AMMONIA AS A CONTAMINANT IN THE PERFORMANCE OF AN INTEGRATED SOFC REFORMER SYSTEM

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ABSTRACT

As supply of natural gas (NG) is limited, more attention is being given to operating fuel cells on syngas derived from gasification of feedstocks such as coal and biomass. Ammonia (NH₃) is one of the problematic contaminants contained in syngas produced from these nitrogen containing feedstocks. NH₃ can be easily oxidized to nitric oxide (NO) in a combustion process and thus if present in the anode exhaust gas would be problematic. The potential effects of NH₃ (particularly at low levels) on fuel cell system performance have not been well studied. The former studies on NH₃ have been limited to either the reforming process alone or testing the fuel cell at the cell level with NH₃ containing gases. No studies have been accomplished on a fuel cell system level basis. Objectives of this work are to obtain a comprehensive understanding of fuel cell system performance on syngas containing NH₃ using an integrated SOFC reformer system. Detailed analysis is conducted within the three major reacting components – indirect internal reformer, SOFC stack and combustion zone. Various simulation tools (etc., CHEMKIN, ASPEN, APSAT) are utilized for analysis. Results show that NH₃ conversion (into N₂ and H₂) in the internal reformer is about 50% when temperature is 750°C. NH₃ conversion (into N₂ and H₂) in the SOFC stack can affect NOₓ emissions significantly. More than 50% NH₃ left from SOFC stack can convert into NOₓ in the combustion zone. Experimental study is also planned to validate the theoretical results.

Keywords: Ammonia (NH₃); Impurity; Nitrogen oxides (NOₓ); Solid Oxide Fuel Cell (SOFC); Coal syngas (CS)

1. INTRODUCTION

It is well recognized that solid oxide fuel cell has a significant advantage of fuel flexibility over the low temperature fuel cells [1]. Various fuels can be processed to produce a reformate (containing primarily H₂ and CO) for direct use in a solid oxide fuel cell. The main fuel sources used to produce this reformate include fossil fuels (e.g., natural gas, oil and coal), and renewable fuels (e.g., biomass and waste). The impacts of multi-fuel operation of integrated SOFC reformer systems on component performance, design point selection, thermal management and overall system efficiency were discussed [2]. However, the potential effects of one major fuel impurity – NH₃, haven’t been studied well.

Depending on the gasifier design, operating conditions and the fuel bound N₂ content, the concentration of NH₃ in the coal syngas can be as high as 0.5 mol% [3-7]. Water based NH₃ removal systems involve cooling the syngas to around 400K, and can remove a substantial amount of NH₃, with residual levels of up to 400ppm as reported [4]. Although the sensible heat recovered in this cooling process may be effectively utilized elsewhere, the process results in reduced cycle efficiency and is not preferable in the advanced power generation design. High temperature clean up systems, which can provide higher efficiency and have less serious tar issues, however remove very little or no NH₃ at all [4, 8].

In the state-of-the-art integrated coal gasification, high temperature fuel cell and gas turbine hybrid systems, NH₃ contained in the cleaned coal gas is first passed through fuel cell before entering gas turbine. Any remaining NH₃ after the fuel cell stack may be converted to nitrogen oxides in the gas turbine combustor. Understanding of NH₃ performance in the
SOFC system is thus important for coal based SOFC hybrid systems.

In addition to being present in coal derived syngas, NH₃ is also present in gas derived from pyrolysis of nitrogen bearing feedstocks such as biomass [8, 13].

Recently, a number of research groups [9-12] have been showing great interest in NH₃ as a H₂ carrier or a direct fuel for fuel cells, which are, however, beyond the current scope of this study.

The former studies on NH₃ conversion are limited to either reforming processes or the fuel cell [10, 12-15] but none on a system level basis. Very little literature work can be found to have detailed study on NH₃ reaction at very low partial pressure (<2.6 torr) in the reformer. Objectives of this work are to theoretically study the performance of low content NH₃ within a pre-commercial integrated SOFC system. Detailed study will be conducted within the three major components – reformer, SOFC stack and combustion zone. In the further step, strategies on NOₓ emissions control within integrated coal gasification, fuel cell and gas turbine combined cycle will be proposed. Experimental study is also planned based on the theoretical results.

2. SOFC SYSTEM DESCRIPTION

A typical integrated SOFC reformer system, the Siemens Westinghouse 25 kW SOFC system [2], is studied in this work. Figure 1 presents an overall system schematic and details of the SOFC stack design based on natural gas fuel. Compressed and desulfurized natural gas is fed to indirect internal reformers (or pre-reformers) with part of spent fuel from an anode off-gas recirculation plenum near the top of the fuel cell stack. In the nickel-based reformers, methane (CH₄) or any higher hydrocarbons react with the steam brought with spent fuel at a temperature as high as 750°C, and are converted to H₂, CO, CO₂, and remaining CH₄. This reformed fuel mixture then enters a fuel manifold at the bottom of the stack where it flows upwards and is distributed to the outside surface of the tubular cells. Meanwhile, after preheating in a recuperator, air is fed by an injection tube and flows upwards along the inside surface of the tubular cells. With fuel on the outside and oxygen from the air on the inside electrochemical reactions take place along the length of the cells. The temperature inside the module and along the length of each cell varies somewhat but the maximum temperature is generally kept below 980°C – 1050°C. Anode off-gas enters the recirculation plenum where a fraction of it is recirculated and the balance flows into the combustion plenum to mix with the depleted air. The small amount of remaining anode off-gas is combusted with the depleted air to preheat the air through the recuperator and provide heat to the reformers before it is exhausted. Notice that Figure 1 just presents the overall concept for stack design. More details about mixing phenomena for combustion zone will be described and discussed in the following modeling section.

The main interest of this work is to investigate the performance of NH₃ as an impurity within the integrated SOFC system, which contains three major components where NH₃ reactions can occur: the reformer, SOFC stack and combustor. The process flow diagram among those three reactors is shown in Figure 2. The detailed configuration of each component will be described in the following sections. Other components, such as recuperator and heater, are not presented in this diagram.

Figure 1: System schematic and SOFC module details of the Siemens Westinghouse 25 kW SOFC system [2]

Figure 2: Process diagram for SOFC with anode recycle
3. NH₃ REACTION MECHANISMS

3.1. Reformer

Four identical reformers with nickel based catalyst are used within 25kW SOFC system, each per quadrant of SOFC stack. Operating temperature is maintained within the range of 720-750°C. The reformer annular geometry (see Figure 3) is: inside radius \( r_{in} = 6.6 \text{ cm} \), outside radius \( r_{out} = 8.4 \text{ cm} \), length \( L = 40 \text{ cm} \).

Based on the previous studies [14, 16-21], the working conditions within 25kW SOFC internal reformer consisting of high temperature (up to 750°C), low pressure (~1.1 bar), and presence of nickel-based catalyst used for steam reformation, can promote the decomposition of NH₃ via the following overall endothermic reaction:

\[
2NH_3 \rightarrow N_2 + 3H_2 \quad H = 11 \text{ kcal/mol} \tag{1}
\]

![Figure 3: Reformer geometry and internal flow configuration](image)

Commercial NH₃ cracking units are designed based on the above reaction mechanism to produce mixture of H₂ and N₂ from anhydrous NH₃. When reaction takes place on nickel catalyst at a temperature of 850°C to 900°C, most of the NH₃ is cracked and residual NH₃ content is rather low, less than 100ppm without requiring additional purifier as reported [18, 22].

Due to the lower reaction temperature and much lower NH₃ concentration compared to the commercial NH₃ cracking units, however, the internal reformer might not convert most of the NH₃ into H₂ and N₂ before it enters the SOFC stack. Quantitative assessment of residual NH₃ level in the reformer outlet requires a further understanding of NH₃ decomposition mechanism under the reaction conditions unique to the reformer.

In this work, NH₃ contained in the fuel is at impurity level of less than 0.5% by volume. At low NH₃ concentrations, reaction mechanism for NH₃ decomposition can be described using the following sequence [10, 23]:

Step 1: \( NH_3(\text{ad}) \stackrel{k_1}{\rightarrow} \text{NH}_3(\text{ad}) \) \tag{2}
Step 2: \( \text{NH}_3(\text{ad}) + H(\text{ad}) \rightarrow \text{NH}_4(\text{ad}) + H(\text{ad}) \) \tag{3}
Step 3: \( \text{NH}_4(\text{ad}) \rightarrow \text{NH}_3(\text{ad}) + H(\text{ad}) \) \tag{4}
Step 4: \( \text{NH}(\text{ad}) + H(\text{ad}) \rightarrow N(\text{ad}) + 3H(\text{ad}) \) \tag{5}
Step 5: \( 2H(\text{ad}) \rightarrow H_2(\text{ad}) \) \tag{6}
Step 6: \( 2N(\text{ad}) \rightarrow N_2(\text{ad}) \) \tag{7}

where \( \text{(ad)} \) denotes that the species is adsorbed on the catalyst surface.

Depending on the reaction temperature, rate limiting step in catalytic NH₃ decomposition can be the NH₃ adsorption (1), the recombinative desorption of N₂ (step 6), or both. Step 2-5 are found kinetically insignificant [17, 19, 23].

a) Low Operating Temperature

When the temperature is low (<727°C based on nickel catalyst), the decomposition rate is independent of NH₃ partial pressure, where the rate-limiting step is the recombinative desorption of N₂, with activation energies around 125-210 kJ/mol [19, 21]. The NH₃ decomposition rate is closely approximated by [21]:

\[
r_{NH_3} = n_0 \cdot k_6 \tag{8}
\]

where, \( n_0 \) is the nickel surface atom density and is given as \( 1.5 \times 10^{13} \text{ cm}^{-2} \); \( k_6 \) is the rate constant for the N₂ recombination in step 6, and is given as [21]:

\[
k_6 = 1 \times 10^3 \text{ s}^{-1} \cdot \exp\left(\frac{-211 \text{ kJ mol}^{-1}}{RT}\right) \tag{9}
\]

b) High Operating Temperature

When the temperature is high (>727°C based on nickel catalyst), the decomposition rate is first-order dependent on NH₃ partial pressure and the rate-limiting step is the NH₃ adsorption, with activation energies in the range of 16-42 kJ/mol [19, 21]. When partial pressure of NH₃ is low, the decomposition rate is independent of N₂ and H₂ partial pressures [19, 24].

Based on the above observations, a power law rate model was suggested [19, 21] to express the NH₃ decomposition rate at high temperature and low NH₃ partial pressure:

\[
r_{NH_3} = k_1 \cdot p_{NH_3} \tag{10}
\]

where, \( k_1 \) is rate constant for NH₃ adsorption in the step 1 of NH₃ decomposition, and \( p \) is the partial pressure. \( k_1 \) is given as [21]:

\[
k_1 = 4.07 \times 10^{16} \text{ molecules cm}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1} \tag{11}
\]

At temperature higher than 520°C, rate constant was obtained to fit experimental data for NH₃ decomposition using a nickel based catalyst [19]:

\[
k_1 = 1.309 \times 10^{12} \cdot \exp\left(\frac{-2.06 \times 10^5 \text{ kJ mol}^{-1}}{RT}\right) \tag{12}
\]

In this work, NH₃ partial pressure is less than 2.6 torr (0.05 psi). The reformer operates at a temperature range of 720°C-750°C, within the high temperature region as discussed before. Therefore, NH₃ conversion can be regarded as dominated by NH₃ adsorption (step 1).

Other than expressed as a series of elementary reactions, surface reactions are also described and studied using global reactions. To seek a simple global rate expression, kinetics of
NH₃ decomposition on Ni/Al₂O₃ catalysts are described using the Temkin-Pyzhev mechanism [25-27]:

\[ r_{NH_3} = k_0 \cdot \exp \left( \frac{-E}{RT} \right) \cdot \left( \frac{P_{Ni}}{K_{eq}} \right)^{\beta} \cdot \left( \frac{P^{3}_{NH_3}}{P^{2}_{N_2}} \right)^{\beta} \]  \( (13) \)

where, \( K_{eq} \) is the thermodynamic equilibrium constant defined as:

\[ \log(K_{eq}) = \frac{-2250.322}{T} + 0.85340 + 1.51049 \log T + 25.8987 \times 10^{-5} T - 14.8961 \times 10^{-8} T^2 \]

Kinetic parameters, the pre-exponential factor \( k_0 \), the activation energy \( E \) and exponent constant \( \beta \) are measured experimentally in the pressure range 9-36 bar and a temperature range of 400-550°C [28]:

\[ k_0 = 5.744 \times 10^{13} \text{ mol/(m}^3 \cdot \text{s} \cdot \text{Pa}^{0.674}) \]

\[ E = 2.304 \times 10^2 \text{ kJ/mol} \]

\[ \beta = 0.674 \]

Kinetics of NH₃ decomposition on various catalysts, vanadium nitride (VN), palladium (Pd) and Iridium (Ir), have also been studied and expressed in Langmuir-Hinshelwood format [29-31].

However, none of the global rate expressions was found appropriate for reaction conditions of interest in this work, very low pressure and relatively high temperature (~750°C).

### 3.2. SOFC

All the NH₃ remained after the reformer will enter SOFC stack. Or, if a SOFC system is designed to operate directly on coal syngas without external or internal reformers, then the NH₃ contained in the coal syngas will be a potential concern for SOFC stack, either degrade the SOFC performance or generate nitrogen oxides (NOₓ).

NH₃ as a fuel contaminant in coal syngas or biogas has been tested on SOFCs and showed no strong association of cell degradation [13, 32]. Instead, NH₃ has been considered as a direct fuel for fuel cell based on the reaction (18). In 1980, Farr at al. [12, 15] constructed and tested a solid electrolyte fuel cell operating on NH₃ fuel to generate electric energy and nitric oxide (NO) for the production of HNO₃. It was shown that the fuel cell, [NH₃, NO, N₂, Pt/ZrO₂ (8% Y₂O₃)/Pt, air], produced mainly NO when operating at temperature around 1100K, and showed that Pt based catalyst has high selectivity to convert NH₃ into NO via electrochemical oxidation. Instead of producing NO, more recent research efforts are to avoid the NO formation in SOFC. The more recent concept for using NH₃ as a direct fuel in SOFC is sending NH₃ directly to SOFC anode surface containing a catalyst, such as iron oxide, Fe₂O₃, or nickel-based compound. NH₃ is first cracked into N₂ and H₂, and the generated H₂ is then utilized for the electrochemical generation of electricity. Based on the experimental results using silver anode and platinum anode with or without iron-based catalyst, Wojcik et al. [14] predicted that NH₃ could work very well in an SOFC system based on nickel anodes, although no actual experimental work has been conducted on nickel anode SOFC in their work. NH₃ performance in a SOFC with Ni/8YSZ anode was studied by Dekker et al. [10]. In their cell tests, the fuel cell outlet gas was measured and analyzed for NOₓ and NH₃ to determine the NH₃ conversion. It was concluded that at operating temperature of 800-1000°C, the conversion of NH₃ is higher than 99.996% due to the withdrawal of H₂ by the electrochemical reaction and is close to the thermodynamic equilibrium. Most of the NH₃ is cracked into H₂ and N₂. The NOₓ outlet concentration of the fuel cell was measured to be below 0.5 ppm at temperature up to 950°C and around 4 ppm at 1000°C.

Some researchers [10, 13] argue that NH₃ as a fuel or fuel impurity can be completely converted into N₂ and H₂ over the SOFC nickel based anode when temperature is high (> 590°C as found in [13]). However, other research groups [19, 21] found out that NH₃ conversion on nickel based catalyst can be high but never reach an equilibrium level even with nickel based catalyst and within high temperature range (>500°C). For example, NH₃ conversion on Ni-Pt/Al₂O₃ catalyst was measured higher than 80% but less than 99% in the temperature range of 520-690°C [19]. From theoretical understanding, high operating temperature of SOFC helps increase reaction rate, however, the overall limiting step for NH₃ conversion can be the mass transfer. Slow NH₃ diffusion especially at low concentration can limit the reach of NH₃ to catalyst surface and therefore leads to lower conversion. Moreover, H₂ existing at anode site, with much higher concentration and diffusivity compared to NH₃, can compete with NH₃ to reach catalyst surface, and further limit NH₃ conversion. Therefore, an accurate prediction of NH₃ conversion within SOFC stack should cover the effects of various factors including catalyst, temperature, residence time and fuel composition, especially, H₂ concentration and NH₃ concentration.
SOFC anode side (fuel gas and anode surface) in this study contains the following species: H₂, CO, CO₂, H₂O, N₂, CH₄, NH₃ and O²⁻. It is noteworthy that nickel, an active catalyst for NH₃ cracking as introduced before, is contained in both anode and interconnection contact, as shown in Figure 4 [33].

