian Krum
Renewable fuels such as biomass and municipal waste have received growing interest, to reduce the share of coal in heat and power production. However, the emissions of nitrogen oxides, i.e. NO\textsubscript{x} (NO and NO\textsubscript{2}), from combustion of these fuels continue to be an environmental concern, as NO\textsubscript{x} leads to formation of photochemical smog and acid rain. A commonly used technology to reduce NO\textsubscript{x} from stationary facilities is the selective non-catalytic reduction (SNCR) process. In this process, a chemical reducing agent, e.g. NH\textsubscript{3} or urea (CO(NH\textsubscript{2})\textsubscript{2}), is added to the post-combustion region, to reduce NO to N\textsubscript{2}. An additional challenge in combustion of biomass and waste fuels arises due to the content of inorganic matter (e.g. alkali and heavy metals) and chlorine in the fuels. Vaporized alkali salts released during combustion can generate sticky and corrosive ashes, which may deposit in the post-combustion region, and potentially cause shutdown of the power plant. Addition of sulfur containing compounds is known to decrease these issues, by converting alkali chlorides to less corrosive alkali sulfates. For this reason, ammonium sulfate ((NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4}) has been suggested as an additive in the SNCR process, which upon decomposition yields NH\textsubscript{3} for reduction of NO, and SO\textsubscript{2}/SO\textsubscript{3} for sulfating metals.

NO\textsubscript{x} emissions from mobile sources, i.e. marine and automotive diesel engines, are typically reduced by employing the selective catalytic reduction (SCR) process, using urea as additive. However, formation of undesirable byproducts during urea decomposition is known to cause deposition in the exhaust system, and may lead to shutdown of the SCR operation. It has therefore been of interest to develop computational tools for the description of urea decomposition and byproduct formation. The goal of these tools are to gain an improved understanding of the process, and to predict optimal operating conditions that reduces the risk of deposition in urea-SCR systems. Previous models for urea decomposition are mainly limited to low heating rate conditions (2-20 °C/min). Such low heating rates are not representative of practical urea-SCR systems, where the urea-water-solution (UWS) droplets of <100 µm may be heated by up to 10\textsuperscript{5} °C/min. The high heating rate is expected to have a significant influence on the process. Therefore, it has been of particular interest in this work to develop models that reliably extends to higher heating rates.

The SNCR performance of ammonium sulfate (AS) has been investigated experimentally in a flow reactor setup under well-controlled conditions. Additionally, a detailed kinetic reaction model for the SNCR chemistry was developed, containing subsets for H/N/O, H\textsubscript{2}/O\textsubscript{2}, H\textsubscript{2}S/O\textsubscript{2}, alkali/sulfur/chlorine and N/S interactions, along with a decomposition reaction for ammonium sulfate. As an important prerequisite for studying the SNCR process with ammonium sulfate, the effects of sulfur oxides on NO reduction was investigated. For SNCR experiments using NH\textsubscript{3} in absence and presence of SO\textsubscript{2}, it was found that SO\textsubscript{2} has a negligible effect on the NO reduction, in line with numerical results of the model. SNCR experiments using ammonium sulfate was demonstrated to achieve up to 95 % NO reduction, in a temperature interval of 1025-1075 °C at AS/NO molar ratios of 1.1-2.3. The model accurately predicted the operating temperature window for efficient NO reduction, but slightly underestimated the NO reduction at temperatures above the optimum. Increasing the residence time by a factor of 40 caused a downwards shift in the operating temperature window by approximately 150
°C, which was well captured by the model. Finally, it was desired to investigate the effect of KCl on NO reduction, as well as the KCl sulfation potential when using ammonium sulfate. Addition of 390 ppm KCl was found to have a promoting effect on NO reduction, by shifting the operating temperature window by 100 °C towards lower temperatures, while attaining a similar degree of NO reduction to that without addition of KCl. However, this promoting effect was not captured by the model, and more work is required to solve this issue, and to determine if the effect is caused by gas phase or condensed phase interactions of KCl with the SNCR chemistry. Finally, the results implied that 60 % of the added KCl was converted by ammonium sulfate at temperatures between 800-1025 °C.

The urea decomposition process was investigated experimentally, by thermogravimetric analysis (TGA), Fourier-transformed Infrared Spectroscopy (FTIR), and Raman spectroscopy. Based on the results of these methods, it was indicated that urea mainly decomposes directly from condensed phase, whereas evaporation of urea is negligible. A kinetic reaction scheme including 14 reactions for urea decomposition and formation of biuret (H₂N-CO-NH-CO-NH₂), cyanuric acid (HOCN)₃, and ammelide (C₃H₄N₄O₂), was developed. The kinetic parameters in the reaction scheme were derived from fitting to TGA experiments under low to medium heating rate conditions (5-500 °C/min). The model yielded a good description of the urea, biuret, and cyanuric acid TGA curves for all investigated heating rates. Moreover, the results implied that an increasing heating rate causes a shift in production of cyanuric acid to ammelide, while reducing the overall deposit formation. Additionally, isothermal TGA experiments of urea extending over 96 hours demonstrated that 280 °C is insufficient to attain fully decompose urea, whereas 380 °C yielded complete decomposition within 55 hours. The model yielded a precise description of the isothermal characteristics of urea at 280 °C, but slightly overestimated the decomposition rate at 380 °C.

A model for UWS droplet evaporation and decomposition in urea-SCR systems was developed, including the reaction scheme for byproduct formation as described above. The water evaporation model compared favorably with experimental evaporation rates of 0.82-0.92 mm UWS droplets at ambient temperatures of 200-400 °C. The decomposition rates of urea particles were generally underestimated, most pronounced at higher temperatures. The model discrepancies were mainly attributed to the experimentally observed micro-explosions of UWS droplets, which is not captured by the present model. The model was further used to predict the evaporation and decomposition behavior of practical UWS droplets of 7-70 µm at 200-400 °C. The numerical results indicate that it is favorable for the conversion of UWS droplets to minimize the droplet size, while operating at high ambient temperature. However, the residence time of the droplets in the exhaust gas before reaching the catalyst is typically too short to attain high conversion of urea. Therefore, the results indicate that considerable amounts of urea and byproducts will reach the catalyst in practical urea-SCR systems.
Dansk resumé

Som led i den grønne omstilling af energisektoren og udfasning af fossile brændsler, har der været en stigende interesse for bæredygtige alternativer såsom biomasse og kommunalt affald. Dog giver forbrændning af disse brændsler stadig anledning til bekymringer, da disse også er kendt for at udlede nitrogenoxider, NO₅ (NO og NO₂). Udledning af NO₅ er forbundet med skadelige virknings på miljøet, da de indgår i dannelsen af fotokemisk smog og syreregn. NO₅ udledning fra forbrændingsanlæg bliver typisk reduceret ved anvendelse af processen ”selective non-catalytic reduction” (SNCR). I denne proces tilsættes et reducerende kemisk middel til røggassen over forbrændingskammeret. De mest anvendte reduktionsmidler er NH₃ og urea (CO(NH₂)₂), der begge kan reducere NO til N₂ under specifikke betingelser. I forbindelse med forbrænding af biomasse og affald opstår der en yderligere udfordring, idet brændslernes høje indhold af metaller og klor har tendens til at danne klistrende og korrosive asker. Sådanne asker kan forårsage belægninger i systemet, der potentielt leder til nedlukning af anlægget. Tilsætning af svovlholdige stoffer kan omdanne alkali klorider til mindre korrosive alkali sulfater, og dermed reducere graden af belægningsdannelse og korrosion. I denne forbindelse er ammonium sulfat ((NH₂)₂SO₄) blevet foreslået som tilsætningsmiddel i SNCR processen. Ammonium sulfat (AS) dekomponerer til NH₃ og svovloxider (SO₂/SO₃) under opvarmning, og kan potentielt både reducere NO og omdanne alkali klorider til mindre korrosive alkali sulfater.

Udledning af NO₅ fra transportindustrien bliver typisk reduceret ved at anvende processen ”selective catalytic reduction” (SCR), med urea som tilsætningsmiddel. Et praktisk problem ved denne proces er, at urea under dekomponering kan danne uønskede biprodukter, og lede til belægningsdannelse i udstødningssystemet og på katalysatoren. Det har i dette projekt været af særlig interesse at udvikle beregningsværktøjer, til at beskrive dekomponeringen af urea samt dannelsen af biprodukter. Formålet med sådanne værktøjer er at opnå en bedre forståelse for processen og udlede optimale betingelser, der reducerer risikoen for belægningsdannelse i systemet. Tidligere modeller for dekomponering af urea er primært udledt ved lave opvarmningshastigheder (2-20 °C/min), som ikke er repræsentative for de praktiske forhold i urea-SCR systemer. I praksis bliver urea tilsat som små urea-vand (UWS) dråber i en diameter under 100 µm. Dette kan medføre opvarmning af dråberne op til 10⁵ °C/min, hvilket forventes at have en stor betydning for processen. Det har derfor været af særlig interesse at udvikle modeller, som er pålidelige ved højere opvarmningshastigheder.

Effektiviteten af AS i SNCR processen blev undersøgt igennem flow reaktor eksperimenter under kontrollerede betingelser. Desuden er en kinetisk reaktions model blevet udviklet til beskrivelse af SNCR kemien. Modellen indeholder mekanismer for interaktioner mellem H/N/O, H₂/O₂, H₂S/O₂, alkali/svovl/klor og N/S, samt en reaktion for dekomponering af ammonium sulfat. Som en vigtig forudsætning for brugen af AS, blev det undersøgt om SO₂ har en indflydelse på NO reduktion. Ved SNCR forsøg med NH₃, med og uden SO₂, blev det vist at SO₂ har en ubetydelig effekt på NO reduktion. Modellen forudså ligeledes ingen effekt af SO₂ på NO reduktionen ved de anvendte betingelser. SNCR eksperimenter med AS viste en høj grad af NO reduktion op til 95 % i et temperaturinterval på 1025-1075 °C for AS/NO molære forhold mellem 1.1-2.3. Modellen gav generelt en god beskrivelse af temperaturvinduet for effektiv NO reduktion, men gav dog en afvigelse ved tem-


En dråbemodel blev udviklet for UWS fordampning og dekomponering i urea-SCR systemer. Modellen inkluderede reaktionsskemaet for urea dekomponering og dannelse af biprodukter, som beskrevet ovenfor. Modellen gav præcise beskrivelser af fordampningshastigheden af 0.82-0.92 mm UWS dråber ved temperaturer mellem 200-400 °C, men underestimerede dekomponeringshastigheden ved disse temperaturer. Afvigelserne blev primært forklaret ud fra eksperimentelt observerede mikro-ekspllosioner af dråberne. Modellen blev yderligere anvendt til at forudsige fordampning og dekomponering af mindre UWS dråber på 7-70 µm ved temperaturer mellem 200-400 °C. Simuleringerne indikerede at det er favorabelt for omdannelsen af UWS dråber at minimere dråbestørrelsen, og opretholde en høj temperatur af udstødningsgassen. Opholdstiden af dråberne i udstødningsrøret før katalysatoren er dog typisk for kort til at opnå tilstrækkelig omdannelse af urea. På baggrund af disse resultater kan det derfor forventes, at betydelige mængder af urea og biprodukter vil danne belegning på katalysatoren i praktiske urea-SCR systemer.
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## Abbreviations and Symbols

### Abbreviations

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<tr>
<td>AS</td>
<td>Ammonium sulfate</td>
</tr>
<tr>
<td>BAT</td>
<td>Best Available Techniques</td>
</tr>
<tr>
<td>CCD</td>
<td>Charge-coupled device</td>
</tr>
<tr>
<td>CFB</td>
<td>Circulating fluidized bed</td>
</tr>
<tr>
<td>CFD</td>
<td>Computational fluid dynamics</td>
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<tr>
<td>CSTR</td>
<td>Continuously stirred tank reactor</td>
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<tr>
<td>CYA</td>
<td>Cyanuric acid</td>
</tr>
<tr>
<td>DL</td>
<td>Diffusion limited</td>
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<tr>
<td>EFR</td>
<td>Entrained flow reactor</td>
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<tr>
<td>FBN</td>
<td>Fuel-bound nitrogen</td>
</tr>
<tr>
<td>FBR</td>
<td>Fixed bed reactor</td>
</tr>
<tr>
<td>FGR</td>
<td>Flue gas recirculation</td>
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<td>FTIR</td>
<td>Fourier-transformed infrared spectroscopy</td>
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<tr>
<td>HPLC</td>
<td>High-performance liquid chromatography</td>
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<tr>
<td>NO&lt;sub&gt;x&lt;/sub&gt;</td>
<td>NO and NO&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td>NRTL</td>
<td>Non-random two-liquid</td>
</tr>
<tr>
<td>RM</td>
<td>Rapid mixing</td>
</tr>
<tr>
<td>SCR</td>
<td>Selective catalytic reduction</td>
</tr>
<tr>
<td>SNCR</td>
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<td>VLN</td>
<td>Very Lean NO&lt;sub&gt;x&lt;/sub&gt;</td>
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### Symbols

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<td>( \lambda )</td>
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1

Introduction

1.1 Background and motivation

Due to the green transition in the energy sector, it has been of increasing interest to reduce the share of coal in heat and power production. Alternatives to coal include biomass and waste fuels, which are considered renewable fuels that do not contribute to a net increase in the CO\textsubscript{2} emission. Combustion of waste has an additional positive effect on the environment by reducing the disposable amount of waste. However, the emission of nitrogen oxides, i.e. NO\textsubscript{x} (NO and NO\textsubscript{2}), from combustion of these fuels continues to be a major environmental concern. NO\textsubscript{x} have been shown to participate in the formation of acid rain and photochemical smog, depletion of the ozone layer [1], and can have a harmful effect on human health [2]. Due to the adverse effects of NO\textsubscript{x}, stringent legislations have been implemented to control their emissions. In the European Union, the daily average NO\textsubscript{x} emissions from stationary 100-300 MW\textsubscript{th} power plants are to be limited from 250 mg/Nm\textsuperscript{3} to 50-150 mg/Nm\textsuperscript{3} for waste combustion and 100-220 mg/Nm\textsuperscript{3} for biomass combustion [3–5]. In the maritime industry, the regulations on NO\textsubscript{x} emissions have also been tightened, with the recent introduction of Tier III emission standards in the MARPOL Annex VI [6], as presented in Table 1.1.

<table>
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<th>Tier</th>
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<td></td>
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<td>n&lt;130</td>
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<td>2000</td>
<td>17</td>
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<tr>
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<td>Tier III</td>
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For stationary power plants, the most commonly applied technology for reduction of NO\textsubscript{x} is the selective non-catalytic reduction (SNCR) process. This process involves injection of a chemical additive, typically ammonia or urea (CH\textsubscript{4}N\textsubscript{2}O), into the post-combustion chamber to reduce NO\textsubscript{x} to N\textsubscript{2}. The SNCR process offers a cheaper alternative to the selective catalytic reduction (SCR) process, as it utilizes the energy from the hot gas to overcome the energy barriers of the chemical reactions, and therefore does not require a catalyst. Although the SNCR process has been studied extensively [7], the increasing interest in alternative fuels such as biomass and waste has introduced more unknowns and uncertainties. Due to the nature of these fuels, high levels of inorganic matter is released upon combustion. A good understanding of the interactions between inorganic matter, e.g. alkali and heavy
metals, with the SNCR chemistry is still lacking. It is therefore desirable to gain an improved understanding of these interactions. Moreover, the presence of alkali and heavy metals in the post-combustion chamber is known to induce agglomeration of ash particles, and accelerate corrosion of heat-transfer surfaces [8–12]. Current control measures for reducing deposition and corrosion involves addition of sulfur containing additives, which can convert the most problematic species into less corrosive species (eg. KCl into K$_2$SO$_4$) [13–19]. A promising additive is ammonium sulfate, which upon thermal decomposition yields ammonia and SO$_2$/SO$_3$ for simultaneous reduction of NO$_x$, and sulfating of metals [20,21]. However, the feasibility of ammonium sulfate in the SNCR process has not yet been demonstrated on a fundamental level, and the knowledge of the metal/sulfur interactions under SNCR conditions is scarce.

In the maritime industry, NO$_x$ is typically reduced by employing the SCR process, using urea as chemical reducing agent. For mobile sources, urea has been the preferred additive, due to advantages in storage and handling. Urea is typically dissolved in water, and injected as fine droplets into the exhaust pipe upstream of the SCR unit. The heat from the exhaust causes the droplets to evaporate, and further decompose into ammonia and isocyanic acid (HNCO) [22–24]. However, formation of undesirable byproducts during urea decomposition has been shown to cause issues with deposition, potentially leading to shutdown of the SCR system [25–28]. Extensive experimental efforts [29–37] and computational efforts [38–41] have been conducted, in order to determine optimal operating conditions to reduce the risk of deposition. However, most studies are limited to low heating rate conditions, which are not representative of a real urea-SCR system. It is desirable to gain a deeper understanding of the mechanisms leading to byproduct formation, in order to develop accurate computational tools for optimization of operating conditions.

1.2 Project objectives

This PhD project aims at investigating the potential use of ammonium sulfate for the SNCR process, and improving the current understanding of the urea decomposition process in SCR applications. Specifically, this work focuses on

- the use of ammonium sulfate as alternative additive for the SNCR process.
- the impact of vaporized alkali metals on the SNCR chemistry.
- modeling of the SNCR chemistry using ammonium sulfate as additive, and the influence of alkali metals.
- the physical and chemical processes involved in decomposition of urea.
- modeling of urea decomposition and byproduct formation under high heating rates.
- modeling of evaporation, decomposition, and byproduct formation of urea-water-solution droplets.
1.3 Structure of this thesis

Including the introduction, this thesis is divided into six chapters.

Chapter 2: Literature study

This chapter provides an overview of NO formation processes during combustion, and reviews different NO reduction technologies for stationary and mobile applications. For stationary power plants, the SNCR process is reviewed, summarizing the chemistry and effect of operating conditions. For automotive and oceangoing units, the urea-SCR process is reviewed, summarizing the issues related to urea decomposition at SCR conditions.

Chapter 3: Selective non-catalytic reduction of NO\textsubscript{x} using alternative additives

This chapter presents experimental results from laboratory scale SNCR experiments using ammonium sulfate as alternative additive. In addition, the influence of sulfur oxides and vaporized KCl on the SNCR chemistry was investigated. A detailed chemical kinetic model was developed to describe the SNCR experiments.

Chapter 4: Kinetic modeling of urea decomposition and byproduct formation

This chapter summarizes the experimental and numerical results on urea decomposition under high heating rate conditions. Moreover, the competition between urea evaporation and decomposition was investigated experimentally. A kinetic model was developed to describe the thermal behavior of urea, as well as the formation of heavy-molecular byproducts including biuret, cyanuric acid, and ammelide.

Chapter 5: Modeling the decomposition and byproduct formation of a urea-water-solution droplet

This chapter presents the numerical results of a developed model for the description of evaporation, decomposition and byproduct formation of a UWS droplet. The model was evaluated against available experimental data, and was further used to predict the decomposition behavior of UWS droplets at typical urea-SCR conditions.

Chapter 6: Concluding remarks and future prospects

This chapter provides a summary of the main conclusions from this PhD project, and suggestions for future work.
Introduction
This chapter provides an overview of the NO\textsubscript{x} formation mechanisms during combustion processes. Furthermore, several techniques for NO\textsubscript{x} reduction in stationary applications are described with emphasis on biomass and waste combustion, along with the effects of important process parameters. In addition, the urea-SCR technique for NO\textsubscript{x} reduction in mobile applications is described, along with proposed numerical models for prediction of urea decomposition and byproduct formation.

### 2.1 Formation of NO

Three unique reaction pathways are responsible for formation of NO during combustion processes. These are: (1) thermal NO formed by combination of atmospheric nitrogen and oxygen at high temperatures; (2) prompt NO formed by reactions between hydrocarbon fragments in the fuel with atmospheric nitrogen; and (3) fuel NO formed from oxidation of fuel-bound nitrogen \[42\]. A simplified reaction path diagram illustrating the major steps in NO formation of these mechanisms is presented in Figure 2.1. Thermal NO is produced by oxidation of atmospheric N\textsubscript{2} at high temperatures, prompt NO is formed by reaction between atmospheric N\textsubscript{2} and hydrocarbon radicals, and fuel NO is formed from the nitrogen found in the fuel which is released during combustion. Each of these mechanisms will be reviewed in the following sections.

![Figure 2.1: Simplified reaction path diagram illustrating the major steps in the formation of thermal, prompt, and fuel NO.](image)

---

Figure 2.1: Simplified reaction path diagram illustrating the major steps in the formation of thermal, prompt, and fuel NO \[7\].
2.1.1 Thermal NO

Thermal NO, also known as the Zeldovich mechanism [43], is governed by chain reactions between atmospheric nitrogen and oxygen. The mechanism is initiated by attack of a free oxygen atom on N₂ (R 2.1), producing NO and a free nitrogen atom. Once formed, the nitrogen atom is rapidly oxidized to NO by O₂ (R 2.2) or OH (R 2.3):

\[
\begin{align*}
N₂ + O & \leftrightarrow NO + N \quad \text{R 2.1} \\
N + O₂ & \leftrightarrow NO + O \quad \text{R 2.2} \\
N + OH & \leftrightarrow NO + H \quad \text{R 2.3}
\end{align*}
\]

The forward reaction rate of R 2.1 has a relatively large activation energy (319 kJ/mol) [44], and is the rate determining step in the mechanism. Experimental work on characterization of thermal NO under well-controlled conditions is scarce. Arai et al. [45] conducted experimental investigations of the N₂/O₂ system in an isothermal flow reactor, which indicated that temperatures above 1300 °C is required for formation of thermal NO. Predictions from a kinetic model developed by Glarborg et al. [7] described the experiments by Arai et al. with good agreement, as shown in Figure 2.2. Additionally, it was recently shown by Strobel et al. [46] that an increase of the adiabatic flame temperature from 1300 °C to 1400 °C, during combustion of municipal solid waste, had no significant impact on the formation of thermal NO.

![Figure 2.2](image)

**Figure 2.2:** Comparison of experimental data by Arai et al. [45] and numerical predictions by the model of Glarborg et al. [7] for formation of thermal NO in a flow reactor as function of temperature and oxygen concentration. Experimental data are shown as symbols, while modeling predictions are shown as lines.
2.1 Formation of NO

2.1.2 Prompt NO

The mechanism for formation of prompt NO is initiated by attack of CH radicals on N\textsubscript{2} [47,48]. In early modeling studies, this reaction was believed to form HCN + N as precursors in the formation of prompt NO [49,50]. However, the reaction was later shown to proceed via insertion of CH into the N\textsubscript{2} molecule [51,52]:

\[ \text{CH} + \text{N}_2 \rightarrow \text{NCN} + \text{H} \quad \text{R 2.4} \]

The knowledge of the subsequent oxidation of NCN to NO have been studied in shock tube experiments by Friedrichs and coworkers, and involve reactions with the O/H radicals [53,54], O\textsubscript{2} [55], and NO [56]. A reaction path diagram for prompt NO (Figure 2.3) was proposed by Glarborg et al. [7], based on a kinetic model simulation of jet-stirred reactor experiments by Bartok et al. [57].

![Reaction Path Diagram for Prompt NO](image)

**Figure 2.3**: Reaction path diagram for prompt NO proposed by Glarborg et al. [7] under the conditions of the jet-stirred reactor experiments by Bartok et al. [57]. A reaction sequence from NCN through HNC to the amine pool has been omitted in the diagram.

For low temperatures and fuel-rich conditions, fuel radicals are typically produced at a faster rate, which promotes the formation of prompt NO. However, under lean conditions, the oxidation rate of the fuel is typically sufficiently rapid to limit the extent of fuel radicals, resulting in negligible amounts of prompt NO\textsubscript{x} [42]. For the combustion of solid fuels such as coal, biomass, and waste, it is generally believed that prompt NO has an insignificant contribution to the overall NO formation, and that fuel NO\textsubscript{x} is the major contributor [48,58].
2.1.3 Fuel NO

Fuel-bound nitrogen (FBN) is by far the major source of NO formation from combustion of fuels with high nitrogen content, such as oils, coal, coke, and municipal solid waste [58–60]. It is generally believed that fuel-bound nitrogen compounds thermally decomposes into low-molecular-weight nitrogen compounds prior to combustion. Miller and Bowman proposed a detailed scheme for reaction pathways in conversion of fuel-N to final N-containing combustion products, including NO, N₂ and NH₃, as depicted in Figure 2.4 [50].

![Proposed reaction pathways leading to formation of NO from fuel nitrogen in rich hydrocarbon flames (equivalence ratios between 1.0 and 1.5). The thick arrows illustrate the dominant reaction pathways [50].](image)

Based on the reaction scheme proposed by Miller and Bowman [50], the initial step of fuel-N conversion is believed to be thermal decomposition of the fuel-N molecules into HCN. HCN is then converted into NCO, primarily by collision with an O radical. NCO is then further converted into NH₁ by collision with an H radical. Depending on the combustion conditions, NH₁ is converted into either NO (for oxidizing conditions) or N₂ (for reducing conditions). There are several recycling pathways, where NO can be converted back into HCN, depending on the conditions. Under lean conditions, NCO and CN may react with O radicals, leading to direct formation of NO.

In a recent numerical study by Frank and Castaldi [60], it was indicated that fuel NO was the dominating formation mechanism in a reciprocating-grate waste combustion. In this study, HCN was predicted to be the most important precursor for formation of fuel NO, in line with the proposal by Miller and Bowman [61].

![Predominant reaction pathway leading to formation of fuel NOₓ, based on CFD analysis of a municipal waste combustion plant, using a detailed chemical kinetic model, adapted from [60].](image)
2.2 Control techniques for NO emissions from stationary sources

There are two main categories for the control of NO\(_x\) emissions: (i) combustion control techniques, which focuses on optimizing combustion conditions with respect to NO\(_x\) formation, and (ii) post-combustion (or flue gas treatment) techniques, which focuses on reducing NO\(_x\) in the free-board above the fuel bed. Figure 2.6 shows some of the most commonly applied techniques for NO\(_x\) abatement [62]. In this section, state of the art techniques for controlling the NO\(_x\) emissions from stationary sources, i.e. combustion of alternative fuels such as biomass and waste, are reviewed.

![Diagram of control techniques for reduction of NO\(_x\)](image)

**Figure 2.6**: Overview of control techniques for reduction of NO\(_x\) [62].

### 2.2.1 Staged combustion

As discussed in 2.1.3, the fate of fuel-N depends largely on the combustion conditions. FBN may end up primarily as either NO (under oxidizing conditions) or as N\(_2\) (under reducing conditions). Thus, the goal of staged combustion is to optimize the combustion conditions to promote the reaction path leading to formation of N\(_2\). In air staging, air is supplied stepwise at different locations in the system, in order to manipulate the primary excess air ratio, and prevent complete combustion from taking place in the primary combustion zone, as illustrated in Figure 2.7.

From investigations on fixed bed combustion of wood [63] and waste [64], it has been shown that optimal conditions in the reduction zone are obtained with a primary excess air/fuel ratio of 0.7 to 0.8, a temperature of 1100 to 1200 °C, and a mean residence time of 0.5 s. In general, NO\(_x\) formation is enhanced for increasing amount of combustion air. However, a certain amount of combustion air is required, in order to maintain complete combustion of the fuel. Therefore, the supply of air to the combustion process becomes an optimization problem, to minimize NO\(_x\) formation while maintaining complete combustion of the fuel. A total excess air/fuel ratio of 1.6 has been found to be optimal for air staging in fixed bed and grate-fired combustion biomass combustion [65,66]. The NO\(_x\) reduction potential using air staging in fixed bed and grate fired combustion of biomass and waste is typically around 50-70 % [66–69].


2.2.2 Flue gas recirculation

In flue gas recirculation (FGR), a part of the flue gas is recycled back to the secondary combustion zone. The main goals of FGR is to (1) reduce NO$_x$ emissions and (2) increase boiler efficiency. The recirculated flue gas mainly contains products of complete combustion such as CO$_2$, H$_2$O, and low levels of O$_2$ and N$_2$. Typically, FGR is employed when the recirculated flue gas temperature is considerably lower than the temperature in the combustion chamber. Thus, mixing of the flue gas with the combustion air causes a decrease in temperature and a reduction of the oxygen availability in the reaction zone. If the temperature in the combustion zone without FGR is high enough (e.g. above 1500 °C), the decrease in temperature when using FGR may reduce the formation of thermal NO$_x$. Furthermore, a reduction of the oxygen availability limits the NO$_x$ formation from fuel-N. Another effect of FGR is an increased turbulence in the system, which can improve the efficiency of post-combustion techniques such as the selective non-catalytic reduction process (which is reviewed in section 2.2.4). FGR is often combined with air staging, where the recirculated flue gas is injected through overfire air ports, and thus replaces parts of the secondary air supply. Installation of FGR has been demonstrated in a grate-fired waste combustion plant to reach NO$_x$ reductions up to 30-37 % [70]. More recent work on grate-fired combustion of biomass showed that adding FGR to an existing air staged combustion system only reduced NO$_x$ emissions by an additional 5-10 % [67]. This study indicated that FGR has a higher NO$_x$ reduction potential when it is employed with the secondary air supply, rather than the primary air supply.

A disadvantage of FGR is that the reduced oxygen availability in the combustion chamber may lead to increased emissions of CO and other products of incomplete combustion (PICs). However, implementations of FGR have not been widely reported to cause problems with enhanced CO emissions, indicating that the enhanced mixing of air and flue gas typically compensates for the reduced oxygen availability [71].

2.2.3 Very Lean NO$_x$ (VLN) process

The Very Lean NO$_x$ (VLN) process is a patented process developed in 2008 by MARTIN GmbH in cooperation with its partner companies CNIM (FR), Covanta Energy [72] and MHIEC. The concept of the VLN process is based on a combination of staged air combustion and flue gas recirculation. In this process, some of the flue gas from the rear area of the combustion chamber (at the end of the grate) is extracted and recirculated back to the upper area of the furnace (see Figure 2.8). Martin et
2.2 Control techniques for NO emissions from stationary sources

al. [69,73] showed that recirculation of flue gas from the rear end of the grate leads to favorable combustion conditions that limits the formation of fuel NO. At the same time, recirculation of the cold flue gas provided mixing and cooling in the upper furnace region. Martin et al. [73] reported that installation of the VLN process to waste combustion plants can yield NO\textsubscript{x} emission values in the scale of 120-180 mg/Nm\textsuperscript{3}. By further applying SNCR, NO\textsubscript{x} emission values down to 80 mg/Nm\textsuperscript{3} with NH\textsubscript{3} slips below 10 mg/Nm\textsuperscript{3} have been reported [69,73]. In addition, the VLN process is expected to have a positive effect on boiler corrosion, by reducing the fly ash entrained in the flue gas [69].

Figure 2.8: Comparison of (a) a conventional staged combustion system and (b) the VLN process. The parameter $\lambda$ is the stoichiometric air/fuel ratio [74].

2.2.4 Selective non-catalytic reduction of NO

The selective non-catalytic reduction (SNCR) process is a post-combustion technique for reduction of NO\textsubscript{x}. Generally, SNCR is more expensive to employ than the primary combustion control techniques, such as air staging, FGR and VLN described in sections 2.2.1 - 2.2.3. However, due to the stringent legislation on NO\textsubscript{x} emissions from stationary combustion plants, it is often necessary to also employ a post-combustion technique. For stationary sources, SNCR is the most commonly applied post-combustion technique for NO\textsubscript{x} control, and will be reviewed in detail in this section.

In the SNCR process, a chemical reducing agent is injected into the flue gas in the post-combustion region. Here, the reagent mixes and reacts selectively with the NO\textsubscript{x} through homogeneous gas phase reactions, where the NO\textsubscript{x} is reduced to nitrogen. Typical reducing agents include gaseous NH\textsubscript{3} (Thermal DeNO\textsubscript{x} [75,76]), urea (NO\textsubscript{x}Out [77]), and cyanuric acid (RapReNO\textsubscript{x} [78]). Under stoichiometric conditions, the global reactions for the SNCR process when using NH\textsubscript{3} and urea (CO(NH\textsubscript{2})\textsubscript{2}) can be expressed as [79]:

\[
2\text{NH}_3 + 2\text{NO} + \frac{1}{2}\text{O}_2 \rightarrow 2\text{N}_2 + 3\text{H}_2\text{O}
\]

\[
\text{CO(NH}_2\text{)}_2 + 2\text{NO} + \frac{1}{2}\text{O}_2 \rightarrow 2\text{N}_2 + \text{CO}_2 + 2\text{H}_2\text{O}
\]

Cyanuric acid, (HOCN)\textsubscript{3} is an alternative to NH\textsubscript{3} and urea, which above 330 °C decomposes to HNCO, which at sufficiently high temperature can be active in the reduction of NO [7,80].
Literature study

The SNCR process has been studied extensively, and is known to be influenced by many factors. Important process parameters include the reaction temperature [58,76], residence time [81], reagent injection rate [33,77,82], presence of O₂ [81,83], SO₂ [84,85], combustible additives [86–91], alkali metals [92–95], and more. The influences of various important factors on the SNCR chemistry are reviewed in the following sections 2.2.4.1 - 2.2.4.8.

Several detailed chemical kinetic models for description of NOₓ chemistry have been proposed. One of the early and most cited models is the mechanism developed by Miller and Bowman in 1989 [50]. This model includes description of NO formation, as described in section 2.1, and degradation of NO through the thermal DeNOₓ and RAPRENOₓ processes. A newly developed mechanism by Glarborg et al. [7], based on the work on nitrogen chemistry reported over the last 40 years. Parts of this mechanism dates back to Miller and Bowman mechanism [50], but has been updated from recent advances in the knowledge of thermochemistry and reaction rates. The most important subsets of the mechanism have been determined from investigations on the chemistry of C₁-C₂ hydrocarbons [96,97], amines [98], cyanides [99], and hydrocarbon-nitrogen interactions [100–102]. In the following sections, experimental studies on the influence of various important process parameters in the SNCR process are reviewed, along with numerical descriptions of Glarborg et al. [7] model.

2.2.4.1 Operating window of the SNCR process

It is widely supported that the SNCR process has a narrow temperature window of effective operation, roughly in the range of 800-1100 °C [58,68,69,71,79,103–107]. The outcome in NO concentration is governed by competing consumption and production reactions of NO during the NH₃ oxidation. In the low-temperature end, NO reduction is mainly caused by the following (simplified) reaction sequence [86].

\[
\begin{align*}
\text{NH}_3 + \text{OH} & \leftrightarrow \text{NH}_2 + \text{H}_2\text{O} & \text{R} \ 2.5 \\
\text{NH}_2 + \text{NO} & \leftrightarrow \text{NNH} + \text{OH} & \text{R} \ 2.6 \\
\text{NH}_2 + \text{NO} & \leftrightarrow \text{N}_2 + \text{H}_2\text{O} & \text{R} \ 2.7 \\
\text{H} + \text{O}_2 & \leftrightarrow \text{O} + \text{OH} & \text{R} \ 2.8 \\
\text{O} + \text{H}_2\text{O} & \rightarrow 2\text{OH} & \text{R} \ 2.9
\end{align*}
\]

Below roughly 800 °C, the chain branching fraction of the NH₂ + NO reaction (i.e. the fraction that produces NNH + OH) is low [108], and the reaction sequence becomes chain terminating, resulting in low NO reduction and high NH₃-slip. For increased temperature, the branching fraction of the NH₂ + NO reaction becomes more significant. The key amine radical, NH₂, reacts almost exclusively with NO, and thus a significant NO reduction can be obtained within a specific temperature window. However, when the temperature is increased beyond an optimum value, the oxidation of NHᵢ radicals to NO is promoted, resulting in a shift from NO reduction to NO production [86]. Early studies have shown that the oxidation of NHᵢ becomes more dominant at temperatures greater than 1100 °C [77]. Thus, the SNCR process has to be operated within a specific temperature window in order to achieve efficient NO reduction. However, this temperature window is influenced by various operating parameters, which will be reviewed in the following sections.
2.2 Control techniques for NO emissions from stationary sources

2.2.4.2 Impact of residence time

The impact of residence time on the SNCR performance was recently investigated in a laminar flow reactor by Liang et al. [81]. It was shown that up to a certain value, increasing the residence time progressively shifted the optimum temperature to lower values, while increasing the NO reduction (see Figure 2.9). For sufficiently long residence time, the optimum temperature and NO reduction level approached a final asymptotic value. Generally, a change in the residence time was found to have the highest impact on NO reduction at lower temperatures (conceivably due to enhanced radical production), while it is less sensitive at temperatures above the optimum for NO reduction. The Glarborg et al. [7] model was used to simulate the experiments by Liang et al. [81], which showed an overall good agreement. A similar trend of increasing the residence time, with a downwards shift in the temperature window, was predicted by the model. However, the NO reduction was generally overestimated, particularly for the lower residence times. Duo et al. [109] found a similar impact of the residence time on NO reduction in flow reactor SNCR experiments in the range of 0.039-0.227 s, in the same order of magnitude as those used by Liang et al. [81].

![Figure 2.9: Experimental results on the impact of residence time on NO reduction in the SNCR process conducted by Liang et al. [81]. The experiments were simulated using the Glarborg et al. model. [7]. The inlet conditions were: NO<sub>i</sub> = 400 ppm, NH<sub>3</sub> = 480 ppm, O<sub>2</sub> = 3 vol. %, balance gas N<sub>2</sub>.](image-url)
2.2.4.3 Impact of NH3/NO molar ratio

The impact of the NH3/NO molar ratio ($\beta_{\text{NH3}}$) on NO reduction was studied in a flow reactor by Muzio et al. [77] (see Figure 2.10). From their investigations, the NO reduction was found to be promoted for increasing $\beta_{\text{NH3}}$, up to a value around 2. Increasing $\beta_{\text{NH3}}$ above 2 did not yield a further increase in the NO reduction, whereas the NH3-slip increased significantly. A similar trend of the NH3/NO molar ratio was found by Javed et al. [82], who showed that a $\beta_{\text{NH3}}$ of 1.5 yielded the optimal NO reduction, while increasing $\beta_{\text{NH3}}$ further did not cause a significant effect on NO reduction. The experimental results by Muzio et al. [77] are not fully captured by the Glarborg et al. model [7]. The model predicts an off-set in the operating temperature window by approximately 75 °C as compared to the experiments. Similar model deviations have been found by Glarborg et al. [7] in simulation of a dry NO/NH3/O2 experiment conducted by Duo [110]. However, the model has been shown to predict NO fairly accurately in presence of water vapor [7], while it tends to underestimate the temperature for onset of reaction in dry conditions. The reason for this discrepancy has not yet been determined. Glarborg et al. [7] suggests that loss of O radicals on the wall may have an influence under dry conditions, while presence of H2O presumably alters the surface condition and inhibits recombination of O radicals on the SiO2 surface. However, an experimental study on the influence of surface reactions on the thermal DeNOx process by Lyon and Benn [111] showed that reaction rates for the NO/NH3/O2 system were largely unaffected by variations in the surface/volume ratio.

Wang et al. [112] investigated the SNCR performance of urea in a flow reactor for varying urea/NO molar ratios. It was found that a normalized stoichiometric ratio (assuming complete decomposition of urea into NH3 and HNCO) of 1.5 was sufficient to reach optimal NO reduction, similar to the trends observed by Muzio et al. [77] and Javed et al. [82]. Thus, comparison of the performance of different additives in the SNCR process may be possible for similar NH3/NO ratios.

Figure 2.10: Experimental results on the impact of $\beta_{\text{NH3}}$ (NH3/NO molar ratio) on NO reduction in the SNCR process conducted by Muzio et al. [77]. The experiments were simulated with the Glarborg et al. [7] model. The inlet conditions were: NO_in = 300 ppm, O2 = 4 %, H2O = 0 %, balance gas N2.
2.2 Control techniques for NO emissions from stationary sources

2.2.4.4 Impact of O₂

The influence of oxygen concentration on the SNCR process was studied experimentally by Kasuya et al. [113] in a flow reactor (see Figure 2.11). It was shown that an increase in oxygen concentration shifted the operating window towards lower temperatures and widened it, while at the same time decreased the maximum amount of NO removal. These characteristics was described well by the Glarborg et al. model [7], although the predicted onset temperature of reaction was slightly less sensitive towards oxygen concentration than experimentally observed.

Similar results were shown by Lu and Lu [83], who studied the impact of oxygen concentration on the SNCR process in a flow reactor. Their results indicated that a trace amount of O₂ (0.01 %) was sufficient to replenish the radical pool and yield high NO reductions up to 95 %. However, the onset of NO reduction with trace amounts of O₂ occurred at higher temperatures (i.e. 1000 °C). Increasing the oxygen concentration slightly to 0.3 % shifted the onset temperature of reaction by roughly 100 °C. Below the optimum temperature, the NO reduction was found to be highly sensitive to variations in the O₂ concentration, and the NO reduction was promoted in rich O₂ atmospheres. This behavior has also been reported in a recent study by Liang et al. [81], who showed a similar influence of oxygen on NO reduction in the SNCR process.

![Figure 2.11: Comparison of experimental data from flow reactor experiments by Kasuya et al. [113], and numerical predictions by Glarborg et al. [7] for the effect on O₂ on NO reduction by NH₃ in a flow reactor. The inlet conditions were: NOᵣ = 500±30 ppm, NH₃ = 1000±60 ppm, H₂O = 5%, balance N₂. Residence time = 88/T(K) s.](image-url)
2.2.4.5 Impact of SO$_2$

The impact of SO$_2$ on the SNCR process was investigated by Dagaut and Nicolle [84] in a jet-stirred reactor. In this study, NO was reduced by ammonia with initial SO$_2$ concentrations ranging from 0-1000 ppm (see Figure 2.12). Their results indicated that presence of SO$_2$ has a minor effect on the SNCR process. A slight shift in the temperature window to higher temperatures for increasing SO$_2$ concentration was observed, but the maximum NO reduction was unaffected. This observation is in agreement with earlier studies performed by Silver [114] and Lucas and Brown [115]. Dagaut and Nicolle [84] explained this effect by proposing that SO$_2$ interferes with the O/H radical pool, mainly through the following reactions:

\[
\begin{align*}
\text{SO}_2 + O(\pm\text{M}) & \leftrightarrow \text{SO}_3(\pm\text{M}) & \text{R 2.10} \\
\text{H} + \text{SO}_2 + \text{M} & \leftrightarrow \text{HOSO} + \text{M} & \text{R 2.11} \\
\text{SO}_2 + \text{NH}_2 & \leftrightarrow \text{NH}_2\text{SO}_2 & \text{R 2.12} \\
\text{HOSO} + \text{O}_2 & \leftrightarrow \text{HO}_2 + \text{SO}_2 & \text{R 2.13}
\end{align*}
\]

Here, M is any gas-phase component that may act as a collision partner. The sequence of reactions R 2.11 and R 2.13 is equivalent to H+O$_2$+M = HO$_2$+M, resulting in a reduction of the radical pool, which in turn causes a lower degree of NH$_3$ oxidation. This mechanism has been proposed to cause the shift in the temperature window toward higher temperatures for increasing SO$_2$ concentration. Their model, which was based on the H/N/O subset by Skreiberg et al. [116] and a subset for sulfur oxides [117] taken largely from Glarborg and coworkers [118], qualitatively captured the observed influence of SO$_2$ on the onset temperature of reaction.

![Figure 2.12: Comparison of experimental and numerical results on the impact of SO$_2$ on NO reduction by Dagaut and Nicolle [84]. The inlet conditions were: NO$_\text{in} = 500$ ppm, NH$_3 = 500$ ppm, O$_2 = 0.625$ vol. %, balance gas N$_2$. The residence time was approximately 0.1 s.](image_url)
2.2.4.6 Impact of combustible additives

Wenli et al. [91] studied the effect of combustible additives including various alkanes, alcohols, ketones, aldehydes and amines on the SNCR process. From their results, it was found that addition of alkanes shift the onset of reaction to lower temperatures, while slightly suppressing the NO reduction (see Figure 2.13). The effect on NO reduction was further shown to be dependent on the type of additive, as well as the concentration. In O\textsubscript{2} rich conditions, combustible additives such as alkanes may be ignited at lower temperatures than NH\textsubscript{3}. Hence, more radicals are produced at lower temperatures when feeding combustible additives to the SNCR system, which promotes the oxidation of NH\textsubscript{3} to NH\textsubscript{2}. This mechanism has been proposed to cause of the downward shift in the temperature window when feeding additives to the SNCR system.

![Figure 2.13: Experimental results on the impact of alkanes on the SNCR performance. Initial conditions were: NO\textsubscript{in} = 507 ppm, NH\textsubscript{3} = 832 ppm, O\textsubscript{2} = 4.0 vol. %, balance gas N\textsubscript{2}. Adapted from [91].](image)

The effect of oxygenated additives on the urea-SNCR process, including H\textsubscript{2}O\textsubscript{2}, C\textsubscript{2}H\textsubscript{5}OH, C\textsubscript{2}H\textsubscript{4}(OH)\textsubscript{2} and C\textsubscript{3}H\textsubscript{5}(OH)\textsubscript{3}, was investigated experimentally by Javed et al. [119]. Addition of these additives (molar additive/NO ratios ranging from 0 to 2.0) generally caused a significant downwards shift in the temperature window for NO reduction by up to 150-330 °C while also broadening the temperature window. It is likely that addition of the oxygenated additives yields more OH radicals, which in turn produce more NH\textsubscript{2} radicals at lower temperatures. However, the downwards shift in temperature was accompanied with a decrease in the NO reduction efficiency and increased CO emissions.

The presence of CO in the SNCR process has been shown to shift the onset temperature of reaction towards lower temperatures, while narrowing the temperature window of efficient NO reduction [76,86,87,120], as reflected in Figure 2.14. It has been suggested that this effect is due to a branching behavior of CO oxidation, which replenishes the radical pool [86]:

![Diagram showing the impact of CO on the SNCR process.](image)
Literature study

\[ \text{CO} + \text{OH} \leftrightarrow \text{CO}_2 + \text{H} \quad \text{R 2.14} \]

\[ \text{H} + \text{O}_2 \leftrightarrow 0 + \text{OH} \quad \text{R 2.15} \]

\[ \text{O} + \text{H}_2\text{O} \leftrightarrow 2\text{OH} \quad \text{R 2.16} \]

From reactions R 2.14 - R 2.16 it can be seen that the CO oxidation is chain branching, and thereby replenishes the O/H radical pool, which in turn promotes the SNCR chemistry at lower temperatures by producing more NH₂ radicals. However, the increase of radicals also promotes the oxidation of NH₃ to NO at higher temperatures, resulting in a more narrow temperature window of efficient NO reduction. As seen from Figure 2.14, the Glarborg et al. [7] model captures both the shift in temperature for onset of reaction, and narrowing of the temperature operating window for increasing CO concentration. However, the model tends to overestimate NO at the high temperature end for high CO concentrations.

![Figure 2.14](image_url)

**Figure 2.14**: The impact of CO on the SNCR performance when using NH₃. The symbols denotes experimental data [86], while solid lines denotes model predictions by the Miller and Glarborg model [108], combined with a subset describing the moist oxidation of CO [121]. Initial conditions were: NO\textsubscript{in} = 300 ppm, NH₃ = 300 ppm, O₂ = 4.0 vol. %, H₂O = 4.5 vol. %, balance gas N₂. The residence time at 927 °C was approximately 150 ms.

### 2.2.4.7 Impact of alkali metals

Zamansky et al. [92] investigated the impact of adding Na species to the SNCR process in a pilot scale entrained flow reactor while using NH₃ as reducing agent. Their experiments showed that small amounts of Na₂CO₃, in the order of 5-15 ppm, yielded a promoting effect on NO reduction, mostly pronounced at temperatures below the optimum of NO reduction (see Figure 2.15). However, addition of larger amounts did not increase the promotor efficiency. The effect of the different Na species (including HCOONa, CH₃COONa, NaNO₃, and Na₂CO₃) was similar, when added in equimolar amounts. Based on kinetic modeling, they suggested that the promoting effect could be explained by
a sequence of gas-phase reactions, in which Na species are initially converted into NaOH, which is the most stable gas-phase Na compound under these conditions (in absence of Cl and S). NaOH further participates in a sequence of reactions leading to formation of OH radicals;

\[
\begin{align*}
\text{NaOH} + O_2 &\leftrightarrow \text{NaO}_2 + \text{OH} & \text{R 2.17} \\
\text{NaO}_2(+M) &\leftrightarrow \text{Na} + \text{O}_2(+M) & \text{R 2.18} \\
\text{Na} + \text{NO}_2 &\leftrightarrow \text{NaO} + \text{NO} & \text{R 2.19} \\
\text{NaO} + \text{H}_2\text{O} &\leftrightarrow \text{NaOH} + \text{OH} & \text{R 2.20}
\end{align*}
\]

Yielding a net effect; \( \text{H}_2\text{O} + \text{HO}_2 \rightarrow 3\text{OH} \). The OH radicals are more active than the HO\(_2\) radicals, and promote NO reduction by forming NH\(_2\) radicals via R 2.5 and reduce NO via R 2.6 and R 2.7. The same promoting effect of Na species on the urea-SNCR process has been demonstrated experimentally [122,123] and numerically [124].

![Experimental results on the impact of Na\(_2\)CO\(_3\) on NO reduction in the SNCR process][1] [92]. The initial conditions were: NO\(_{in}\) = 500 ppm, NH\(_3\) = 725 ppm, O\(_2\) = 3.9 %, H\(_2\)O = 15.0 %, CO\(_2\) = 7.0 %. The residence time was 187/T(K) s.

Hao et al. [94] compared the effects of various Na and K species (including Na\(_2\)CO\(_3\), NaCl, and KCl) on the SNCR process through experiments in an entrained flow reactor (Figure 2.16), and ordered the promotor efficiency on NO reduction as Na\(_2\)CO\(_3\) > KCl > NaCl. As Na\(_2\)CO\(_3\) is expected to be rapidly converted into NaOH at SNCR conditions, it is indicated that alkali hydroxides are more active in the SNCR process as compared to alkali chlorides. As suggested by Zamansky et al. [92], this is conceivably due to a higher production rate of OH radicals from the reaction sequence R 2.17 - R 2.20.
Figure 2.16: Experimental results on the effect of Na/K additives on the SNCR process, adapted from Hao et al. [94]. The inlet conditions were: NO$_{in}$ = 400 ppm, NH$_3$ = 400 ppm, O$_2$ = 4 %, H$_2$O = 4 %, balance N$_2$. The residence time was kept constant at 0.6 s.

Entrained flow reactor experiments by Guo et al. [95] indicated that Na species have a slightly stronger promoting effect on NO reduction than K species, which is supported by experiments of Lu et al. [125]. Guo et al. [95] further used the Na and K mechanisms proposed by Zamansky et al. [92] and Hindiyarti et al. [93], respectively, to simulate the effect of Na and K species on NO reduction. As seen from Figure 2.17, the model predicted a small promoting effect of Na$_2$CO$_3$, but was unable to capture the promoting effect of K$_2$CO$_3$ on NO reduction, thus illustrating the short-comings in the mechanism for K species proposed by Hindiyarti et al. [93].

Figure 2.17: Comparison of experimental and numerical results for the effects of Na$_2$CO$_3$ and K$_2$CO$_3$ on the SNCR process, adapted from Guo et al. [95]. The inlet conditions were: NO$_{in}$ = 400 ppm, NH$_3$ = 600 ppm, O$_2$ = 2.8 %, H$_2$O = 6 %, balance N$_2$. The residence time was about 3–4 s.
2.2 Control techniques for NO emissions from stationary sources

2.2.4.8 Impact of mixing

The reduction of small amounts of NO, typically in the concentration range of 150-500 ppm, requires efficient mixing of the reducing agent and the flue gas. This can be challenging to facilitate over a wide space, such as full-scale SNCR applications. Thus, the SNCR performance is strongly influenced by the mixing conditions. This is typically also reflected by the differences in reported NO reduction levels between laboratory studies, e.g. those described in sections 2.2.4.1 - 2.2.4.7 (up to 100 %), and full-scale SNCR applications (up to 70 %) [103].

Lv et al. [126] studied techniques for enhancing global mixing between the reducing agent and the flue gas, by CFD simulation of an SNCR system. Increasing the droplet size was shown to cause a more homogeneous mixing of the flue gas and reducing reagent at a global scale (enhanced macro-mixing). However, the SNCR performance also depends on the effective micro-scale mixing between reagent droplets and flue gas. Increasing the droplet size has a negative impact on the micro-scale mixing, since the surface area per volume of the reagent is reduced. Consequently, the determining the reagent droplet size for optimal NO reduction at the global scale is an optimization problem, to facilitate both macro-scale and micro-scale mixing of the reducing agent with the flue gas.

Lv et al. [126] further investigated the optimization potential in NO reduction by rearranging the injection nozzles. A multi-level nozzle arrangement for injection of reducing reagent at different levels in the furnace, which effectively increased the macro-scale mixing of the reagent with the flue gas, was shown to enhance the SNCR performance. On the basis of this concept, Hitachi Zosen Inova developed a controlled multi-level reagent feed system for the SNCR process named DyNOR™ [105]. This control system measures local temperature variations in the furnace, and selects the injection locations that will have the highest impact on the overall NO reduction. The reagent injection rate is controlled based on stack NO emission measurements. A shortcoming of the DyNOR system is the lack of CO measurements in the SNCR section. As discussed in section 2.2.4.6, CO has an adverse effect on the SCNR chemistry by narrowing the temperature window of efficient NO reduction. Therefore, the reducing reagent should preferably be injected at a location where the CO has been fully oxidized. Thus, the implementation of an in situ CO measurement could potentially be an advantageous feature to the DyNOR system. However, installation of in-situ gas analyzers in full-scale combustion plants is challenging and expensive.
2.2.4.9 SNCR with ammonium sulfate

Fuels with high alkali chlorine content such as biomass and municipal waste have shown a tendency to enhance deposit formation in the post-combustion chamber, and may accelerate corrosion on heat-transfer surfaces [8–12]. Broström et al. [13] showed, in experiments with a 25 MW biomass fired circulating fluid bed (CFB) boiler, that such problems can potentially be reduced by adding ammonium sulfate (\((\text{NH}_4\text{)}_2\text{SO}_4\)) to the post-combustion region. Ammonium sulfate decomposes spontaneously into \(\text{NH}_3\) and sulfur oxides at SNCR conditions, and can thereby be active both in the reduction of NO, and in the sulfation of alkali chlorides. Extensive mechanisms for alkali chloride sulfation have been proposed previously [92,93,127,128], as described briefly in section 2.2.4.7.

Building on the work of Broström et al. [13], Kassman et al. [18–20] performed SNCR experiments with ammonium sulfate, \(\text{NH}_3\), and urea in a 12 MW biomass fired CFB boiler (see Figure 2.18). Their results indicated a SNCR performance of ammonium sulfate comparable to that of \(\text{NH}_3\) and urea. It was further showed that KCl sulfation is promoted for increasing excess air ratio \((\lambda_{\text{air}})\) and S/Cl molar ratio, and obtained 80 % reduction of KCl with \(\lambda_{\text{air}}=1.4\) and S/Cl=2. Thus, the results of Kassman et al. clearly illustrates the advantages of using ammonium sulfate as additive in the SNCR process. However, the SNCR performance using ammonium sulfate has not yet been investigated under controlled conditions.

![Figure 2.18](image_url)

**Figure 2.18:** Reduction of NO in a CFB boiler at 870 °C by injection of ammonium sulfate, urea, and \(\text{NH}_3\) [20].
2.3 Urea decomposition and byproduct formation

This section provides an overview of the urea decomposition process, which is important in the urea-SCR process for control of NOx emissions from mobile sources. The mechanisms and reaction pathways of urea decomposition and byproduct formation are reviewed, along with mathematical models describing the chemical and physical processes.

2.3.1 Urea-SCR process

The selective catalytic reduction (SCR) process using urea (CH\textsubscript{4}N\textsubscript{2}O) as reducing agent is a common and effective method to reduce NOx on mobile sources. In this process, a urea-water-solution (UWS) is injected as small droplets in the range of 1-150 µm \([129,130]\) into the exhaust pipe upstream of the SCR unit, and releases NH\textsubscript{3} upon heating from the exhaust, as illustrated in Figure 2.19.

![Illustration of a urea-SCR system. A UWS spray is injected into the exhaust pipe upstream of the SCR unit, where the UWS droplets undergo evaporation and chemical decomposition \([130]\).](image)

The temperature of the exhaust gas from diesel engines varies in the range of 200-450 °C, depending on the engine load. The injected UWS supplies the SCR unit with NH\textsubscript{3}, which is used as the active reducing agent through the standard (R 2.21) and fast (R 2.22) SCR reactions \([131,132]\):

\[
4\text{NH}_3 + 4\text{NO} + \text{O}_2 \xrightarrow{\text{cat}} 4\text{N}_2 + 6\text{H}_2\text{O} \quad \text{R 2.21}
\]

\[
2\text{NH}_3 + \text{NO} + \text{NO}_2 \xrightarrow{\text{cat}} 2\text{N}_2 + 3\text{H}_2\text{O} \quad \text{R 2.22}
\]

The SCR process is influenced by several parameters such as reaction temperature, NH\textsubscript{3}/NO molar ratio, residence time of the gas in the catalyst bed, and active catalyst surface area. At optimal conditions, the SCR process can potentially reduce up to 90% of NOx emissions. The typical temperature window for SCR operation is 250-450 °C \([131]\), which corresponds well to the exhaust gas temperatures in diesel engines on ships and automotive vehicles, as shown in Table 2.1.
Table 2.1: Typical SCR conditions in marina and automotive applications.

<table>
<thead>
<tr>
<th>Property</th>
<th>Marine applications [133]</th>
<th>Automotive applications [39]</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Exhaust gas</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature</td>
<td>300-450 °C</td>
<td>130-730 °C</td>
</tr>
<tr>
<td>Absolute humidity</td>
<td>0.03-0.04</td>
<td>Not available</td>
</tr>
<tr>
<td>Pressure</td>
<td>1.5-4.5 bar</td>
<td>1 bar</td>
</tr>
<tr>
<td><strong>UWS spray</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Droplet diameter</td>
<td>1-100 µm</td>
<td>20-150 µm</td>
</tr>
<tr>
<td>Injection temperature</td>
<td>~ 40 °C</td>
<td>25-80 °C</td>
</tr>
<tr>
<td>Slip velocity</td>
<td>0-10 m/s</td>
<td>Not available</td>
</tr>
<tr>
<td>Urea concentration</td>
<td>0.4 kg/kg</td>
<td>0.325 kg/kg</td>
</tr>
</tbody>
</table>

Unfortunately, using urea as additive for the SCR process has been shown to introduce some challenges. Urea is known to produce solid byproducts during decomposition, which in SCR applications can deposit on surfaces and potentially cause severe operational problems, as illustrated in Figure 2.20.

![Illustration of deposit formation in a urea-SCR system [130].](image)

When atomized into a hot exhaust gas, the water from UWS droplets is initially evaporated, yielding solid urea particles. Continued heating above 133 °C causes urea to melt and subsequently decompose into ammonia and isocyanic acid (HNCO) [22]:

\[
\text{CO(NH}_2\text{)}_2(\text{l or g}) \rightarrow \text{NH}_3(\text{g}) + \text{HNCO}(\text{g})
\]

Despite decades of research, the state of urea during decomposition is still controversial. Most studies support the decomposition of urea directly from solid or liquid state [23,26,134–136]. However, some
2.3 Urea decomposition and byproduct formation

studies suggest that urea evaporates and consecutively decomposes in the gas phase [137–139]. Finally, some studies indicate that urea decomposes into ionic species NH4⁺ and NCO−, which further react to form gaseous NH₃ and HNCO [25,41]. A better understanding of the physical processes involved in urea decomposition is essential, in order to develop accurate numerical simulation tools. Therefore, one of the main objectives in the present work has been to investigate the competition between urea decomposition and evaporation.

HNCO is highly stable in the gas phase [22], but can easily hydrolyze over an SCR catalyst in presence of water [140–143]:

\[
\text{HNCO(g)} + \text{H}_2\text{O}^{\text{cat}} \rightarrow \text{NH}_3(g) + \text{CO}_2(g)
\]

HNCO is highly reactive in the liquid phase, and can react with unconverted urea to form undesired byproducts [29,144–146]. Previous experimental investigations have shown that the main byproducts of urea decomposition include biuret, cyanuric acid (CYA), ammelide, and ammeline (see Table 2.2) [25–27,146]. These byproducts are more thermally resistant than urea, and can deposit on surfaces in the urea-SCR system, potentially causing fouling of the catalyst or blocking of the UWS injection nozzles. Proposed reaction pathways leading to the formation of these byproducts, and how these are influenced by certain operating conditions, are reviewed in section 2.3.2.

<table>
<thead>
<tr>
<th>Trivial name</th>
<th>Urea</th>
<th>Biuret</th>
<th>CYA</th>
<th>Ammelide</th>
<th>Ammeline</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>CH₄N₂O</td>
<td>C₂H₅N₃O₂</td>
<td>C₃H₂N₃O₃</td>
<td>C₃H₄N₄O₂</td>
<td>C₃H₅N₃O</td>
</tr>
<tr>
<td>Structure</td>
<td>H₂N(CONH₂)</td>
<td>H₂N(CONH₂)₂</td>
<td>C₃N₂O₂H₂OH</td>
<td>C₃N₃O₃H₂OH</td>
<td>C₃N₃O₂H₂OH</td>
</tr>
</tbody>
</table>

2.3.2 Reaction pathways for byproduct formation

The decomposition of urea and byproduct formation have been extensively studied in the past few decades. Common methods for investigating the urea decomposition behavior include thermal gravimetric analysis (TGA), often combined with high liquid chromatography (HPLC) for analysis of the residue composition, and Fourier-transformed infrared spectroscopy (FTIR) for analysis of gas phase products. Urea decomposition has been studied in TGA at low heating rate conditions (2-20 °C/min) by several groups [25,27,34,40]. The TGA curve of urea (see Figure 2.21) is characterized by several plateaus, due to formation of byproducts from urea decomposition (see Table 2.2). As illustrated in Figure 2.21, the overall shape of the urea TGA curves obtained from different studies is consistent, and indicates formation of a secondary byproduct at around 225 °C, which is thermally stable up to
around 300 °C. Urea is typically completely decomposed at temperatures above 450 °C, but the process is highly sensitive to variations in the conditions such as sample mass, surface area, and heating rate. Thus, comparison of urea TGA curves from different studies has to be conducted by carefully considering any differences in the experimental conditions.

Figure 2.21: Comparison of urea TGA curves conducted at a heating rate of 10 °C/min. In the data of Krum [147], the sample mass was 50 mg with a surface area of 89.9 mm². In the data of Brack et al. [40], the sample mass was 45 mg with a surface area 30.2 mm². In the data of Schaber et al. [25], the sample mass was 30 mg, with an unspecified surface area.

Schaber et al. [25] studied the decomposition behavior of urea and its main byproducts including biuret, CYA, ammelide by TGA at low heating rate conditions, HPLC to analyze condensed phase products, and FTIR to analyze gas phase products. Based on the TGA curve of urea at 10 °C/min (Figure 2.21), Schaber et al. [25] argued that urea decomposition can be divided into four main temperature regions, which will be described below.

The first reaction region is defined from 25-190 °C. The TGA curve of urea in this temperature region indicated that the mass loss of urea begins in earnest at temperatures above the melting point 133 °C. The FTIR spectra of the effluent gas revealed small characteristic [NCO·] and [NH₄⁺] absorption peaks (2156 cm⁻¹ [148] and 3333 cm⁻¹ [149], respectively), indicating a very small degree of decomposition prior to the melting point, which has also been observed in the study of Chen et al. [150]. Schaber et al. [25] reported that the mass loss between 140 °C and 152 °C is primarily associated with evaporation of urea, while decomposition becomes dominant above 152 °C, indicated by a vigorous increase in intensity of the [NCO·] and [NH₄⁺] absorption peaks in the FTIR signal. Thus, the initial step in the decomposition process was proposed to be the decomposition into ammonium cyanate salt, which has also been observed by Carp [151].

\[
\text{urea(l)} \xrightarrow{T > 152 \degree C} \text{NH}_4^+\text{NCO}^-(l) \rightarrow \text{NH}_3(g) + \text{HNCO}(g)
\]  

R 2.25
Above 160 °C, Schaber et al. [25] reported the production of biuret based on an absorption peak in the FTIR signal unique for biuret at 1325 cm\(^{-1}\). They proposed that biuret is produced between 160-190 °C by reaction of HNCO with unconverted urea according to:

\[
\text{urea(l) + HNCO(g) \rightarrow biuret(l)}
\]

It is generally agreed that biuret is the first byproduct produced from urea decomposition [25,27,28,152]. The chemistry of biuret between 160-190 °C is complex, and still controversial. Two main reaction paths of biuret have been proposed to occur in this temperature region, to produce either CYA or ammelide [25,146].

\[
\text{biuret(l) + HNCO(g) \rightarrow CYA(s) + NH}_3(g)
\]

\[
\text{biuret(l) + HNCO(g) \rightarrow ammelide(s) + H}_2O(g)
\]

However, only small amounts of CYA and ammelide have been detected prior to decomposition of biuret. TGA of urea at low heating rates (2-20 °C/min) have shown that production of CYA via reaction R 2.27 is favored, while reaction R 2.28 runs in parallel at a lower extent. The chemistry of biuret is conceivably influenced by several factors such as heating rate and surface area of the sample. It is of interest in the present project to determine if the production of CYA and ammelide can be influenced and potentially minimized by increasing the heating rate of the urea sample.

The second reaction region is defined from 190-250 °C. This reaction region is characterized by an increase in biuret decomposition (R 2.29), followed by an increase in production of CYA and ammelide. CYA and ammelide have been shown from TGA to be thermally stable up to approximately 250 °C, which explains the plateau of stable mass in the urea TGA curve (Figure 2.21) at 225-250 °C. The physical appearance of the sample in this temperature range was a sticky solid matrix, which solidified above 250 °C [25]. This physical behavior indicates that sample in temperature interval 225-250 °C consists of a liquid/solid mixture of biuret, CYA, and ammelide, which transforms into a solid mixture of CYA and ammelide above 250 °C.

\[
\text{biuret(l) \rightarrow urea(l) + HNCO(g)}
\]

Urea produced from biuret decomposition is unstable at this temperature, and will itself decompose according to reaction R 2.25. In this temperature region, Schaber et al. [25] proposed that auto-condensation reactions associated with biuret decomposition becomes competitive for production of CYA and ammelide:

\[
2\text{biuret(l) \rightarrow CYA(s) + HNCO(g) + 2NH}_3(g)
\]

\[
2\text{biuret(l) \rightarrow ammelide(s) + HNCO(g) + NH}_3(g) + H}_2O(g)
\]

Trace amounts of ammeline was also detected in this reaction region, which is likely produced via amination of ammelide:
Literature study

\[
\text{Ammelide(s) + NH}_3(g) \xrightarrow{T>193 \, ^\circ \text{C}} \text{ammeline(s) + H}_2\text{O(g)} \quad \text{R 2.32}
\]

Schaber et al. [25] identified melamine in residues above 250 °C by HPLC. Two possible routes for production of melamine are the amination of ammeline (R 2.33) and the trimerization of cyanamide (R 2.34):

\[
\text{Ammeline(s) + NH}_3(g) \xrightarrow{T>250 \, ^\circ \text{C}} \text{melamine(s) + H}_2\text{O(g)} \quad \text{R 2.33}
\]

\[
3\text{H}_2\text{NCN(g)} \xrightarrow{T>250 \, ^\circ \text{C}} \text{melamine(s)} \quad \text{R 2.34}
\]

Ammination of ammeline is conceivably the dominating route to melamine production, as cyanamide has not been isolated from urea decomposition at normal conditions [25].

The third reaction region is defined from 250-360 °C. In this temperature range, CYA, ammelide and trace amounts of ammeline make up most of the residue. As the temperature is increased above 260 °C, another large mass loss is observed in the urea TGA curve (Figure 2.21), which is mainly associated with CYA sublimation and/or decomposition:

\[
\text{CYA(s) ↔ CYA(g)} \quad \text{R 2.35}
\]

\[
\text{CYA(s) ↔ 3HNCO(g)} \quad \text{R 2.36}
\]

Whether CYA first sublimes and decomposes in the gas phase, or decomposes directly from solid phase is still controversial. Schaber et al. [25] suggests that sublimation of CYA is responsible for most of the mass loss, while Schmidt [153] suggested that CYA decomposes directly from solid phase. Since reaction R 2.36 is reversible at lower temperatures (i.e. below 250 °C) [154], it is challenging to prove which mechanism is dominant. Sublimation and/or decomposition of CYA continues up to approximately 350 °C, where most of the CYA has been depleted from the residue. As the decomposition of ammelide and ammeline begins in earnest at approximately 360 °C, a small plateau of stable mass is observed in the urea TGA curve (Figure 2.21) at 350-360 °C.

The fourth reaction region is defined as above 360 °C. This reaction region is characterized by the continued sublimation and/or decomposition of CYA, ammelide and ammeline. Schaber et al. [25] state complete elimination of CYA, ammelide, and ammeline at 380 °C, 600 °C and 700 °C, respectively. The high temperature residues produced from ammelide and ammeline above 500 °C have been suggested to consist of condensation products of melamine (C₉H₆N₆), e.g. melam (C₆H₉N₁₁), melem (C₆H₆N₁₀), melon (C₆H₃N₉), or higher [29,155–157], as illustrated in Figure 2.22. However, the extent of such polymerized byproducts under typical urea-SCR conditions are expected to be insignificant, as the urea TGA curve (Figure 2.21) shows complete decomposition at approximately 450 °C.
2.3 Urea decomposition and byproduct formation

Figure 2.22: Proposed reaction scheme for melamine self-condensation into heavy-molecular polymerized products [155].

2.3.3 Urea decomposition and byproduct formation in SCR systems

Although analytical methods such as TGA in combination with HPLC/FTIR have been helpful to study the urea decomposition chemistry at a fundamental level, the conditions of such methods are typically not representative of practical urea-SCR systems. A different approach to gaining a better understanding of this process has been to conduct experiments in pilot scale urea-SCR facilities, and to investigate the effects of various process and design parameters on the byproduct formation.

2.3.3.1 Influence of exhaust temperature

Eakle et al. [29,144] investigated the deposition of byproducts from urea decomposition in a Diesel test engine (224 kW). Deposits in the exhaust pipe were collected from experiments operating approximately 1 hour at varying exhaust temperatures from 200-360 °C. The deposition yield was found to decrease linearly with increasing exhaust temperature. Furthermore, the appearance of the deposits shifted in color from white to yellow/brown for increasing exhaust temperature, and the water solubility decreased from 100 % at 200 °C to 58 % at 360 °C. In addition, a significant increase in iron content (600-1000 ppm) was detected in the deposits generated at 340-360 °C by Proton Induced X-ray Emission (PIXE) analysis, indicating a corrosive behavior of these deposits. An HPLC analysis of the deposits (see Figure 2.23) showed that the deposits generated below 250 °C mainly consist of unreacted urea. For exhaust temperatures between 250-340 °C, the deposits were a mixture of urea, biuret, and CYA, while the deposit generated at 360 °C mainly consisted of CYA. Ammelide could only be detected in trace amounts at temperatures above 280 °C.
2.3.3.2 Influence of wall wetting

Strots et al. [32] investigated the formation of urea-derived deposits in a test engine urea-SCR system. By employing thermocouples at the wall of the exhaust system, they observed a decrease in the wall temperature by 20 °C when injecting the UWS spray to the exhaust pipe. Deposits in the exhaust pipe were collected for varying exhaust temperatures, and it was found that increasing the temperature from 220 °C to 350 °C caused a drastic reduction in deposit yield from 65 % to 1.5 %. They argued that formation of a liquid film of water and urea-derived deposits at the wall may occur at lower temperatures, due to restricted space for evaporation of water. In order to reduce this wall wetting effect, a wire mesh was installed to reduce the impingement of droplets on the wall. This approach was reported to cause halve the amount of deposition at lower temperatures. It is conceivable that the formation of a stable wall film facilitates the condensed phase reactions described in section 2.3.2, thus increasing the risk of byproduct deposition.

2.3.3.3 Influence of exhaust design

In order to reduce the risk of deposition in practical urea-SCR systems, it is important to develop a design of the exhaust system, which minimizes the degree of wall wetting. Wall wetting occurs when droplets of the UWS spray impinge and accumulate on the wall, due to restricted space for evaporation and decomposition. Parameters that affect wall wetting include the exhaust temperature, and spray characteristics such as droplet size, flow rate, velocity, and injection angle.

Zheng et al. [36,158,159] investigated the influence of various injection system designs in a urea-SCR test facility on the deposit formation. Two different injection designs were used in the experiments (see Figure 2.24); a 45° injection mounted on a straight pipe, and a coaxial injection mounted
on an S-shaped pipe. It was found that using a coaxial injection of the spray resulted in lower deposition than using a 45° injection, indicating that a more direct injection can reduce the degree of wall wetting. Thus, an S-shaped conformation with a coaxial injection of the spray may be advantageous to reduce the risk of deposition, but requires a bend of the exhaust pipe that may not be ideal in practical urea-SCR systems.

Additionally, Zheng et al. [36,158,159] showed that installation of mixing units could increase the wall temperature by 20 °C, due to increased heat transfer to the wall from the enhanced turbulence. They reported a small decrease in deposition when employing the mixing units, and attributed the effect to a lower degree of wall wetting. Conceivably, the increased turbulence when using mixers may also have had a promoting effect on the convective heat transfer to the droplets, thereby increasing the evaporation rate.

![Figure 2.24: Illustration of a 45° injection mounting geometry on a straight pipe (left) and a coaxial injection mounting on an S-shaped pipe (right) [158].](image)

### 2.3.4 Modeling of urea decomposition and byproduct formation

Development of predictive simulation tools to describe urea decomposition and byproduct formation has been of increasing interest. One approach to describe the urea decomposition process has been to derive kinetic reaction schemes, including reactions for byproduct formation, based on TGA experiments. However, such kinetic models are not very useful on a practical level, since they are not representative of practical urea-SCR systems. Therefore, efforts have also been made to develop predictive models for the description of UWS droplet evaporation and decomposition in SCR systems. This section reviews and evaluates different models for kinetic description of urea decomposition and byproduct formation, as well as UWS droplet depletion in SCR systems.

#### 2.3.4.1 Kinetic modeling

Ebrahimian et al. [41] made the first attempt at deriving a kinetic reaction scheme for urea decomposition and formation of biuret, CYA, and ammelide. They proposed a reaction scheme consisting of 12 reactions involving ionic interactions with urea, biuret, CYA, and ammelide. The kinetic parameters for urea thermolysis; urea $\rightarrow$ NH$_4^+$ + NCO$^-$ was taken from the work of Kieke et al. [160], while the kinetic parameters for the remaining reactions involving biuret, CYA, and ammelide were derived from TGA data by Schaber et al. [25] and Fang et al. [161]. The reaction scheme was simulated in a
continuously stirred tank reactor (CSTR), to describe the TGA experiments of Schaber et al. [25]. As seen from Figure 2.25, the model by Ebrahimian et al. [41] performs well for describing urea decomposition under low heating rate conditions (10 °C/min). However, the model underestimates the mass loss for decomposition of biuret, and shows significant discrepancies for decomposition of CYA and ammelide. For ammelide decomposition, a decrease in the mass loss rate is observed around 450 °C, indicating formation of more thermally resistant species. However, this cannot be captured by the model of Ebrahimian et al. [41], since reactions leading to formation of such species have not been included in the model.

![Figure 2.25: Comparison of modeling results from Ebrahimian et al. [41] and TGA data from Schaber et al. [25] of urea, biuret, CYA, and ammelide, with a heating rate of 10 °C/min. The initial sample masses for all data sets were 30 mg.](image)

Brack et al. [40] developed a kinetic reaction scheme for urea decomposition and byproduct formation based on 15 reactions including urea, biuret, CYA, ammelide, and triuret. In contrast to the reaction scheme proposed by Ebrahimian et al. [41], their model did not involve ionic interactions. The reaction rates were fitted to TGA data of urea and byproducts under heating rates of 2-20 °C/min, and a Hertz-Knudsen term was used to describe HNCO evaporation [162]. Their model compared favorably to the urea TGA curve, and yielded an improved description of the byproduct TGA curves (see Figure 2.26), as compared to the model of Ebrahimian et al. [41]. Furthermore, the model could accurately predict changes in the experimental conditions, such as heating rate, sample mass, and sample surface area.
2.3 Urea decomposition and byproduct formation

Overall, the kinetic models by Ebrahimian et al. [41] and Brack et al. [40] are capable of describing the chemistry of urea decomposition reasonably well, and can satisfactorily predict the byproduct formation for increasing temperature. However, the studies are restricted to low heating rate conditions, which are not representative of practical urea-SCR systems. In a numerical study by Abu-Ramadan et al. [38], it was indicated that the heating rate of UWS droplets may be in the order of $10^5$ °C/min, depending on the conditions (see section 2.3.4.2). It is expected that the heating rate has a significant influence on urea decomposition and byproduct formation, and it is questionable if the kinetic models from Ebrahimian et al. [41] and Brack et al. [40] can be extrapolated to practical heating rates of UWS droplets.

2.3.4.2 UWS droplet depletion modeling

This section summarizes previous numerical efforts to describe the depletion of a UWS droplet suspended in a heated environment. The process involves evaporation of water, followed by melting and decomposition of urea, and potentially formation of secondary byproducts. The system is generally modelled as a spherical multicomponent droplet surrounded by a thin gas film. As illustrated in Figure 2.27, the evaporation and decomposition processes are driven by a heat flux from the environment to the droplet. The UWS droplet is characterized by a uniform size, temperature, and species mass fraction ($r_d$, $T_d$, and $Y_i$), whereas the environment is specified as a hot gas mixture with uniform temperature, pressure, and species ($T_\infty$, $P_\infty$, and $Y_{i,\infty}$). Experimental results on UWS droplet depletion have shown that evaporation of water and decomposition of urea occurs in two distinct phases [33,163]. Therefore, the process is often modelled in two separate steps [39,41,164–167]. In contrast, Abu-Ramadan et al. [38] treated the process as multicomponent evaporation system, where water and urea evaporates simultaneously. In the following, description of droplet vaporization will be reviewed mainly through the model proposed by Abu-Ramadan et al. [38]. Various approaches for depletion of urea, including evaporation and kinetic modeling, will also be reviewed.
Droplet vaporization model

Modeling the evaporation of water in a multicomponent droplet includes mathematical description of the gas phase, the gas-liquid interface, and the liquid phase, and will be presented chronologically in that order.

For the gas phase analysis, a quasi-steady state assumption is typically employed, to setup an energy conservation equation:

\[ \dot{Q}_g + \dot{Q}_{rad} = \dot{Q}_d + \dot{Q}_{vap} \]  \hspace{1cm} (E.2.1)

Here, \( \dot{Q}_g \) and \( \dot{Q}_{rad} \) are the heat transfer from the gas phase to the droplet by convection, conduction, and radiation, while \( \dot{Q}_d \) and \( \dot{Q}_{vap} \) are the heat consumption for heating and evaporation of the droplet. Although most studies disregard the radiation term, Abu-Ramadan [38] argued that radiation may be important for automotive SCR systems, and included it in the energy balance (E.2.2). The heat transfer to the droplet, \( \dot{Q}_g \), may include both convective and conductive heat transfer terms, which has been treated differently in various modeling studies. Abu-Ramadan et al. [38] omitted the convective contribution to the heat transfer, due to the assumption of a stagnant environment (zero slip velocity), leading to an expression for \( \dot{Q}_g \) only including a conduction term (E.2.3). For urea-SCR systems, it may be reasonable to assume zero slip velocity, as the small droplets are expected to follow the trajectory of the exhaust. The heat consumed for heating and vaporization of the droplet are expressed by E.2.4 and E.2.5.

\[ \dot{Q}_{rad} = \pi d_r \sigma \varepsilon (T_{wall}^4 - T_{d,s}^4) \]  \hspace{1cm} (E.2.2)

\[ \dot{Q}_g = 2\pi d_r N u_g \lambda_g (T_{\infty}^4 - T_{d,s}^4) \]  \hspace{1cm} (E.2.3)
2.3 Urea decomposition and byproduct formation

\[
\dot{Q}_{vap} = \sum_{i=1}^{n} m_i L_{vap,i} \quad \text{E 2.4}
\]

\[
\dot{Q}_d = m_d c_{p,d} \frac{\Delta T_{d,s}}{\Delta t} \quad \text{E 2.5}
\]

Here, \(d_d\) is the droplet diameter, \(\sigma\) is the Stefan-Boltzman constant, \(\varepsilon\) is the emissivity, \(T_{wall}\) is the wall temperature of the exhaust pipe, \(T_{d,s}\) is the droplet surface temperature, \(N_{u_g}\) is the Nusselt number, \(\lambda_g\) is the conductivity of the gas phase, \(T^\infty\) is the ambient temperature, \(m_i\) is the mass flux of water vaporized from the droplet, \(L_{vap,i}\) is the latent heat of vaporization, \(m_d\) is the mass of the droplet, and \(c_{p,d}\) is the heat capacity of the droplet.

As Abu-Ramadan et al. [168] considered the environment to be stagnant, the mass transfer rate was expressed based on a diffusion term. The total evaporation rate, summing over all evaporating species in the multicomponent droplet, was expressed as:

\[
m = \frac{\sum_{i=1}^{n} j_{i,g}}{1 - \sum_{i=1}^{n} Y_{i,g}} \quad \text{E 2.6}
\]

Here, \(j_{i,f}\) and \(Y_{i,f}\) are the diffusion rate and mass fractions of species \(i\) in the gas phase. The diffusion rate is driven by the concentration gradient in the gas phase, calculated by:

\[
j_{i,g} = \pi d_d \rho_g \Gamma_{i,g} Sh_{i,g} (Y_{i,g} - Y_i^\infty) \quad \text{E 2.7}
\]

Here, \(\rho_g\) is the density of the gas phase, \(\Gamma_{i,g}\) is the mass diffusion coefficient, and \(Sh_{i,g}\) is the Sherwood number. Due to the temperature gradient in the film region, the physical properties of the gas film are typically evaluated at reference temperature using the 1/3 rule [169]:

\[
T_g = T_{d,s} + 1/3(T^\infty - T_{d,s}) \quad \text{E 2.8}
\]

For the gas-liquid interface analysis, Abu-Ramadan et al. [38] treated both the gas and liquid phases as ideal and in thermodynamic equilibrium. This allows for calculation of the vapor fractions of evaporating species at the droplet surface by Raoult’s law (E 2.9 and E 2.10). In contrast, Ebrahimian et al. [41] argued that UWS droplets should be treated as a nonideal liquid, and thus employed a non-random two-liquid (NRTL) local composition model to estimate the vapor fractions.

\[
X_{i,g,s} = x_{i,d,s} \frac{P_{sat,i}(T_{d,s})}{P^\infty} \quad \text{E 2.9}
\]

\[
Y_{i,g,s} = \frac{x_{i,g,s} M_i}{\sum_{j=1}^{n} x_{j,g,s} M_j} \quad \text{E 2.10}
\]

Here, \(x\) is the liquid fraction, \(P_{sat,i}\) is the saturation vapor pressure, \(P^\infty\) is the ambient pressure far from the droplet, and \(M\) is the molar weight.
For the liquid phase analysis, Abu-Ramadan et al. [38] employed a rapid mixing (RM) model and a diffusion limited (DL) model to describe the temperature and concentration distribution in the droplet. In the RM model, infinitely high thermal and mass diffusivities of the liquid phase are assumed, resulting in spatially uniform temperature and species concentration distributions in the droplet. The temporal variation in the droplet temperature and species concentration, $T_d(t)$ and $Y_{i,d}(t)$, are then determined from the mass and energy balances described in E 2.5 and E 2.6. In contrast, the DL model does not assume infinitely fast diffusivities, and thus considers spatial variations of temperature and species concentration in the droplet. This results in a system of partial differential equations, where the transport properties of the droplet vary spatially and temporally. Thus, the complexity of the calculations are significantly increased when using the DL model as compared to the RM model. However, the numerical results from Abu-Ramadan et al. [38] indicated a highly similar impact of the RM and DL models on the overall UWS depletion. Therefore, the RM model is an attractive alternative to the DL model due to its simplicity, and has also been employed in other numerical UWS depletion studies [41,165].

Models for urea depletion in a droplet

Different models for depletion of urea has been proposed. In the multicomponent droplet vaporization model proposed by Abu-Ramadan et al. [38], urea depletion was described as an evaporation process similar to E 2.4, with an expression for the latent heat of vaporization of urea:

$$L_{vap,u}(T_{d,s}) = L_{vap,u}(T_{std}) + \int_{T_{std}}^{T_{d,s}} (C_{p,u}(g) - C_{p,u(l)})dT$$

(E 2.11)

As a secondary approach, Abu-Ramadan et al. [38] attempted to model the depletion of urea as a decomposition process, where urea is decomposed directly from condensed phase to NH$_3$ and HNCO. The term for urea decomposition was implemented in the energy balance through $m_u H_{th,u(l)}$, where the enthalpy of reaction was calculated as:

$$H_{th,u(l)}(T_{d,s}) = H_{th,u(l)}(T_{std}) + \int_{T_{std}}^{T_{d,s}} (C_{p,NH_3(g)} + C_{p,HNCO(g)} - C_{p,u(l)})dT$$

(E 2.12)

The decomposition rate of urea, $\dot{m}_u$, was described by a first-order reaction model for the single reaction urea(l)→NH$_3$(g) + HNCO(g), and thus did not include the formation of byproducts:

$$\dot{m}_u = -A \cdot \exp\left(-\frac{E_a}{RT}\right) m_u$$

(E 2.13)

Here, $A$ and $E$ are the pre-exponential factor and activation energy of the urea decomposition reaction. The derivation of kinetic parameters were based on TGA data under low heating rate conditions (10 °C/min) [24,25].

Gan et al. [165] attempted to model the decomposition of urea in a UWS droplet based on a kinetic reaction model, slightly modified from the proposed scheme by Ebrahimian et al. [41]. Thus, the model takes byproduct formation during urea decomposition into account, including biuret, CYA,
and ammelide, but the derivation of the kinetic parameters was restricted to low heating rate TGA data.

Figure 2.28 shows a comparison of UWS droplet depletion experiments by Wang et al. [33] with the simulation results by Abu-Ramadan et al. [38] and Gan et al. [165]. From the comparison, it can be seen that the models generally describe the evaporation of water from UWS droplets accurately, and follows the d^2 law (d^2 decreases linearly with time) [170]. However, the evaporation rate is slightly underestimated by the models of Abu-Ramadan et al. [38] at 400 °C. The experimental data from Wang et al. [33] shows fluctuations and an overall increase in the droplet size when the droplet is close to fully dried, indicating distortion of the droplets. This behavior was attributed to micro-explosions of the droplets, caused by entrapment of water due to formation of a urea shell on the surface. A similar behavior of UWS droplets was recently documented by Surendran et al. [163], who showed occurrence of micro-explosions for UWS droplets exposed to temperatures above 250 °C. Ryddner and Trujillo [167] suggested that the internal concentration gradients are slower to equilibrate at higher temperatures, causing the solidification of urea at the surface to be faster, and thereby enhancing the micro-explosion effect for higher temperatures.

The UWS depletion models by Abu-Ramadan et al. [38], Gan et al. [165], and Lundström et al. [166] generally underestimate the decomposition rate of urea in the experiments by Wang et al. [33], mostly pronounced for higher temperatures. The model discrepancies for urea decomposition may partly be attributed to experimental uncertainties related to the micro-explosions. The occurrence of micro-explosions are expected to have had a significant effect on the observed decomposition rate by Wang et al. [33], due to fragmentation of the droplet. Furthermore, the experiments by Wang et al. [33] may have been influenced by conductive heat transfer through the fibers, which is not accounted for in the models. However, as discussed in section 2.3.4.1, it is questionable whether the kinetic models proposed by Abu-Ramadan et al. [38] and Gan et al. [165] can reliably be extrapolated to higher heating conditions, as the kinetic parameters were derived under 2-20 °C/min heating rate conditions.

**Figure 2.28:** Comparison of UWS droplet depletion experiments by Wang et al. [33] with numerical results from Gan et al. [165] and Abu-Ramadan et al. [38] with a kinetic model and a vaporization model for depletion of urea, under the following conditions: a) T° = 300 °C, P° = 1 atm, Y_u,0 = 0.325, T_d,0 = 25 °C, and d_d,0 = 0.92 mm; and b) T° = 400 °C, P° = 1 atm, Y_u,0 = 0.325, T_d,0 = 25 °C, and d_d,0 = 0.87 mm.
2.4 Summary of literature study

NO can be formed during combustion processes via three unique mechanisms, namely thermal NO, prompt NO, and fuel NO. In combustion of biomass and waste fuels, the oxidation of fuel bound nitrogen is the major contributor to NO emissions. Several methods for reduction of NO emissions exist, including primary control measures such as air staging and flue gas recirculation, and secondary control measures such as the SNCR and SCR processes. In this literature study, special emphasis was given to the SNCR process employed in stationary combustion plants, and the SCR process employed in mobile sources.

The SNCR process can be employed by using NH₃, urea, CYA, or other amine-containing additives. The process is characterized by a narrow operating temperature window of efficient NO reduction. This operating window is typically located around 800-1100 °C, but can be influenced by several important process parameters, including the residence time, NH₃/NO molar ratio, O₂ concentration, and presence of SO₂, combustible additives, and alkali metals. The SNCR chemistry is very sensitive to O/H radicals, and the effects of various process parameters can typically be described based on their influence on the radical pool. In general, an increase of O/H radicals increase the NO reduction efficiency below the optimum temperature by promoting the NH₂+NO reaction. However, above the optimum temperature, an increase of O/H radicals leads to increased NH₃ oxidation, which can result in a net increase of NO. The effects of residence time, O₂, and NH₃/NO molar ratio on the radical pool are fairly well established, whereas the effects of sulfur oxides and alkali metals are less understood. Studies on multifunctional countermeasures tackling both NO reduction and alkali chlorine induced corrosion are scarce. Ammonium sulfate has been demonstrated to facilitate NO reduction and conversion of KCl to K₂SO₄ simultaneously in the SNCR process during CFB combustion of biomass. However, investigations of the SNCR process with ammonium sulfate under well-controlled conditions are lacking.

The SCR process is typically employed for reduction of NO from marine and automotive diesel engines. For such mobile applications, urea is the preferred ammonia carrier, due to advantages in storage and handling. However, the decomposition of urea is known to cause issues with formation of byproducts. The main byproducts of urea decomposition include biuret, CYA, and ammelide. These compounds are more thermally resistant than urea, and may deposit in the exhaust system. The reaction mechanisms of urea decomposition and byproduct formation have been studied extensively through TGA in combination with HPLC and/or FTIR under low heating rate conditions, while TGA data at high heating rates are scarce. The process is mainly temperature dependent, but is also influenced by parameters such as sample mass, surface area, and heating rate. Investigations in test engine setups indicate that formation of liquid pools on the wall may be a major contributor to the overall deposit formation. Several kinetic models for urea decomposition and byproduct formation have been proposed, but are limited to low heating rate conditions. Moreover, models for UWS evaporation are well established, which yield good descriptions of water evaporation. However, the models generally underestimate the urea decomposition rate, and do not include byproduct formation. Development of models that reliably extrapolate to higher heating rates is necessary, in order to accurately describe the depletion of UWS droplets in practical urea-SCR systems.
Selective non-catalytic reduction of NO$_x$ with alternative additives

This chapter has been written as a manuscript containing unpublished results from work on the SNCR process using ammonium sulfate as additive. Experimental and numerical results of the SNCR performance using ammonium sulfate, along with the effects of SO$_2$ and alkali metals on NO reduction, are presented.

Abstract:

The selective non-catalytic reduction (SNCR) process was investigated using ammonium sulfate as additive, for the simultaneous reduction of NO$_x$, deposition, and corrosion in stationary combustion plants. The SNCR performance of ammonium sulfate was evaluated through experiments in a laboratory-scale flow reactor, and compared with experiments using the more common additives ammonia and urea. SO$_2$, which is a decomposition product of ammonium sulfate, was found to have a negligible effect on the NO reduction by NH$_3$. SNCR experiments with 5wt. % and 10wt. % aqueous ammonium sulfate solutions yielded NO reductions up to 95% in a temperature interval of 1025 °C to 1075 °C. It was indicated that sulfur from ammonium sulfate is mainly released as SO$_3$ below 1000 °C, while SO$_2$ is gradually produced at temperatures above 1000 °C. The experiments were further simulated with a newly developed kinetic model. The numerical results for SNCR using NH$_3$ in dry conditions compared well with the experiments, but yielded an off-set in the onset temperature of reaction by 50 °C towards lower temperatures. The SNCR experiments using ammonium sulfate were accurately described by the model, although the predicted NO reductions at the optimum were slightly underestimated. Addition of KCl to the SNCR process was shown to have a promoting effect on the NO reduction at lower temperatures, by extending the temperature window for efficient reduction by 50 °C. Furthermore, ammonium sulfate facilitated KCl sulfation, demonstrating the potential of using ammonium sulfate to simultaneously reduce NO$_x$ and corrosion in full-scale combustion plants.

3.1 Introduction

Combustion of alternative fuels such as biomass and waste is a competitive method for production of heat and electricity. However, emission of nitrogen oxides (NO$_x$) from combustion of such fuels continues to be a major environmental concern. In the developed countries, the regulations on NO$_x$ emission limits have become increasingly stringent, and continue to be a driving force for research and development of new and improved methods for NO$_x$ abatement [7,171,172]. A commonly used technology for reduction of NO$_x$ emissions from stationary combustion sources is the selective non-catalytic reduction (SNCR) process [173]. The SNCR process is classified as a post-combustion treatment.
of the flue gas, where additional chemical agents are sprayed into the flue gas in the post-combustion region to react with NO. The most common chemical agents for the SNCR process are gaseous ammonia and aqueous urea (CO(NH$_2$)$_2$) solution, which can both react selectively with NO. The SNCR process with these additives have been demonstrated to achieve up to 70% NO$_x$ reduction in commercial power plants [173,174]. Under stoichiometric conditions, the overall reactions for the SNCR process when using ammonia and urea are described by [175]:

$$2\text{NH}_3 + 2\text{NO} + \frac{1}{2}\text{O}_2 \rightarrow 2\text{N}_2 + 3\text{H}_2\text{O}$$

$$\text{CO(NH}_2)_2 + 2\text{NO} + \frac{1}{2}\text{O}_2 \rightarrow 2\text{N}_2 + 2\text{H}_2\text{O} + \text{CO}_2$$

The SNCR process is known to be strongly temperature dependent, with a narrow temperature window of effective NO$_x$ reduction, typically located around 850-1100 °C. The SNCR process has been studied extensively in the past, and is considered a mature technology for NO$_x$ reduction in stationary sources [7]. Previous studies have shown that important process parameters for the SNCR process include temperature [176], residence time [81], injection rate of the chemical reducing agent [77], mixing of reagent with the flue gas [105,126], oxygen concentration [81,83], presence of combustibles [86–90,177,178], and alkali metals [14,128,179]. Also the impact of the SO$_2$ concentration has been investigated [84,85].

An additional challenge in combustion of biomass and waste fuels arises due to the content of inorganic matter (e.g., alkali and heavy metals) in the fuel [180,181]. Alkali salts released during combustion can act as a glue to induce agglomeration of ash particles, and can thus generate highly sticky and corrosive deposits in the boiler [182,183]. The partitioning of alkali and heavy metals in the boiler is a determining factor for the amount of ash deposition and composition, and has been studied extensively in the past [180,184,185]. Build-up of deposits may increase the pressure drop, and eventually cause shutdown of the boiler. Furthermore, the deposits are typically highly corrosive and can cause rupture of heat transfer tubes in the boiler. Techniques for reducing deposition and corrosion in boilers operating with waste fuels are scarce. However, in previous studies it has been shown that addition of sulfur containing additives can reduce the extent of deposition and corrosion in the boiler [11,14,16]. Sulfur may be added as elemental sulfur to the fuel [17], or through injection of SO$_2$ [186] or ammonium sulfate [13,15] into the flue gas. Kassman et al. [19] showed that ammonium sulfate was more efficient than elemental sulfur for the sulfation of gaseous KCl in a biomass fired circulating fluidized bed (CFB) boiler, indicating that SO$_3$ is of greater importance than SO$_2$ for the sulfation of KCl.

Techniques for the simultaneous reduction of NO$_x$ emissions, deposition and corrosion have recently come of interest. One possibility involves injection of additives that are active both in the SNCR process and in sulfating corrosive alkali metals. Ammonium sulfate (AS) has been proposed as an additive, which upon decomposition yields NH$_3$ for the reduction of NO, and SO$_2$/SO$_3$ for sulfating metals. Results for the use of AS as SNCR agent are reported for pilot-scale conditions [20,187], while its use for sulfation of alkali metals has been studied in pilot and full-scale [13,19,188]. These results provide an understanding of the overall behavior and the potential of the additive, but due to the complexities of flow and mixing in larger scale, they are less useful for kinetic model development.
and validation. In the present work, SNCR experiments using ammonium sulfate were conducted in a laboratory flow reactor as a function of temperature, AS/NO ratio and residence time. Also, the impact of KCl on the SNCR process, as well as the sulfation of KCl by ammonium sulfate, was investigated. The results were interpreted in terms of a detailed chemical kinetic model for both the SNCR process and KCl sulfation using ammonium sulfate as additive.

3.2 Experimental work

3.2.1 Experimental setup

A flow reactor setup was developed for the purpose of studying the SNCR process with the use of solvable additives. The setup, illustrated in Figure 3.1, is comprised of 1) a homogeneous flow reactor, 2) a feeding system capable of pre-mixing a liquid stream of the reducing agent with a gas stream, and 3) gas analysis by Fourier-transform infrared spectroscopy (FTIR).

A closed cylindrical tank of approximately 1.5 L was used to store 500 ml aqueous solutions of ammonium sulfate ((NH₄)₂SO₄). Additionally, an SNCR experiment using a 5 wt. % urea-water-solution as additive has been conducted as reference; these data are shown in Appendix A. Circulation of cooling water was installed in an outer shell, to avoid heating of the solution from the oven. A 24 V ultrasonic humidifier was used to generate a fine mist of the aqueous solution. The droplet size distribution of the mist was recorded by a high-speed camera, and the average droplet size was determined as ~1 µm (see Appendix A). The droplet size distribution was not influenced by the additive concentration. The droplets were transported to the reactor with a carrier N₂/O₂ gas flow.

A mixing unit was installed above the reactor, where the mist was mixed with gas reactants before entering the reactor. Two quartz flow reactors with inner diameters of 6 mm and 2.1 cm were used in the experiments. The reactors were surrounded by three separate heating elements, which facilitated a uniform temperature profile over a length of 30 cm. The gas residence times were 6686/T(K) s for the large reactor and 151/T(K) s for the small reactor.

The concentrations of NO, NO₂, SO₂, H₂O, and HCl in the flue gas from the reactor were continuously monitored by on-line FTIR spectroscopy (MultiGas 2030). Due to the presence of NH₃, SO₃ and H₂O in the outlet stream, sulfurous acid and/or sulfuric acid can potentially be formed by condensation between approximately 115 and 170 °C [189]. In order to avoid condensation of water and sulfur containing species, the outlet tube was heat traced to 180 °C.
Selective non-catalytic reduction of NOx with alternative additives

3.2.2 Estimation of the additive feeding rate

The additive was supplied to the reactor as micron sized droplets generated by a humidifier suspended in an aqueous solution of the additive. However, as the feeding rate of the additive to the reactor could not be actively controlled, it was necessary to make accurate determinations of the actual feeding rate. The NH$_3$ measurement was not considered reliable, due to uncertainties arising from adsorption and/or condensation in the outlet tube. Instead, the feeding rate of additive to the reactor was investigated by two methods, which are described in sections 3.2.2.1 and 3.2.2.2.

3.2.2.1 Water measurement

The feeding rate was estimated based on the H$_2$O measurement by the FTIR gas analyzer, along with the known additive concentration in the aqueous solution. However, the gas flow in the tank was found to cause some degree of H$_2$O evaporation, despite continuous cooling of the tank below 20 °C, thus introducing an uncertainty to this estimation method. Evaporation of water from the tank was observed by non-zero water levels, when feeding the carrier gas through the tank while the humidifier was idle, as illustrated in Figure 3.2. When the humidifier was activated, the H$_2$O concentration increased rapidly to a higher level, indicating feeding of mist to the reactor.

The additive feeding rate was estimated by subtracting the initial H$_2$O concentration, corresponding to water evaporation, from the final steady state concentration, as illustrated in Figure 3.2. The mist feeding rate was thereby determined as 0.26 mg/s.

The hypothesis that water was evaporating from the tank was further supported by conductivity measurements of a 20 wt. % AS solution, which had been used for SNCR experiments. After approximately 20 hours of active operation, the AS concentration of the solution was measured to 25.7 wt. %, indicating an up concentration due evaporation of water.
3.2 Experimental work

Figure 3.2. Water concentration during an SNCR experiment with 5 wt.% AS/H₂O solution using the thin reactor (diameter of 6 mm). A gas flow of 800 ml/min N₂ was sent through the tank to carry the mist to the reactor. The dashed lines indicate when the mist generator is activated (bottom) and the average water concentration during the experiment (top). The mist generator was turned off at approximately 100 min, and the gas flow was set to bypass the mist tank at 155 min.

3.2.2.2 Urea decomposition experiment

In addition to the estimation method explained in section 3.2.2.1, it was attempted determine the additive feeding rate based on a UWS decomposition experiment. A 5 wt. % UWS was decomposed at 1200 °C at varying O₂ and NO conditions, while using a similar gas flow through the tank similar to that of the experiment described in section 3.2.2.1. Urea is known to fully decompose into NH₃ and HNCO at high temperatures [190], while HNCO is further oxidized to CO/CO₂ in presence of O₂. The effect of NO was investigated, as it is known to enhance the HNCO conversion to CO/CO₂ [7]. The CO, CO₂, O₂ and NO concentrations in the flue gas from decomposition of urea were continuously monitored by on-line gas analyzers (NGA2000, Fisher-Rosemount). Steady-state results for the varying conditions during decomposition of UWS are presented in Figure 3.3. The feeding rate of urea to the reactor was determined from a carbon mole balance using the ideal gas law, assuming complete conversion of urea into CO/CO₂ at the highest O₂ and NO concentrations. The total mist flow rate based on this method was determined to be 0.23 mg/s, which is comparable with the estimation based on water measurement, as described in section 3.2.2.1.
Selective non-catalytic reduction of NOx with alternative additives

Figure 3.3. Production of CO and CO₂ from UWS decomposition at 1200 °C at varying conditions. A gas flow of 800 mls/min N₂ was sent through the tank to carry the mist to the reactor, and the total gas flow rate was 1000 mls/min.

3.2.2.3 Concluding remarks on the estimation of additive feeding rate

The additive feeding rate to the reactor at conditions similar to the SNCR experiments was estimated by two methods, as described in sections 3.2.2.1 and 3.2.2.2. The two methods yielded comparable results for the mist feeding rate, with flow rates around 0.25 mg/s. Although the UWS decomposition experiment was considered a more reliable method to determine the mist feeding rate, it was decided to use the H₂O measurement method, due to the convenience that H₂O is measured in every experiment. The H₂O measurements for all experiments is provided in Appendix A.

3.3 Modeling Work

Simulations of the SNCR experiments were conducted in ANSYS Chemkin Pro [191], using a one-dimensional plug flow reactor configuration. At the inlet to the reactor, all reactants were assumed to be gaseous, following immediate evaporation of water aerosols upon entering the isothermal zone of the reactor. The gas temperature was assumed to be equal to the oven temperature, as the measurements were obtained at steady state conditions.

The simulations were conducted with a detailed chemical kinetic model for the reduction of NO by ammonium sulfate. The model was based on the extensive mechanism for nitrogen chemistry by Glarborg et al. [7]. In addition to the nitrogen chemistry, the model contained subsets for H₂/O₂, H₂S/O₂, alkali/sulfur/chlorine [14,128,179], and N/S interactions [192]. In the present work, a small subset for ammonium sulfate conversion was developed, as discussed below. The full model, including thermodynamic properties, can be provided upon request by the authors. For simulations with KCl, it was assumed that KCl sublimes instantaneously at the inlet for temperatures above 770 °C. This assumption is supported by the study of Knudsen et al. [193], who investigated the release of K species from combustion of biomass in a fixed-bed reactor, and showed that all fuel chlorine was
3.3 Modeling Work

released to the gas phase above 800 °C. A recent study by Simonsson et al. [194] showed that alkali salts with low lattice energies (i.e. NaCl and KCl) rapidly dissociate when passing through a flame, which further supports the assumption of a fast KCl sublimation.

A decomposition reaction, presented in Table 3.1, for ammonium sulfate was included in the mechanism, with the rate constant drawn from recent work by Wu et al. [188]. It is assumed that ammonium sulfate decomposes into NH₃, SO₃, and H₂O as the sole products, even at the highest temperatures studied. While this assumption provided the best agreement with the present experimental results, it is not consistent with the findings of Wu et al. [188], who reported that the sulfur is mainly released as SO₂ at temperatures above 900 °C. It is conceivable that the dissociation reaction occurs in condensed phase, and differences in condensed particle size and reaction conditions may affect the SO₂/SO₃ ratio, but more work is required to solve this issue.

The introduction of ammonium sulfate as an additive means that the sulfur oxide levels in the process are significant. Presumably there are interactions between the amine and the sulfur chemistry. The N/S subset was drawn largely from Glarborg [192], but extended in the present work. Dagaut and Nicolle [84] proposed that formation of NH₂SO₂ might be important for the interactions between amines and SO₂. Consequently, a subset for NH₂SO₂ was established and implemented in the model. This subset, along with the kinetic parameters, is presented in Table 3.1. The NH₂SO₂ adduct is formed by recombination of NH₂ and SO₂ (2). The kinetic data for this reaction were adopted from the study of Gao et al. [195]. There are no information reported about consumption reactions for NH₂SO₂. Rate constants for H-abstraction reactions to form NHSO₂ were estimated under the assumption that the NH₂SO₂ + radical reactions are analogous to the corresponding NH₃ + radical reactions. The rate constant for dissociation of NHSO₂ was estimated in the reverse direction, assuming that NH + SO₂ (+M) behaves similarly to O + SO₂ (+M).

Table 3.1. Kinetic model parameters for the decomposition of ammonium sulfate and NH₂SO₂ subset, to be used in a modified Arrhenius expression of the form \( k = A \cdot T^\beta \cdot \exp(-E/[R \cdot T]) \). *A units: mol, cm, s, K. **E units: cal/mol.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>A*</th>
<th>β</th>
<th>E**</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) ((\text{NH}_4)_2\text{SO}_4 \rightarrow 2\text{NH}_3 + \text{H}_2\text{O} + \text{SO}_3)</td>
<td>9.2E+06</td>
<td>0.00</td>
<td>13042</td>
<td>[188]</td>
</tr>
<tr>
<td>(2) (\text{NH}_2 + \text{SO}_2(+M) ↔ \text{NH}_2\text{SO}_2(+M))</td>
<td>9.7E+12</td>
<td>0.00</td>
<td>0</td>
<td>[188]</td>
</tr>
<tr>
<td>Low pressure limit</td>
<td>6.1E+18</td>
<td>-0.83</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>(3) (\text{NH}_2\text{SO}_2 + \text{O}_2 ↔ \text{NHSO}_2 + \text{HO}_2)</td>
<td>2.0E+13</td>
<td>0.00</td>
<td>11700</td>
<td>Estimated</td>
</tr>
<tr>
<td>(4) (\text{NH}_2\text{SO}_2 + H ↔ \text{NHSO}_2 + \text{H}_2)</td>
<td>6.4E+05</td>
<td>2.39</td>
<td>10171</td>
<td>Estimated</td>
</tr>
<tr>
<td>(5) (\text{NH}_2\text{SO}_2 + \text{O} ↔ \text{NHSO}_2 + \text{OH})</td>
<td>9.4E+06</td>
<td>1.94</td>
<td>6460</td>
<td>Estimated</td>
</tr>
<tr>
<td>(6) (\text{NH}_2\text{SO}_2 + \text{OH} ↔ \text{NHSO}_2 \text{H}_2\text{O})</td>
<td>2.0E+06</td>
<td>2.04</td>
<td>566</td>
<td>Estimated</td>
</tr>
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<td>(7) (\text{NH}_2\text{SO}_2 + \text{HO}_2 ↔ \text{NHSO}_2 + \text{H}_2\text{O}_2)</td>
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<td>22000</td>
<td>Estimated</td>
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<td>(8) (\text{NH} + \text{SO}_2(+M) ↔ \text{NHSO}_2(+M))</td>
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<td>1689</td>
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<td>Low pressure limit</td>
<td>2.9E+27</td>
<td>-3.58</td>
<td>5206</td>
<td></td>
</tr>
</tbody>
</table>
### 3.4 Results and Discussion

The experimental and numerical results are presented and discussed in this section. The results include investigations of the SNCR performance of ammonium sulfate at varying AS/NO molar ratios, along with investigations of the influence of SO₂, KCl, and residence time on the SNCR chemistry.

#### 3.4.1 SNCR with NH₃ and the impact of SO₂

Since ammonium sulfate decomposes into NH₃ and sulfur oxides, it is an important prerequisite for studying the SNCR process with ammonium sulfate, to first look into the impact of SOₓ on the NO reduction. Figure 3.4 shows results for SNCR experiments using NH₃ with a β₉₃ (NH₃/NO) value of 1.5 in dry conditions with and without addition of SO₂. In the absence of SO₂, reaction is initiated above 850 °C and the NO reduction is very efficient in the temperature range 900-1000 °C. The observed NO reduction efficiency compares well with other studies [83,110,113,196]. The influence of SO₂ on the NO reduction is small. The onset of NO reduction is shifted slightly downwards in temperature when adding 289 ppm SO₂, but the difference is within the experimental uncertainty. The NO reduction is only slightly affected by the presence of SO₂; above the optimum temperature, SO₂ was found to have a small promoting effect on the oxidation of NH₃ to NO, in agreement with other studies [84,85].

![Graph showing NO reduction efficiency](image)

**Figure 3.4.** Comparison of numerical and experimental results of SNCR using NH₃ with and without presence of SO₂. The inlet conditions in the experiment without SO₂ were: NOₐ = 530 ppm, NH₃ = 800 ppm, O₂ = 2 vol. %, balance N₂. The inlet conditions in the experiment with SO₂ were: NOₐ = 430 ppm, NH₃ = 800 ppm, O₂ = 2 vol. %, SO₂ = 289 ppm. The residence time in the reactor was 151/T(K) s in both experiments.

The experimental results are not fully captured by the model. The temperature window for efficient NO reduction is predicted to be located at approximately 850-950 °C, providing a 50 °C off-set from the experiments. Moreover, the predicted increase in NO concentration above the optimum temperature is steeper than experimentally observed. This level of discrepancy has also been observed in
earlier work for SNCR with NH$_3$ under dry conditions [7], and is attributed to short-comings in the H/N/O subset of the model.

Figure 3.5 shows a sensitivity analysis for NO just above the onset temperature of reaction (840 °C) and above the optimum temperature (1000 °C). The predictions are very sensitive to the branching ratio of the NH$_2$ + NO reaction. Below the optimum temperature for the process, the chain branching reaction NH$_2$ + NO → NNH + OH is favorable to NO reduction, while the chain terminating reaction NH$_2$ + NO → N$_2$ + H$_2$O is equally unfavorable. Above the optimum temperature, the sensitivity of the NH$_2$ + NO reactions is reversed; here, an increase in the radical pool promotes the conversion of NH$_2$ to NO. Thus, the steeper increase in NO above the optimum temperature, as predicted by the model, indicates an overestimation of the O/H radical pool.

In agreement with the observation that the influence of SO$_2$ on the NO reduction is small, none of the S/N reactions show up among the most sensitive steps. The thermal stability of NH$_2$SO$_2$ is not sufficient for this component to play a role under the investigated conditions. The small impact of SO$_2$ is caused by its interaction with the O/H radical pool, involving terminating sequences such as SO$_2$ + X (+M) → XSO$_2$ (+M), XSO$_2$ + Y → SO$_2$ + XY, where X and Y are radicals [197].

**Figure 3.5.** Sensitivity coefficients for prediction of NO in the SNCR process using NH$_3$ and SO$_2$.

### 3.4.2 SNCR with ammonium sulfate

In this section, the experimental and numerical results for the SNCR process using ammonium sulfate with varying AS/NO molar ratio at two different residence times are presented. The effect of KCl on NO reduction and the sulfation of KCl by ammonium sulfate, was also investigated.

#### 3.4.2.1 The impact of AS/NO molar ratio on NO reduction

Figure 3.6 shows the experimental and numerical results of SNCR with a 5 wt. % and a 10 wt. % AS/H$_2$O solution at a short residence time of 151/T(K) s. To the knowledge of the authors, these experiments represent the first laboratory-scale experiments, i.e. under controlled conditions, of the
Selective non-catalytic reduction of NOx with alternative additives

SNCR performance using ammonium sulfate as additive. The onset of reaction was found to occur at around 900 °C, with the highest NO reduction at around 1050 °C. NO reductions of up to 95% were achieved in a somewhat narrow temperature window, which could be slightly broadened by increasing the AS/NO molar ratio. The present results are similar to those of Kassman et al. [20], who also reported a large reduction of NO using ammonium sulfate in a CFB boiler.

The onset for formation of SO2 occurs around 1000 °C. Above this temperature, the SO2 concentration increases linearly with temperature above 1000 °C, reaching levels corresponding to more than 50% conversion of AS to SO2. The behavior is qualitatively similarly to that observed by Wu et al. [188] for decomposition of ammonium sulfate in a tube reactor. However, the results are not directly comparable, because the experiments of Wu et al. [188] were conducted in an inert atmosphere. Under the present conditions, the O/H radical pool formed by the interaction of NH3, O2, and NO strongly enhances reduction of SO3 to SO2.

The experimental results shown in Figure 3.6 are described satisfactorily by the model. However, the onset for reaction occurs at around 25 °C lower than predicted. Furthermore, NO is overpredicted at higher temperatures, indicating issues with overestimation of the O/H radical pool similar to those for using NH3 as additive (Figure 3.4). The onset for formation of SO2 at 1000 °C is well captured, but the SO2 concentration is strongly overestimated above 1050 °C; a further indication that the predicted chain branching is too strong.

![Figure 3.6](image_url)

Figure 3.6. Comparison of modeling and experimental results of SNCR using a 5 wt. % (left) and a 10 wt. % (right) AS/H2O solution. The initial conditions with a 5 wt. % AS solution were: NOin = 400 ppm, (NH4)2SO4 = 430 ppm, O2 = 1 %, H2O = 9.5 %, balance N2. The initial conditions with a 10 wt. % AS solution were: NOin = 400 ppm, (NH4)2SO4 = 908 ppm, O2 = 1 %, H2O = 9.5 %, balance N2. The residence time in both experiments were 151/T(K) s.

Figure 3.7 shows sensitivity analyses for NO and SO2 above the onset temperature of reaction (1000 °C) and above the optimum temperature (1100 °C) for the SNCR process using a 5 wt. % AS solution. Similarly to the SNCR results using NH3 (Figure 3.5), predicted NO is most sensitive below the optimum temperature. The NO reduction is again dominated by the NH2 + NO reaction, with a smaller sensitivity to the chain branching reaction H + O2 ↔ O + OH. Prediction of SO2 is also very sensitive to the NH2 + NO reaction, due to its influence on the radical pool. Generally, more radicals lead to a higher production rate of SO2 via SO3 + H ↔ SO2 + OH. This is also reflected in the SNCR results.
3.4 Results and Discussion

(Figure 3.6), which show an increase of SO$_2$ above 1000 °C. Above the optimum temperature, the sensitivity of NO and SO$_2$ is reversed. In general, the chain branching and propagating reactions that lead to an increase in the radical pool promotes the NO formation via NH$_2$ oxidation.

Figure 3.7: Sensitivity coefficients for prediction of NO (left) and SO$_2$ (right) in the SNCR process using ammonium sulfate.

The impact of the AS/NO molar ratio was also investigated at longer residence times, but for lower AS/NO ratios. Figure 3.8 shows experimental and numerical results of SNCR using ammonium sulfate solutions (2.5 wt. %, 5 wt. %, and 10 wt. %) in a larger reactor with a residence time of 6686/T(K) s, corresponding to 3-5 s at the relevant temperatures. It was found that the long residence time shifted the temperature window significantly towards lower temperatures, in agreement with the findings of Liang et al. [81] who investigated the impact of residence time on NO reduction using NH$_3$. The NO reduction levels are lower than those obtained with a low residence time (Figure 3.6), due to the lower additive feeding rate. The temperature for the onset of reaction, and the temperature for highest NO reduction, are both satisfactorily predicted by the model for all three AS solution concentrations.

Figure 3.8. Comparison of modeling and experimental results of SNCR using a varying AS in H$_2$O solutions. The inlet conditions were: NO$_{in}$ = 400 ppm, O$_2$ = 1.3 %, H$_2$O = 4.0 %, balance gas N$_2$. The residence time was 6686/T(K) s.
3.4.2.2 The impact of KCl on NO reduction and sulfation of KCl by ammonium sulfate

The influence of KCl on the SNCR process was investigated by using an aqueous solution containing 5 wt. % AS and 2.5 wt. % KCl. Figure 3.9 shows a comparison of SNCR results using ammonium sulfate in presence and absence of KCl. The addition of 390 ppm KCl was found to have a strong promoting effect on NO reduction at lower temperatures. It shifts the onset of reaction from approximately 900 °C to 800 °C and broadens the temperature window by 50 °C. Also the formation of SO$_2$ is promoted at lower temperatures by addition of KCl.

A promoting effect of various Na/K additives (chlorides, carbonates, and hydroxides) on NO reduction has been demonstrated in flow reactor SNCR experiments using NH$_3$ [92,94,95] and urea [122] as additives. Hao et al. [94] found that addition of 125 ppm KCl promoted the NO reduction by 15 % at 850 °C, which is in line with the present experiments. Guo et al. [95] showed that addition of 25 ppm Na$_2$CO$_3$ promoted the NO reduction at 750 °C from 20 % to 70 %. The effect was captured qualitatively by the Na mechanism proposed by Zamansky et al. [92] The effect of Na$_2$CO$_3$, which rapidly decomposes and forms NaOH in presence of water vapor; Na$_2$CO$_3$ → Na$_2$O + CO$_2$, Na$_2$O + H$_2$O → 2NaOH, was attributed mainly to a sequence gas phase reactions leading to an increase of OH radicals; NaOH + O$_2$ ↔ NaO$_2$ + OH, NaOH(+M) ↔ Na + OH(+M), and NaO + H$_2$O ↔ NaOH + OH. Addition of 25 ppm K$_2$CO$_3$ yielded similar results similar to those obtained with Na$_2$CO$_3$. Despite the fact that the K mechanism proposed by Hindiyarti et al. [93] is very similar to that proposed for Na by Zamansky et al. [92], the promoting effect of K$_2$CO$_3$ on NO reduction was strongly underpredicted at 750 °C [95]. Guo et al. [95] proposed that one reason for the difference could be the lower rate constant for KOH dissociation compared to that of NaOH, but more work is needed to solve this issue.

The present model uses an alkali/sulfur/chlorine subset [14,128,179], drawn to a large extend from the mechanism proposed by Hindiyarti et al. [93] As seen from Figure 3.9, the present model underestimates the promoting effect of KCl on NO reduction at lower temperatures. It qualitatively captures the effect of KCl on SO$_2$ production, but underestimates the effect. A sensitivity analysis of predicted SO$_2$ at 1000 °C indicated that SO$_2$ is mainly sensitive to the reactions SO$_3$ + H ↔ SO$_2$ + OH and KOSO$_2$(+M) ↔ KO + SO$_2$(+M). The intermediate KOSO$_2$ is produced from association of K atoms with SO$_3$; K + SO$_3$(+M) ↔ KOSO$_2$(+M). Thus, the addition of KCl presumably promotes the reduction of SO$_3$ to SO$_2$ both through its influence on the radical pool and by direct K/S interactions, but this influence is underestimated by the model.
3.4 Results and Discussion

Figure 3.9. Comparison of modeling and experimental results of SNCR using a 5 wt. % AS and a 5 wt. % AS + 2.5 wt. % KCl in H₂O solution. The inlet conditions without KCl were: NO_{in} = 400 ppm (NH₄)₂SO₄ = 430 ppm, O₂ = 1 %, H₂O = 9.0 %, balance gas N₂. The inlet conditions with KCl were: NO_{in} = 410 ppm, (NH₄)₂SO₄(g) = 430 ppm, KCl(g) = 390 ppm, O₂ = 1 %, H₂O = 9.0 %, balance gas N₂. The residence time was 151/T(K) s.

Figure 3.10 shows the measured HCl and predicted alkali metal concentrations during the SNCR experiment using a 5 wt. % AS + 2.5 wt. % KCl in H₂O solution (giving a S/Cl molar ratio of 1.1). Hydrogen chloride is not detected below 900 °C. This observation is likely due to a reaction between HCl and NH₃, occurring downstream of the reactor. At the low temperature (~160 °C) in the tubes between the reactor and the analyzer, conditions are favorable for formation of NH₄Cl aerosols by the direct reaction NH₃ + HCl → NH₄Cl(s). This reaction has been demonstrated to proceed rapidly at 25 °C [198–200]. With a residence time of approximately 4-5 s in the outlet tube downstream of the reactor, HCl can be expected to be largely depleted when NH₃ is in excess. This explanation is further in line with the NO measurement (Figure 3.9) that indicates consumption of NH₃ above 850 °C, corresponding to the onset of HCl detection (Figure 3.10). The measured HCl concentration is found to be highest between 975-1075 °C, corresponding to the optimum temperature for NO reduction where the consumption of NH₃ is high. Thus, the HCl measurement is only considered reliable at temperatures above 1025 °C, where NH₃ is close to fully consumed.

At temperatures lower than the sublimation point (770 °C), a significant fraction of the KCl is expected to remain in condensed form. For temperatures above the sublimation point, the sublimation rate of KCl can be assumed to be fast due to the small droplet size (~1 µm), in line with the results from Knudsen et al. [193]. Still, it is desirable in future work to validate this assumption, e.g., by estimating the required time for complete sublimation of KCl for this droplet size at temperatures between 770-850 °C. Since the present results do not provide evidence of KCl sublimation at the investigated conditions, it cannot be concluded whether the observed promoting effect of KCl on NO production is due to gas-phase interactions, or due to catalytic effects of KCl aerosols.

Due to the uncertainty of the HCl results in presence of NH₃, the measurement cannot be reliably used to interpret the KCl sulfation below 975 °C (corresponding to the optimum temperature for NO reduction). At 1025-1050 °C, the measured HCl concentration of 230 ppm indicated a 60 % conversion of KCl, corresponding to a lower limit of the sulfation. The model predicts a high conversion of
KCl to K$_2$SO$_4$ and KHSO$_4$ between 800-1050 °C, but KHSO$_4$ is gradually converted back to KCl above 800 °C. Above 1050 °C, the sulfation of KCl becomes thermodynamically restricted, with production of KOH favored [128].

![Figure 3.10](image_url) Measured and predicted concentration of HCl (left) and predicted concentrations alkali metals (right) during the SNCR experiment using a 5 wt. % AS + 2.5 wt. % KCl in H$_2$O solution.

Figure 3.11 shows a reaction pathway analysis for K transformation during the SNCR process using the AS/KCl solution (Figure 3.9), conducted at 1025 °C and 1150 °C. The gas-phase chemistry of K species is fast, and quickly reaches equilibrium upon entering the reactor. According to the model, the initial step in the gaseous K$_2$SO$_4$ formation is an association reaction; KCl + SO$_3$ (+M) ↔ KSO$_3$Cl (+M). The alkali oxysulfur chloride complex further reacts in a sequence of shuffle reactions leading to formation of K$_2$SO$_4$; KSO$_3$Cl + H$_2$O ↔ KHSO$_4$ + HCl, KHSO$_4$ + KCl ↔ K$_2$SO$_4$ + HCl. Theoretical evaluations have indicated that KSO$_3$Cl and KHSO$_4$ are sufficiently stable in the gas phase up to 1100 °C to act as precursors for K$_2$SO$_4$ [127].

Since SO$_3$ is assumed to be a direct product from decomposition of ammonium sulfate, the oxidation of SO$_2$ to SO$_3$ is not rate-limiting for the KCl sulfation in the present model. However, the SO$_2$ concentration was found to increase linearly with temperature above 900 °C in the SNCR experiment with AS/KCl solution (see Figure 3.9). Thus, the KCl sulfation may in reality be limited by reduction of SO$_3$ to SO$_2$ above 900 °C.

At 1150 °C, the alkali chemistry is notably more complex, and involves several recycle sequences. KCl is mainly converted to KOH through the following reaction sequence; KCl + H ↔ K + HCl, K + O$_2$ (+M) ↔ KO$_2$ (+M), KO$_2$ + OH ↔ KOH + O$_2$. The intermediate KO$_2$ is also formed through a sequence of association reactions with SO$_2$; K + SO$_2$ (+M) ↔ KOSO (+M), O$_2$ + KOSO (+M) ↔ KOSO$_3$ (+M), KOSO$_3$ (+M) ↔ KO$_2$ + SO$_2$ (+M). A small amount of K$_2$SO$_4$ is also produced through a reaction sequence started by association of K with SO$_3$; K + SO$_3$ (+M) ↔ KOSO$_2$ (+M), OH + KOSO$_2$ (+M) ↔ KHSO$_4$ (+M), KHSO$_4$ + KCl ↔ K$_2$SO$_4$ + HCl. However, under these conditions parts of the consumed KCl is replenished from reactions of K$_2$SO$_4$ with Cl and KOH with HCl. As a consequence, ammonium sulfate is not as efficient in the sulfation of KCl at 1150 °C as compared to 1025 °C.
Figure 3.11. Pathway analysis for gas-phase alkali transformation in the SNCR process using ammonium sulfate. The analysis was conducted at a) 1025 °C and b) 1150 °C.
3.5 Conclusion

The use of ammonium sulfate in the SNCR process was investigated in a laboratory-scale flow reactor setup, using a liquid feeding system for the supply of additive to the reactor. In addition, a detailed kinetic model was developed, including descriptions of the SNCR chemistry as well as decomposition of ammonium sulfate.

The SNCR performance was evaluated at (NH$_4$)$_2$SO$_4$/NO molar ratios of 1.1 and 2.3, which both demonstrated NO reductions up to 95% in a temperature interval of 1025-1075 °C. The NO reductions by ammonium sulfate were overall well described by the model, with a small offset by 25 °C in the predicted onset of reaction. However, the model slightly underestimated the NO reduction at high temperatures, conceivably due to overestimation of the O/H radical pool.

SNCR experiments using ammonia, in presence and absence of SO$_2$, showed a negligible influence of SO$_2$ on NO reduction. Furthermore, the model did not show an effect of SO$_2$ on NO reduction, indicating that the SNCR chemistry is not sensitive to the developed NH$_2$SO$_2$ subset.

The impact of increasing the residence time from 151/T(K) s to 6686/T(K) s on the SNCR process when using ammonium sulfate was investigated. The increase in residence time resulted in a downwards shift in temperature for the onset of reaction, which was well captured by the model. The results demonstrated that ammonium sulfate may also be a feasible additive for the SNCR process at longer residence times.

Addition of 390 ppm KCl was found to promote NO reduction, by shifting the onset temperature of reaction towards lower temperatures by 100 °C, while widening the operating window. However, the effect could not be captured by the model, and it has not been determined if it is caused by gas phase or condensed phase interactions of KCl. The discrepancy is mainly attributed to an underestimation of the influence of K species on the O/H radical pool at lower temperatures. The results further indicated a favorable degree of KCl sulfation up to 60% at an optimum temperature of 1025 °C.
Kinetic modeling of urea decomposition and byproduct formation

This chapter has been written in a manuscript format. A slightly modified version of this manuscript has been published in the peer-reviewed journal *Chemical Engineering Science* as,


**Abstract:** A kinetic model for urea decomposition and byproduct formation was developed and validated against thermogravimetric analyses (TGA) of urea and urea-derived byproducts, including biuret and cyanuric acid, at heating rates up to 500 °C/min. The model provided a good description of urea decomposition at all investigated heating rates. The results indicate that an increase in heating rate causes a shift in production of cyanuric acid into ammelide and limits the overall byproduct formation. Additionally, it is shown that a long reaction time is necessary to fully decompose urea at temperatures corresponding to SCR applications.

### 4.1 Introduction

The recent emission regulations for lean burning engines require appropriate aftertreatment of the exhaust gas from heavy-duty engines, to reduce emissions of nitrogen oxides (NO\textsubscript{x}) [201]. An effective technology to reduce NO\textsubscript{x} is the selective catalytic reduction process (SCR), which requires the supply of NH\textsubscript{3} as reducing agent [22,30,202]. For mobile sources, urea is the preferred additive, as it is non-toxic, can be dissolved in water, and releases NH\textsubscript{3} upon heating [23,31]. Unfortunately, urea is known to produce solid byproducts at temperatures corresponding to SCR conditions, potentially causing severe operational problems, e.g. clogging of the injection nozzles and fouling of the catalyst [26,27,32]. Therefore, development of numerical simulation tools is important, to assess the risk of deposit formation, and to predict optimal operational conditions.

The major byproducts from urea decomposition are known to be biuret, cyanuric acid (CYA), and ammelide. The reaction pathways leading to the formation of these byproducts during urea decomposition are known [25,145,146,152,203]. However, knowledge of the physical processes involved is scarce, and it is still unclear what phase urea is in during decomposition. Most studies support decomposition of urea directly from either solid or liquid phase [23,26,134–136]. In contrast, Bernhard et al. [138,139] studied urea evaporation in a flow reactor at 50-250 °C, and identified urea in the gas phase by Fourier transformed infrared spectroscopy (FTIR). Therefore, a better understanding
of the physical processes is important to make accurate model predictions of urea decomposition and deposit formation.

Schaber et al. [25] performed thermogravimetric analyses (TGA) of decomposition of urea, along with its most important byproducts including biuret, CYA, ammelide and triuret. Their work showed that urea decomposition is a complex multi-step process, with the formation of byproducts being highly dependent on the reaction temperature. Also other process parameters can influence the decomposition behavior of urea, e.g., heating rate, surface area, and initial sample size [40,41,204].

Ebrahimian et al. [41] made the first attempt to derive a reaction scheme for urea decomposition. Their model, which was based on ionic reactions, was tested against data from Schaber et al. [25] and Lundström et al. [204]. It was able to reproduce the urea TGA curve with reasonable accuracy but it failed to describe the decomposition behavior of the urea-derived byproducts including biuret, CYA, and ammelide. Brack et al. [40] recently developed a reaction mechanism for urea decomposition and formation of biuret, CYA, ammelide, and triuret based on non-ionic species. Their model described well low heating rate TGA data (5-20 °C/min), including the effect of changes in crucible geometry and sample mass.

The modeling studies by Ebrahimian et al. [41] and Brack et al. [40] were restricted to low heating rates of 5-20 °C/min. However, a numerical study by Abu-Ramadan et al. [38] indicates that the heating rate of a UWS droplet in a practical urea-SCR system may be in the order of 10^5 °C/min, depending on the droplet size and exhaust temperature. The heating rate can be expected to have a major impact on the urea decomposition and byproduct formation. Conceivably, a higher heating rate can reduce the formation of byproducts by minimizing the extent of side-reactions.

In the present work, a kinetic model for urea decomposition and byproduct formation is developed, based on the proposed reaction scheme by Brack et al. [40]. The model is validated against TGA data over a wider range of heating rates (5-500 °C/min). As part of the work, the physical behavior of urea is investigated to determine the relative importance of evaporation and decomposition of urea. Three experimental methods are employed: a TGA-FTIR setup, a fixed bed reactor coupled with FTIR, and a solid state Raman spectroscopy setup.

### 4.2 Experimental section

#### 4.2.1 Thermogravimetric analysis

Urea (>99.5% purity), biuret (>97.0% purity), and CYA (>99% purity) were purchased from Sigma-Aldrich Co., and used without further purification. Samples for TGA were prepared by grinding and fractionating the materials to 106-108 µm size intervals, and the typical sample mass was 50 mg. Two different crucible types were used, allowing variation in the surface area of the sample for constant mass (0.283 cm² and 0.899 cm²). The TGA experiments were performed on a Netzsch STA 449 F1 Jupiter. The setup consisted of a furnace capable of high heating rates of up to 1000 °C/min. In the present work, the heating rate was limited to 5-500 °C/min, as higher heating rates imposed significant
fluctuations in the measurements. During operation, the furnace was purged by 100 ml/min N₂. The experiments were designed to investigate the influence of the heating rate and sample surface area on the urea decomposition. Additionally, isothermal TGA experiments were conducted to investigate the long-term thermal stability of urea.

A study of the gas phase products from urea decomposition was conducted on a combined TGA-FTIR setup. The setup consisted of a Netzsch STA 449 C Jupiter, and an Equinox 55 FTIR spectrometer from Bruker. A 50 mg urea sample was heated to 140 °C at 10 °C/min, and held isothermally at 140 °C for 3 hours. The gas was continuously measured by FTIR in the spectral range of 400-4000 cm⁻¹, at an operational temperature of 140 °C.

### 4.2.2 Solid state Raman spectroscopy

This setup was comprised of a reactor vessel and a Raman spectrometer, as illustrated in Figure 4.1. A removable ceramic sample holder was placed within a reaction cell, which could be heated up to 1000 °C at a maximum heating rate of 100 °C/min. A quartz glass window was installed above the sample holder. 12.5 ml/min N₂ was used to purge the produced gases during decomposition experiments. A porous support material was used to carry a quartz crucible, 4 mm in diameter and 2 mm in height. The reactor vessel was positioned on a motorized stage beneath the Raman laser.

The purpose of the thin transparent quartz glass plate above the reaction cell was twofold. Firstly, it acted as a window to enable observation of the sample during decomposition. Secondly, the surface temperature of the glass plate was colder than the average reactor temperature, due to direct contact with the ambient. Thus, the glass plate simultaneously acted as a condensation surface for evaporated species.

The following procedure was applied for all experiments: A 10 mg sample was loaded in the crucible, heated to a specified temperature at 10 °C/min, and held isothermally for 15 min. The sample was then cooled rapidly to room temperature, and the solid phases in the crucible and on the glass plate were analyzed separately by Raman spectrometry. Then, the remaining sample mass in the crucible was fed back to the reactor, and the procedure was repeated for increasing temperatures (50 °C increments) until the sample had been fully decomposed.
Figure 4.1: Simplified schematic drawing of the reaction cell. The sample is loaded in a quartz crucible, and placed on a porous support material. A glass plate (illustrated by a blue square) is installed at the top of the reaction cell. A laser beam from the Raman spectrometer (illustrated by a green line) is used to acquire Raman spectra of the sample during decomposition. Vapors generated from the sample during decomposition (illustrated by red lines) are carried away by a 12.5 ml/min sweeping N\textsubscript{2} gas flow.

The Raman spectrometer used in this setup was a Labram HR Evolution Raman Spectrometer (Horiba), with a spectral range of 200-2200 nm (UV-VIS-NIR). It used a blazed holographic plane grating (Pyrex, coated with aluminum), with a groove density of 1800 l/mm, and a blaze wavelength of 500 nm. Furthermore, it used a deep cooled CCD (Syncerity) detector for spectral detection from ultraviolet (UV) to near-IR (200 nm to 1100 nm). The Raman filter was 532 nm Edge with a cut off at 50 cm\textsuperscript{-1}. The laser type was an air-cooled frequency doubled Nd:YAG 532 nm 100 mW from Oxxius. Instrument control, data acquisition, analysis and display were all managed in the LabSpec 6 package software.

4.2.3 Fixed bed reactor coupled with FTIR spectroscopy

A fixed bed reactor setup was used to conduct transient decomposition experiments of solid samples with online gas phase measurement by FTIR, operated at 191 °C and 1 bar. The reactor design is illustrated in Figure 4.2. The experiments were designed to investigate if HNCO, produced from decomposition of CYA, can recombine with NH\textsubscript{3} to form condensed phase species. Thus, CYA particles were fed to the reactor at 400 °C, where they decomposed in the presence of 900 ppm NH\textsubscript{3}. Sand, which had been pretreated at 600 °C for 2 hours, was used to assist the transport of the sample during feeding.
4.3 Modeling section

4.3.1 Kinetic modeling of urea decomposition and byproduct formation

A kinetic model for urea decomposition and byproduct formation has been developed, based on the reaction scheme by Brack et al. [40]. In the present work, it has been of interest to improve the model prediction at higher heating rates. Thus, kinetic parameters of selected reactions have been adjusted to obtain a better agreement with the higher heating rate experimental data of the present work. The reaction scheme of the present model is listed in Table 4.1.

In the optimization of the kinetic parameters, it was assumed that the initial mass loss of urea is dominated by urea decomposition; urea(m) \( \rightarrow \) HNCO(l) + NH\(_3\)(g) (reaction 1), and the subsequent formation of biuret; urea(m) + HNCO(l) \( \rightarrow \) biuret(m) (reaction 2). Therefore, the kinetic parameters of reaction 1 and reaction 2 were fitted to the initial mass loss of urea TGA curves for 5, 10, 50, and 500 °C/min. Similarly, the kinetic parameters of the CYA decomposition reaction; CYA(s) \( \rightarrow \) HNCO(g) (reaction 5) were fitted to TGA data of CYA for heating rates of 10, 50, and 500 °C/min. Furthermore, the biuret matrix decomposition reaction; biuret(matrix) \( \rightarrow \) 2HNCO(g) + NH\(_3\)(g) (reaction 12) was fitted to the initial mass loss of biuret for TGA heating rates of 10, 50, and 500 °C/min. The term matrix refers to a solid matrix-like aggregate state of biuret, which has been observed to occur at approximately 215-220 °C [40]. Finally, the kinetic parameters of ammelide sublimation
Kinetic modeling of urea decomposition and byproduct formation

(Reaction 14) were fitted to isothermal data of a urea sample, which had been heated to 280 °C with a heating rate of 500 °C/min.

Table 4.1: Kinetic scheme and parameters for the urea decomposition model. States of aggregation: (s): solid, (l): liquid/dissolved, (g): gaseous. For reactions with two reactants, the reaction order \( \gamma_j \) of each reactant is specified in the order in which the reactants are listed in the chemical reaction. \( pw \) represents present work.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>( \gamma_j )</th>
<th>( \Lambda )</th>
<th>( Ea ) (kJ/mol)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>urea(l) ( \rightarrow ) HNCO(l) + NH_3(g)</td>
<td>1</td>
<td>1.0 ( \cdot ) 10^{-1} l/s</td>
<td>120.0</td>
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<td>2</td>
<td>urea(l) + HNCO(l) ( \rightarrow ) biuret(l)</td>
<td>1/1</td>
<td>3.5 ( \cdot ) 10^{11} ml/mol/s</td>
<td>80.0</td>
</tr>
<tr>
<td>3</td>
<td>biuret(l) ( \rightarrow ) urea(l) + HNCO(l)</td>
<td>1</td>
<td>1.1 ( \cdot ) 10^{20} l/s</td>
<td>208.2</td>
</tr>
<tr>
<td>4</td>
<td>biuret(l) + HNCO(g) ( \rightarrow ) CYA(s) + NH_3(g)</td>
<td>1/1</td>
<td>9.4 ( \cdot ) 10^{20} ml/mol/s</td>
<td>158.7</td>
</tr>
<tr>
<td>5</td>
<td>CYA(s) ( \rightarrow ) 3HNCO(g)</td>
<td>0</td>
<td>1.0 ( \cdot ) 10^{3} mol/s</td>
<td>115.0</td>
</tr>
<tr>
<td>6</td>
<td>2biuret(l) ( \rightarrow ) ammelide(s) + HNCO(l) + NH_3(g) + H_2O(g)</td>
<td>2</td>
<td>3.6 ( \cdot ) 10^{-26} l/s</td>
<td>257.8</td>
</tr>
<tr>
<td>7</td>
<td>urea(l) + 2HNCO(l) ( \rightarrow ) ammelide(s) + H_2O(g)</td>
<td>1/2</td>
<td>1.3 ( \cdot ) 10^{20} ml^2/mol^2/s^2</td>
<td>110.4</td>
</tr>
<tr>
<td>8</td>
<td>biuret(l) + HNCO(g) ( \rightarrow ) triuret(s)</td>
<td>1/1</td>
<td>1.1 ( \cdot ) 10^{15} ml/mol/s</td>
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<tr>
<td>9</td>
<td>triuret(s) ( \rightarrow ) CYA(s) + NH_3(g)</td>
<td>1</td>
<td>1.2 ( \cdot ) 10^{18} l/s</td>
<td>194.9</td>
</tr>
<tr>
<td>10</td>
<td>biuret(l) ( \rightarrow ) biuret(matrix)</td>
<td>1</td>
<td>8.2 ( \cdot ) 10^{-26} l/s</td>
<td>271.5</td>
</tr>
<tr>
<td>11</td>
<td>biuret(matrix) ( \rightarrow ) biuret(l)</td>
<td>1</td>
<td>3.2 ( \cdot ) 10^{9} l/s</td>
<td>112.0</td>
</tr>
<tr>
<td>12</td>
<td>biuret(matrix) ( \rightarrow ) 2HNCO(g) + NH_3(g)</td>
<td>1</td>
<td>5.6 ( \cdot ) 10^{24} l/s</td>
<td>255.0</td>
</tr>
<tr>
<td>13a</td>
<td>urea(s) ( \rightarrow ) urea(l) (T &gt; 133 °C)</td>
<td>1</td>
<td>1.0 ( \cdot ) 10^{15}.T^{-1.5} l/s</td>
<td>160.0</td>
</tr>
<tr>
<td>13b</td>
<td>urea(l) ( \rightarrow ) urea(s) (T &lt; 133 °C)</td>
<td>1</td>
<td>1.0 ( \cdot ) 10^{15}.T^{-1.5} l/s</td>
<td>160.0</td>
</tr>
<tr>
<td>14</td>
<td>ammelide(s) ( \rightarrow ) ammelide(g)</td>
<td>1</td>
<td>1.0 ( \cdot ) 10^{14} ml/mol/s</td>
<td>209.0</td>
</tr>
</tbody>
</table>

Notably, there is a significant difference in the kinetic parameters for reaction 1 between the present model and the model by Brack et al. [40]. From simulations of urea TGA curves with higher heating rates (up to 500 °C/min) using the model of Brack et al., it was found that the shift in onset of decomposition was overestimated. This behavior indicates that the activation energy for the initial decomposition of urea (reaction 1) has been set too low in the model of Brack et al. Furthermore, Brack et al. treat reaction 1 as a 0.3 order reaction, while it is treated as a first order reaction in the present work.

The rate of formation of each species was calculated from equation E 4.1:
Here, $V$ is the total volume of species in the condensed phase, diminishing over time. $\nu_{ik}$ is the stoichiometric coefficient of the $i$’th species in the $k$’th reaction. $A_k$ and $E_{a,k}$ are the pre-exponential factor and activation energy of the $k$’th reaction. $c_j$ and $\gamma_j$ are the concentration and reaction order of the $j$’th species, respectively. Finally, $j_i$ is the evaporation rate of the $i$’th species. The densities and molar weights of the components were used in the model to calculate the total volume of the condensed phase species. Based on experimental observations from the FBR-FTIR (section 4.4.1.3) and TGA-FTIR (section 4.4.1.2) setups, it was concluded that the extent of urea evaporation is insignificant. Therefore, HNCO is the only condensed phase species considered to evaporate in the current model (see below).

### 4.3.2 Evaporation of HNCO

The evaporation of HNCO was calculated from the Hertz-Knudsen equation [207]. The Hertz-Knudsen equation assumes that the gas phase can be described as ideal, and that the gas velocity follows a Maxwell distribution. The flux of HNCO from the liquid to the gas phase is calculated by equation E.4.2 [207]:

$$j_{\text{HNCO}} = \frac{1}{4} \alpha \cdot v \cdot \frac{c_{\text{HNCO}}}{h} \cdot A_s$$  \hspace{1cm} (E.4.2)

$\alpha$ is an evaporation coefficient, $v$ is the velocity of gas molecules, $c$ is the concentration in the condensed phase, $h$ is the Henry constant, and $A_s$ is the surface area. The parameters in the Hertz-Knudsen equation were calculated by equations E.4.3 - E.4.4 [207]:

$$v = \sqrt{\frac{8 \cdot R \cdot T}{\pi \cdot M_{\text{HNCO}}}}$$  \hspace{1cm} (E.4.3)

$$h = \frac{\rho_{\text{HNCO}}}{(p_{\text{HNCO}}^0 \cdot M_{\text{HNCO}} / (R \cdot T))}$$  \hspace{1cm} (E.4.4)

The evaporation of HNCO is modelled with an evaporation constant of $\alpha = 0.001$, and a vapor pressure $p_{\text{HNCO}}^0$ according to equation E.4.5 [208]:

$$p_{\text{HNCO}}^0 \text{bar} = 10^{(4.69 - \frac{1252.195}{T / \text{K} - 29.167})}$$  \hspace{1cm} (E.4.5)
**4.4 Results and discussion**

**4.4.1 Competition between urea decomposition and evaporation**

One of the aims of the present work has been to gain a better understanding of the physical processes governing the depletion rate of urea, by investigating the relative importance of urea evaporation and decomposition. This insight is necessary to develop a reliable model for urea decomposition and to assess the risk of deposition. For this purpose, three experimental methods were employed: a solid state Raman spectroscopy setup, a fixed bed reactor setup coupled with FTIR spectroscopy, and a TGA-FTIR setup.

**4.4.1.1 Analysis of urea decomposition by solid state Raman spectroscopy**

The reaction cell setup (Figure 4.1) was used to assess the importance of urea evaporation during the early stages of urea depletion. The experiment was designed to identify evaporated species, as well as residue species, from a urea sample at various decomposition temperatures. Solid state Raman spectra were acquired of the recondensed vapors and residues generated at the following holding temperatures: 175, 225, 275, 325, and 370 °C. The holding temperatures were selected to emphasize different stages and mixture compositions during the decomposition, based on the urea TGA results.

Figure 4.3 shows the cumulative mass yields of the sample residue and accumulated recondensed vapors on the glass plate, which was kept at close to ambient temperature. Notably, up to 50 % of the initial sample mass was recovered as recondensed species on the glass plate. It was observed that the recondensed vapors were generated when the temperature increased above the melting point of urea (133 °C), and increased at an almost linear rate for increasing decomposition temperature.

![Figure 4.3: Mass yields of the sample residues and recondensed vapors, obtained from urea decomposition in the Raman experiments. The sample was kept isothermally for 15 min at each temperature, and cooled to room temperature in-between the temperature intervals, for analysis by Raman spectroscopy. The initial sample mass was 10 mg pure urea.](image)
The residues and recondensed vapors generated at each temperature were analyzed separately by solid state Raman spectroscopy. To identify the species, the spectra were compared to reference data on urea, as well as the main urea-derived byproducts, i.e., biuret, CYA, and ammelide (see Appendix B). Table 4.2 summarizes the results of the analysis. Urea was positively identified among the recondensed species generated at temperatures up to 275 °C. Above 275 °C, CYA was detected in the recondensed sample, while urea was no longer present. The Raman spectra of the recondensed vapors indicated also the presence of other species, which could not be identified from the database. The residue species showed presence of CYA at temperatures above 225 °C, in agreement with the findings of Schaber et al. [25]. Additionally, the Raman spectra of the recondensed vapors generated above 275 °C indicated presence of CYA. These results show that CYA either sublimes or decomposes from solid state at temperatures above 275 °C, and can recondense or recombine into solid CYA when impacting on a colder surface.

The presence of urea among the recondensed species yields the immediate perception that urea simultaneously experiences both evaporation and decomposition to byproducts. However, there are two possible sources of the species that were collected in condensed form on the glass plate. In addition to species evaporating from the urea sample and recondensing on the glass plate, it is also possible that gas phase products from decomposition recombine during cooling and then deposit on the glass plate. If the latter is the case, then the observed generation of recondensed vapors does not give evidence of urea evaporation. The feasibility of recombination of gaseous products from urea decomposition is further investigated and discussed in section 4.4.1.3.

Table 4.2: Identification of species produced during urea decomposition experiments at varying temperature ranges. The analysis is conducted by solid state Raman spectroscopy.

<table>
<thead>
<tr>
<th>Temperature range [°C]</th>
<th>Residue species</th>
<th>Recondensed vapor species</th>
</tr>
</thead>
<tbody>
<tr>
<td>25-175</td>
<td>Urea + other</td>
<td>Urea + other</td>
</tr>
<tr>
<td>175-225</td>
<td>CYA</td>
<td>Urea + other</td>
</tr>
<tr>
<td>225-275</td>
<td>CYA</td>
<td>Urea + other</td>
</tr>
<tr>
<td>275-325</td>
<td>CYA + other</td>
<td>CYA + other</td>
</tr>
<tr>
<td>325-370</td>
<td>Unidentified</td>
<td>CYA + other</td>
</tr>
</tbody>
</table>

4.4.1.2 Gas phase products of urea decomposition

In order to further investigate the urea decomposition and evaporation behavior, decomposition of a urea sample has been conducted in a TGA-FTIR setup. In this experiment, 50 mg of urea was heated to 140 °C, and kept isothermally for 3 h to investigate if urea could be detected in the gas phase. The FTIR spectrum of the produced gases was continuously measured during the experiment, as shown in Figure 4.4. By analyzing the evolution in the absorption intensity, the most rapid gas release was seen to occur at around 2500 s. At this time, two broad peaks around 800-1200 cm⁻¹ and 1500-1700
cm\(^{-1}\) indicate the presence of NH\(_3\) [209]. The sharp peak observed at 2260 cm\(^{-1}\) corresponds to the OCN\(^{-}\) stretch, which indicates the presence of HNCO [210]. Finally, the weaker intensity band observed around 3500 cm\(^{-1}\) corresponds to the N – H stretch, which is also characteristic for HNCO. However, the IR spectrum does not show clear indications of the characteristic C = O and C – N stretching frequencies of the urea molecule, at 1677 cm\(^{-1}\) and 1453 cm\(^{-1}\), respectively [211]. These results support that decomposition of urea is the dominating mechanism at 140 °C, due to the observed intensity of the characteristic HNCO and NH\(_3\) peaks. Evaporation of urea is therefore assessed to be negligible, since urea could not be detected in the gas phase.

![Figure 4.4: IR spectrum of gases produced by TGA of 50 mg urea at 140 °C over 3 h (top), and the FTIR spectrum of the TGA gas after 2500 s (bottom). Reference FTIR spectra of gaseous HNCO [212], NH\(_3\) [209], and urea [213] are shown for comparison.](image)

#### 4.4.1.3 Recombination of gaseous products from urea decomposition

To reconcile the observation of urea in the recondensed products (section 4.4.1.1) with the lack of gaseous urea detected in the decomposition products (section 4.4.1.2), it was investigated if gaseous products from urea decomposition could undergo chemical recombination to form solid products. Gaseous decomposition products of urea are known to include HNCO and NH\(_3\). Recombination of HNCO and NH\(_3\) was studied in the fixed bed reactor setup coupled with FTIR spectroscopy. CYA, which is known to decompose into HNCO at temperatures above 300 °C, was used as a precursor for HNCO. CYA samples of 1.44, 1.73, 2.44, and 4.2 mg, respectively, were fed to the reactor at 400 °C in 900 ppm NH\(_3\), using a total gas flow of 500 ml/\(\text{min}\).

The results from the experiments are presented in Figure 4.5. From the transient FTIR measurements, it can be seen that the decomposition time scale of CYA is consistently around 40-60 s. As the HNCO measurements exceed the calibration range (0-400 ppm), they are not considered quantitatively reliable. However, the measured HNCO peaks are qualitatively seen to be strongly correlated with a decrease in the NH\(_3\) measurement. It is observed that the NH\(_3\) consumption increases for increasing CYA sample amount, while the HNCO peaks stagnate around 2000 ppm for increasing sample mass.
Since feeding of 4.2 mg CYA yields only around 6.5 ml HNCO over a reaction time of approximately 50 s, the contribution to the total gas volume of 500 ml/min is very small and dilution can be neglected. Thus, the trends, consistent throughout the four tests, support the occurrence of a fast recombination reaction between NH$_3$ and HNCO. Such a reaction is expected to occur only at lower temperatures, i.e., in the outlet tube which was heat traced to 140 °C.

![Figure 4.5](image_url)

**Figure 4.5:** Gas phase analysis by FTIR of CYA decomposition in the FBR setup at 400 °C in 900 ppm NH$_3$.

The consistency of the experiments is further checked by plotting the NH$_3$ consumption against the amount of CYA fed to the reactor, as shown in Figure 4.6. The amount of consumed NH$_3$ has been calculated based on an integration of the inverse peak of the NH$_3$ measurement for all four experiments. The integration values are then used together with the ideal gas law:

\[
    n_{NH_3} = \int_{t_1}^{t_2} y_{NH_3} \cdot d t \cdot \frac{P \cdot Q}{R \cdot T}
\]

Here, $n_{NH_3}$ (mol) is the consumed amount of NH$_3$ in the experiment. $y_{NH_3}$ is the mole fraction NH$_3$ measured by the FTIR. $t_1$ and $t_2$ are the integration limits, defining the time span of the gas release from the decomposition of the sample. P, R, Q, and T are the pressure, gas constant, volumetric flow rate (500 ml/min), and temperature at standard conditions (0 °C), respectively. As shown in Figure 4.6, there is a strong correlation between the NH$_3$ consumption and the amount of fed CYA.
Kinetic modeling of urea decomposition and byproduct formation

Experimental results clearly support that gas-phase recombination of HNCO and NH₃ into condensable products can occur at low temperature. The species produced by recombination of HNCO and NH₃ have not been identified, but is suggested to be partly urea, based on the investigation described in section 4.4.1.1.

![Figure 4.6: Correlation between the amount of NH₃ consumed from feeding CYA samples at 400 °C. Initial NH₃ is 900 ppm.](image)

4.4.1.4 Concluding remarks on evaporation vs. decomposition

The competition between urea evaporation and decomposition was investigated by three experimental methods. The presence of urea among the recondensed vapors generated in the Raman setup indicated that urea evaporation is competitive, in agreement with the observations of Bernhard et al. [138,139]. However, the TG-FTIR results confirmed the presence of only HNCO and NH₃ in the gas phase, while urea could not be detected. It was shown that gaseous HNCO and NH₃ can recombine into condensable products at lower temperatures, offering an alternative reaction path to urea in the recondensed species in the solid state Raman setup. Based on these investigations, it is concluded that decomposition is the dominating mechanism in the depletion of urea, while the evaporation of urea is negligible and can be disregarded in the model, in agreement with the assumptions of Brack et al. [40].

4.4.2 Influence of surface area on urea decomposition

The kinetic model is validated against TGA data from the present work and other sources. In these experiments, crucibles with varying surface area were used and it is important that the model is able to capture the impact of surface area on urea decomposition. A surface area dependence was included in the decomposition of CYA into HNCO (reaction 5 in Table 4.1), and in the evaporation of HNCO...
modeller by the Hertz-Knudsen model. Additionally, the decaying surface area of the sample during decomposition, due to the crucible geometry, has been taken into account.

TGA experiments of urea have been conducted by using two different crucible types, yielding a variation in the surface area for constant sample size (0.283 cm$^2$ and 0.899 cm$^2$, respectively). The two samples were subjected to the same temperature program, heating at 10 °C/min up to 140 °C, where the temperature was held isothermally for 3 h. By comparing the two experiments, shown in Figure 4.7, it is observed that a larger surface area will cause a faster depletion rate of the sample. The depletion rate of the samples resembles that of an exponential decay, indicating the formation of more thermally resistant byproducts. Since a larger surface area increases the HNCO evaporation rate, the concentration of HNCO in the condensed phase is reduced, leading to less formation of byproducts. The model captures the experimental trends, but underestimates the influence of the surface area. This discrepancy can be attributed to uncertainties in the surface area measurement, or inaccurate HNCO evaporation modeling by the Hertz-Knudsen equation. However, it has not been possible to improve the model further in regards to the HNCO evaporation, as the available data are very limited. Additional experimental data on vapor pressure correlations for HNCO are required to improve the model, and this has not been prioritized in the present work. This shortcoming must be kept in mind when comparing modeling results to TGA data.

![Figure 4.7: Model validation of the surface area dependence. TGA experiments of urea with similar sample mass but varying surface area. The samples are heated at 10 °C/min up to 140 °C and kept isothermally for 3 h. The sample surface area of large crucible is 0.899 cm$^2$, and decays over time due to a round-bottom geometry of the crucible. The sample surface area of small crucible is 0.283 cm$^2$, and is constant over time due to a cylindrical geometry of the crucible.](image)

### 4.4.3 Influence of the heating rate on urea decomposition

It is a central hypothesis of the present work that the heating rate will influence the decomposition behavior of urea and the resulting byproduct formation. Thus, the impact of the heating rate on urea decomposition was studied by TGA, with heating rates of 5, 10, 50 and 500 °C/min. It is observed
from the results shown in Figure 4.8 that the general shape of the TGA curves is similar for varying heating rates. However, the decomposition is shifted towards higher temperatures for increasing heating rate, in line with the work by Brack et al. [40]. The initial mass loss of the TGA curves is seen to be increasing for higher heating rates; this is well captured by the model. The results indicate that an increased heating rate limits the production of the byproduct species that cause the first plateau in the TGA curves. This effect is most pronounced for the highest heating rate. The first plateau consists mainly of CYA [25]. Thus, the results indicate that an increasing heating rate can lead to a reduced production of CYA.

The present model is intended to be applied in models for decomposition of urea-water-solution droplets [38,41,165]. Based on simulations by Abu-Ramadan et al. [38], there is still a significant gap between the heating rates used in the present work (5-500 °C/min), and that of a real urea-SCR system (approximately 10^5 °C/min). The applicability of the present kinetic scheme in droplet models is still not well understood, and is a topic of ongoing research.

![Figure 4.8: Comparison of model simulations and experimental TGA curves for urea decomposition at varying heating rate. The initial sample mass was 50 mg, with a surface area of 0.899 cm².](image)

Figure 4.9 compares predictions of the present model and that of Brack et al. [40] with TGA data for 10 °C/min and 500 °C/min, respectively. Low heating rate data are shown from the present work as well as from Schaber et al. [25]. The differences seen between the experimental data sets obtained at 10 °C/min may be attributed to differences in sample mass, crucible surface area, etc. The model by Brack et al. [40] describes well the low heating rate TGA data from [25], but does not extrapolate accurately to high heating rate conditions. The present model provides satisfactory predictions of the urea TGA curves for a wide range of heating rates up to 500 °C/min. The onset of fast decomposition is predicted correctly for both heating rates, but the width of the plateau is overestimated, mostly pronounced at the high heating rate.
4.4 Results and discussion

Figure 4.9: Comparison of simulations performed with the present model and the model by Brack et al. [40]. The models are validated against TGA curves for urea decomposition from the present work (pw) and from Schaber et al. [25]. In the present work, the initial sample mass and surface area in all experiments and model simulations were 50 mg and 0.899 cm², respectively. The typical sample mass of experiments from Schaber et al. [25] was 30-50 mg, while the sample surface area was unspecified.

Figure 4.10 shows the formation of the individual byproducts, as predicted by the present model. The calculations show a shift in production from CYA to ammelide for increasing heating rate. According to the predictions, an increased heating rate reduces the production of biuret. Consequently, the production of CYA via reaction 4 in Table 4.1 is reduced, while the production of ammelide via reaction 6 and 7 in Table 4.1 is promoted.

Figure 4.10: Simulation of urea TGA at varying heating rates with 50 mg initial sample mass and a surface area of 0.899 cm².
4.4.4 Decomposition of urea-derived byproducts

To gain a better understanding of the decomposition and formation mechanisms occurring during urea decomposition, analysis of the main urea-derived byproducts is important. While the decomposition behavior of biuret and CYA has been investigated previously by TGA at low heating rates [25,40], data at higher heating rates have not been reported. Therefore, TGA curves for biuret and CYA were obtained at heating rates in the range 10-500 °C/min.

Figure 4.11 shows that the initial decomposition of biuret begins around 193 °C; this is captured well by the model. When biuret is heated at a low heating rate, i.e., 10 °C/min, it is seen to produce stable species at 225 °C. This is consistent with the formation of a solid matrix at this temperature, as reported by Schaber et al. [25]. The solid matrix decomposes by further heating, while CYA is subsequently produced. CYA is thermally stable up to around 290 °C, thus yielding a second plateau of stable mass in the biuret TGA curve. However, when the heating rate of the biuret sample is increased to 50 °C/min, there is no indication of solid matrix formation; the reaction leading to a biuret matrix at 225 °C is apparently limited at high heating rates. The TGA mass at the plateau, corresponding to a mixture of CYA and ammelide, is seen to increase significantly for increasing heating rate of biuret. This behavior is in conflict with previous observations from urea TGA at varying heating rates, as presented in Figure 4.8, and also with modeling predictions. The model is unable to capture the thermal stability of the biuret matrix at 225 °C, as well as the increased production of CYA for increased heating rate, and more work is required to explain this discrepancy.

The decomposition of pure CYA (Figure 4.11) is seen to be monotonic in the mass loss, indicating that no byproducts are formed. The decomposition is shifted towards higher temperatures for increasing heating rate, in line with previous studies [25,40,152]. The model predicts satisfactorily the general shape and trends of the CYA TGA curves, even though the impact of heating rate is not captured quantitatively.

Figure 4.11: Comparison of model simulation with TGA data of pure biuret (left) and CYA (right) at varying heating rates. The initial sample mass was 50 mg, with a surface area of 0.899 cm².
4.4 Results and discussion

4.4.5 Long-term thermal stability of urea

The long-term thermal stability of urea has been investigated by TGA. Figure 4.12 shows the TGA curves of two urea samples (50 mg), which were heated at 500 °C/min to 280 °C and 380 °C, respectively, and kept isothermally for 96 hours. For the experiment at 280 °C, the majority of the mass loss (~70%) occurs within the first minute. After the initial mass loss, the mass loss rate is seen to decrease drastically, with the TGA mass decreasing further to ~9.5% within a couple of hours. After 96 hours, the TGA mass has decreased to ~6.2% of the initial sample mass. From these results, deposit formation can be expected to occur at exhaust temperatures of 280 °C or below, corresponding to low engine load of maritime diesel engines. The model is seen to accurately describe the initial mass loss, while also capturing the slow decomposition rate after the initial mass loss. It predicts that mainly ammelide is present in the deposit at this temperature, whereas the produced CYA is decomposed after a reaction time of 3 hours. This observation is consistent with the TGA curve of pure ammelide, showing that ammelide begins to decompose at temperatures above 300 °C [25].

For the experiment at 380 °C, the TGA mass is seen to drop to ~3% within the first minute. The sample is seen to be fully decomposed after a reaction time of approximately 50 hours. The model accurately describes the initial mass loss, but overestimates the decomposition rate, as it shows full decomposition after 1 hour. This is likely due to omission of reactions in the model leading to formation of more thermally resistant byproducts.

These results imply that deposit formation in urea-SCR systems can be avoided by keeping the exhaust temperature at 380 °C or above, which corresponds to full engine load of maritime diesel engines [39]. Unfortunately, conclusions from TGA experiments cannot be reliably extrapolated to continuous urea-SCR systems. Therefore, it is not possible to conclude if urea deposition will show similar behavior in practical urea-SCR operation. Nevertheless, the observations made from this analysis have improved the understanding of the deposit behavior under longer reaction times at varying temperatures. It is thus implied that an increased operation temperature can reduce the risk of deposition.

Figure 4.12: Comparison of TGA experiments and simulation of two 50 mg urea samples, heated to 280 °C and 380 °C, respectively. The heating rate was 500 °C/min.
4.5 Conclusions

A kinetic reaction model for urea decomposition was developed, based on a global reaction scheme proposed by Brack et al. [40]. The kinetic parameters of selected reactions have been revised to describe more accurately high heating rate TGA data. The competition between urea evaporation and decomposition was investigated in a solid state Raman spectroscopy setup, a fixed bed reactor, and a TG-FTIR setup. The results showed that decomposition is the dominating mechanism in the process, whereas the extent of urea evaporation is negligible.

The model was validated against TGA data of urea, biuret, and CYA, at heating rates up to 500 °C/min. The results imply that an increasing heating rate causes a shift from production of CYA into ammelide, while reducing the overall deposit formation.

Isothermal TGA of urea extending over 96 hours was performed to investigate the long-term thermal stability of urea. It was shown that a reaction temperature of 280 °C is insufficient to fully decompose urea, whereas at 380 °C urea is fully decomposed after 55 hours.

The developed model is able to give accurate descriptions of the performed TGA with constant heating rate TGA, as well as isothermal TGA experiments. Thus, a reliable model description of the urea decomposition process at higher heating rates, which more closely resembles SCR applications, is possible for the first time.
Modeling the decomposition and byproduct formation of a urea-water-solution droplet

This chapter has been written in a manuscript format. The manuscript has been submitted for publication to the peer-reviewed journal *Chemical Engineering Science* as,


**Abstract:**

A mathematical model for urea-water-solution (UWS) droplet evaporation and decomposition, including a semi-detailed kinetic scheme for byproduct formation, was developed. The model provided a good description of experimental UWS evaporation and decomposition rates. The depletion of 7-70 µm UWS droplets was investigated at ambient temperatures of 200-400 °C corresponding to urea-SCR conditions. The results indicate that the risk of deposition may be reduced by minimizing the droplet size and maximizing the exhaust temperature and reaction time. The present work can provide guidance for designing an efficient evaporation system, to facilitate a stable SCR operation with high NO reduction.

**5.1 Introduction**

Selective catalytic reduction (SCR) of nitrogen oxides (NO<sub>x</sub>) is commonly used in various applications to reduce NO<sub>x</sub> emissions. For mobile sources, a urea-water-solution (UWS, contains 32.5 wt.% urea; brandname: Adblue) has been the preferred additive. In the urea-SCR process, the UWS is sprayed into the exhaust pipe upstream of the catalyst as small droplets in the range of 7-100 µm [39,214]. For marine engines, the exhaust temperature is typically in the range of 200-400 °C depending on the engine load. When the UWS droplets are injected into the hot exhaust, they undergo evaporation and decomposition into NH<sub>3</sub> and HNCO. HNCO is highly reactive in the condensed phase, and is known to participate in a series of reaction pathways leading to the formation of biuret, cyanuric acid (CYA), ammelide, and other heavy-molecular compounds [25,146]. If not minimized, the formation of these byproducts can cause operational problems, e.g., clogging of the injection nozzles and fouling of the catalyst [26,27,32]. These issues have introduced the need for computational tools to optimize operational conditions and minimize the risk of deposition.

A common approach in previous computational efforts has been to treat the depletion of UWS droplets in two separate phases, as documented by Kim et al. [215] and Wang et al. [33]. In the first phase,
water is completely evaporated from the UWS droplet, in a process where intermolecular forces between water and urea are neglected. This evaporation process can be treated in various ways, but generally includes analysis of the gas phase, the liquid phase, and the gas-liquid interface. In the second phase, dry urea undergoes decomposition, which according to Emel’yanenko [216] and Bernhard et al. [138] begin in earnest at 133 °C. This two-stage approach was first employed in the work of Birkhold et al. [39], and later adopted in other modeling studies [38,166,217,218].

Abu-Ramadan et al. [38] questioned whether the presence of urea could be ignored during the water evaporation stage. They pointed to a gradual surface enrichment of urea during evaporation of water, due to diffusion limitations. Eventually, this would lead to entrainment of water in the droplet due to precipitation of urea at the droplet surface. This further causes an increase in the surface temperature, which can initiate decomposition of urea prior to the complete evaporation of water. Vaporization of the entrapped water may also potentiate distortion and micro-explosions of the droplet, as observed experimentally by Wang et al. [33]. This behavior was studied numerically by Ryddner and Trujillo [167], who estimated that the pressure difference inside a UWS droplet may rise to 10 kPa, which cannot be easily equilibrated due to the surface solidification. Their results show that increasing pressure differences can be expected for increasing ambient temperature, in agreement with the observations from Wang et al. [33].

Another common topic of investigation is the urea depletion model. Urea depletion has been treated either as an evaporation process or a decomposition process. Abu-Ramadan et al. [38] found that an evaporation approach gave a higher model accuracy than a decomposition approach based on kinetic expressions adopted from Birkhold et al. [39]. The evaporation approach was also advocated by Lundström et al. [166], who predicted the depletion rates of UWS droplets in the study of Wang et al. [33] with good accuracy by using a vapor pressure model for the evaporation of urea. Bernhard et al. [138] studied evaporation of urea in a flow reactor and measured urea in the gas phase, indicating that urea evaporation may be important. However, in a recent study Krum et al. [219] could not detect gas-phase urea in a combined thermogravimetric analysis (TGA) / Fourier transformed infrared spectroscopy (FTIR) study. Additionally, they showed that gaseous HNCO and NH₃ can recombine into condensable products at lower temperatures, offering an alternative reaction path to urea in the recondensed species. They concluded that decomposition is the dominating mechanism in the depletion of urea.

The decomposition approach was preferred in several computational studies to describe urea depletion [41,165,217]. In the recent study by Gan et al. [165], the decomposition of UWS droplets was modelled by including a kinetic scheme based on ionic reactions to describe the formation of biuret, CYA, and ammelide during urea decomposition. The model was able to accurately describe the evaporation phase in the experimental data from Wang et al. [33], but generally underestimated the decomposition rate of urea. Their calculations, focusing on larger droplets and longer residence times than representative of practical systems, indicated that the ambient temperature was the decisive factor for the required time to reach complete decomposition.
In the present work, a model for UWS evaporation and decomposition including byproduct formation is presented. A kinetic reaction model based on non-ionic species is adopted from previous work Krum et al. [219], and combined with an energy balance based on the work of Abramzon and Sirignano [168]. The kinetic model of Krum et al. [219] was developed to describe TGA mass loss data for urea at medium heating rate conditions (up to 500 °C/min.), while earlier models [41,165] employed kinetic parameters derived based on low heating rate TGA data (≤ 20 °C/min.). For this reason, the present kinetic model presumably extrapolates better to the high heating rate conditions in urea-SCR applications, which based on numerical results from Abu-Ramadan et al. [38] may be in the order of 10^5 °C/min. The model is evaluated against experimental data from Wang et al. [33] and used to investigate the decomposition behavior of UWS droplets at urea-SCR conditions.

5.2 Modeling section

A model for evaporation and decomposition of a spherically symmetric UWS droplet in a heated environment is presented in this section. The model includes a water evaporation model and a kinetic reaction scheme to describe urea decomposition and byproduct formation. The kinetic model includes formation and decomposition of biuret, CYA, ammelide, and triuret, as described in recent work [219]. The initial UWS droplet is characterized by a specified uniform size \( d_0 \), temperature \( T_{l,0} \), and species mass fraction \( Y_{u,0} \). The evaporation and decomposition processes are driven by heat transported from the environment to the droplet. The environment is specified as a hot gas mixture with uniform temperature, pressure, and species (\( T^\infty \), \( P^\infty \), and \( Y_{i,\infty} \)).

5.2.1 Modeling assumptions

The physical and chemical processes involved in the evaporation and decomposition of a UWS droplet are complex. In order to reduce the computational time, a series of simplifying assumptions are introduced:

1. The gas phase is in quasi-steady state due to a much higher thermal diffusivity of the gas phase compared to the liquid phase.
2. The slip velocity between the droplet and the gas phase is zero.
3. The gas phase and liquid phase are both treated as ideal, and at thermodynamic equilibrium at the gas/liquid interface.
4. The heat and mass transfer in the liquid phase are infinitely fast (rapid mixing), resulting in uniform droplet temperature and species concentration profiles.
5. Heat transfer by radiation can be neglected.
6. The water evaporation and urea decomposition can be modelled separately.
5.2.2  Modeling of water evaporation

5.2.2.1  Mass transfer

By employing the assumption of a quasi-steady state gas phase, the mass loss rate of water from the droplet can be determined from the following expression [168]:

\[ \dot{m}_{H_2O} = \pi d_d \rho_g \Gamma_{wv,g} Sh_c \ln(1 + B_M) \cdot (T^\infty / 673) \]  

\( d_d \) is the droplet diameter, \( \rho_g \) is the density of the gas phase, \( \Gamma_{wv,g} \) is the diffusion coefficient of water vapor in air, \( Sh_c \) is the modified Sherwood number, \( B_M \) is the dimensionless mass Spalding number, and \( T^\infty \) is the ambient temperature. Adopting the adjustment coefficient \((T^\infty / 673)\) was found by Gan et al. [165] to provide more accurate results for the evaporation rate of UWS droplets at varying ambient temperatures. The dimensionless mass Spalding number, \( B_m \), for mass transfer by convection and diffusion is defined by:

\[ B_m = \frac{Y_{wv,s} - Y_{wv}^\infty}{1 - Y_{wv,s}} \]  

\( Y_{wv,s} \) and \( Y_{wv}^\infty \) are the mass fraction of water vapor at the surface of the droplet, and far from the droplet, respectively.

5.2.2.2  Heat transfer

An energy balance was established for the UWS droplet including terms for convection, conduction, and evaporation:

\[ \dot{Q}_g = \dot{Q}_{vap} + \dot{Q}_d \]  

The heat transferred from the environment to the droplet by convection was described by [168]:

\[ \dot{Q}_g = -\dot{m}_{H_2O} C_{p,wv} T^\infty - T_d \frac{T^\infty - T_d}{B_T} \]  

Here, \( C_{p,wv} \) is the heat capacity of the water vapor, and \( B_T \) is the dimensionless heat Spalding number, \( B_T \), defined by:

\[ B_T = (1 + B_M)^\varphi - 1 \quad , \quad \varphi = \frac{C_{p,wv} Sh_c}{C_{p,g} Nu_c Le} \]  

\( \varphi \) is a dimensionless parameter, \( C_{p,g} \) is the heat capacity of the gas phase, \( Nu_c \) is the modified Nusselt number, and \( Le \) is the Lewis number.

As the intermolecular forces between water and urea were neglected, the heat of vaporization was calculated from the evaporation enthalpy of water:
5.2 Modeling section

\begin{equation}
\dot{Q}_{vap} = -\dot{m}_{H_2O} \Delta H_{vap,w} \tag{E 5.6}
\end{equation}

The conductive heat transfer in the droplet was described by:

\begin{equation}
\dot{Q}_d = m_d C_{p,d} \dot{T}_d \tag{E 5.7}
\end{equation}

\(C_{p,d}\) is the heat capacity of the liquid mixture. By substituting equations E 5.4 - E 5.7 into equation E 5.3 and rearranging, an expression was found for the temporal change in the droplet temperature:

\begin{equation}
\dot{T}_d = -\frac{\dot{m}}{m_d C_{p,d}} \left( C_{p,\text{vw}} \cdot \frac{T^\infty - T_d}{B_T} - \Delta H_{vap,w} \right) \tag{E 5.8}
\end{equation}

### 5.2.2.3 Dimensionless parameters

The evaporation model includes several dimensionless parameters, including the Spalding numbers \(B_M\) and \(B_T\), which were introduced in section 5.2.2.1 and 5.2.2.2. In this work, the mass and heat transfer are calculated from the modified Sherwood and Nusselt numbers, \(Sh_c\) and \(Nu_c\),

\begin{align*}
Sh_c &= 2 + \frac{Sh_0 - 2}{F_M}, \quad F_M = (1 + B_M)^{0.7} \frac{\ln(1 + B_M)}{B_M} \tag{E 5.9} \\
Nu_c &= 2 + \frac{Nu_0 - 2}{F_T}, \quad F_T = (1 + B_T)^{0.7} \frac{\ln(1 + B_T)}{B_T} \tag{E 5.10}
\end{align*}

\(F_M\) and \(F_T\) are correction factors for the modified Sherwood and Nusselt numbers. The standard Sherwood and Nusselt numbers, \(Sh_0\) and \(Nu_0\), were calculated from the Frossling correlations:

\begin{align*}
Sh_0 &= 2 + 0.552 Re^{1/2} Sc^{1/3} \tag{E 5.11} \\
Nu_0 &= 2 + 0.552 Re^{1/2} Pr^{1/3} \tag{E 5.12}
\end{align*}

The Reynolds, Schmidt, Prandtl, and Lewis numbers were calculated according to:

\begin{align*}
Re &= \frac{\rho_g u_{\text{slip}} d_d}{\mu_g} \tag{E 5.13} \\
Sc &= \frac{\mu_g}{\rho_g \Gamma_{\text{vw},g}} \tag{E 5.14} \\
Pr &= \frac{C_{p,g} \mu_g}{\lambda_g} \tag{E 5.15} \\
Le &= \frac{Sc}{Pr} = \frac{\lambda_g}{C_{p,g} \rho_g \Gamma_{\text{vw},g}} \tag{E 5.16}
\end{align*}

\(u_{\text{slip}}\) is the slip velocity between the gas and the droplet, \(\mu_g\) is the dynamic viscosity of the gas, and \(\lambda_g\) is the thermal conductivity of the gas. Notably, \(Sh_c\) and \(Nu_c\) become equal to 2 when employing
the assumption of zero slip velocity. However, if a slip velocity is taken into account, the calculation of \( \text{Sh}_c \) and \( \text{Nu}_c \) becomes iterative.

5.2.3 Modeling of urea decomposition

The decomposition of a dry urea particle was calculated based on a kinetic model originally proposed by Brack et al. [40] for low heating rate conditions (2-20 °C/min). This scheme was recently modified by Krum et al. [219] to extend its range of validity to higher heating rates, up to 500 °C/min. This range is still well below the values of \( 10^5 \) °C/min estimated for UWS droplets in urea-SCR systems [38], but the model of Krum et al. [219] is expected to provide a more reliable extrapolation. It consists of 14 global reactions for urea decomposition, including formation and decomposition of biuret, CYA, triuret, and ammelide.

An energy balance was established to simulate the conditions of a practical urea-SCR system. The temporal change in the particle temperature was described by equation E 5.17 [165]:

\[
\frac{dT_d}{dt} = \frac{1}{m_d c_p, d} \left( 2\pi r_d \text{Nu}_0 \lambda_d \left(T^\infty - T_d \right) + \dot{m}_d \Delta H_{H, d} \right)^{2/3}
\]

E 5.17

The temporal mass change of the particle was calculated by the kinetic model, based on the depleting volume. The modified Nusselt number, \( \text{Nu}_c \), has been replaced by the Nusselt number for a non-evaporating urea particle, \( \text{Nu}_0 \). The correlations for the physical properties of the particle are presented in section 5.2.4. The surface area of the depleting particle is calculated based on spherical geometry:

\[
A_s = 4\pi \left( \frac{3}{4\pi} V \right)^{2/3}
\]

E 5.18

5.2.4 Material and transport properties

All properties of the individual components in the gas phase and condensed phases during evaporation and decomposition are temperature dependent. Correlations for the gas and liquid phases during evaporation and decomposition are presented in this section.

5.2.4.1 Physical properties of film region

To simplify the calculation of the physical properties of the film region, it was assumed that the droplet is surrounded by dry air. Thus, water vapor from evaporation, and other species from the exhaust gas, were neglected in the calculation of the film properties. A reference temperature of the film was calculated, using an averaging parameter \( A_r \) of 1/3, which has been shown to provide an accurate description of the evaporation of n-heptane droplets [218]:

\[
T_{ref} = T_d + A_r (T^\infty - T_d)
\]

E 5.19
The reference temperature is further used to calculate the physical properties of the film region, including the density, heat capacity, thermal conductivity, viscosity, and diffusion coefficient of water vapor in air, which can be found in Appendix C.

### 5.2.4.2 Physical properties of the liquid phase

The physical properties of the liquid phase during evaporation of water are presented in this section. Because the droplet consists of urea dissolved in water, the physical properties during water evaporation are calculated as a mixture of water and urea. All physical properties of the droplet are temperature dependent, and are calculated based on the droplet temperature. The droplet temperature is assumed to be uniform, but increases over time in a heated environment. Due to evaporation of water, the concentration of urea in the droplet changes transiently. Thus, the physical properties of the droplet are not constant and are evaluated at every time step in the model.

\[
\rho_d = \frac{1}{\sum_{i=1}^{N} \frac{Y_{i,d}}{\rho_{i,d}}} \quad \text{E 5.20}
\]

\[
\rho_w = DT_d^3 + CT_d^2 + BT_d + A \quad \text{E 5.21}
\]

\[
\rho_u = 1278.2 \text{ kg/m}^3 \quad \text{E 5.22}
\]

\[
C_{p,d} = \sum_{i=1}^{N} Y_{i,d}C_{p,i,d} \quad \text{E 5.23}
\]

\[
C_{p,i,d} = DT_d^3 + CT_d^2 + BT_d + A \quad \text{E 5.24}
\]

\[
\Delta H_{vap} = CT_d^2 + BT_d + A \quad \text{E 5.25}
\]

\[
\Delta H_{th,u} = 3096 \text{ kJ/kg} \quad \text{E 5.26}
\]

\[
P_{sat}^{H_2O} = 10^{A-B/(T+C)} \quad \text{E 5.27}
\]

The constants used in the calculations of the physical properties of the liquid phase are presented in Table 5.1.
Modeling the decomposition and byproduct formation of a urea-water-solution droplet

Table 5.1: Parameters for calculating the density and heat capacity of the liquid phase. Due to lack of data, the constants for urea has been used for HNCO, while the constants for CYA has been used for ammelide.

<table>
<thead>
<tr>
<th>Property</th>
<th>Range [°C]</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \rho_w ) [kg/m(^3)]</td>
<td>0-390</td>
<td>1.25 \times 10^3</td>
<td>1.91</td>
<td>5.51 \times 10^{-3}</td>
<td>6.73 \times 10^{-6}</td>
<td>[220]</td>
</tr>
<tr>
<td>( C_{p,w(l)} ) [J/(kg K)]</td>
<td>25-230</td>
<td>5.35 \times 10^3</td>
<td>6.66</td>
<td>7.36 \times 10^{-3}</td>
<td>6.29 \times 10^{-6}</td>
<td>[221]</td>
</tr>
<tr>
<td>( C_{p,u(s)} ) [J/(kg K)]</td>
<td>75-85</td>
<td>197.3</td>
<td>4.73</td>
<td>1.01 \times 10^{-3}</td>
<td>0</td>
<td>[222]</td>
</tr>
<tr>
<td>( C_{p,u(l)} ) [J/(kg K)]</td>
<td>133-290</td>
<td>1.61 \times 10^4</td>
<td>84.90</td>
<td>1.67 \times 10^{-1}</td>
<td>1.06 \times 10^{-4}</td>
<td>[223]</td>
</tr>
<tr>
<td>( C_{p,HNCO(l)} ) [J/(kg K)]</td>
<td>-75-85</td>
<td>197.3</td>
<td>4.73</td>
<td>1.01 \times 10^{-3}</td>
<td>0</td>
<td>[222]</td>
</tr>
<tr>
<td>( C_{p,biuret(l)} ) [J/(kg K)]</td>
<td>175-45</td>
<td>212.1</td>
<td>3.32</td>
<td>1.86 \times 10^{-3}</td>
<td>3.51 \times 10^{-6}</td>
<td>[224]</td>
</tr>
<tr>
<td>( C_{p,CYA(s)} ) [J/(kg K)]</td>
<td>180-75</td>
<td>147.6</td>
<td>3.04</td>
<td>2.75 \times 10^{-4}</td>
<td>0</td>
<td>[225]</td>
</tr>
<tr>
<td>( C_{p,ammelide(s)} ) [J/(kg K)]</td>
<td>180-75</td>
<td>147.6</td>
<td>3.04</td>
<td>2.75 \times 10^{-4}</td>
<td>0</td>
<td>[225]</td>
</tr>
<tr>
<td>( C_{p,triuret(s)} ) [J/(kg K)]</td>
<td>25-1225</td>
<td>253.6</td>
<td>3.46</td>
<td>1.94 \times 10^{-3}</td>
<td>2.10 \times 10^{-7}</td>
<td>[226]</td>
</tr>
</tbody>
</table>

5.3 Results and discussion

5.3.1 Model Assessment

The model has been evaluated against selected experimental data from Wang et al. [33] and Surendran et al. [163] in the temperature range 200-400 °C, corresponding to practical urea-SCR conditions (Figure 5.1). The experiments by Wang et al. [33] were conducted by suspending UWS droplets on quartz fibers with a diameter of 0.125 mm inside an electrically heated furnace at 100 °C to 600 °C. The furnace was continuously purged by dry air during experiments, thereby removing vapors generated from the droplet yielding dry conditions. The relative velocity between the purge gas and the droplet was unspecified, and is therefore considered an uncertainty in the modeling. The experiments were designed to minimize heat transfer by radiation by using radiative shields. Thus, most of the heat transfer to the droplets was attributed to convection. A small degree of heat transfer by conduction can be suspected due to the size of the quartz fiber. However, the conduction is not expected to cause a significant uncertainty, and has not been included in the modeling. The experiments by Surendran et al. [163] were also conducted by suspending UWS droplets on a quartz fiber, and are generally similar to the experiments by Wang et al. [33]. However, the fiber diameter in the experiments of Surendran et al. [163] was considerably lower (25 µm), largely eliminating the heat transfer by conduction. Furthermore, Surendran et al. [163] report a relative slip velocity in the range of 1.1-4.3 m/s, which has been included in the modeling.
The UWS droplet sizes and ambient temperatures in the selected experiments from Wang et al. [33] and Surendran et al. [163] were in the range of 0.815-1.00 mm and 200-400 °C, respectively. In practical urea-SCR systems, the UWS droplets are typically in the range of 1-100 µm [39,214]. Thus, the droplets used in the experiments by Wang et al. [33] and Surendran et al. [163] are not representative of a practical urea-SCR system, but are included for comparative purposes.

