NOx Pollution Analysis for a Sulfur Recovery Unit Thermal Reactor

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Abstract. A sulfur recovery unit (SRU) thermal reactor is the most important equipment in a sulfur plant. It is negatively affected by high temperature operations. In this paper, NOx emissions from the SRU thermal reactors are simulated. Both the prototype thermal reactor and its modifications, including changing fuel mass fraction, changing inlet air quantity, changing inlet oxygen mole fraction, and changing burner geometry, are analyzed to investigate their influences on NOx emissions. In respect of the fuel mass fraction, the simulation results show that the highest NO emission occurs at a zone 1 fuel mass fraction of 0.375, around which the reactor maximum temperature and the zone 1 average temperature reach maximum values. Concerning the inlet air quantity, the highest NO emission occurs when the inlet air quantity is 2.4 times the designed inlet air quantity. This is very close to the inlet air quantity at which the maximum average temperature occurs. Regarding the inlet oxygen mole fraction, the NO emission increases as the inlet oxygen mole fraction increases. With regard to the burner geometry, the NO emission increases as the clearance of the burner acid gas tip increases. In addition, the NO emission increases as the swirling strength increases.

1. Introduction
A SRU thermal reactor is the most important equipment in a sulfur plant. It converts the NH₃, H₂S and hydrocarbons in the reactants into sulfur. Most of the sulfur elements are recovered from the SRU thermal reactor. The first section of a SRU that uses the Claus process is composed of a burner, a thermal reactor and a waste heat exchanger. The configuration and dimensions of the first section of a SRU for a typical petroleum refinery are shown in figure 1.

Figure 1. The configuration and dimensions of the first section of the SRU for a typical petroleum refinery.
SRU thermal reactors are negatively affected by high temperature operations because high temperature can damage the refractory and the heat exchanger tubes. Our experience of operating a practical SRU thermal reactor in Taiwan shows that the refractories at the zone 1 corner and the choke ring are the parts of the thermal reactor that experience the greatest deterioration. The zone 1 corner has a suddenly expanded geometry and a recirculation zone forms behind it. The temperature at the zone 1 corner can exceed the maximum service temperature of the refractory and cause collapse or deformation. The choke ring is subjected to a bending moment from the rapid combustion gas stream and can collapse or deform.

Nitrogen oxide (NOx) is one of the major sources of air pollution. It is generated mainly from the high temperature combustion processes and may result in acid rain and cause damage to the atmospheric ozone layer. In addition, NOx has been recognized as one of the major causes of excessive peroxide concentration in the atmosphere. Thus, there is a common consensus that NOx control has become a worldwide problem. Normann et al. [1] reviewed available techniques for controlling both the emission of NOx to the atmosphere and the content of NOx in the captured carbon dioxide. They indicated that for a first generation of oxy-fuel power plants, conventional primary NOx control should be sufficient to meet today’s emission regulations, if based on emission per unit of fuel supplied. However, there are several opportunities for new methods of NOx control in oxy-fuel plants, depending on future emission and storage legislation for carbon capture schemes. Javed et al. [2] presented a review of NOx removal techniques with particular reference to SNCR technology. A review of various features related to selective non-catalytic gas phase injection of ammonia and ammonium salts (as reducing agent) was presented. Computational fluid dynamics (CFD) modeling was also applied to SNCR. In addition, a two-stage NOx removal strategy to control un-reacted ammonia slip and to improve overall efficiency was discussed and a summary highlighted various areas needing further research was given. Other reviews for NOx emissions and controls can be found in the author’s previous study [3].

In this paper, NOx emissions from the SRU thermal reactors are simulated. Practical operating conditions from a petrochemical corporation in Taiwan are used as the designed conditions for the discussion. Both the prototype SRU thermal reactor and its modifications, including changing fuel mass fraction, changing inlet air quantity, changing inlet oxygen mole fraction, and changing burner geometry, are analyzed to investigate their influences on NOx emissions.