In the typical SOFC system operating on natural gas, anode reactions are generalized as:

\[ H_i + O^{2-} \rightarrow H_iO + 2e^- \]  \hspace{1cm} (14)
\[ CO + O^{2-} \rightarrow CO_2 + 2e^- \]  \hspace{1cm} (15)
\[ CH_i + 4O^{2-} \rightarrow CO_2 + 2H_2O + 8e^- \]  \hspace{1cm} (16)

Due to the existence of NH₃ and nickel catalyst, the following additional anode reactions are considered based on the suggestions by different studies [10, 12, 14, 15]:

a. NH₃ cracking:
\[ 2NH_3 \rightarrow N_2 + 3H_2 \]  \hspace{1cm} (1)

b. Electrochemical reaction:
\[ 2NH_3 + 5O^{2-} \rightarrow 2NO + 3H_2O + 10e^- \]  \hspace{1cm} (17)

c. NH₃ reduction via NO:
\[ 4NH_3 + 6NO \rightarrow 5N_2 + 6H_2O \]  \hspace{1cm} (18)

Selectivity to NO or N₂ for NH₃ reaction depends on: catalyst, temperature, O²⁻ diffusivity and NH₃ diffusivity, residence time and NH₃ molar flow rate (content and total fuel flow rate). Within the temperature range of 700-1000°C, it was observed [34] that NO formation reaction (17) is selective with platinum based catalyst. NH₃ cracking reaction (1) is selective with nickel based catalyst.

Since none of the test results show that NH₃ would degrade SOFC performance, the only concern about NH₃ in SOFC stack is its possible causes for NOx generation. No report has been found showing that significant amount of NOx can be produced within fuel cell stack itself. Instead, NOx may be produced when the depleted fuel cell anode gas containing NH₃ is combusted in a combustor before entering turbine. Theoretical study and experimental work are needed to determine the significance of NH₃ content within anode depleted gas on NOx production or reduction (reaction (17) or (18)).

3.3. Combustion zone

Geometry and internal flow pattern of combustion zone are depicted in Figure 5 based on the schematics of the 25kW SOFC system provided by Siemens Westinghouse Power Corporation [33, 35], though the exact configuration and dimensions were not well known. The zone outlets were assumed to be through the sides of the zone (as shown in Figure 1), based on knowledge of the unit. Combustion zone outlet temperature is observed about 860°C, where the anode depleted fuel meet with cathode depleted gas (~16% O₂) and combust to generate heat. NH₃ at that temperature range can react to generate various products (etc., N₂, NO, N₂O) as discovered in various studies [36, 37].

No catalysts are utilized within the combustion zones. Therefore, the study focuses on non-catalytic reaction of NH₃. Actually, NH₃ is commonly used as a reducing agent for NO in both selective catalytic reduction (SCR) and selective non-catalytic reduction (SNCR). It was found that when NH₃ is injected into a fuel-lean zone, which is the case in this work, NO is reduced by the reactions (18) and (19) [37]:

\[ 4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O \]  \hspace{1cm} (19)

It was also reported that NH₃ gives effective reduction of NO emission within a narrow temperature window around 750-850°C. Average temperature (~860°C) of combustion zones studied in this work is slightly out of the temperature range. One negative effect is that if NH₃ is excess, NO and N₂O can be formed via the following overall reactions:

\[ 4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O \]  \hspace{1cm} (20)
\[ 4NH_3 + 4O_2 \rightarrow 2N_2O + 6H_2O \]  \hspace{1cm} (21)

4. MODELING

4.1. Overall strategy and tools

ASPEN PLUS, a widely used commercial simulation tool for process engineering, is applied to determine the reaction kinetics within the reformer. ASPEN PLUS enables the users to define detailed reaction mechanisms and reactor conditions to predict reaction conversions, and understand reaction behavior. Detailed reformer model will be described in the later sections.

Reactions within SOFC stack are studied in two steps using two analysis tools:

1. Major reactions and products from SOFC stack, except those associated with NH₃ kinetics, are determined using a validated simulation tool – Advanced Power Systems Analysis Tool (APSAT). Details about APSAT and SOFC model can be seen in [38, 39].

2. As mentioned before, NH₃ decomposition under SOFC reaction conditions can be from 80% to 99.996%. Detailed model on NH₃ reaction and conversion is not investigated.
in this work. Instead, different conversion levels are considered.

A model comprised of a series of perfectly stirred reactors (PSR) and a plug flow reactor (PFR) from CHEMKIN 4.0.2 is built for simulating the combustion zone.

### 4.2. Reformer

#### 4.2.1 Reactor model setup

Geometry description and flow configuration of the annular steam reformer are shown in Figure 3. The detailed parameters and specifications are listed in Table 1.  Reformer geometry was determined from the observed data [33, 40, 41], while the catalyst information was assumed based on the reference work [42]. The reformer is simulated as a plug flow reactor using RPlug model provided by APSEN PLUS (see Figure 6).

![Figure 6: Reformer model setup (ASPEN RPlug)](Downloaded From: http://proceedings.asmedigitalcollection.asme.org/ on 02/18/2016 Terms of Use: http://www.asme.org/about-asme/terms-of-use)

#### Table 1: Reformer Description

| Parameter | Value | Description |
|-----------|-------|-------------|
| \( r_{in} \) | 6.6 cm | Inside radius of reformer can |
| \( r_{out} \) | 8.4 cm | Outside radius of reformer can |
| \( L \) | 0.4 m | Length of reformer |
| \( \rho_c \) | 2355 kg/m³ | Bulk density of catalyst |
| \( \varepsilon \) | 0.528 | Catalyst bed void fraction |
| \( \alpha \) | 9.3 m²/gcat | Catalyst surface area per unit of mass |

#### Table 2: Reformer operating conditions

| Parameter | Value | Description |
|-----------|-------|-------------|
| Fresh fuel flow rate, g/s | 0.211 | Natural gas | 1.21 | Coal syngas |
| reformer inlet flow rate, g/s | 1.262 | Natural gas | 1.54 | Coal syngas |
| NH₃ content in fresh fuel, % | 0.2 | 0.2 |
| Operation temperature, °C | 750 | 750 |
| Pressure, bar | 1.14 | 1.14 |

Reformer operating conditions and flow information based on both cases of natural gas and coal syngas are summarized in Table 2.  Constant operating pressure and temperature are assumed to approximate the actual steady-state operating conditions.  A typical NH₃ content of 0.2% was assumed based on the reference work [3-7].  Coal syngas fresh fuel flow rate is much higher than natural gas due to its lower fuel heat value.  Anode recirculation ratio is 0.55 for natural gas case and 0.15 for coal syngas.  Those design details can be seen in the former work [2].

#### 4.2.2 Reaction kinetics

Reaction mechanisms and rate expressions for NH₃ decomposition within reformer were discussed in the former section.  Global reaction (1) is incorporated into the ASPEN PLUS model, and different reaction rate expressions are considered and compared.

Due to the low content of NH₃ existing in the reformer, NH₃ decomposition is interesting, however, not a dominating reaction.  A complete model of reformer need include all the other possible reactions.  Major reactions over a nickel supported catalyst within a steam reformer were widely adopted as a three-step mechanism:

1. Endothermic steam reforming reaction,
   \[
   CH_{4} + H_{2}O \leftrightarrow CO + 3H_{2}
   \]  (22)

2. Exothermic water gas shift reaction,
   \[
   CO + H_{2}O \leftrightarrow CO_{2} + H_{2}
   \]  (23)

3. Endothermic full steam reforming plus shift reaction,
   \[
   CH_{4} + 2H_{2}O \leftrightarrow CO_{2} + 4H_{2}
   \]  (24)

Langmuir–Hinshelwood mechanism, a mechanism for surface catalysis in which the reaction occurs between species that are adsorbed on the surface, is commonly applied to determine the reaction rates [26, 42-44].  Typical kinetic rate equations for steam reforming of methane are derived by Xu and Froment, whose work was carried out over a commercial catalyst (Ni/MgAl₂O₄, 15.2% nickel) [42, 43]:

\[
\begin{align*}
    r_1 &= k_1 \left( \frac{P_{CH_4} P_{H_2O}}{P_{H_2}^{0.5}} \right) K_{p1} / DEN^2 \\
    r_2 &= k_2 \left( \frac{P_{CO} P_{H_2O}}{P_{H_2} K_{p2}} \right) / DEN^2 \\
    r_3 &= k_3 \left( \frac{P_{CH_4} P_{H_2O}}{P_{H_2}^{0.5}} \right) K_{p3} / DEN^2
\end{align*}
\]  (25-27)

\[
DEN = 1 + K_{p1} P_{CO} + K_{p2} P_{CH_4} + K_{p3} P_{H_2O} / P_{H_2}
\]  (28)

where, \( p \) is partial pressure of each species in the reactor; \( r_1, r_2, r_3 \) stand for reaction rates for reactions (25), (26) and (27); \( k_1, k_2, k_3 \) are kinetic factors for each reaction; \( K_{p1}, K_{p2}, K_{p3} \) are equilibrium constants; \( K \) as shown in ‘DEN’ term is adsorption constant for each species.
Kinetic factors $k_1, k_2, k_3$ and adsorption constants $K_i$ are defined in Arrhenius format:

$$k_i = A_i \cdot \exp\left(-E_i / RT\right)$$  \hspace{1cm} (29)

$$K_i = A_i \cdot \exp\left(-\Delta H_i / RT\right)$$  \hspace{1cm} (30)

Table 3: Activation energy and pre-exponential factors for kinetic factors $k_i$

| Kinetic Factors | Activation Energy $E_i$ (kJ/mol) | Pre-Exponential Factor $A_i$ |
|-----------------|---------------------------------|----------------------------|
| $k_1$           | 240.1                           | $3.711 \times 10^{14}$ (kmol-Pa$^{0.5}$/kg$_{cat}$s) |
| $k_2$           | 67.13                           | $5.431 \times 10^{3}$ (kmol/kg$_{cat}$s-Pa) |
| $k_3$           | 243.9                           | $8.944 \times 10^{13}$ (kmol-Pa$^{0.5}$/kg$_{cat}$s) |

Table 4: Heat of adsorption and pre-exponential factors for adsorption constant $K_i$

| Adsorption Constant | Heat of Adsorption $\Delta H_i$ (kJ/mol) | Pre-Exponential Factor $A_i$ |
|---------------------|------------------------------------------|----------------------------|
| $K_{CO}$            | -70.65                                   | $8.23 \times 10^{4}$ (MPa)$^{-1}$ |
| $K_{CH_4}$          | -38.28                                   | $6.65 \times 10^{3}$ (MPa)$^{-1}$ |
| $K_{H_2O}$          | 88.68                                    | $1.77 \times 10^{5}$ (unit less) |
| $K_{H_2}$           | -82.9                                    | $6.12 \times 10^{8}$ (MPa)$^{-1}$ |

Table 5: Equilibrium constant $K_{pi}$

| Equilibrium Constant $K_{pi}$ | Units |
|--------------------------------|-------|
| $K_{p1}$                       | $1.198 \times 10^{11} \cdot \exp(-26830/T)$ (MPa)$^2$ |
| $K_{p2}$                       | $1.77 \times 10^{-2} \cdot \exp(4400/T)$ (MPa)$^0$ |
| $K_{p3}$                       | $K_{p1} \cdot K_{p2}$ (MPa)$^2$ |

The constants used in the current model for each of the chemical expressions of interest are presented in Table 3, Table 4 and Table 5, which are derived from literatures [42-44]. It is noteworthy that the above rate equations for the major reactions are dealing with intrinsic kinetics of methane-steam reforming and water-gas shift on the nickel based catalyst, and do not account for diffusion limitations. A more accurate reformer model needs to combine both reaction kinetics and diffusion limitations to have a more accurate prediction. However, the focus of current study is on the NH$_3$ conversion within reformer. NH$_3$ rate expressions as given in equations (10) and (12) were derived from experimental data, which accounted for diffusion effects.

4.3. SOFC stack

Detailed kinetic modeling of NH$_3$ reaction within SOFC stack is not considered in the current work. Instead, conversion ratio of NH$_3$ based on reference work is investigated and summarized as reference for consideration. A complete model of NH$_3$ reaction including consideration of chemical kinetics, mass transfer, and heat transfer will be built in the future.

