Integrated Flue Gas Purification and Latent Heat Recovery for Pressurized Oxy-Combustion

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Project Overview

Project Objectives

Develop an enabling technology for simultaneous recovery of latent heat and removal of SOx and NOx from flue gas during pressurized oxy-coal combustion.

Funding

Total award: $1,291,964

DOE share: $996,652
Cost share: $295,312

Project Performance Dates

09/01/2015 - 08/31/2018 (extended)

Project Participants

Washington University
Technology Background
SPOC Process

courtesy of Electric Power Research Institute
Latent Heat Recovery – Direct Contact Cooler (DCC)

- Flue gas
- Cooling water (cw)
- Flue gas exit temperature from DCC (°C)
- Pressure
- Flue gas moisture condensation (%)
- Wet flue gas
- Cw + condensate

Diagram:
- DCC wash column
- Pressure levels: 35 bar, 25 bar, 15 bar, 10 bar, 1 bar
SOx and NOx Removal

Knowledge Gaps:
- There are discrepancies about the role of N\textsubscript{2}O\textsubscript{3} and N\textsubscript{2}O\textsubscript{4} in NO\textsubscript{x} dissolution
- Aqueous phase kinetics and mechanism remain unclear
Questions

• What is the optimum design for the DCC for pressurized oxy-combustion?

• What is the expected removal efficiency at the proposed operating conditions for SPOC?

• What are the optimal operating & inlet conditions for the DCC?
  o Inlet NOx/SOx ratio
  o pH
  o Temperature

• What are the critical and rate limiting reactions?

• Can faster/more efficient capture be achieved using catalysts?

• Is one column sufficient?
Project Objectives

• Develop a predictive model for reactor design & operation.
• Experimentally determine critical reactions and rates.
• Design, build and test prototype DCC for 100 kW pressurized combustor at WUSTL.
• Conduct parametric study to optimize process.
• Estimate capital and operating costs of the DCC for a full-scale SPOC plant.
Project Organization

Project Management
  Richard Axelbaum
  Ben Kumfer

Chemical Mechanisms and Kinetics

Modeling
  Lead: Gregory Yablonsky
  Oleg Temkin
  Piyush Verma

Experiment
  Lead: Young-Shin Jun
  Yujia Min
  David Stokie

Process Modeling
  Lead: Richard Axelbaum
  Akshay Gopan
  Piyush Verma

Prototype DCC
  Lead: Ben Kumfer
  David Stokie
Technical Approach/Project Scope
Technical Approach

- Continuously stirred tank reactor - CSTR (bench-scale)
- Prototype DCC (100 kW)

Experiment

Modeling

- Kinetic model & reduced mechanism development
- DCC model w/ chemistry & transport

Results

Design

Scale

- 100 kW SPOC Facility
- SPOC process & econ. model (550 MWe)
Technical Approach:
Mechanism and Kinetics
Normann et al. proposed a detailed mechanism containing 34 reactions. (Intern. J. of Greenhouse Gas Control, V. 12, January 2013, pp.26-34.)

- contains many intermediates
- produces large discrepancies with experimental data in the literature (up to 700%)
- kinetic expressions need verification

A reduced model has been constructed.
Proposed Mechanism

**NO\textsubscript{x} Reactions**

*Gas Phase*

1. \(2\text{NO} (g) + \text{O}_2 (g) \rightarrow 2\text{NO}_2 (g)\)
2. \(2\text{NO}_2 (g) \leftrightarrow \text{N}_2\text{O}_4 (g)\)
3. \(\text{NO}(g) + \text{NO}_2 (g) \rightarrow \text{N}_2\text{O}_3 (g)\)

*Gas + Liquid Phase*

4. \(2 \text{ NO}_2 (g) + \text{H}_2\text{O} (g, aq) \rightarrow \text{HNO}_2 (aq) + \text{HNO}_3 (aq)\)
5. \(\text{N}_2\text{O}_4 (g) + \text{H}_2\text{O} (g, aq) \rightarrow \text{HNO}_2 (aq) + \text{HNO}_3 (aq)\)
6. \(\text{N}_2\text{O}_3 (g) + 2\text{H}_2\text{O} (g, aq) \rightarrow 2 \text{HNO}_2 (aq)\)
7. \(3 \text{HNO}_2 (aq) \rightarrow \text{HNO}_3 (aq) + 2 \text{NO} (g, aq) + \text{H}_2\text{O} (g, aq)\)

**SO\textsubscript{x} Reactions**

8. \(\text{SO}_2 (g) + \text{H}_2\text{O} (g, aq) \rightarrow \text{HSO}_3^- (aq) + \text{H}^+ (aq)\)

**SO\textsubscript{x} + NO\textsubscript{x} