Modeling the Fate of Nitrogen in Supercritical Water Oxidation

by

Jinzhou Fan

Department of Civil and Environmental Engineering
Duke University

Date:_______________________
Approved:

_________________________
Marc Deshusses

_________________________
Claudia Gunsch, Advisor

_________________________
Michael Howard Bergin

Thesis submitted in partial fulfillment of
the requirements for the degree of
Master of Science in the Department of
Civil and environmental Engineering in the Graduate School
of Duke University

2020
ABSTRACT

Modeling the Fate of Nitrogen in Supercritical Water Oxidation

by

Jinzhou Fan

Department of Civil and Environmental Engineering
Duke University

Date: ____________________

Approved:

___________________________
Marc Deshusses

___________________________
Claudia Gunsch, Advisor

___________________________
Michael Howard Bergin

An abstract of a thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in the Department of Civil and environmental Engineering in the Graduate School of Duke University

2020
Abstract

Supercritical water oxidation (SCWO) is an emerging transformative technology for the treatment of all kinds of organic wastes. When treating substances containing nitrogen such as municipal sludge, ammonia and nitrous oxide are frequently observed in the outlet streams of SCWO systems. In this study, a mathematical model was established to simulate nitrogen reactions during SCWO in order to understand the kinetics of ammonia formation and reduce nitrous oxide generation. The final model was validated with actual data obtained with the Duke pilot SCWO system and served to provide guidance on SCWO operation.

The research presented herein showed that the assumed kinetics and simplified model can predict the outcome of the Duke SCWO system well. The prediction results for the ammonia, nitrate in effluent and COD conversion rate was close to the experiment data.

According to the model, increasing temperature can reduce the ammonia, nitrate and N₂O production rate, and promote nitrogen conversion to N₂. To control the emission of N₂O, the operation can focus on increasing reactor temperature and finding conditions, additives or catalyst that promote NO₂ radical decomposition.
Contents

Abstract .................................................................................................................................................. iv

List of Tables .......................................................................................................................................... vii

List of Figures ......................................................................................................................................... viii

1. Introduction ........................................................................................................................................ 1

2. Objective ............................................................................................................................................ 6

3. Methodology ....................................................................................................................................... 7

   3.1 Apparatus .................................................................................................................................... 7

   3.2 Inorganic nitrogen measurements and baseline performance ...................................................... 9

   3.3 Organic nitrogen and FTIR test for basic characterization ........................................................... 10

4. Modeling the fate of N species during SCWO ..................................................................................... 12

   4.1 Chemical reaction and kinetics background ................................................................................. 13

      4.1.1 N species in the inlet and outlet of the reactor .................................................................... 14

      4.1.2 Organic nitrogen reactions ................................................................................................. 15

      4.1.3 Denitrification pathway ....................................................................................................... 16

      4.1.4 Nitrate reduction ................................................................................................................. 17

      4.1.5 NO\textsubscript{2} consumption ............................................................................................... 18

      4.1.6 Hydroxyl radical and oxygen generation ............................................................................. 18

   4.2 Model structure ............................................................................................................................ 20

      4.2.1 Mass balance structure ....................................................................................................... 21

      4.2.2 Mass balance of the organics with -NH\textsubscript{2} in first CSTR ........................................... 22
List of Tables

Table 1: Laboratory nitrogen test method ................................................................. 9
Table 2: Standard curve of FTIR .............................................................................. 11
Table 3: Porportion of nitrogen functional groups in biosolids ............................... 35
Table 4: Operation parameters for two experiments ............................................... 41
Table 5: Output of Experiment 1 and model simulation ......................................... 42
Table 6: Output of Experiment 2 and model simulation .......................................... 42
Table 7: Exhausted gas of model and Experiment ..................................................... 43
List of Figures

Figure 1: Schematic diagram of Duke SCWO system .......................................................... 7
Figure 2: FTIR test and functional group adsorption ............................................................ 11
Figure 3: High level pathways for nitrogen reaction ............................................................ 13
Figure 4: Proposed pathways for the kinetic modeling of nitrogen reaction in SCWO . 19
Figure 5: Modeling the turbular reactor by discretizing space ........................................... 20
Figure 6: Array CSTR model ............................................................................................... 20
Figure 7: Density of water at from 650K to 1500K and 250 bar ........................................... 30
Figure 8: Density of air at from 650K to 880K and 250 bar ................................................ 30
Figure 9: Heat capacity of water from 650K to 1500K and 250 bar ..................................... 33
Figure 10: Heat capacity of air at from 650K to 880K and 250 bar ...................................... 34
Figure 11: Example of FTIR test including amine standard curve and sludge test ........... 36
Figure 12: Amine standard curve development in FTIR ...................................................... 36
Figure 13: Nitro group standard curve development in FTIR ............................................. 37
Figure 14: Nitrogen mass balance ....................................................................................... 40
Figure 15: Parametric plot of the ammonia and nitrate flow rate vs reactor temperature ... 44
Figure 16: Parametric plot of the R4 reaction rate vs reactor temperature ......................... 45
Figure 17: N2 and N2O molar flow rate (mol/s) in outlet vs temperature ......................... 46
Figure 18: Parametric plot of the R6 and R11 reaction rates vs temperature ....................... 47
Figure 19: N2O molar flow rate (mol/s) in outlet vs R11 activation energy ....................... 48
1. Introduction

Supercritical water oxidation (SCWO) is an emerging advanced oxidation technology for the treatment of organics found in a wide range of wastes. Supercritical water (SCW) refers to water above its critical point of 374 °C and 22.1 MPa. In this condition, the thermodynamic properties of supercritical water make it completely miscible with all organics and gases, as well as a superior medium for oxidation processes. (Al-Duri, Alsoqyiani, & Kings, 2016; Chern, 2013; Schmieder & Abeln, 1999)

In supercritical water oxidation, organics, air (or oxygen), and water are mixed and pressurized typically around 220 bar and temperatures above 400 °C. At these conditions, oxidation is initiated spontaneously and the heat of oxidation results in a temperature increase to 550-650 °C depending on the concentration of the organics undergoing treatment and their calorific content. (Webley, Tester, & Holgate, 1991) Organics are destroyed rapidly with conversions to carbon dioxide at yields above 99.99% at residence times of less than 1 min, more frequently in the order of 5-10 seconds. Inorganics are oxidized and precipitated out of solution as inorganic salts. (Thomason & Modell, 1984) Additionally, SCWO has other advantages, such as little toxic emissions, few ash formation, and no pre-drying requirement. (Al-Duri et al., 2016) Furthermore, SCWO is exothermic, producing energy from the oxidation of organics to achieve self-sustained treatment. (Cocero, Alonso, Sanz, & Fdz-Polanco, 2002) Such advantages potentially place SCWO as a promising alternative technology of
incineration, landfill and disposal (Defra, 2015) in treating toxic and bio-refractory wastes, such as biocides (Baur, Schmidt, Krämer, & Gerber, 2005), wastewater, sewage sludge (Goto, Nada, Kodama, & Hirose, 1999) and waste leachate (Zou et al., 2013).

Although organic substances destruction has been frequently studied in supercritical water reactors, little research efforts have been placed on reactions of other elements common to waste streams. Nitrogen, in particular, is present in many waste streams of interest. (Dell’Orco, Gloyna, & Buelow, 1997) Although SCWO is highly efficient for organics oxidation, its end products, which include ammonia, nitrate, and nitrogen oxides (in particular nitrous oxide which is a greenhouse gas), can be factors limiting its application to large-scale processes. (Segond, Matsumura, & Yamamoto, 2002)

On one hand, ammonia has been proved as a predominant and stable product from several waste streams targeted for treatment with SCWO. Shanableh and Gloyna (Shanableh & Gloyna, 1991) and Tongdhamachart (Tongdhamachart, 1990) applied SCWO to treat industrial and municipal sludges, reporting ammonia as a refractory reaction product at a temperature over 400 °C. In a more basic study on SCWO, Webley demonstrated that ammonia was primarily unreacted at temperature even over 600 °C and pressure at 248 bar. (Webley et al., 1991) The same result was also reported in Takahashi and Hong’s research on treating metabolic wastes. (Hong, Fowler, Killilea, & Swallow, 1987; Takahashi, Wydeven, & Koo, 1989) On the other hand, due to the high
content of nitrogen in sludge and in air (when air is used as oxidant), the oxidation process in SCWO could lead to a significant amount of nitrogen oxides, and particularly to nitrous oxide (N\textsubscript{2}O) which is a toxic compound and a greenhouse gas (with a global warming potential which is 298 times that of carbon dioxide over 100 years) (Marias, Benzaoui, Vaxelaire, Gelix, & Nicol, 2015). Benjaminet et al. investigated the oxidation of methylamine at 250 bar and 390–500 °C, and concluded that the major N-containing products were N\textsubscript{2}, NH\textsubscript{3}, N\textsubscript{2}O (Benjamin & Savage, 2005b). Li and Oshima studied the elementary reaction of methylamine in SCWO system, showing that NH\textsubscript{3} and N\textsubscript{2} were the major products, meanwhile trace amounts of NO\textsubscript{x}, like N\textsubscript{2}O and NO\textsubscript{2}, were detected (H. Li & Oshima, 2005).

Considering the regulation of discharging ammonia and nitrate into the received stream, and the toxicity and environmental concerns of nitrous oxides, the fate of nitrogen in SCWO needs to be better understood to advance the development and the industrial application of SCWO process. To date, some research exists on SCWO of N-containing compounds such as ammonia, nitrate, aniline, nitrophenol, indole, quinazoline etc. (B. Yang, Cheng, Tang, & Shen, 2018). Benjamin et al. studied the oxidation of methylamine and concluded the products as N\textsubscript{2}, NH\textsubscript{3}, N\textsubscript{2}O (Benjamin & Savage, 2005a, 2005b). Shimoda et al. increased the conversion of ammonia to nitrogen gas and nitrate by adding methanol at 250 bar and 530 °C. (Shimoda, Fujii, Hayashi, & Oshima, 2016) Guo et al. investigated the reaction of indole in SCW in the lab-scale and
found that hydrogen and carbon organic compounds gasification rate up to 79% and 20%, respectively, under 550-700°C (Liu, Jin, Wei, & Guo, 2016). Killilea et al. investigated the decomposition of NH₃ with ethanol, taking urea as a sample to generate NH₃. At 690 °C and 23 MPa, complete decomposition of NH₃ was observed in the presence of ethanol.

At a temperature range of 525-608 °C, N₂O was produced more than N₂ (Killilea, Swallow, & Hong, 1992). Cocero et al. studied the nitrogen fate from the decomposition of some N-containing compounds with 2-propanol as co-fuel using SCWO. Results showed that nitrate presented in effluent at 645 °C and 25 MPa but N₂O was not tested (Cocero, Alonso, Torio, Valvelado, & Fdz-Polanco, 2000). Dell’Orco et al.’s research on nitrate salts mixed with ammonia in SCW without oxygen showed that NO₂ radicals reacted with NH₂ radical, generated from NH₃, to produce N₂ and NOₓ (Dell’Orco et al., 1997). A similar result was observed in the research by Proesmans et al., who explored the hydrothermal oxidation process of organics, such as methanol and phenol, associated with NH₄NO₃. The products included N₂, NO₂ as well as NOₓ (Proesmans, Luan, & Buelow, 1997). Lee et al. investigated the activation energy of 4-nitroaniline decomposition and obtained 128 ± 35 kJ mol⁻¹ and 159 ± 25 kJ mol⁻¹ in SCW with and without oxygen, respectively (Lee, Park, Nam, Kim, & Lee, 1997). Zhang et al. tested nitrobenzene reaction in SCWO and estimated activation energy as 36 ± 5 kJ mol⁻¹ (Zhang & Hua, 2003). Furthermore, some researchers believed that the oxidation of
ammonia was the rate-limiting step for the conversion of organic nitrogen to nitrogen gas, and increasing pressure, temperature and reaction time could promote this conversion. (Lee & Do Park, 1996; Pérez, Rogak, & Branion, 2004; Zhang & Hua, 2003).

Even though N-containing compounds were investigated by several researchers, the majority of the studies were on pure compounds and at lab-scale. The composition of sludge or other wastes candidates for SCWO treatment is expected to be a complicated organic mixture, which makes the SCWO process hard to predict and control. Only a few works have been done about N-containing organic mixture reaction in SCWO. Yujia el at. investigated N-containing organics oxidation and their end products. The study demonstrated that the end products highly depend on the composition of sludge, particularly the types of N-containing organic functional group. Yujia el at. also summarized the nitrogen radical fate on denitrification in SCWO. However, in the SCWO process, the factors that affect N₂O generation are still unclear and the exact fate of nitrogen fate remains unknown, except for a handful of pure N-containing organic compounds tested at the lab-scale (Tan et al., 2020).

More studies on nitrogen reaction of sludge in SCWO process are needed to predict and control the generation of ammonia, nitrate, and nitrous oxide (especially for N₂O) in pilot-scale or even industrial application. A tool to contribute achieving such goal can be a mathematical model. Indeed, using a model of SCWO, one can begin to understand how ammonia, nitrate N₂O are produced from the nitrogen embedded in the
initial sludge, and how the SCWO process could be designed and operated to reduce
N₂O generation (Gómez-Barea & Leckner, 2010; Gómez-Barea & Leckner, 2013; Nilsson,
In this study, a mathematical model was developed, building on previous works
mentioned above, with a specific focus on nitrogen reactions during the SCWO process.
This mathematical model was calibrated with data from the Duke SCOW pilot system
operated by the Duke Sanitation group. The final model was compared to actual data
obtained from this system for validation.

2. Objective

The overall objective of this research is to explore the kinetics and nitrogen
reaction pathway in SCWO treating municipal sludge and to develop a model to predict
the outputs of the SCWO system depending on the operation and the input. By
achieving these goals, the generation mechanism of N₂O emission in SCWO can be
clarified, and the lessons learned can be applied to optimize the operation of SCWO
systems.
3. Methodology

3.1 Apparatus

A schematic diagram of the Duke SCWO system is shown in Fig. 1. The continuous tubular reactor was designed to be operated at maximum pressure and temperature of 240 bar and 650 °C, respectively. The tubular reactor has a 15.6 mm inner diameter (ID) and is 4 m long, resulting in a volume of approximately 0.760 L.

Firstly, the sludge, mixture of water and air are pumped by two separate pumps and a compressor at the design flow rate, respectively. Then, the sludge is pre-heated by a heat exchanger before being mixed with water and air at the entrance of the reactor. A
furnace and another heat exchanger ahead of the entrance of the reactor can heat the water mixed with air to supercritical temperature. The furnace maintains the stability of the temperature of the mixture before its entering reactor and can reach its desired temperature in a few minutes. It was also installed to compensate for heat losses and the fact that the pilot system does not include complete heat and energy recovery options. Finally, air, water, and sludge mixed at the entrance of the reactor react as they move through the reactor; the temperature of the reactor increases as a result of the exothermic reaction. The temperature in the reactor is monitored and recorded by 5 temperature sensors, to keep the temperature stable and constant. The pressure is controlled by a back-pressure regulator at a value of around 240 bars.

A high-pressure separator splits gas and liquid after the different heat exchangers. The liquid passes through a sieve to retain possible large particles and is discharged through capillaries as the effluent of the SCWO system. Samples in the effluent are collected, then tested and measured in the lab for various species. The gas is exhausted from the back-pressure regulator and is monitored by various electronic sensor before being vented.
3.2 Inorganic nitrogen measurements and baseline performance

For sludge, the solid percentage, ammonia, nitrate, nitrite, and total nitrogen were measured in the lab using standard methods (Table 1). The solid percentage for digested sludge used in the Duke SCWO system ranged approximately from 10% to 18%. The ammonia and nitrate were averaging from 15.8% and 2.4%, respectively, of the total nitrogen in the sludge, which indicates that organic nitrogen is the majority of nitrogen compounds in the sludge feed.

For the effluent, ammonia, nitrate, nitrite, and total nitrogen were also measured in the lab using standard methods (Table 1). Ammonia was the majority (generally about 80%) of total nitrogen; nitrate and nitrite were relatively low, sometimes even below the detection limit. The fraction of the total nitrogen that is denitrified (i.e., conversion to N₂ gas) in Duke SCWO system is approximately 50%.

**Table 1. Laboratory nitrogen test method**

<table>
<thead>
<tr>
<th>description</th>
<th>method</th>
<th>method number</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-NH₄⁺</td>
<td>Ammonia nitrogen</td>
<td>Salicylate Method</td>
</tr>
<tr>
<td>N-NO₃⁻</td>
<td>Nitrate nitrogen</td>
<td>Chronotropic Acid Method</td>
</tr>
<tr>
<td>N-TN</td>
<td>Total nitrogen</td>
<td>Persulfate Digestion Method</td>
</tr>
</tbody>
</table>
3.3 Organic nitrogen and FTIR test for basic characterization

As mentioned in section 3.2, the proportion of organic nitrogen in the feed was estimated to be above 60% of the total nitrogen. This high proportion of organic nitrogen requires further definition of the sludge organic composition in order to accurately model the nitrogen reactions when sludge undergoes SCWO since the speciation (e.g., nitro vs. amino group) of nitrogen is expected to affect the fate of the nitrogen. Little is known about the details of N speciation in biosolids.

An adequate approach to analyze the organic composition of sludge may be an elementary test for sample fraction. (Blumer, Kleffner, Lucke, & Zander, 1980; Boenigk, Haenel, & Zander, 1990) However, the elementary composition of sludge contributes less to the development of kinetics and the prediction of the types and quantities of outcome substances. Therefore, another method is required to analyze the more detailed composition of sludge (Guillén, Iglesias, Domínguez, & Blanco, 1995).

Fourier-transform infrared spectroscopy (FTIR) (Griffiths & De Haseth, 2007) is a technique used to obtain an infrared spectrum of absorption or emission of a solid, liquid or gas. This method is widely applied in the qualification of bonds and functional groups in an organic mixture, and could be used for sludge (Guillen, Iglesias, Domínguez, & Blanco, 1992). Some studies combined IR spectroscopy with other techniques to quantify nitrogen functional groups in coal tar pitches. (Fei, Sakanishi, Yamashita, & Mochida, 1990; Wallace, Bartle, & Perry, 1989)
In the present study, FTIR was applied to identify and quantify the nitrogen functional groups (NFG) that are present in sludge as shown in Fig.2. A standard curve was developed, by substance containing NFG, to calculate the concentrations of NFG in sludge as shown in Table.1. Pre-drying of sludge before carrying out FTIR was required to remove the inference of water on amino-group quantification.

<table>
<thead>
<tr>
<th>Functional group</th>
<th>Standard sample</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amine (-NH, -NH₂)</td>
<td>Urea (CH₄N₂O)</td>
<td>dimethylsulfoxide</td>
</tr>
<tr>
<td>Nitro (-NO₂)</td>
<td>Nitrobenzene (C₆H₅NO₂)</td>
<td>DMSO</td>
</tr>
</tbody>
</table>
4. Modeling the fate of N species during SCWO

In this study, a mathematical model was developed to simulate the nitrogen reactions of sludge in the reactor under supercritical conditions. Once validated, the model, which can be applied to optimize the operation for the supercritical water system and predict the nitrogenous outlet based on inlet data at steady-state. The parameters and calibration and validation data for this model were collected from several sources: (1) data of configuration and nitrogen experiments carried out in Duke SCWO system.
related research about nitrogen fate in SCWO or, when not available, in combustion systems.

4.1 Chemical reaction and kinetics background

Sludge from wastewater treatment plants can be regarded as a mixture of a variety of organic and inorganic compounds. To model the sludge reaction in supercritical water oxidation, a significant hurdle is caused by the complexity of sludge composition. Most sludge SCWO kinetic studies focused on the carbon reaction, like the study of Christopher et al (Martino & Savage, 1997). For nitrogen kinetics, the majority of studies are only considering pure organic or inorganic substances, which cannot be used to simulate sludge reaction. The complexity and challenges of defining all nitrogenous substances that exist in sludge and to modelling the fate them in the reaction can’t be overstated.

Yujia el at. investigated N-containing organics oxidation and their end products in supercritical water oxidation, and demonstrated that the end products highly depended on the composition of sludge, particularly the types of N-containing organic functional group. Based on the results and conclusion of Yujia’s study, we can simplify the composition of sludge. Yujia el at. found that different nitrogen functional groups generate corresponding inorganic products. Therefore, the reaction model can be
divided into two pathways (the organic and inorganic pathways), as shown in Fig.3. (B. Yang, Cheng, Tang, et al., 2018)

![Diagram showing high level pathways for nitrogen reaction in SCWO]

**Fig.3.** High level pathways for nitrogen reaction in SCWO

**4.1.1 N species in the inlet and outlet of the reactor**

The sludge treated in the SCWO unit was analyzed as reported above. Generally, organic nitrogen accounted for the main fraction of total nitrogen in the sludge used as feed for the Duke SCWO system. Ammonia and nitrate detected in the sludge, and nitrogen gas in the inlet air were three main inorganic nitrogen substances in the inlet.

The outlet of SCWO is commonly reported to contain ammonia, nitrate and nitrogen gas. Trace NOx was detected in Dell’Orco’s, Li and Oshima’s studies about the
elementary reaction of methylamine in SCWO system. (H. Li & Oshima, 2005))

Relatively high-level N₂O were measured in Killilea and Benjamin studies about oxidation reaction in SCWO system, and some levels of N₂O were also frequently detected in the Duke SCWO system used in this research. (Killilea et al., 1992) Therefore, the outlet species considered for the model are assumed to be NH₄⁺, NO₃⁻, N₂, N₂O.

4.1.2 Organic nitrogen reactions

The reactions for organic nitrogen are simplified by using nitrogen functional groups. Yujia el at. investigated the relationship between nitrogen functional group in SCWO inlet with inorganic outlet. They found organics with the amino group will generate ammonia during SCWO as the majority product, while nitro groups lead to the significant formation of nitrate. The diazo group and the heterocyclic group mainly produce nitrogen gas and some ammonia and nitrate. They also pointed the functional group will generate the radicals. However, the kinetics was still not clear for such reactions, which will be developed in the future. (B. Yang, Cheng, Tang, et al., 2018).

To simplify and generalize the reaction, we assume the diazo group and the heterocyclic group only produce nitrogen gas. Based on the assumptions, reactions of organic nitrogen can be expressed as follows:

\[
\begin{align*}
\alpha_1 C_x - NH_2 + \beta_1 \cdot OH + \gamma_1 \cdot O & \rightarrow \alpha_1 NH_4^+ + x\alpha_1 CO_2 + x_1 H_2O \quad \Delta H_1 \quad R1 \\
\alpha_2 C_x - NO_2 + \beta_2 \cdot OH + \gamma_2 \cdot O & \rightarrow \alpha_2 NO_3^- + x\alpha_2 CO_2 + x_2 H_2O \quad \Delta H_2 \quad R2
\end{align*}
\]
\[ \alpha_3 C_x - N - + \beta_3 \cdot OH + \gamma_3 \cdot O \rightarrow 0.5\alpha_3N_2 + x\alpha_3 CO_2 + X_3H_2O \quad \Delta H_3 \quad \text{R3} \]

### 4.1.3 Denitrification pathway

The denitrification pathway in supercritical water oxidation has been investigated by several researchers. NH\textsuperscript{+} and NO\textsuperscript{−} have been reported by Takahashi et al. (Takahashi et al., 1989) as refractory substances in the SCWO system for their thermal stability. Paul et al. studied the oxidation of ammonia in supercritical water oxidation and suggested an oxidation pathway of ammonia. (Webley et al., 1991) Based on this, Bowen and Philip (Gopalan & Savage, 1995; B. Yang, Cheng, Yuan, & Shen, 2018) investigated the denitrification pathway of nitrate with ammonia in supercritical water, and expressed it as the following reaction (R4–R8).

Ammonia in supercritical water reacts with hydroxyl radicals, which are generated by the reaction between oxygen and water in high-temperature conditions and convert it to \( \cdot \text{NH}_2 \), the aminyl radical as shown in R4. Yu et al. and Jason et al. reported that \( \cdot \text{NH}_2 \) will be further oxidized to form NO (nitrogen oxide) and \( \cdot \text{NO}_2 \) radical as expressed in R5 and R6. (Ploeger, Green, & Tester, 2008; Song et al., 2016)

\[ \text{NH}_4^+ + \cdot OH \rightarrow \cdot \text{NH}_2 + 2H_2O + H \quad \Delta H_4 \quad \text{R4} \]
\[ \cdot \text{NH}_2 + \cdot O \rightarrow \text{NO} + H_2O + 2H \quad \Delta H_5 \quad \text{R5} \]
\[ \text{NO} + \cdot O \rightarrow \cdot \text{NO}_2 \quad \Delta H_6 \quad \text{R6} \]
Finally, \( \cdot \text{NH}_2 \) radical is proposed to interact with NO and \( \cdot \text{NO}_2 \) to produce \( \text{N}_2 \) and \( \text{N}_2\text{O} \) (R7 and R8). This denitrification pathway was also detected in a fluidized bed reaction, which had a similar temperature and reaction condition.

\[
\cdot \text{NH}_2 + \cdot \text{NO}_2 \rightarrow \text{N}_2 \text{O} + \text{H}_2\text{O} \quad \Delta H_7 \quad \text{R7}
\]

\[
\cdot \text{NH}_2 + \text{NO} \rightarrow \text{N}_2 + \text{H}_2\text{O} \quad \Delta H_8 \quad \text{R8}
\]

### 4.1.4 Nitrate reduction

Except for the denitrification reaction of ammonia, Dell’Orco et al.’s research, about nitrate salts mixed with ammonia in SCW, pointed out the nitrate effect of improving denitrification (Dell’Orco et al., 1997). The denitrification rate is lower than 20%, when ammonia and nitrate exist alone. However, when those two substances coexist, the denitrification rate increases significantly. Bowen et al. investigated the synergistic mechanism of denitrification in SCWO and the decomposition of nitrate was detected. The nitrate can produce \( \cdot \text{NO}_2 \) and OH radicals (B. Yang, Cheng, Yuan, et al., 2018). This was included in the model too (R9).

\[
\text{HNO}_3 \rightarrow \cdot \text{NO}_2 + \cdot \text{OH} \quad \Delta H_9 \quad \text{R9}
\]

Furthermore, Yujia’s study on nitrogen transformation of 41 organic compounds during SCWO showed the oxidation of amino organics can produce nitrate as well, which indicated that the decomposition of nitrate and should be reversible; it was represented in our model as R10. Furthermore, according to Bowen’s study (B. Yang,
Cheng, Yuan, et al., 2018) and the experiment result in Duke SCWO system on nitrate, adding nitrate can improve the denitrification rate and increase the nitrogen gas in the outlet, which indicates that decomposition of NO$_2$ in SCWO plays an important role (B. Yang, Cheng, Tang, et al., 2018). This led to the inclusion of R11.

\[
\begin{align*}
NO_2 + \cdot OH & \rightarrow HNO_3 & \Delta H_{10} & \text{R10} \\
\cdot NO_2 & \rightarrow NO + \cdot O & \Delta H_{11} & \text{R11}
\end{align*}
\]

### 4.1.5 NO$_2$ consumption

Although the generation of N$_2$O through the denitrification pathway was studied by several researchers, the pathway generation of N$_2$O by oxidation of N$_2$ is still not clear. William et al. studied the fate of nitrogen in supercritical water oxidation and observed the nitrogen gas oxidation reaction (Killilea et al., 1992). N$_2$O generation from nitrogen alongside combustion was also detected in the Duke SCWO system when oxidizing isopropyl alcohol (IPA) alone with air as the oxidant. This is represented by the reaction R12.

\[
\begin{align*}
2N_2 + O_2 & \rightarrow 2N_2O & \Delta H_{12} & \text{R12} \\
N_2O + \cdot O & \rightarrow 2NO & \Delta H_{13} & \text{R13}
\end{align*}
\]

### 4.1.6 Hydroxyl radical and oxygen generation

The generation mechanism of hydroxyl radicals is well studied in fluidized bed combustion, but somehow less studied in supercritical water oxidation. Eric et al. (Brock
& Savage, 1995) studied detailed chemical kinetics of carbon, hydrogen, and oxygen, and reported that oxygen can react with water, generating two hydroxyl radicals (R14). The same reaction is reported in Pinwei’s study about NOx emission in fluidized bed combustion (P.-W. Li & Chyang, 2020). Furthermore, Ding et al. studied the catalytic SCWO process and reported the decomposition of oxygen triggered by the supercritical water media and metals as catalysts. The oxygen radicals play a significant role in the transformation of NO to NO2 radical (R6), and the oxidation of organics (R1-R3).

\[
\begin{align*}
2H_2O + O_2 & \rightarrow 2 \cdot OH & \Delta H_{14} \\
O_2 & \rightarrow 2 \cdot O & \Delta H_{15} \\
2 \cdot O & \rightarrow O_2 & \Delta H_{16}
\end{align*}
\]

Putting it all together, the main reactions concerned with the fate of nitrogen in supercritical water oxidation can be mapped, as in Fig.4.

---

**Fig.4.** Proposed pathways for the kinetic modeling of nitrogen reactions in SCWO
4.2 Model structure

The focus of the model developed in this study is the sludge reaction in the tubular reactor, in order to predict the effluent concentration based on inlet concentrations and operating conditions. Due to the significant change of physical properties for water and air from sub-supercritical to supercritical conditions, this study will only simulate the reaction under a supercritical condition in a steady-state. This is because simulating the sub to supercritical phase transition is far too complex. The rapid phase transition in the system that was studied, and the quasi absence of reaction before reaching supercritical conditions makes this assumption acceptable. In a supercritical reactor at steady state, the pressure of the whole system remains constant and the temperature at every spot in the reactor is stable.

![Diagram of the tubular reactor](image)

**Fig.5.** Modeling the tubular reactor by discretizing space

An array model was applied, which means the reactor is regarded as a series of 5 small sections as shown in Fig. 5. Each section is regarded as a continuous stirred tank reactor (CSTR), and the effluent concentration equals the concentration inside each reactor (Fig. 6)
The influent stream contains sludge, NH$_4^+$, NO$_3^-$, air, water. The effluent contains CO$_2$, NH$_4^+$, NO$_3^-$, O$_2$, N$_2$, N$_2$O, NO$_2$. The flow enters the reactor and the reaction proceeds while the reactants pass through the reactor.

### 4.2.1 Mass balance structure

Based on the kinetic scheme and the array of reactors representing the tubular reactor, mass balances for each substance can be derived. The mass balance equation follows a generic form:

\[ \text{Mass change in CSTR} = \text{Mass flowed in} - \text{Mass flowed out} - \text{Reaction consumption} \]

The equation expresses the conservation of mass of each substance in one CSTR. Take the organics as an example, the changing mass of organics in a CSTR equals to the mass flowing into CSTR minus the mass flowing out and minus the amount consumed...
in the reaction. The different mass balance equations for each nitrogen species can be
developed using partial differential equations.

4.2.2 Mass balance of the organics with \(-\text{NH}_2\) in first CSTR

\[
V \frac{dC_{\text{organicNH}_2[1]}}{dt} = FC_{\text{organicNH}_2 \text{ in}} - QC_{\text{organicNH}_2[1]} + VR_{\text{organicNH}_2[1]}
\]

\(V\)-volume of CSTR element (L)

d\(t\)-increment of time (s)

\(F\)-total inlet mass flow rate (g/s)

\(Q[1]\)-total volumetric flow rate out of first CSTR (L/s)

\(C_{\text{organicNH}_2 \text{ in}}\)-concentration of the organics with \(-\text{NH}_2\) in the inflow (mol/g)

\(C_{\text{organicNH}_2[1]}\)-concentration of organics with \(-\text{NH}_2\) in the first CSTR (mol/L)

\(R_{\text{organicNH}_2[1]}\)-reaction rate of organics with \(-\text{NH}_2\) in the first CSTR (mol/L·s)

4.2.3 Mass balance of the organics with \(-\text{NH}_2\) in the other CSTRs

\[
V \frac{dC_{\text{organicNH}_2[i]}}{dt} = Q[i - 1]C_{\text{organicNH}_2[i - 1]} - Q[i]C_{\text{organicNH}_2[i]} + VR_{\text{organicNH}_2[i]}
\]
$Q[i - 1]$- total volumetric flow rate out of "i − 1" CSTR ($i \in [2,3,4,5]$) (L/s)

$Q[i]$- total volumetric flow rate out of "i" CSTR ($i \in [2,3,4,5]$) (L/s)

$C_{organicNH_2}[i - 1]$- concentration in "i − 1" CSTR ($i \in [2,3,4,5]$) (mol/L)

$C_{organicNH_2}[i]$-concentration in "i" CSTR ($i \in [2,3,4,5]$) (mol/L)

$R_{organicNH_2}[i]$-reaction rate in "i" CSTR ($i \in [2,3,4,5]$) (mol/L.s)

### 4.2.4 The reaction of organics with -NH$_2$ in each CSTR

The reaction rate of organics with -NH$_2$ can be expressed with the Arrhenius relationship.

$$R_{organicNH_2}[i] = -k_1[i]C_{organicNH_2}[i]^{\alpha_1}C_{OH}[i]^{\beta_1}C_O[i]^{\gamma_1}$$

$$k_1[i] = A_1 e^{\frac{E_{a_1}}{RT[i]}}$$

$k_1[i]$- Reaction R1 rate constant in "i" CSTR ($i \in [1,2,3,4,5]$)

$C_{OH}[i]$- ·OH radical concentration in "i" CSTR ($i \in [1,2,3,4,5]$) (mol/L)

$C_O[i]$- ·O radical concentration in "i" CSTR ($i \in [1,2,3,4,5]$) (mol/L)

$\alpha_1$- Stoichiometric Coefficient in R1

$\beta_1$- Stoichiometric Coefficient in R1

$\gamma_1$- Stoichiometric Coefficient in R1

$A_1$- Pre-exponential factor
\( E_{a1} \) - The activation energy (J mol\(^{-1}\))

\( T[i] \) - The temperature in "i" CSTR (\( i \in [1,2,3,4,5] \)) (K)

\( R \) - Universal gas constant (J mol\(^{-1}\)K\(^{-1}\))

### 4.2.5 Mass balance for all substances in SCWO

By separating the reactor into 5 CSTRs, we can establish the model for all target substances (like organics with -NH\(_2\)) reacting and flowing through the reactor, which when solved, will provide the concentration profile of those substances in the SCWO system. Based on the model developed above, the mass balance of all substances in the reaction can be derived in partial differential equation form in a similar structure as well.

\[
V \frac{dC_{organicNO_2}[1]}{dt} = FC_{organicNO_2 in} - Q[1]C_{organicNO_2}[1] + VR_{organicNO_2}[1]
\]

\[
V \frac{dC_{organicNO_2}[2..5]}{dt} = Q[i - 1]C_{organicNO_2}[i - 1] - Q[i]C_{organicNO_2}[i] + VR_{organicNO_2}[i]
\]

\[
R_{organicNO_2}[i] = -k_2[i]C_{organicNO_2}[i]^\alpha_2C_{OH}[i]^\beta_2C_O[i]^{\gamma_2}
\]

\[
V \frac{dC_{organicNN}[1]}{dt} = FC_{organicNN in} - Q[1]C_{organicNN}[1] + VR_{organicNN}[1]
\]

\[
V \frac{dC_{organicNN}[2..5]}{dt} = Q[i - 1]C_{organicNN}[i - 1] - Q[i]C_{organicNN}[i] + VR_{organicNN}[i]
\]

\[
R_{organicNN}[i] = -k_3[i]C_{organicNN}[i]^\alpha_3C_{OH}[i]^\beta_3C_O[i]^{\gamma_3}
\]

\[
V \frac{dC_{NH_4}[1]}{dt} = FC_{NH_4 in} - Q[1]C_{NH_4}[1] + VR_{NH_4}[1]
\]

24
\[
V \frac{dC_{NH_4}[2..5]}{dt} = Q[i - 1]C_{NH_4}[i - 1] - Q[i]C_{NH_4}[i] + VR_{NH_4}[i]
\]

\[
R_{NH_4} = k_1[i]C_{organicNH_4}[i]\alpha_1 C_{OH}[i]^{\beta_1} C_O[i]^{\gamma_1} + k_3[i]C_{organicN}[i]\alpha_3 C_{OH}[i]^{\beta_3} C_O[i]^{\gamma_3}
\]

\[
- k_4[i]C_{NH_4}[i]C_{OH}[i]
\]

\[
V \frac{dC_{NO_3}[1]}{dt} = FC_{NO_3,in} - Q[1]C_{NO_3}[1] + VR_{NO_3}[1]
\]

\[
V \frac{dC_{NO_3}[2..5]}{dt} = Q[i - 1]C_{NO_3}[i - 1] - Q[i]C_{NO_3}[i] + VR_{NO_3}[i]
\]

\[
R_{NO_3}[i] = k_2[i]C_{organicNO_2}[i]\alpha_2 C_{OH}[i]^{\beta_2} C_O[i]^{\gamma_2} - k_9[i]C_{NO_3}[i] + k_{10}[i]C_{NO_2}[i]C_{OH}[i]
\]

\[
V \frac{dC_{N_2}[1]}{dt} = FC_{N_2,in} - Q[1]C_{N_2}[1] + VR_{N_2}[1]
\]

\[
V \frac{dC_{N_2}[2..5]}{dt} = Q[i - 1]C_{N_2}[i - 1] - Q[i]C_{N_2}[i] + VR_{N_2}[i]
\]

\[
R_{N_2}[i] = 0.5 k_3[i]C_{organicN}[i]\alpha_3 C_{OH}[i]^{\beta_3} C_O[i]^{\gamma_3} + k_8[i]C_{NH_4}[i]C_{N_0}[i] - k_{12}[i]C_{N_2}[i]C_{OH}[i]
\]

