Incineration of Ammonia Wastewater and The Effect to The Environment

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Abstract. Wastewater containing ammonia is normally sent to the wastewater treatment system in a chemical plant for the removal of ammonia compound. Alternatively, it is proposed to remove the ammonia compound by incinerating the wastewater using the existing incinerator system. However, it is essential to ensure that the gaseous and aqueous emission produced by the incinerator system do not exceed the Clean Air Regulations (CAR) 2014 and Industrial Effluent Regulations (IER) 2009 limits, especially the nitrogen oxides (NOx) content and unburnt ammonia compound. A process simulation model of the incinerator system was developed using a Gibbs energy minimization reactor approach coupled with Gasification property package to predict the products of the incineration process. Two case study runs were conducted to evaluate the impact of incinerator operating temperature and ammonia concentration in the wastewater feed. Theoretically, there are two causes of NOx production; from thermal NOx (oxidation of nitrogen at high temperature) and fuel NOx (oxidation of liberated nitrogen from ammonia). The study showed that the thermal NOx effect is significantly higher than fuel NOx effect through this study. This is because the total liberated nitrogen molecules from the intended concentration of ammonia in the aqueous water is comparatively small when compared with the amount of nitrogen molecules in the combustion air. Based on the case study results, there is very minimal impact of ammonia injection on total NOx production as the incinerator temperature is commonly controlled on a fixed set point. There is also opportunity to reduce fuel gas requirement because the heating value of the waste streams increases through the combustion of hydrogen molecules in ammonia.

I. INTRODUCTION

A local petrochemical plant produces wastewater containing ammonia that is treated by an internal wastewater treatment system. The wastewater treatment has been designed to remove any ammonia compound prior to release to the environment. As part of an on-going operational improvement initiative, a proposal is raised to remove the ammonia compound by incinerating the wastewater using the existing incinerator. This would avoid plant turndown and enable continuous plant production in the event when the wastewater treatment system needs to undergo maintenance. However, it is essential to ensure that the gaseous and aqueous emission produced by the incinerator system do not exceed the Clean Air Regulations (CAR) 2014 and Industrial Effluent Regulations (IER) 2009 limits, especially the nitrogen oxides (NOx) content and unburnt ammonia compound. Theoretically, there are two contributors of NOx production; from thermal NOx (oxidation of nitrogen at high temperature) and fuel NOx (oxidation of liberated nitrogen from ammonia). A study using process simulation model was commissioned to evaluate the theory of NOx production and predict the stack emissions of the incinerator system with ammonia injection. The simplified process flow diagram of the incinerator system is illustrated in Figure 1.
II. SIMULATION MODEL DEVELOPMENT

A simulation model of the incinerator system using iCON simulation software was first developed based on the plant design case. This step is crucial to select the appropriate thermodynamic property package and equipment modelling approach. The Gasification property package is selected as it best matches the design heat and material balance (HMB) for the two main streams in the system: burned gas from incinerator thermal oxidizer and stack emissions. The incinerator thermal oxidizer equipment is modelled based on Gibbs Free Energy Equilibrium Reactor approach. The reactor solves the system with a Gibbs Free Energy minimization calculation based on atom balances as constraints. The Gibbs Free Energy is the thermodynamic potential of the chemical reactions and is represented by Equation 1.

**Equation 1**

\[ \Delta G = \Delta H - T \Delta S \]

where:

- \( G \) = Gibbs Free Energy
- \( \Delta H \) = Heat of Reaction
- \( T \) = Temperature
- \( S \) = Entropy

Based on the design case model, an actual case model of the incinerator system was then developed by tuning the model to match actual data from the plant. The actual data is based on a period when plant conditions are similar to the expected conditions for future ammonia injection. These data include waste feed flows and content, fuel gas flow, combustion air flow, incinerator temperature and stack emissions. The actual combustion controls were also included into the simulation model to replicate the plant behavior. The combustion controls include incinerator temperature control by fuel gas flow, primary combustion air flow control by combustible feed flows and excess oxygen (O2) control by cooling air flow.