2. Numerical methods and physical models

In this study, the FLUENT commercial code is used to simulate the reacting and fluid flow in a SRU thermal reactor. The SIMPLE algorithm by Patankar [4] is used to solve the governing equations. The discretizations of convection terms and diffusion terms are respectively performed using the power-law scheme and the central difference scheme. In terms of physical models, considering the accuracy and stability of the models and the evaluations of other researchers, the standard k-ε Model [5], the P-I radiation model [6] and the non-premixed combustion model with β–type probability density function [7] are respectively used for the turbulence, radiation and combustion simulations. The standard wall functions [8] are used to resolve the flow quantities (velocity, the temperature, and the turbulence quantities) at the near-wall regions. The detailed governing equations and convergence criterion were described in a previous study by the author [9].

In this study, the numerical model of a SRU thermal reactor is constructed using an unstructured grid. Figure 2 shows the numerical model of the prototype SRU thermal reactor. In figure 2, the heat exchanger section consists of 19 cooling tubes, which have a diameter of 0.5m, as shown schematically in figure 3. The heat absorption rate for each heat exchanger tube is 40,000 W/m² and the other walls are adiabatic. No slip condition is applied on any of the solid walls. The exit of the heat exchanger section is connected to other equipment at 300 K and 1 atm by a pipe that is 1.372m in diameter and 11.5m in length.
In this study, two types of oxygen supplies are investigated: an oxygen-normal supply and an oxygen-rich supply. An oxygen-rich supply increases sulfur recovery. The designed conditions (including the species compositions, the temperature, the pressure and the velocity) at the acid gas inlet holes of zone 1 and zone 2 and at the air inlet hole are listed in the author’s previous studies[10,11]. These conditions are practical operating conditions that are used by a petrochemical corporation in Taiwan. The turbulence kinetic energy is 10% of the inlet mean flow kinetic energy and the turbulence dissipation rate is computed using Eq.(1).

\[ \varepsilon = C_{\mu} \frac{k^{3/2}}{l} \]  

where \( l=0.07L \) and L is the hydraulic diameter.

### 3. Results and discussion

#### 3.1. Prototype SRU thermal reactor

The exit NO concentration, maximum temperature and average temperature for the prototype SRU thermal reactor are listed in table 1. This result will be used as the basis for comparison in the subsequent discussions.

| NOexit | T\text{\textsubscript{max}} | T\text{\textsubscript{avg}} |
|--------|----------------|----------------|
| 1.18   | 1931           | 1548           |
|        | 14.7           | 1598           |

**Table 1.** Exit NO concentration, maximum temperature and average temperature for the prototype SRU thermal reactor.
3.2. Effect of fuel mass fraction

To investigate the effect of fuel mass fraction on NO emission, the zone 1 fuel mass fraction is defined as the mass ratio of the zone 1 acid gas to the total acid gas (acid gas to zone 1 plus acid gas to zone 2). The designed zone 1 fuel mass fractions are 0.875 for an oxygen-normal supply and 0.895 for an oxygen-rich supply.

Figure 4 shows the exit NO concentrations for SRU thermal reactors with different zone 1 fuel mass fractions. The air is kept at the designed condition. Thermal NOx arises from the nitrogen in air when the temperature exceeds 1600°C. From the author’s previous study [10], it was found that the maximum temperature and the average temperature reach maximum values at a zone 1 fuel mass fraction of about 0.375, as shown in figure 5, which implies that the stoichiometric fuel mass fraction is around 0.375. The temperature decreases when the zone 1 fuel mass fraction deviates from the stoichiometric fuel mass fraction. It can be observed from figure 4 that the highest NO emission occurs at a zone 1 fuel mass fraction of 0.375, around which the reactor maximum temperature and the zone 1 average temperature reach maximum values.

Figure 4. Exit NO concentrations for SRU thermal reactors with different zone 1 fuel mass fractions.

Figure 5. A comparison of the maximum and zone 1 average temperatures for SRU thermal reactors with different zone 1 fuel mass fractions.
3.3. Effect of inlet air quantity

To investigate the effect of inlet air quantity on NO emission, 25 inlet air quantities ranging from 0.1-2.5 times the designed inlet air quantity are investigated. The fuel (acid gas to zone 1 and zone 2) is maintained at the designed conditions.