4.4. Combustion zone

Mixing phenomena and reaction modes are shown in Figure 7, where depleted fuel from recirculation zone is mostly reacted in the area between SOFC tubes. Gas from that area is mixed and reacted with more air in the area between air feed tubes. SOFC tube has an external diameter of 2.2cm, while distance between SOFC tubes is about 3.3cm.

Figure 7: Mixing phenomena and modeling zones

A kinetic model for simulating the combustion zone was achieved using CHEMKIN 4.0.2 for both cases of natural gas and coal syngas (see Figure 8). Mass flow rates and temperatures for model inlets and outlet were predicted using APSAT simulation tool (See [2]). To approximate the mixing
phenomena when anode depleted fuel enters the combustion zone, a series of Perfectly Stirred Reactors (PSRs) with stepwise addition of air are considered. Major reaction zone between SOFC tubes is equally divided into three zones and simulated using three PSR models. Total residence time for those three reactors is about 0.1 second. Area between air feed tubes is simulated with another PSR, with a residence time about 0.5 second. The phenomena including gas composition change due to the heat exchange and temperature drop after combustion products leaving the combustion zone are simulated using a Plug Flow Reactor (PFR). Reaction mechanisms (GRI 3.0) are provided in CHEMKIN, which can predict potential fuel NOx from NH3 as well as thermal NOx. PSR model is applied due to its simplicity and also because it provides solutions to flame problems more quickly [45].

5. RESULTS AND DISCUSSIONS

5.1. Preliminary equilibrium analysis

The equilibrium model from CHEMKIN 4.0.2, coupled with steady state analysis tool APSAT, was firstly used to estimate the gas composition after each of the three reacting components – reformer, SOFC stack and combustor. Typical coal syngas from Wabash coal gasification project is considered [1,46]. Major results are summarized in the Table 6, which suggest:

a) Most of the NH3 is cracked into N2 and H2 before entering combustion zone. In case of coal syngas containing 0.2% NH3, only 13ppm NH3 remains in the reformate stream and enters SOFC stack, while NH3 conversion within the reformer is 99.2%. More NH3 conversion is found in SOFC stack assuming chemical equilibrium is reached, which leaves only 0.3ppm NH3 entering the combustion zone.

b) When comparing NOx levels after the combustion zone with and without NH3 contained in the fuel stream, it is found that NH3 is not the major contributor to the significant amount of NO and NO2 predicted at the combustor outlet. Due to the high conversion based on equilibrium analysis, very little NH3 (0.3ppm) remains after reacting in the reformer and SOFC, and therefore generates negligible fuel NOx at combustion zone. NOx level after combustion zone is predicted to be lower in the coal gas case than natural gas case due to lower combustor temperature.

c) NOx level (less than 0.02ppm) in the system exhaust obtained from the equilibrium analysis is much underestimated when it is compared to the observed data. NOx emissions have never observed to be higher than 1ppm, but still higher than 0.1ppm in the exhaust of 25kW SOFC system based on natural gas fuel [35], which suggests that a more detailed analysis of combustion zone should be conducted. In this work, a kinetics model is set up for such a detailed study with consideration of mixing and reaction phenomena.

d) CHEMKIN equilibrium analysis of NH3 reaction in the reformer can provide reference values but inaccurate results for actual NH3 conversion due to the low NH3 concentration and short residence time (<0.5 second). More detailed kinetics study is necessary, and the results are shown in the following section.

Table 6: Results from CHEMKIN equilibrium analysis

| Stream No. | Fresh Fuel | Ref. in | Ref. out | Anode out | Comb. in | Comb. out | Exhaust | Comb. in | Comb. out | Exhaust | Comb. in | Comb. out | Exhaust |
|------------|------------|--------|---------|-----------|---------|----------|---------|---------|----------|---------|---------|----------|---------|
| H2 %       | 34.80      | 30.15  | 28.89   | 4.38      | 0.38    | 0.38     | 0.78    |         |          |         |          |          |         |
| O2 %       |            |        |         |           |         | 16.80    | 16.90   | 16.90   | 16.80    | 16.23   | 16.23   | 17.30    | 16.71   | 16.71   |
| N2 %       | 2.00       | 2.00   | 2.03    | 1.94      | 74.73   | 78.32    | 78.32   | 74.73   | 75.19    | 75.19   | 76.96   | 77.46    | 77.46   |
| H2O %      |            |        |         |           |         | 4.90     | 8.01    | 32.02   | 2.81     | 3.40    | 3.40    | 3.27     | 3.27    | 3.85    |
| CH4 %      | 1.90       | 1.66   | 0.36    | 0.31      | 0.03    | 0.03     | 0.02    |         |          |         |          |          |         |
| CO %       | 45.30      | 39.84  | 44.56   | 9.6       | 0.83    | 0.83     | 0.51    |         |          |         |          |          |         |
| CO2 %      | 15.80      | 21.19  | 16.15   | 51.16     | 4.42    | 1.36     | 1.36    | 4.42    | 5.31     | 5.31    | 1.42    | 1.97     | 1.97    |
| NH3%       | 0.20       | 0.169  | 0.0013  | 3ppm      | 0.3ppm  | 68.44    | 0.007   | 65.71   | 0.007    | 81.95   | 81.95   | ~0       |         |
| NO, ppm    |            |        |         |           |         |          |         |         |          |         |         |          |         |
| NO2(15%O2), ppm |        |        |         |           |         | 126      | 0.134   | 100     | 0.105    | 146     | 146     | 0.02     |         |
| M, gram/s  | 4.86       | 6.17   | 6.17    | 8.81      | 79.07   | 79.07    | 79.07   | 79.07   | 79.07    | 79.07   | 73.84   | 73.84    | 73.84   |
| T, °C      | 17         | 750    | 750     | 911       | 815     | 815      | 297     | 815     | 815      | 297     | 836     | 836      | 145     |
| P, Bar     | 2.7        | 1.14   | 1.14    | 1.12      | 1.085   | 1.085    | 1.032   | 1.085   | 1.085    | 1.032   | 1.085   | 1.085    | 1.032   |

1: Combustion with NH3 injection (Coal syngas case)
2: Combustion without NH3 injection (Coal syngas case)
3: Combustion without NH3 injection (Natural gas case)
5.2. **Reformer: kinetics results**

The performance of reformer in natural gas case with SOFC anode recirculation is first analyzed using the ASPEN reformer kinetics model (see Figure 9). Methane reformation and reverse water shift reaction reach equilibriums at a reformer length ~0.3 meter. Due to the high reformer operating temperature (750°C), a significant content of CO (~21%) remains when exiting the reformer.