\[
V \frac{dC_{N_2O}[1]}{dt} = FC_{N_2O,in} - Q[1]C_{N_2O}[1] + VR_{N_2O}[1]
\]

\[
V \frac{dC_{N_2O}[2..5]}{dt} = Q[i - 1]C_{N_2O}[i - 1] - Q[i]C_{N_2O}[i] + VR_{N_2O}[i]
\]

\[
R_{N_2O}[i] = k_7[i]C_{NH_2}[i]C_{NO_2}[i] + k_{12}[i]C_{N_2}[i]C_{OH}[i] - k_{13}[i]C_{N_2O}[i]C_O[i]
\]

\[
V \frac{dC_{O_2}[1]}{dt} = FC_{O_2,in} - Q[1]C_{O_2}[1] + VR_{O_2}[1]
\]

\[
V \frac{dC_{O_2}[2..5]}{dt} = Q[i - 1]C_{O_2}[i - 1] - Q[i]C_{O_2}[i] + VR_{O_2}[i]
\]

\[
R_{O_2} = - k_{15}[i]C_{N_2}[i]C_{O_2}[i] + 0.5 k_{16}[i]C_{N_2}[i]C_O[i]^2
\]

\[
V \frac{dC_{CO_2}[1]}{dt} = FC_{CO_2,in} - Q[1]C_{CO_2}[1] + VR_{CO_2}[1]
\]

\[
V \frac{dC_{CO_2}[2..5]}{dt} = Q[i - 1]C_{CO_2}[i - 1] - Q[i]C_{CO_2}[i] + VR_{CO_2}[i]
\]
\[ R_{CO_2} = x \ k_1[i]C_{organicNH2}[i]\beta_1C_{OH}[i]^{\alpha_1}C_{OH}[i]^{\gamma_1} + x \ k_2[i]C_{organicNO3}[i]\beta_2C_{OH}[i]^{\alpha_2}C_{OH}[i]^{\gamma_2} + x \ k_3[i]C_{organicNN}[i]\alpha_3C_{OH}[i]^{\alpha_3}C_{OH}[i]^{\gamma_3} \]

\[ V \ \frac{dC_0[1]}{dt} = FC_{0\ im} - Q[1]C_0[1] + VR_0[1] \]

\[ V \ \frac{dC_0[2..5]}{dt} = Q[i - 1]C_0[i - 1] - Q[i]C_0[i] + VR_0[i] \]

\[ R_0[i] = -\frac{\gamma_1}{\alpha_1} k_1[i]C_{organicNH2}[i]\alpha_1C_{OH}[i]^{\beta_1}C_{OH}[i]^{\gamma_1} - \frac{\gamma_2}{\alpha_2} k_2[i]C_{organicNO3}[i]\alpha_2C_{OH}[i]^{\beta_2}C_{OH}[i]^{\gamma_2} \]

\[ V \ \frac{dC_{OH}[1]}{dt} = FC_{OH\ im} - Q[1]C_{OH}[1] + VR_{OH}[1] \]

\[ V \ \frac{dC_{OH}[2..5]}{dt} = Q[i - 1]C_{OH}[i - 1] - Q[i]C_{OH}[i] + VR_{OH}[i] \]

\[ R_{OH}[i] = -\frac{\beta_1}{\alpha_1} k_1[i]C_{organicNH2}[i]\alpha_1C_{OH}[i]^{\beta_1}C_{OH}[i]^{\gamma_1} - \frac{\beta_2}{\alpha_2} k_2[i]C_{organicNO3}[i]\alpha_2C_{OH}[i]^{\beta_2}C_{OH}[i]^{\gamma_2} \]

\[ V \ \frac{dC_{NH2}[1]}{dt} = FC_{NH2\ im} - Q[1]C_{NH2}[1] + VR_{NH2}[1] \]

\[ V \ \frac{dC_{NH2}[2..5]}{dt} = Q[i - 1]C_{NH2}[i - 1] - Q[i]C_{NH2}[i] + VR_{NH2}[i] \]

\[ R_{NH2}[i] = k_4[i]C_{NH4}[i]C_{OH}[i] - k_5[i]C_{NH2}[i]C_{OH}[i] - k_7[i]C_{NH2}[i]C_{NO2}[i] - k_8[i]C_{NH2}[i]C_{NO}[i] \]

\[ V \ \frac{dC_{NO}[1]}{dt} = FC_{NO\ im} - Q[1]C_{NO}[1] + VR_{NO}[1] \]
\[
V \frac{dC_{NO}[2.5]}{dt} = Q[i - 1]C_{NO}[i - 1] - Q[i]C_{NO}[i] + VR_{NO}[i]
\]

\[
R_{NO}[i] = k_5[i]C_{NH_2}[i]C_0[i] - k_6[i]C_{NO}[i]C_0[i] - k_8[i]C_{NH_2}[i]C_{NO}[i] + k_{11}[i]C_{NO_2}[i]
+ 2k_{13}[i]C_{N_2O}[i]C_0[i]
\]

\[
V \frac{dC_{NO_2}[1]}{dt} = FC_{NO_2 \text{ in}} - Q[1]C_{NO_2}[1] + VR_{NO_2}[1]
\]

\[
V \frac{dC_{NO_2}[2..5]}{dt} = Q[i - 1]C_{NO_2}[i - 1] - Q[i]C_{NO_2}[i] + VR_{NO_2}[i]
\]

\[
R_{NO_2}[i] = k_6[i]C_{NO}[i]C_0[i] - k_7[i]C_{NH_2}[i]C_{NO_2}[i] + k_9[i]C_{NO_2}[i] + k_{10}[i]C_{NO_2}[i]C_{OH}[i]
- k_{11}[i]C_{NO_2}[i]
\]

### 4.2.6 Thermodynamic properties

The properties of water and air mixtures at supercritical conditions are not well characterized. For example, the flow behavior in the reactor complicated and not well known. Similarly, the thermodynamic and kinetic constants for the transformation process of sludge in supercritical water are not well known. Most of the research assumes that thermodynamic properties of mixtures are that of pure substances, and generally the properties of water is assumed to be representative of those of the whole mixture (Cocero & Martinez, 2004; Moussiere et al., 2007). In the Duke SCWO system, during regular operation, the mass flow rate of water is roughly twice that of the airflow or that of the sludge flow. Generally, the solid percentage of sludge undergoing treatment is 10~19% dry mass. Considering the unique property of supercritical water
and a large proportion of water in inlet, it is acceptable to assume the mixture of gas and water can be the representative of the whole mixture.

Nermin and Klose (Nermin et al., 2012; Klose et al., 1986) studied the properties of organic in SCW. They stated that, when the temperature and pressure reaches the supercritical point, the hydrogen bonds break down, changing the property of water. Water becomes less polar and it acts like an organic solvent, which makes solubility of organics and gases in SCW increase dramatically.

(1) **Volumetric flow rate**

The reactor is assumed to be consisting of 5 CSTRs in series. Although the mass flow rate of the mixture is along the reactor, the volumetric flow rates vary. This is due to the variation of density, which is caused by the changes in temperature and composition of the mixture along the reactor, as the reaction proceeds. The volumetric flow rate is defined as:

\[
Q = \frac{F}{\rho}
\]

\(F\)-total mass inflow rate (g/s)

\(Q[i]\)- total volumetric flow rate out of "i" CSTR \((i \in [1,2,3,4,5])\) (L/s)

\(\rho[i]\)- the density of mixture in "i" CSTR \((i \in [1,2,3,4,5])\) (g/L)
(2) **Density of the mixture**

To calculate the volumetric flow rate, the density of the mixture is needed. The density of the mixture can be defined as:

$$\rho = \frac{(F_w + F_s) \cdot \rho_w + F_{air} \cdot \rho_{air}}{F_w + F_s + F_{air}}$$

- $F_w$ - water mass flow rate (g)
- $F_{air}$ - air mass flow rate (g)
- $F_s$ - sludge mass flow rate

- $\rho_w[i]$ - density of water in "i" CSTR ($i \in [1,2,3,4,5]$) (g/m³)
- $\rho_{air}[i]$ - density of gas in "i" CSTR ($i \in [1,2,3,4,5]$) (g/m³)

(3) **Density of water and gas in each CSTR**

The $\rho_w[i]$ and $\rho_{air}[i]$ can be calculated from polynomial approximations of the density which were developed by the Duke SCWO project group:

$$\rho_w = a + \frac{b}{T_{in} - h} + d \cdot TR[i] \quad (kg/m^3)$$

$$\rho_{air} = -0.13 \cdot TR[i] + 203.16 \quad (kg/m^3)$$

a = 68.15617696, b = 4265.654464, h = 365.4923128, d = -0.03
However, the density of air is different from the density of gas because of different compositions. The oxidation of sludge causes the consumption of O$_2$ and
generation of CO$_2$ which changes the composition through the reactor. The density of gas can be calculated as follows:

\[ P \cdot V = n \cdot R \cdot T \Rightarrow \rho = \frac{M_a \cdot \rho}{RT} \]

Therefore \( \rho_{gas} = \frac{M_{gas}}{M_{air}} \rho_{air} \)

\[ M_{gas} = \frac{m_g}{n_g} = \frac{C_{O_2}[i] \cdot M_{O_2} + C_{N_2}[i] \cdot M_{N_2} + C_{CO_2}[i] \cdot M_{CO_2}}{C_{O_2}[i] + C_{N_2}[i] + C_{CO_2}[i]} \rho_{gas} = \frac{M_{gas}}{M_{air}} \rho_{air} \]

\[ M_{air} \text{- the average molar mass of air (g/mol)} \]