III. CASE STUDIES
Two sets of case study were conducted to evaluate the impact of incinerator operating temperature and ammonia concentration in the wastewater feed. The actual case model was used as the basis model for case study. In both cases, the excess O2 and incinerator temperature are controlled at normal operating values of 0.37 mol% and 1050 °C via the combustion controllers.

**Case Study 1: Decreasing Incinerator Operating Temperature**

The first case study run on decreasing the incinerator temperature was aimed at finding out the threshold incinerator temperature at which unburnt ammonia is evident at the stack and its impact on NOx production. This was achieved by gradually reducing the incinerator temperature control set-point. Results from the case study show that no unburnt ammonia is evident at stack even at zero fuel gas flow with a resultant incinerator temperature of 890 °C. It is also observed from Figure 2 that NOx production at stack is highly dependent on the incinerator temperature; i.e. lower incinerator temperature reduces NOx production. This strengthens the theory that the bulk of NOx at stack is caused by thermal oxidation of N2 in air because ammonia concentration was kept unchanged in this case study. This is considering ideal and complete combustion in the Gibbs reactor.

**Case Study 2: Increasing Ammonia Concentration**

A constant direct aqueous flow with varying ammonia concentration was set for this run. The impact to NOx production, unburnt ammonia, fuel gas and combustion air was observed and discussed. The fuel gas flow rate and combustion air reduces with increase in ammonia concentration as shown in Figure 3. This is because the hydrogen molecules in ammonia increases the heating value in the feed streams, thus, less fuel gas is required to meet the specified incinerator temperature. No unburnt ammonia was also observed even at high ammonia concentration. No significant changes in NOx was also observed with increased ammonia concentration as shown in Figure 4, proving that the bulk of NOx at stack is due to thermal oxidation of N2 composition in air at very high temperature. This is because the total liberated nitrogen molecules from the intended concentration of ammonia in the aqueous water is comparatively small when compared with the amount of nitrogen molecules in the combustion air. The chemical reaction equations in Equation 2 to Equation 6 show the possible reactions related to Ammonia reaction and NOx production.

**Equation 2**
4NH₃ + 3O₂ → 2N₂ + 6H₂O  \[ \Delta H_{r} = -316.8 \text{ kJ/mol NH₃ (oxidation)} \]

**Equation 3**
2NH₃ → N₂ + 3H₂  \[ \Delta H_{r} = 46.1 \text{ kJ/mol NH₃ (pyrolysis)} \]

**Equation 4**
N₂ + O₂ → 2NO  \[ \Delta H_{r} = 180.6 \text{ kJ/mol N₂} \]

**Equation 5**
N₂ + 2O₂ → 2NO₂  \[ \Delta H_{r} = 65.1 \text{ kJ/mol N₂} \]

**Equation 6**
2H₂ + O₂ → 2H₂O  \[ \Delta H_{r} = -242.0 \text{ kJ/mol H₂} \]

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**IV. CONCLUSION**

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**Figure 3**: Effect of ammonia concentration injection on fuel gas flow and combustion air flow

**Figure 4**: Effect of ammonia concentration injection on NOx concentration at stack
Based on ideal thermodynamic laws, the iCON simulation model has shown that there are two causes of NOx production; thermal NOx (oxidation of N2 at high temperature) and fuel NOx (oxidation of liberated N2 from ammonia). It was observed that the thermal NOx effect is significantly higher than fuel NOx effect for this study. This is because the total liberated N2 molecules from the intended concentration of ammonia in the aqueous water is comparatively small when compared with the amount of N2 molecules in the combustion air. Based on the case study results, there is very minimal impact of ammonia injection on total NOx production as the incinerator temperature is commonly controlled on a fixed set point. There is also opportunity to reduce fuel gas requirement because the heating value of the waste streams increases through the combustion of hydrogen molecules in ammonia.

V. FUTURE WORK

An actual performance test run for ammonia injection is planned at the site to validate the desktop study of ammonia injection into the incinerator system. As ammonia in water is a weak base solution that will result in alkali waste production, it is also important to check the capability of the existing incinerator refractory to withstand this condition.

References

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