![Figure 9: Reformer process stream profiles for natural gas](image)

**Figure 9: Reformer process stream profiles for natural gas**

Due to the high CO content (~21%) when exiting the reformer, a shift reactor may be considered to couple with SOFC stack when operating on coal syngas for converting CO into H₂ and provide some flexibility to help relieve the challenge of thermal management within SOFC stack.

Residence times for natural gas and coal syngas are compared in Figure 11. Due to the lower inlet flow rate (see Table 2), reformer on coal syngas show a smaller residence time at the beginning compared to natural gas. At the very end of the reformer, coal syngas case shows a higher residence time, because coal syngas composition doesn’t change much along the reformer, however, molar flow rate keeps increasing in natural gas case when steam reformation occurs.

![Figure 11: Residence time comparison](image)

**Figure 11: Residence time comparison**

NH₃ reaction is considered and its conversion in the reformer is predicted based on the reaction mechanism and rate constant introduced in equations (10) and (12). For coal syngas case, as shown in Figure 12, the NH₃ reaction does not reach equilibrium within the reformer reactor, and the NH₃ conversion is limited to about 50% at the end of reformer (temperature = 750°C). For natural gas case, NH₃ reaction almost reaches equilibrium at the end of reformer due to its high CO content (~40%). Instead, since CO content is very high (>40%) and water gas shift reaction is exothermic, a shift reactor may be considered to couple with SOFC stack when operating on coal syngas for converting CO into H₂ and provide some flexibility to help relieve the challenge of thermal management within SOFC stack.

![Figure 12: NH₃ conversion along the reformer](image)

**Figure 12: NH₃ conversion along the reformer**

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lower inlet NH3 content, which is highly diluted by the recirculated anode depleted fuel.

It is noteworthy that NH3 conversion has a nearly linear dependence on the reformer operating temperature. The increase of temperature enhances the conversion (see Figure 13), because NH3 decomposition is endothermic. When temperature is lowered to 700°C from 750°C, the NH3 conversion within the reformer will decrease to 16% from 50% for coal syngas case, and from 45% to 15% for natural gas case.

**Figure 13: Dependence of NH3 conversion on reformer temperature**

Temkin-Pyzhev mechanism and rate constant based on equation (13) have also been incorporated into the reformer model, and the results show that NH3 reaction reaches thermodynamic equilibrium very quickly (less than 0.0001 second). Considering equation (13) is derived at very high pressure, this fast reaction mechanism is not adapted in this work.

### 5.3. SOFC

As introduced before, an accurate prediction of NH3 reactions and conversion in SOFC stack requires a comprehensive understanding of all different factors that could affect NH3 reaction formats and rates, which could be very complicated and need a separate study. In this work, the following two assumptions are made for simplification based on the results shown in literature [10, 13, 19, 21]:

- All the reacted NH3 is cracked into H2 and N2.
- NH3 conversion (with the formation of N2) is in the range of 80-99.996%.

### 5.4. Combustion zone

NOx predictions from combustion zone model are summarized in Table 7, which are generated based on different cases with various fuel types, NH3 contents and NH3 conversions in SOFC stack. All NOx values are adjusted to a 15% O2 dry bases.

When typical natural gas is used as the fuel (case NG 1), thermal NOx emissions are predicted to be about 0.3ppm which is close to the observed data of 0.35ppm [35]. When 0.2% NH3 is added into natural gas (case NG 2), and 80% NH3 conversion in the SOFC stack is assumed, then NOx level is about 3.5ppm. Combustion zone in Case NG 2 has almost the same operating conditions (e.g., temperature, residence time...) as Case NG 1 due to the negligible effects of low content of NH3. Therefore, the thermal NOx emissions from Case NG 2 can be considered the same as in Case NG 1 – about 0.3ppm. The increased NOx in Case NG 2, fuel NOx, is sourced from the adding of NH3. The conversion of NH3 to NOx in the combustion ozone is about 53% (see Table 8), where the left part of NH3 is converted into N2.

For coal syngas cases, thermal NOx, as shown in case CS 1, is about 0.16ppm, lower than NG Case 1 due to the lower temperature. Fuel NOx is found significantly depended on the NH3 conversion in the reformer and SOFC stack. When NH3 conversion in the reformer is about 50% as predicted by the model at a temperature of 750°C and the NH3 conversion in SOFC is low (80%), 0.2% NH3 contained in the coal syngas can cause 17ppm total NOx for a SOFC system integrated with a reformer, and 37ppm NOx without a reformer. Therefore, a reformer can help reduce NOx emissions when NH3 conversion is not very high at SOFC stack.