### 4.3 Heat transfer

Heat balances need to be written to have accurate representation of the tem along the reactor. The balances take the form of:

Energy Accumulation = Energy flowed in – Energy flowed out – Energy released by the reaction

\[ (m_w[i] + m_g[i])C_p[i] \frac{dT[i]}{dt} = F(C_p[i] - 1)T[i] - C_p[i]T[i]) + V \left( \sum R_n[i] \cdot \Delta H_n[i] \right) \]

\( C_p[i] \text{------ } C_p \text{ for each part, the heat capacity of the mixture, kJ/g*K} \)

\( \Delta H_n[i] \text{------ reaction enthalpy, kJ/mol} \)
4.3.1. Mass of water and air in each CSTR

To calculate the density of the mixture, the masses of gas mixture and water are needed. To simplified the model, we can assume the total mass of gas equals the sum mass of oxygen, nitrogen and carbon dioxide, as expressed below:

\[ m_g[i] = V \cdot (C_{O_2}[i] \cdot M_{O_2} + C_{N_2}[i] \cdot M_{N_2} + C_{CO_2}[i] \cdot M_{CO_2}) \]

- \( M_{O_2} \) - O\(_2\) molar mass (32 g/mol)
- \( M_{N_2} \) - N\(_2\) molar mass (28 g/mol)
- \( M_{CO_2} \) - CO\(_2\) molar mass (44 g/mol)

To calculate the mass of water in each CSTR, we have to assume that the volume of water equals the volume of the CSTR. Then we can develop the mass of water:

\[ m_w[i] = V \cdot \rho_w[i] \]

4.3.2. Heat capacity of the mixture

As same as the density, the heat capacity of the mixture changes with temperature and it can be calculated in the same way:

\[ C_p[i] = \frac{m_w[i] \cdot C_{pw}[i] + m_g[i] \cdot C_{pg}[i]}{m_w[i] + m_g[i]} \ (kJ/g \ K) \]

- \( m_w[i] \) ---- mass of water in CSTR\([i]\) (g)
- \( m_g[i] \) ---- mass of gas in CSTR\([i]\) (g)
- \( C_{pw}[i] \)---- heat capacity of water in CSTR\([i]\) (kJ/g K)
- \( C_{pg}[i] \)---- heat capacity of gas in CSTR\([i]\) (kJ/g K)
(1) Heat capacity of water and air in each CSTR

The $C_{pw}[i]$ and $C_{pair}[i]$ can be calculated from the simulation of heat capacity which is from Duke SCWO project group:

$$C_{pw}[1..5] = (e + \frac{f}{T[i]} - g) \times 10^{-4} \text{ (kJ/g K)}$$

\[e = 2.137539497, f = 222.01184, g = 391.7878136\]

$$C_{pa\text{ir}}[1..5] = 1 \times 10^{-4} \cdot T[i] + 1.05 \text{ (kJ/g K)}$$

Because the generation of CO$_2$, the heat capacity of gas from that of air, therefore, we introduce a correction factor $\varepsilon$, which expressed as:

$$C_{pg}[i] = \varepsilon \cdot C_{pa\text{ir}}[i]$$

Fig. 9. Heat capacity of water from 650 K to 1500 K and 250 bar
5. Results and Discussion

5.1 N functional groups determination in sludge by FTIR

FTIR of biosolids was conducted at Duke SMIF to determine N functional groups. The results showed that FTIR peaks for the amine functional group suffered interferences by water peaks. According to the literature, the absorption peak of the hydroxyl group ranges from 3200 cm\(^{-1}\) to 3500 cm\(^{-1}\), while the amine group ranges from 3400 cm\(^{-1}\) to 3500 cm\(^{-1}\). Therefore, to conduct FTIR of the sludge, drying was carried out.

Standard curves for amine and nitro functional groups were developed for FTIR, then dried biosolids were tested. The FTIR spectra for biosolids and standard curve of functional group should be tested together to make sure the uniform of the test baseline.
An example is shown in Fig. 11, the range of amine standard curve should contain the sludge peak. The standard curves of amine and nitro groups are shown in Fig. 12 and 13 while the percentages of each group in sludge are listed in Table. 3. The standard curves of amine and nitro groups are linear, which can be used for sludge test.

The rest parts of organic nitrogen in sludge contains nitrile, cyclic nitrogen etc. However, it is hard to measure such nitrogen directly, because with different types of the connecting atom to nitrogen atom, the frequency of absorption varying. Each signals are extremely small which causes error for quantification in FTIR. Because nitrile, dino and cyclic nitrogen still generate nitrogen gas as end product according to Bowen’s study, (Yang et al., 2018) we only can assume the cyclic nitrogen equals the rest parts of organic nitrogen, which is expressed below:

\[
Cyclic \ nitrogen = organic \ nitrogen - amine - nitro
\]

The amine functional group constitutes the majority (53%) of the organic nitrogen, as expected from the presence of amino acids in proteins. Nitrogen in nitro-groups is 15% of the total organic nitrogen in the sludge. The rest of the organic nitrogen is unknown and was assumed to be in some cyclic structures, accounting for approximately 32% of the total organic nitrogen.
Fig. 11. Example of FTIR test including amine standard curve and sludge test

Fig. 12. Amine standard curve development in FTIR
Fig. 13. Nitro group standard curve development in FTIR

Table 3. Proportion of nitrogen functional groups in biosolids

<table>
<thead>
<tr>
<th>Functional group</th>
<th>Frequency range</th>
<th>Percentage of organic nitrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amine (-NH₂)</td>
<td>3500-3300</td>
<td>53%</td>
</tr>
<tr>
<td>Nitro (-NO₂)</td>
<td>1550-1500</td>
<td>15%</td>
</tr>
<tr>
<td>Others (Cyclic-N)</td>
<td>unknown</td>
<td>~32%</td>
</tr>
</tbody>
</table>
5.2 Model verification

The original model includes 5 CSTR reactors to simulate the plug flow nature of the actual system. However, because of the complexity of the system, and uncertainties in the kinetics and lack of data in heat transfer, it was decided to initially simplify the model, to check the validity of the reaction kinetic schematic as shown in Fig. 4, and to check the robustness of the numerical solution. For the solution, all dynamic mass balances were included in a Berkeley Madonna model (https://berkeley-madonna.myshopify.com/) and all dynamic balances were solved numerically until a steady state was obtained, using a stiff algorithm. Values for model parameters are listed in the Appendices.

Thus, the model was first simplified from 5 CSTR to 1 CSTR only to validate the kinetics. The temperature of the single CSTR was assumed to be the average temperature of the tube during steady-state, to make this simplified model closest to the real condition. The heat transfer will also not be included in this simplified model, but will be added in the next section after validating the kinetic schematic.

The density of sludge can be assumed equal to the density of water, because the solid percentage of sludge treated is about 10%, and water flow is controlled in 30%–50% mass of total flow in Duke SCWO system.

The differential equations of this simplified model are expressed below:

$$V \frac{dC}{dt} = F C_{in} - Q_{out} C + VR$$
$Q_{out} = \frac{F}{\rho}$

$\rho \approx \rho_w = a + \frac{b}{T - h} + d \cdot T \quad (g/L)$

$V$ - the total volume of the tube (L)

$C$ - concentration of each substance (mol/L)

$F$ - mass flow rate (sum of sludge, air, and water mass flow rate, g/s)

$Q_{out}$ - volumetric flow out of reactor (L/s)

$\rho$ - density of flow (g/L)

$\rho_w$ - the density of water at temperature $T$ (g/L)

$T$ - average temperature of the reactor

5.2.1 Mass balance, verification of conservation of mass

To validate the reaction model and code, the mass balance equation of nitrogen is developed as follows:

$mb = (77\% \cdot Fa + TN \cdot Fs) - Q \cdot \Sigma N$

$\Sigma N = C_{orgNH2} + C_{orgNO2} + C_{orgCN} + C_{NO3} + C_{NH4} + C_{NO2} + C_{NO} + 2C_{N2} + 2C_{N2O}$

$TN$ - total nitrogen concentration in sludge (mol/g)

$\Sigma N$ - sum concentration of nitrogen substances
Fig. 14 expressed the mass balance for N over time, which shows that at a steady-state, the mass balance value reaches zero. This means that the nitrogen in the inlet equals the nitrogen in the outlet, which validates the mass balance differential equation for the model.
5.2.2 Model validation with experimental data

In this study, the simplified model was established. The reaction parameters including Arrhenius parameters and enthalpies are listed in Appendix B and C. Two experiments were carried out with the Duke pilot SCWO system to provide data and validate the established model. The operation parameters are shown in Table 4. The operating parameters were used as input for the simplified model, the outputs of the model were compared with experiment results, as shown in Table 5 and Table 6.

| Table 4. Operation parameters for two experiments |
|-----------------------------------------|-----------------|-----------------|
|                                          | Experiment NO.1 | Experiment NO.2 |
| Reactor average temperature (°C)         | 572.4           | 555.5           |
| Water flow rate (g/s)                    | 8.43            | 11.53           |
| Air flow rate (g/s)                      | 4.39            | 6.54            |
| Sludge flow rate (g/s)                   | 8.23            | 7.83            |
| Total nitrogen in sludge (mol/g)         | 0.00049         | 0.00047         |
| Ammonia in sludge (mol/g)                | 0.000073        | 0.000076        |
| Nitrate in sludge (mol/g)                | 0.000011        | 0.000012        |
Table 5. Output of Experiment 1 and model simulation