Figure 6 shows the exit NO concentrations for SRU thermal reactors with different inlet air quantities. From the author’s previous study [11], it was found that the temperature increases as the inlet air quantity increases, until a maximum temperature is reached at about 2.3 times the designed inlet air quantity, as shown in figure 7. This demonstrates that the designed conditions are fuel-rich (or air-lean) conditions. From figure 6, it is observed that the highest NO emission occurs when the inlet air quantity is 2.4 times the designed inlet air quantity. This is very close to the inlet air quantity at which the maximum average temperature occurs.

![Figure 6](image)

**Figure 6.** Exit NO concentrations for SRU thermal reactors with different inlet air quantities.

![Figure 7](image)

**Figure 7.** A comparison of the average temperature for a SRU thermal reactor with different inlet air quantities.

3.4. Effect of inlet oxygen mole fraction

Figure 8 shows the exit NO concentrations for SRU thermal reactors with different inlet O₂ mole fractions. The inlet O₂ mole fractions range from 0.16-0.25. For inlet O₂ mole fractions less than or equal to 0.2 (oxygen-lean), the inlet air quantity is equal to the oxygen-normal case. For inlet O₂ mole fractions greater than 0.2 (oxygen-rich), the inlet air quantity is equal to the oxygen-rich case. The fuel
(acid gas to zone 1 and zone 2) conditions are kept at the designed conditions. From the author’s previous study [11], it was found that the temperature increases monotonically as the inlet O\textsubscript{2} mole fraction increases because the chemical reaction is more complete, as shown in figure 9. The average temperature for an inlet O\textsubscript{2} mole fraction of 0.21 is lower than that for an inlet O\textsubscript{2} mole fraction of 0.2 because the inlet air quantity for the oxygen-rich case is less than that for the oxygen-normal case.

From figure 8, it is observed that the NO emission increases as the inlet O\textsubscript{2} mole fraction increases. Because the thermal NO\textsubscript{x} arises from the nitrogen in air when the temperature exceeds 1600°C, the NO emission increases dramatically as the inlet O\textsubscript{2} mole fractions are greater than 0.23 at which the average temperatures in zone 1 are above 1600°C.

![Figure 8](image1.png)

**Figure 8.** Exit NO concentrations for SRU thermal reactors with different inlet O\textsubscript{2} mole fractions.

![Figure 9](image2.png)

**Figure 9.** A comparison of the temperature for a SRU thermal reactor with different inlet O\textsubscript{2} mole fractions.

### 3.5. Effect of burner parameters

To investigate the effect of burner parameters on NO emission, the clearance of the acid gas tip and the inlet air swirler angle are investigated. The fuel (acid gas to zone 1 and zone 2) and air are kept at the designed conditions.

Figure 1(b) shows the configuration and dimension of the burner section, from which it is seen that length of the acid gas tip (L) controls the horizontal clearance between the acid gas tip and the acid gas channel. The horizontal clearance decreases with L. Figure 10 shows the exit NO concentrations for
SRU thermal reactors with different horizontal clearances of the acid gas tip. The vertical clearance is kept constant by setting the height of the acid gas tip (H) at 80mm. Six lengths of the acid gas tip (L) are used and compared, including 25.4mm, 50.8mm, 76.2mm, 101.6mm, 127mm and 152.4mm, among which 127mm is the default L of a petrochemical corporation in Taiwan. From the author’s previous study [12], it was found that a larger petrochemical (smaller L) tends to yield a higher temperature, as shown in figure 11. Slower ejected horizontal clearance (smaller L) tends to yield a higher temperature. In contrast, faster ejected acid gas may retard the mixing with the swirling air. The smallest horizontal clearance (L=152.4mm) leads to the lowest temperature.

From figure 10, it is observed that the NO emission increases as the horizontal clearance increases (L decreases) because a larger horizontal clearance (smaller L) yields a higher temperature.

![Figure 10](image1.png)

**Figure 10.** Exit NO concentrations for SRU thermal reactors with different horizontal clearances of the acid gas tip.

![Figure 11](image2.png)

**Figure 11.** A comparison of the cross-sectional average temperatures for SRU thermal reactors with different horizontal clearances of the acid gas tip.