### Table 7: NH3 conversion and NOx prediction

| Cases | Fresh fuel | Reformer outlet | NH3 conv. in SOFC, % | FC anode outlet | System exhaust |
|-------|------------|----------------|----------------------|----------------|----------------|
| NG 1  | 0          | 0              | N/A                  | 0              | 0.3            |
| NG 2  | 0.002      | 0.00024        | 80                   | 0.000048       | 3.5            |
| CS 1  | 0          | 0              | N/A                  | 0              | 0.16           |
| CS 2  | 0.002      | 0.0009         | 80                   | 0.00018        | 17             |
| CS 3  | 0.002      | N/A            | 80                   | 0.0004         | 37             |
| CS 4  | 0.002      | 0.0009         | 99.996               | 3.6E-08        | 0.16           |
| CS 5  | 0.002      | N/A            | 99.996               | 8.0E-08        | 0.17           |

### Table 8: Analysis results for NH3 to NOx conversion

| Cases | NG 2 | CS 2 |
|-------|------|------|
| Comb. zone inlet NH3, 10^-6 mol/s | 1.79 | 10.5 |
| Comb. zone outlet NH3, 10^-6 mol/s | 2.65 x 10^-5 | 1.68 x 10^-4 |
| Total NOx emissions, 10^-6 mol/s | 1.04 | 6.08 |
| NOx from NH3, 10^-6 mol/s | 0.95 | 6.03 |
| NH3 to NOx, % | 53 | 57 |

When the conversion is high (99.996%), the NOx emissions are very low (less than 0.2ppm) for each case, and concern about NH3 as a contaminant in the coal syngas is not necessary. It suggests that coal syngas from high temperature coal gasifier can be directly sent to SOFC system without special design for NH3 removal. Also, it suggests that if NH3...
conversion is high in SOFC stack, a reformer is not necessary for SOFC system to crack NH₃ when operating on such type of coal syngas.

The mechanism routes for NH₃ to form NOx are plotted in Figure 14 for both cases of natural gas and coal syngas. NH₃ molecule is first broken down into NH₂ species. NH₂ is converted into NH or HNO via reactions with O or OH. NH reacts with O₂ or O to form NO directly, or is converted to HNO. HNO reacts with OH, O₂, O or H to form NO. NO is the only source for forming NO₂ and they can convert to each other. The net increase of NOx (NO & NO₂) comes from either NH or HNO. Natural gas and coal syngas show similar reaction routes for NOx generation from NH₃.

Figure 14: Mechanism analysis for NH₃ to NOx conversion

Table 9: NO formation analysis (reactor PSR 1)

| Cases                  | NG  | CS  |
|------------------------|-----|-----|
| Residence time         | 0.01| 0.01|
| Reactor exit temperature, °C | 1066| 1165|
| NO net formation rate in each reaction, mol/m³/s | 0.26 | 0.02 |
| N+O₂<=>NO+O            | 0.73| 0.53|
| HNO+O<=>NO+OH          | 0.4 | 0.36|
| HNO+H<=>H₂+NO          | 1.5 | 2.0 |
| HNO+OH<=>NO+H₂O        | 2.5 | 2.3 |
| NH+O₂<=>NO+OH          | 0.35| 0.31|
| NH+O<=>NO+H            | 0.2 | 0.18|
| Overall NO net formation rate, mol/m³/s | 5.8 | 5.9 |
| From HNO₂, %           | 88.4| 87 |
| From NH, %             | 9.5 | 8.2 |
| Others, %              | 2.1 | 4.4 |

It is also noteworthy that the NOx reduction mechanism as introduced in equation (19) is insignificant in this combustion zone due to the high local temperature in this study. For both cases of natural gas and coal syngas, the temperatures in different PSRs are higher than 860°C (higher ~1100°C in PSR 1 for both cases of natural gas and coal syngas as seen in Table 9), which is out of the temperature window (750-850°C) for the SNCR reaction to occur.

Quantitative analysis of NO formation in different routes is conducted and the results are summarized in Table 9. Because NO₂ comes from NO, the formation rate analysis of NO is equivalent to NOx. It is found that most of NO is produced in the first PSR reactor (PSR 1). The NO formations in the other PSR reactors are at least 2 orders of magnitude less than PSR 1. Thus, the analysis is focused on PSR 1. For both of natural gas and coal syngas cases, about 90% NO is formed from HNO and the left is mainly from NH. In PSR 1, the residence time is about 0.02 second. Sensitivity analysis shows that the change of residence time affects the net formation rate in each reaction, but doesn’t change much the overall NO net formation rate.

6. CONCLUSIONS

The study of this work suggests the following major conclusions:

1. NH₃ as a contaminant in the SOFC integrated system will not degrade SOFC performance based on literature review, however, potentially causes NOx emissions from combustion zone according to the investigation in this work.

2. NH₃ conversion in the internal reformer is about 50% when temperature is 750°C based on model results.

3. More accurate theoretical understanding and prediction of NH₃ conversion in the SOFC stack need a comprehensive study of mass transfer, heat transfer chemical reactions and electrochemical reactions, which should consider the following major factors: catalyst, temperature, O₂ diffusivity and NH₃ diffusivity, residence time and NH₃ molar flow rate.

4. NH₃ conversion (into N₂ and H₂) in the SOFC stack can affect NOx emissions significantly. The current study shows that when the conversion is high (99.996%) as some research groups suggested, the concern about NOx emissions (less than 0.2 ppm) from NH₃ in the coal syngas is not necessary. It suggests that coal syngas may be directly sent to SOFC system without a reformer.

5. Lower NH₃ conversion in the SOFC stack may cause high fuel NOx. When the conversion is 80%, 0.2% NH₃ contained in the coal syngas can generate 17 ppm NOx with a reformer, and 37 ppm NOx without a reformer.

6. More than 50% NH₃ left from SOFC stack, either natural gas case or coal syngas case, can convert into NOx mainly (~90%) from the following formation route: NH₃ → NH₂ → (NH) → HNO → NO(± NO₂)

7. SOFC system is promising to operate directly on coal syngas without special design on NH₃ removal.

8. An external or internal reformer is not necessary for SOFC system to operate on typical coal syngas, except for some special cases where coal syngas contains significant amounts of CH₄. But a reformer can be helpful for
cracking NH3 and reducing NOx emissions when NH3 conversion in SOFC stack is not high enough.

9. A shift reactor may be considered to couple with SOFC stack when operating on coal syngas for converting CO into H2 and provide some flexibility to help relieve the challenge of thermal management within SOFC stack.

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