<table>
<thead>
<tr>
<th></th>
<th>COD removal</th>
<th>NH$_4^+$</th>
<th>NO$_3^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unit</td>
<td>%</td>
<td>mol/L</td>
<td>mol/L</td>
</tr>
<tr>
<td>Experiment</td>
<td>99.2</td>
<td>0.0509</td>
<td>5.36E-05</td>
</tr>
<tr>
<td>Model</td>
<td>97.8</td>
<td>0.0781</td>
<td>9.87E-05</td>
</tr>
</tbody>
</table>

Table 6. Output of Experiment 2 and model simulation

<table>
<thead>
<tr>
<th></th>
<th>COD removal</th>
<th>NH$_4^+$</th>
<th>NO$_3^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unit</td>
<td>%</td>
<td>mol/L</td>
<td>mol/L</td>
</tr>
<tr>
<td>Experiment</td>
<td>99.5</td>
<td>0.0813</td>
<td>3.52E-05</td>
</tr>
<tr>
<td>Model</td>
<td>97.6</td>
<td>0.0805</td>
<td>6.41E-05</td>
</tr>
</tbody>
</table>

Table 5 and 6 show that the simplified one-CSTR model can reasonably simulate the outcome of the Duke SCWO system. The predicted COD removal rate was lower than the actual removal; similarly nitrate effluent con prediction was higher than the experimental value, and ammonia simulated effluent was close in experiment #1 and slightly lower in experiment #2. Considering that the complexity of the model and that kinetic parameters were collected from others’ works, the fit can be considered to be relatively good. It is possible that the composition of sludge and other uncertainties resulted in the differences observed. Overall, these results show that the simplified
model and reaction pathway and kinetics can be used to predict the nitrogen reaction in the Duke SCWO system.

The data for exhaust gas composition from the Duke SCWO system and model are shown in Table 7. As shown in Table 7, the prediction of nitrogen is the most accurate, and the values of CO$_2$ and O$_2$ from model were about 3% and 2% off, respectively. There is reason for such small deviations, and not necessarily the error in the model. The ratio of carbon and nitrogen in raw sludge in this model was assume to be 5 to 1, which was the global consensus estimated ratio. However, this value should be higher in experiment because the addition of IPA as co-fuel in Duke SCWO system. Therefore, the total carbon and oxygen consumption in model were lower than practical experiment, which caused the predicted CO$_2$:lower and O$_2$: higher than experiment data.

<table>
<thead>
<tr>
<th></th>
<th>CO$_2$ (%)</th>
<th>O$_2$ (%)</th>
<th>N$_2$ (%)</th>
<th>N$_2$O (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exp NO.1</td>
<td>15.2</td>
<td>8.5</td>
<td>about 76%*</td>
<td>about 150*</td>
</tr>
<tr>
<td>Model</td>
<td>12.3</td>
<td>10.1</td>
<td>77.5</td>
<td>833</td>
</tr>
</tbody>
</table>

* Value of nitrogen gas is estimated using 100% minus the oxygen and carbon dioxide, as the N2 sensor is not installed on the system.

*Value is approximate for now, as N2O sensor showed significant interferences with CO$_2$. We have additional GC data pointing to the approximate value reported here.
5.2.3 Model parameter sensitivity

Fig.15. Parametric plot of the ammonia and nitrate flow rate (mol/s) vs reactor temperature

(1). Ammonia and nitrate

The ammonia and nitrate concentration in the effluent was predicted to be 0.078 mol/L and 9.87E-05 mol/L, (Table 5) which correlated with the experiment data of concentration in the Duke SCWO effluent. The parametric sensitivity of the process to the oxygen content and the reactor temperature was investigated next.
Ammonia concentration remains relatively high even the oxygen existing, as shown in (Table 5 and 7), which reflects the refractory properties of ammonia in SCWO (Webley et al., 1991; Hong, Fowler, Killilea, & Swallow, 1987; Takahashi, Wydeven, & Koo, 1989). The predicted ammonia and nitrate levels as a function of temperature are reported in Fig. 15. Although the values are not varying much, the trends showed a decrease with the increasing temperature, which is probably the result from the increasing rate of oxidation of ammonia (R4), as shown in Fig. 16.

Fig. 16. Parametric plot of the R4 reaction rate (L mol⁻¹s⁻¹) vs reactor temperature
Fig. 17 shows the model simulated effluent concentrations of N₂ and N₂O as affected by reactor temperature. The increasing temperature leads to an increase in the molar flow of nitrogen gas and a decrease in the molar flow of N₂O. Similar trends were observed experimentally by our team (results to be confirmed after addressing analytical issues) and by Philip’s work on ammonia reaction in supercritical water oxidation (Savage, 1999). They pointed out the increased N₂O formation, at low temperature,
probably due to the increase rate of formation (R6 in Fig. 18) and decrease rate of decomposition (R11 in Fig. 18) of NO₂ radical.

**Fig.18.** Parametric plot of the R6 and R11 reaction rates vs temperature
5.2.4 N$_2$O emission reduction

Fig. 19. N$_2$O molar flow rate (mol/s) in outlet vs R11 activation energy

To reduce the emission of N$_2$O, a possible solution is thus to increase the temperature according to Fig. 19. However, there are limitations for the materials of construction of the reactor, the reactor temperature should not be higher than 600-650 °C for the Duke SCWO system. Possibly, a catalyst could be used for controlling N$_2$O emissions. Bowen’s study (Yang et al., 2018) about catalysts for denitrification shows the capability of metal salt to catalyze that reaction in SCWO. Tae explored various catalysts' effect on COD conversion and oxidation rate in the SCWO system (Park, T. J et al., 2003). As shown in Fig. 19, the N$_2$O generation rate is positively correlated with the activation
energy of R11 (decomposition of NO$_2$ radical). Therefore, to control the N$_2$O emission, appropriate catalysts that reduce the activation energy of R11 should be sought.
6. Improvement of model

The model that was developed proved useful in describing the SCWO process. Still, it remains a simplification of the actual process. Some improvements are suggested.

1. Energy model will be added after the heating losses are characterized

   In this study, a simplified model was developed and it performed well to predict the nitrogen and COD reactions. However, because of limitation of time, the energy model was not included in this model. By combining the energy model with kinetics, the temperature in the reactor would be able to be predicted.

2. Extend the model reactor from one CSTR to multiple

   In this simplified model, the output of the reaction was predicted. To improve the accuracy of the model further, changing the model from one CSTR to multiple CSTRs will simulate the real plug flow property in the reactor.

3. Consider the carbon dioxide dissolution

   The exhaust gas of the real system is different from the output of the model, due to the dissolution of carbon dioxide in the G/L separator. It is necessary for the model to include the dissolution of carbon dioxide in the liquid effluent, in order to directly validate the output of gas. This will enable pH modeling, which could be beneficial.

4. Explore the pressure effect on the kinetics

   The pressure in the SCWO is generally 230-250 bar, which is poses challenges to find appropriate rate constants for the kinetics in the model. The effects of pressure on
the reaction rate were neglected. However, adding the effects of pressure into the model, may lead to better predictions and allow exploring the effects of pressure on the performance of the system.

5. Explore how inorganic metal affects the nitrogen reaction

Metals may play a significant role as a catalyst to affect the reactions, in particular N₂O formation. By including different metals in the experiments with the pilot SCOW system, possibly means to reduce N₂O can be found, and these effects on kinetics can be included in the model for better representation of the fate of nitrogen.
7. Conclusion

FTIR can be used to quantify the nitrogen functional group in sludge, but the sludge requires dewatering before analysis. The data and results of the FTIR quantification test can be applied to calculate the nitrogen functional group percentage in sludge.

The kinetic schematic and simplified model that was developed could predict the reactions in the Duke SCWO system well and provide information about the mechanism of products and by-products generation. The prediction results for the ammonia, nitrate in effluent and COD conversion rate were relatively close to the experiment data. The prediction COD conversion rate was lower than the experiment result, possibly affected by inorganic salts and properties of fluid undergoing treatment.

Increasing temperature can reduce the ammonia, nitrate, and N₂O production rate, and promote nitrogen conversion to N₂. To control the emission of N₂O, the operation can focus on increasing reactor temperature and applying a catalyst for NO₂ radical decomposition.
## Appendix A