Figure 12 shows the exit NO concentrations for SRU thermal reactors with different vertical clearances of the acid gas tip. The horizontal clearance is kept constant by setting the length of the acid gas tip (L) to 127mm. In figure 1(b), the height of the acid gas tip (H) controls the vertical clearance of the acid gas tip. The vertical clearance decreases with H. Four heights of the acid gas tip (H) are used and compared, including 40mm, 80mm, 160mm and 240mm, among which 80mm is the default H of a petrochemical corporation in Taiwan. From the author’s previous study [12], it was
found that a larger vertical clearance (smaller H) yields a higher temperature, as shown in figure 13. This result is similar to that for a larger horizontal clearance. The smallest vertical clearance (H=240mm) leads to the lowest temperature.

From figure 12, it is observed that the NO emission increases as the vertical clearance increases (H decreases) because a larger vertical clearance (smaller H) yields a higher temperature. This result is similar to that for a larger horizontal clearance.

![Graph](image1)
(a) oxygen-normal supply
![Graph](image2)
(b) oxygen-rich supply

**Figure 12.** Exit NO concentrations for SRU thermal reactors with different vertical clearances of the acid gas tip.

![Graph](image3)
(a) oxygen-normal supply
![Graph](image4)
(b) oxygen-rich supply

**Figure 13.** A comparison of the cross-sectional average temperatures for a SRU thermal reactor with different vertical clearances of the acid gas tip.

Figure 14 shows the exit NO concentrations for SRU thermal reactors with different air swirler angles. The inlet air swirler angle, θ_{sw}, controls the strength of the swirling motion. The swirling strength can be expressed in terms of the radial (v_r) and tangential (v_θ) components of the inlet air velocity by the following equation.

\[
\frac{v_r}{v_\theta} = \tan \theta_{sw}
\]

(2)

A smaller θ_{sw} corresponds to a stronger swirling motion. The length (L) and height (H) of the acid gas tip are kept at 127mm and 80mm, respectively. Four inlet air swirler angles (θ_{sw}) are used and compared, including 10°, 20°, 30° and 60°. From the author’s previous study [12], it was found that a
smaller $\theta_{sw}$ yields a higher zone I temperature, as shown in figure 15. This is because a stronger swirling motion leads to a better mixing, a more complete chemical reaction and hence a higher temperature. The smallest $\theta_{sw}$ (10°) produces the highest zone I temperature.

From figure 14, it is observed that the NO emission increases as the swirling strength increases (swirler angle, $\theta_{sw}$, decreases) because a stronger swirling motion (smaller $\theta_{sw}$) yields a higher temperature.

![Figure 14](image1.png)

**Figure 14.** Exit NO concentrations for SRU thermal reactors with different air swirler angles.

![Figure 15](image2.png)

**Figure 15.** A comparison of the cross-sectional average temperatures for SRU thermal reactors with different inlet air swirler angles.

4. Conclusion
In this paper, NOx emissions from the SRU thermal reactors are simulated. Practical operating conditions from a petrochemical corporation in Taiwan are used as the designed conditions for the discussion. Both the prototype SRU thermal reactor and its modifications, including changing fuel mass fraction, changing inlet air quantity, changing inlet oxygen mole fraction, and changing burner geometry, are analyzed to investigate their influences on NOx emissions. From the simulation results, the following conclusions may be drawn:

1. In respect of the fuel mass fraction, the highest NO emission occurs at a zone 1 fuel mass fraction of 0.375, around which the reactor maximum temperature and the zone 1 average temperature
reach maximum values.

(2) Concerning the inlet air quantity, the highest NO emission occurs when the inlet air quantity is 2.4 times the designed inlet air quantity. This is very close to the inlet air quantity at which the maximum average temperature occurs.

(3) Regarding the inlet oxygen mole fraction, the NO emission increases as the inlet oxygen mole fraction increases.

(4) With regard to the burner geometry, the NO emission increases as the clearance of the burner acid gas tip increases. In addition, the NO emission increases as the swirling strength increases.

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