In accordance with the d^2-law [170], the initial depletion rate of the UWS droplets in Figure 5.1, corresponding to evaporation of water, is seen to be linear. The evaporation rates of UWS droplets in the selected experiments from Wang et al. [33] and Surendran et al. [163] are accurately predicted. The evaporation rates reported by Surendran et al. [163] are significantly higher than those of Wang et al. [33]; this is captured well by the model. The main differences between the two experimental sets are the slip velocity and choice of suspender.

The decomposition rate of urea is seen to be drastically lower than the evaporation rate of water. The higher evaporation and decomposition rates observed by Surendran et al. [163] may be due to the increased convection compared to the experiments by Wang et al. [33]. The increased slip velocity may also enhance the fragmentation of the droplets at higher temperatures, thus accelerating the depletion process. Additionally, previous studies have shown that the choice of suspender may affect the evaporation and decomposition rate [227–230].

The model clearly underestimates the decomposition rates of the UWS droplets from Wang et al. [33] and Surendran et al. [163], but yields comparable results to the modeling studies by Gan et al. [165] and Ryddner and Trujillo [167]. The model cannot capture the distortion of the UWS droplets caused by micro-explosions, which are most pronounced at temperatures above 300 °C. Ryddner and Trujillo [167] suggest that the internal concentration gradients are slower to equilibrate at higher temperatures, resulting in a faster solidification of urea at the droplet surface and thereby enhancing the occurrence of micro-explosions. The occurrence of micro-explosions is expected to increase the decomposition rate, as the initial droplet is fragmented into smaller droplets, which in part explains the underestimated decomposition rates. It is also possible that the model underestimates the effect of slip velocity on the decomposition process, but it seems unlikely that the difference in slip velocity is solely responsible for the observed difference in the evaporation and decomposition rates between the two experimental sets.

Despite the deviations between modeling predictions and observed urea decomposition rates, the model is used in the next section to simulate conditions relevant for practical SCR systems. Under actual SCR conditions, the droplets are much smaller than those used in the experimental work of Wang et al. [33] and Surendran et al. [163] and uncertainties related to micro-explosions, slip velocity, and heat transfer through the droplet holder are largely eliminated.
Figure 5.1: Comparison between the experimental data from Wang et al. (2009) and Surendran et al. [163], and numerical predictions using the present model. The conditions in the experiments by Wang et al. (2009) was: (a) $T_\infty = 200 \, ^\circ\text{C}$, $T_{l,0} = 27 \, ^\circ\text{C}$, $P = 1 \, \text{atm}$, $u = 0 \, \text{m/s}$, $d_0 = 0.870 \, \text{mm}$, $Y_{u,0} = 0.325$, $Y_{w,\infty} = 0$; (b) $T_\infty = 300 \, ^\circ\text{C}$, $T_{l,0} = 27 \, ^\circ\text{C}$, $P = 1 \, \text{atm}$, $u_{slip} = 0 \, \text{m/s}$, $d_0 = 0.920 \, \text{mm}$, $Y_{u,0} = 0.325$, $Y_{w,\infty} = 0$; and (c) $T_\infty = 400 \, ^\circ\text{C}$, $T_{l,0} = 27 \, ^\circ\text{C}$, $P = 1 \, \text{atm}$, $u_{slip} = 0 \, \text{m/s}$, $d_0 = 0.815 \, \text{mm}$, $Y_{u,0} = 0.325$, $Y_{w,\infty} = 0$. The conditions in the experiments by Surendran et al. [163] was: (a) $T_\infty = 200 \, ^\circ\text{C}$, $T_{l,0} = 27 \, ^\circ\text{C}$, $P = 1 \, \text{atm}$, $u_{slip} = 2.4 \, \text{m/s}$, $d_0 = 1.00 \, \text{mm}$, $Y_{u,0} = 0.325$, $Y_{w,\infty} = 0$; (b) $T_\infty = 300 \, ^\circ\text{C}$, $T_{l,0} = 27 \, ^\circ\text{C}$, $P = 1 \, \text{atm}$, $u_{slip} = 3.1 \, \text{m/s}$, $d_0 = 1.00 \, \text{mm}$, $Y_{u,0} = 0.325$, $Y_{w,\infty} = 0$; and (c) $T_\infty = 400 \, ^\circ\text{C}$, $T_{l,0} = 27 \, ^\circ\text{C}$, $P = 1 \, \text{atm}$, $u_{slip} = 4.3 \, \text{m/s}$, $d_0 = 0.92 \, \text{mm}$, $Y_{u,0} = 0.325$, $Y_{w,\infty} = 0$. 

Modeling the decomposition and byproduct formation of a urea-water-solution droplet
5.3.2 UWS droplet decomposition

It is of interest to study the decomposition of UWS droplets at conditions representative of a urea-SCR system, in order to determine optimal urea-SCR conditions. Thus, the modeling was conducted for 7 µm and 70 µm UWS droplets in a temperature range of 200–400 °C. The velocity of the exhaust from marine engines is typically around 30–40 m/s, yielding short gas residence times in the evaporation zone of 10–120 ms [214]. The injected droplets are expected to follow the gas flow with zero slip velocity, and therefore the timespan in the simulations was set to 120 ms. By assuming zero slip velocity, and thus neglecting convective heat transfer, the evaporation and decomposition may be slightly underestimated. The simulations presented in Figure 5.2 show that the evaporation and decomposition rate of a UWS droplet highly depends on the droplet size, ambient temperature, and residence time.

The wet-bulb temperature of the UWS droplets during water evaporation is around 50–70 °C. When the drying is nearly complete, the droplet temperature increases at a high heating rate, and reaches a new equilibrium temperature, when the droplet has been completely dried. The predicted droplet temperature profiles cannot be validated due to lack of experimental data, but are comparable with other modeling studies [38].

It was found that 7 µm UWS droplets experience rapid evaporation of the water at ambient temperatures of 200–400 °C. In contrast, the 70 µm droplets require an ambient temperature of 400 °C to reach complete drying within a reaction time of 120 ms, yielding insufficient time for decomposition of urea. Therefore, minimizing the droplet size may reduce the amount of deposition on the catalyst and the wall. Although impingement on the wall would yield longer reaction times, it is generally undesirable as the wall temperature is lower than the gas temperature. Thus, droplets impinging on the wall would lead to slower evaporation and decomposition rates, which may cause a build-up in the deposition. Minimizing the initial droplet size is therefore assessed to be favorable, in order to reduce the risk of deposition.

As illustrated in Figure 5.2, the evaporation and decomposition processes are also very sensitive to the ambient temperature. Although 200 °C and 300 °C are sufficient to completely dry a 7 µm droplet, the conversion of urea after a reaction time of 120 ms at this temperature is practically zero, increasing the potential for deposition. According to the model, a droplet size of 7 µm, combined with a temperature of 400 °C, still leads to significant decomposition within the given timespan. For these conditions, it was predicted that the deposit consists mainly of ammelide, which is known to be relatively stable at 400 °C. Hence, none of the investigated conditions yielded complete conversion of urea. However, the simulations indicate that the extent of evaporation and decomposition is influenced by several factors, including initial droplet size, ambient temperature, and reaction time. Based on the modeling predictions, it is recommended that the initial droplet size should be minimized, while the ambient temperature should be kept as high and stable as possible. Increasing the reaction time by extending the evaporation zone may also increase the conversion efficiency of urea, but is usually not practically feasible due to lack of space.
Figure 5.2: Numerical predictions for the transient evolution in the droplet mass for varying initial droplet size and ambient temperature. The following conditions are similar for all 6 simulations; $T_{l,0} = 27$ °C, $P = 1$ atm., $u_{slip} = 0$ m/s, $Y_{u,0} = 0.325$, $Y_{w,0} = Y_{w,\infty} = 0$. 
5.4 Conclusion

A model for UWS evaporation and decomposition including byproduct formation was developed. The evaporation process was described by the Abramzon and Sirignano model [168], while the decomposition process was described by the reaction scheme of Krum et al. [219]. Modeling predictions were compared with experimental data from Wang et al. [33] and Surendran et al. [163]. The model accurately predicted the evaporation rates of 0.815-0.920 mm UWS droplets at ambient temperatures of 200-400 °C, but the urea decomposition rates were underestimated. This is explained by the occurrence of micro-explosions in the comparably large droplets in the experiments that is not captured by the model.

The evaporation and decomposition characteristics of UWS droplets were found to depend on the initial droplet size, ambient temperature, and residence time. Generally, smaller droplet size, larger ambient temperature, and larger residence time lead to faster evaporation and decomposition rates. Hence, optimization of the UWS injection system to reduce the droplet size is favorable to reduce the risk of deposition. Additionally, operating at a high non-fluctuating engine load to maintain a high and stable exhaust temperature may also be favorable to reduce the risk of deposition. The results indicate that full conversion may not be possible within the typical range of the process parameters in urea-SCR systems.
Modeling the decomposition and byproduct formation of a urea-water-solution droplet
6 Concluding remarks and future work

6.1 Summary of conclusions

Chapter 2 provides an overview of the NO formation mechanisms, along with existing techniques for NO reduction in stationary combustion sources. Emphasis was given to the SNCR process for NO reduction, reviewing the effects of important process parameters on NO reduction. Furthermore, experimental and numerical efforts on the urea decomposition and byproduct formation process in urea-SCR systems were reviewed.

Chapter 3 presents the experimental and numerical results on SNCR with ammonium sulfate, along with the effects of SO\textsubscript{2} and KCl on NO reduction. Experiments were conducted in a flow reactor setup, with a liquid feeding system to supply the additive. The results were compared with numerical predictions of a newly developed detailed kinetic model, including descriptions of the SNCR chemistry and decomposition of ammonium sulfate. The main conclusions from this work are:

- Ammonium sulfate (AS) can achieve up to 95 % NO reduction in the SNCR process, in a temperature interval of 1025-1075 °C at AS/NO molar ratios of 1.1-2.3. The results were well described by the kinetic model, which predicted a maximum of 90 % NO reduction in a similar operating window as experimentally observed. However, the NO reduction was slightly underestimated above the optimum temperatures, attributed to an overestimation of the O/H radical pool.

- The experimental and numerical SNCR results with NH\textsubscript{3}, in absence and presence of SO\textsubscript{2}, showed a negligible effect of SO\textsubscript{2} on NO reduction for the investigated conditions.

- Prolonging the residence time from 151/T(K) s to 6686/T(K) s caused a downwards shift in the operating temperature window when using ammonium sulfate. The effect of increasing the residence time was well captured by the model.

- The effect of KCl on NO reduction while using ammonium sulfate as additive was investigated. Preliminary results of the investigation showed that addition of KCl has a promoting effect on NO reduction. A similar degree of NO reduction to that without addition of KCl was observed, but the temperature for onset of reaction was shifted by 100 °C towards lower temperatures, and the operating window was widened. However, the effect was not captured by the model, and it was not possible to determine if the effect was caused by gas phase or condensed phase interactions of KCl with the nitrogen chemistry. Finally, the results implied a 60 % degree of KCl sulfation by ammonium sulfate at 1025 °C. These results demonstrated
the potential of ammonium sulfate to simultaneously reduce NO and KCl induced corrosion in practical combustion plants.

Chapter 4 presents experimental investigations of the mechanisms for urea decomposition, along with numerical results from a kinetic reaction model describing urea decomposition and byproduct formation. The kinetic model was derived from TGA experiments of urea, biuret, CYA, and ammelide under low to medium heating rate conditions (5-500 °C/min). The main findings from this work are:

- Experimental investigations of the urea depletion behavior indicated that decomposition is the dominating mechanism, whereas evaporation of urea is negligible.
- TGA results of urea decomposition at 5-500 °C/min implied that an increasing heating rate causes a shift in production of CYA to ammelide, while reducing the overall deposit formation.
- The characteristics of the urea, biuret, and CYA TGA curves are well described by the model for varying heating rates. Thus, the model gives reliable descriptions of the urea decomposition process at medium heating rates that more closely resemble the conditions in practical urea-SCR systems.
- Isothermal TGA experiments of urea extending over 96 hours demonstrated that a reaction temperature of 280 °C is insufficient to fully decompose urea, whereas 380 °C yielded complete decomposition after 55 hours. The model gives accurate description of the isothermal urea TGA data at 280 °C, but overestimates the decomposition rate at 380 °C.

Chapter 5 presents the numerical results of a developed model for UWS evaporation and decomposition in urea-SCR systems. The model was comprised of a droplet evaporation model, combined with a kinetic reaction scheme for urea decomposition and byproduct formation. The main conclusions from this work are:

- The model for UWS droplet evaporation and decomposition was validated against UWS depletion experiments conducted at ambient temperatures of 200-400 °C. The evaporation rates of 0.82-0.92 mm UWS droplets at these temperatures were well described, but the decomposition rates were underestimated, most pronounced at higher temperatures. The model discrepancy was attributed to experimental uncertainties related to the occurrence of micro-explosions of UWS droplets.
- The model was used to predict the evaporation and decomposition behavior of 7-70 μm UWS droplets at 200-400 °C. In general, smaller droplet size, higher ambient temperature, and longer residence time lead to a higher conversion of the UWS droplets. Moreover, the results indicated that full conversion of the droplets may not be possible under typical conditions of urea-SCR systems, and considerable amounts of urea and byproducts can be expected to deposit on the catalyst.
6.2 Suggestions for future work

The results in this work provide an improved understanding of the SNCR process with ammonium sulfate, along with the effects of SO$_2$ and alkali metals on the SNCR chemistry. Furthermore, the work has given valuable insight in the urea decomposition process. However, additional work could be conducted in these fields to shed light on some topics that remain uncertain. A few suggestions for additional investigations are described below.

**Additional SNCR experiments with ammonium sulfate and alkali metals.**

The preliminary results on SNCR with ammonium sulfate and alkali metals show a promising potential for the industrial use of ammonium sulfate in SNCR processes. However, more work is desirable to gain a deeper understanding of the effects of alkali metals on the nitrogen chemistry, as well as the alkali transformations under SNCR conditions. Using the current setup, it could be interesting to collect and analyze particles downstream of the reactor at varying operating temperatures, to determine the composition of the particles. Such experiments could also be used to validate the mechanisms for interactions of alkali metals with the nitrogen chemistry. Additionally, it could be interesting to use the current setup to investigate the effects of other alkali metals on NO reduction.

**Investigation of the KCl sublimation behavior.**

The sublimation rate of KCl under the investigated conditions is expected to be fast, but experimental evidence of KCl in the gas phase is lacking. The sublimation behavior of KCl could possibly be investigated in a fixed bed reactor setup, with addition of solid KCl particles and a mixture of SO$_2$/SO$_3$, while measuring HCl in the effluent gas. In absence of ammonia downstream of the reactor, HCl can presumably be a reliable indication of the KCl sulfation.

In addition, it could be useful to estimate the KCl sublimation rate by employing the UWS droplet evaporation model. By implementing thermodynamic properties of KCl instead of urea, it may be possible to estimate the required time for complete drying and sublimation of aqueous KCl droplets.

**Reliable gas phase analysis of ammonium sulfate decomposition.**

In the present work, ammonium sulfate is assumed to decompose solely into NH$_3$, SO$_3$, and H$_2$O for all investigated temperatures. However, previous work on ammonium sulfate decomposition has indicated that sulfur is released as a mixture of SO$_2$/SO$_3$, and the distribution is temperature dependent. Therefore, it is desirable to further investigate the decomposition behavior of ammonium sulfate under well-controlled conditions, as the yield of SO$_2$ and SO$_3$ has a significant influence on the alkali transformation. However, as NH$_3$ and SO$_3$ may react at lower temperatures to form condensed products, the current setup cannot provide a reliable gas phase analysis of ammonium sulfate decomposition.
Concluding remarks and future work

Temperature measurements of urea samples or UWS droplets in heated environments.

Presently, validation of UWS evaporation and decomposition models rely solely on measurements of the droplet size at varying ambient temperatures. Temperature measurements of decomposing urea samples and UWS droplets are lacking, and therefore it has not been possible to evaluate the predicted droplet temperature profiles. Experimental investigations of the temperature profile during decomposition of urea could improve the understanding of the thermal behavior. One possibility could be to record UWS droplets in heated environments by IR spectroscopy. However, derivation of the temperature profile from such an approach requires details about the emissivity of the droplets and the surrounding, which is not easily obtainable.
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Appendix A – Supplementary material to Paper A

Water measurements in SNCR experiments

Figure A. 1 shows the water measurements of SNCR experiments using aqueous ammonium sulfate solutions in the large reactor with a residence time of $6686/T(K)$ s. For the first 25 min of the experiments, carrier gas was sent through the mist tank while the humidifier was idle. After activating the humidifier at approximately 25 min, the water concentration increased by approximately 1.5 % in each of the experiments.

Figure A. 2 shows the water measurements of SNCR experiments using 5 wt. % AS solutions with and without addition of KCl in the small reactor with a residence time of $151/T(K)$ s. The humidifier was activated after approximately 55 min, resulting in an increase in the water concentration by approximately 6 %.

The difference in water concentration caused by activating the humidifier was used to quantify the additive feeding rate in every experiment.

![Figure A. 1: Water measurements by FTIR spectroscopy in SNCR experiments using aqueous ammonium sulfate solutions as additive in the large reactor with a residence time of 6686/T(K) s.](image)
Figure A. 2: Water measurements by FTIR spectroscopy in SNCR experiments using 5 wt.% AS solutions with and without addition of KCl as additive in the small reactor with a residence time of $151/T(K)$ s.
Droplet size measurements

Figure A. 3 shows the average droplet sizes generated by the humidifier, measured by a high-speed camera (Imperx B2520 CCD Camera). The setup further used a LED light source for illumination of the droplets (Pyrooptic LP-1000). Four different cases were tested, to investigate the influence of additive concentration and tube length on the droplet size. The average droplet size was found to be approximately 1 µm, and the size of droplets was not influenced by the additive concentration or tube length. However, the droplet density was reduced when using the tube, indicating that parts of the droplets deposit in the tube. Therefore, the tube length was minimized in the actual SNCR experiments, to obtain the highest possible additive feeding rate.

Figure A. 3: Average size distributions of droplets generated by the humidifier for different cases. Top left: Droplets of pure water are measured directly upon leaving the tank. Top right: Droplets of pure water are first sent through a 50 cm tube before being analyzed. Bottom left: Droplets of a 20 wt. % AS solution are measured directly upon leaving the tank. Bottom right: Droplets of a 20 wt.% AS solution are first sent through a 50 cm tube before being analyzed.
Urea SNCR experiment

Figure A. 4 shows results for an SNCR experiment using urea as additive. The experiment was conducted with a 5 wt. % UWS, with a total gas flow of 1000 ml/min. The mole fraction of NH₃ and HNCO was calculated to 946 ppm, assuming instantaneous conversion of urea into NH₃ and HNCO at a 1:1 molar ratio upon entering the reactor. The onset of reaction was found to occur at around 925 °C, with the highest NO reduction at around 1100 °C. Despite differences in reactor configuration and conditions, the results agree fairly well with experimental data from Alzueta et al. [231] and Rota et al. [232,233]. However, the results in the present work showed a slightly broader temperature window, located at a slightly higher temperatures. These results demonstrate that the developed additive feeding system works, and can supply the necessary amounts of additive to the reactor for efficient NO reduction.

**Figure A. 4:** Experimental results for SNCR using a 5 wt. % UWS. The inlet composition was: NO = 400 ppm, NH₃ = 946 ppm, HNCO = 946 ppm, O₂ = 1 vol. %, H₂O = 9.5 vol. %, balance N₂. The residence time in the reactor was 151/T(K) s. The results from Alzueta et al. [231] were obtained in a laminar flow reactor with inlet concentrations: urea = 150 ppm, NOᵢₙ = 300 ppm, O₂ = 4 vol. %, H₂O = 4 vol. %, residence time (s) = 200/T(K). The results from Rota et al. [232] were obtained in a jet-stirred reactor with inlet concentrations: urea = 300 ppm, NOᵢₙ = 500 ppm, O₂ = 4 vol. %, H₂O = 19 vol. %, residence time (s) = 200/T(K).
Appendix B – Supplementary material to Paper B

Raman spectroscopy raw data

The material presented in Figure B. 1 - Figure B. 10 show the solid state Raman spectra acquired of recondensed vapors and deposits, generated from urea decomposition experiments at various temperatures. The Raman spectra of the recondensed vapors and deposits are compared with reference Raman spectra of pure urea, biuret, and cyanuric acid (CYA) samples.

![Raman spectrum](image)

**Figure B. 1:** Solid state Raman spectrum of the recondensed vapors generated from urea decomposition at 175 °C, and of a pure urea sample. The spectra are acquired at room temperature. The sample mass was 10 mg, and the heating rate was 10 °C/min.
Figure B. 2: Solid state Raman spectrum of the deposit generated from urea decomposition at 175 °C, and of a pure urea sample. The spectra are acquired at room temperature. The sample mass was 10 mg, and the heating rate was 10 °C/min.

Figure B. 3: Solid state Raman spectrum of the recondensed vapors generated from urea decomposition at 225 °C, and of a pure urea sample. The spectra are acquired at room temperature. The sample mass was 10 mg, and the heating rate was 10 °C/min.
Figure B. 4: Solid state Raman spectrum of the deposit generated from urea decomposition at 225 °C, and of a pure cyanuric acid (CYA) sample. The spectra are acquired at room temperature. The sample mass was 10 mg, and the heating rate was 10 °C/min.

Figure B. 5: Solid state Raman spectrum of the recondensed vapors generated from urea decomposition at 275 °C, and of a pure urea sample. The spectra are acquired at room temperature. The sample mass was 10 mg, and the heating rate was 10 °C/min.
Figure B. 6: Solid state Raman spectrum of the deposit generated from urea decomposition at 275 °C, and of a cyanuric acid (CYA) sample. The spectra are acquired at room temperature. The sample mass was 10 mg, and the heating rate was 10 °C/min.

Figure B. 7: Solid state Raman spectrum of the recondensed vapors generated from urea decomposition at 325 °C, and of a cyanuric acid (CYA) sample. The spectra are acquired at room temperature. The sample mass was 10 mg, and the heating rate was 10 °C/min.
Figure B. 8: Solid state Raman spectrum of the deposit generated from urea decomposition at 325 °C, and of a cyanuric acid (CYA) sample. The spectra are acquired at room temperature. The sample mass was 10 mg, and the heating rate was 10 °C/min.

Figure B. 9: Solid state Raman spectrum of the recondensed vapors generated from urea decomposition at 370 °C, and of a cyanuric acid (CYA) sample. The spectra are acquired at room temperature. The sample mass was 10 mg, and the heating rate was 10 °C/min.
Figure B.10: Solid state Raman spectrum of the deposit generated from urea decomposition at 370 °C, and of a cyanuric acid (CYA) sample. The spectra are acquired at room temperature. The sample mass was 10 mg, and the heating rate was 10 °C/min.
Physical properties of the film region

The following material describes the equations and parameters used in the calculation of the physical properties of the film surrounding the UWS droplet. The density is calculated from the ideal gas law, whereas the other properties are calculated from polynomial correlations:

\[ \rho_{air} = \frac{P_\infty W_{air}}{R T_{ref}} \]

\[ C_{p,air} = DT_{ref}^3 + CT_{ref}^2 + BT_{ref} + A \]

\[ \lambda_{air} = CT_{ref}^2 + BT_{ref} + A \]

\[ \mu_{air} = CT_{ref}^2 + BT_{ref} + A \]

\[ \Gamma_{w,air} = CT_{ref}^2 + BT_{ref} + A \]

The constants used in the correlations for the film properties are presented in Table C.1:

**Table C.1:** Parameters for calculating the physical properties of the film region surrounding the UWS droplet.

<table>
<thead>
<tr>
<th>Property</th>
<th>Range [°C]</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_{p,air} ) [J/(kg K)]</td>
<td>-175-725</td>
<td>1.07\cdot10^3</td>
<td>-0.526</td>
<td>1.17\cdot10^{-3}</td>
<td>-5.79\cdot10^{-7}</td>
<td>[221]</td>
</tr>
<tr>
<td>( \lambda_{air} ) [W/(m K)]</td>
<td>-15-1125</td>
<td>6.78\cdot10^{-3}</td>
<td>6.81\cdot10^{-5}</td>
<td>-5.65\cdot10^{-9}</td>
<td>0</td>
<td>[234]</td>
</tr>
<tr>
<td>( \mu_{air} ) [Pa s]</td>
<td>-15-1125</td>
<td>5.09\cdot10^{-6}</td>
<td>4.83\cdot10^{-8}</td>
<td>-1.05\cdot10^{-11}</td>
<td>0</td>
<td>[234]</td>
</tr>
<tr>
<td>( \Gamma_{w,air} ) [m^2/s]</td>
<td>20-400</td>
<td>-2.78\cdot10^{-5}</td>
<td>1.51\cdot10^{-7}</td>
<td>8.82\cdot10^{-11}</td>
<td>0</td>
<td>[221]</td>
</tr>
</tbody>
</table>