<table>
<thead>
<tr>
<th>PARAMETER</th>
<th>PHYSICAL MEANING</th>
<th>UNIT</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V$</td>
<td>Volume of each CSTR</td>
<td>$L$</td>
</tr>
<tr>
<td>$F$</td>
<td>Mass flow rate through reactor</td>
<td>$kg/L$</td>
</tr>
<tr>
<td>$Q[i]$</td>
<td>Volumetric flow rate in CSTR [i] (i=1,2,3,4,5)</td>
<td>$L/s$</td>
</tr>
<tr>
<td>$C_{in}$</td>
<td>Concentration of substance in inflow</td>
<td>$mol/kg$</td>
</tr>
<tr>
<td>$C[i]$</td>
<td>Concentration of substance in CSTR [i] (i=1,2,3,4,5)</td>
<td>$mol/L$</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>Stoichiometric number of sludges</td>
<td>N/A</td>
</tr>
<tr>
<td>$\beta$</td>
<td>Stoichiometric number of hydroxyl radical</td>
<td>N/A</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>Stoichiometric number of oxygen radical</td>
<td>N/A</td>
</tr>
<tr>
<td>$x$</td>
<td>Carbon ratio over nitrogen in sludge</td>
<td>N/A</td>
</tr>
<tr>
<td>$R[i]$</td>
<td>Reaction rate in CSTR [i] (i=1,2,3,4,5)</td>
<td>$mol/L \cdot s$</td>
</tr>
<tr>
<td>$k[i]$</td>
<td>Reaction rate constant in CSTR [i] (i=1,2,3,4,5)</td>
<td></td>
</tr>
<tr>
<td>$Ea$</td>
<td>Activation energy</td>
<td>$kJ/L$</td>
</tr>
<tr>
<td>$A$</td>
<td>Pre-exponential factor</td>
<td>N/A</td>
</tr>
<tr>
<td>$\rho[i]$</td>
<td>Density in CSTR [i] (i=1,2,3,4,5)</td>
<td>$kg/L$</td>
</tr>
<tr>
<td>$m_{w[i]}$</td>
<td>Total mass of water in CSTR[i] (i=1,2,3,4,5)</td>
<td>$kg$</td>
</tr>
<tr>
<td>$m_{g[i]}$</td>
<td>Total mass of gas in CSTR [i] (i=1,2,3,4,5)</td>
<td>$kg$</td>
</tr>
<tr>
<td>$T[i]$</td>
<td>Temperature of mixture in CSTR [i] (i=1,2,3,4,5)</td>
<td>$K$</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
<td>Unit</td>
</tr>
<tr>
<td>--------</td>
<td>-------------------------------------</td>
<td>-----------------</td>
</tr>
<tr>
<td>$M$</td>
<td>Molar mass</td>
<td>kg/mol</td>
</tr>
<tr>
<td>$a, b, h, d$</td>
<td>Regression constants for water density</td>
<td>N/A</td>
</tr>
<tr>
<td>$C_p[i]$</td>
<td>Heat capacity of mixture in CSTR[i] (i=1,2,3,4,5)</td>
<td>kJ/kg·K</td>
</tr>
<tr>
<td>$e, f, g$</td>
<td>Regression constants for water heat capacity</td>
<td>N/A</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>Gas heat capacity correction factor</td>
<td>N/A</td>
</tr>
<tr>
<td>$\Delta H$</td>
<td>Enthalpy of reaction</td>
<td>kJ/mol</td>
</tr>
</tbody>
</table>
## Appendix B

Reaction mechanism rate coefficients in form $k = AT^z e^{-\frac{E_a}{RT}}$. Units are moles, L, seconds, Kelvins and J/mole.

<table>
<thead>
<tr>
<th>REACTION</th>
<th>$A$</th>
<th>$z$</th>
<th>$E_a$</th>
<th>REFERENCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$\alpha_1 C_x - NH_2 + \beta_1 \cdot OH + \gamma_1 \cdot O \rightarrow \alpha_1 NH_4^+ + x\alpha_1 CO_2 + X_1H_2O$</td>
<td>4.36E+03</td>
<td>0</td>
<td>20.4</td>
</tr>
<tr>
<td>2</td>
<td>$\alpha_2 C_x - NO_2 + \beta_2 \cdot OH + \gamma_2 \cdot O \rightarrow \alpha_2 NO_3^- + x\alpha_2 CO_2 + X_2H_2O$</td>
<td>4.36E+03</td>
<td>0</td>
<td>20.4</td>
</tr>
<tr>
<td>3</td>
<td>$\alpha_3 C_x - N - +\beta_3 \cdot OH + \gamma_3 \cdot O \rightarrow 0.5\alpha_3 N_2 + x\alpha_3 CO_2 + X_3H_2O$</td>
<td>4.36E+03</td>
<td>0</td>
<td>20.4</td>
</tr>
<tr>
<td>4</td>
<td>$NH_4^+ + \cdot OH \rightarrow \cdot NH_2 + H_2O + H$</td>
<td>2.04E+03</td>
<td>2.040</td>
<td>2.326</td>
</tr>
<tr>
<td>5</td>
<td>$\cdot NH_2 + \cdot O \rightarrow NO + 2H$</td>
<td>4.00E+03</td>
<td>2</td>
<td>6.402</td>
</tr>
<tr>
<td>6</td>
<td>$NO + \cdot O \rightarrow \cdot NO_2$</td>
<td>1.30E+12</td>
<td>-0.75</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>$\cdot NH_2 + \cdot NO_2 \rightarrow N_2O + H_2O$</td>
<td>2.60E+15</td>
<td>-2.191</td>
<td>1.904</td>
</tr>
<tr>
<td>8</td>
<td>$\cdot NH_2 + NO \rightarrow N_2 + H_2O$</td>
<td>6.20E+12</td>
<td>-2.19</td>
<td>0</td>
</tr>
<tr>
<td>9</td>
<td>$HNO_3 \rightarrow \cdot NO_2 + \cdot OH$</td>
<td>1.26E+15</td>
<td>0</td>
<td>199.577</td>
</tr>
<tr>
<td>10</td>
<td>$\cdot NO_2 + \cdot OH \rightarrow HNO_3$</td>
<td>1.00E+11.6</td>
<td>-0.85</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Reaction</td>
<td>Rate Constant</td>
<td>E0</td>
<td>A</td>
</tr>
<tr>
<td>---</td>
<td>--------------------------------------</td>
<td>---------------</td>
<td>----</td>
<td>---</td>
</tr>
<tr>
<td>11</td>
<td>( \cdot NO_2 \rightarrow NO \cdot O )</td>
<td>7.60E+18</td>
<td>-1.27</td>
<td>306.645</td>
</tr>
<tr>
<td>12</td>
<td>( N_2 + \cdot OH \rightarrow N_2O + H )</td>
<td>3.2E+09</td>
<td>0</td>
<td>336.8</td>
</tr>
<tr>
<td>13</td>
<td>( N_2O \cdot O \rightarrow 2 NO )</td>
<td>1.00E+11</td>
<td>0</td>
<td>117.2</td>
</tr>
<tr>
<td>14</td>
<td>( H_2O + \cdot O \rightarrow 2 \cdot OH )</td>
<td>1.50E+07</td>
<td>1.14</td>
<td>72.170</td>
</tr>
<tr>
<td>15</td>
<td>( O_2 + N_2 \rightarrow 2 \cdot O + N_2 )</td>
<td>2.09E+9</td>
<td>-1</td>
<td>493.880</td>
</tr>
<tr>
<td>16</td>
<td>( 2 \cdot O + N_2 \rightarrow O_2 + N_2 )</td>
<td>1.89E+7</td>
<td>0</td>
<td>7.481</td>
</tr>
</tbody>
</table>
## Appendix C

Enthalpy values for each reaction, unit as kJ/mol

<table>
<thead>
<tr>
<th>REACTION</th>
<th>ΔH</th>
<th>REFERENCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha_1 C_x - NH_2 + \beta_1 \cdot OH + \gamma_1 \cdot O \rightarrow \alpha_1 NH_4^+ + x\alpha_1 CO_2 + X_1 H_2O$</td>
<td>-835.48</td>
<td>(1)</td>
</tr>
<tr>
<td>$\alpha_2 C_x - NO_2 + \beta_2 \cdot OH + \gamma_2 \cdot O \rightarrow \alpha_2 NO_3^- + x\alpha_2 CO_2 + X_2 H_2O$</td>
<td>-835.48</td>
<td>(1)</td>
</tr>
<tr>
<td>$\alpha_3 C_x - N + \beta_3 \cdot OH + \gamma_3 \cdot O \rightarrow 0.5\alpha_3 N_2 + x\alpha_3 CO_2 + X_3 H_2O$</td>
<td>-835.48</td>
<td>(1)</td>
</tr>
<tr>
<td>$NH_4^+ + 2 \cdot OH \rightarrow NH_2 + 2H_2O$</td>
<td>-465.571</td>
<td>(2)</td>
</tr>
<tr>
<td>$\cdot NH_2 + 4 \cdot OH \rightarrow NO + H_2O$</td>
<td>-352.159</td>
<td>(2)</td>
</tr>
<tr>
<td>$NO + \cdot O \rightarrow \cdot NO_2$</td>
<td>-531.033</td>
<td>(2)</td>
</tr>
<tr>
<td>$\cdot NH_2 + \cdot NO_2 \rightarrow N_2O + H_2O$</td>
<td>74.708</td>
<td>(2)</td>
</tr>
<tr>
<td>$\cdot NH_2 + NO \rightarrow N_2 + H_2O$</td>
<td>-296.776</td>
<td>(2)</td>
</tr>
<tr>
<td>$HNO_3 \rightarrow NO_2 + \cdot OH$</td>
<td>-38.355</td>
<td>(2)</td>
</tr>
<tr>
<td>$NO_2 + \cdot OH \rightarrow HNO_3$</td>
<td>38.355</td>
<td>(2)</td>
</tr>
<tr>
<td>$\cdot NO_2 \rightarrow NO + \cdot O$</td>
<td>531.033</td>
<td>(2)</td>
</tr>
<tr>
<td>$2N_2 + O_2 \rightarrow 2N_2O$</td>
<td>166.61</td>
<td>(2)</td>
</tr>
<tr>
<td>$N_2O + \cdot O \rightarrow 2 NO$</td>
<td>-179.516</td>
<td>(2)</td>
</tr>
<tr>
<td>$2H_2O + O_2 \rightarrow 2 \cdot OH$</td>
<td>497.794</td>
<td>(2)</td>
</tr>
<tr>
<td>$O_2 \rightarrow 2 \cdot O$</td>
<td>485.708</td>
<td>(2)</td>
</tr>
<tr>
<td>$2 \cdot O \rightarrow O_2$</td>
<td>-485.708</td>
<td>(2)</td>
</tr>
</tbody>
</table>

(1) Tested by Duke Sanitation solution group  
(2) NIST JANAF table: https://janaf.nist.gov/
References


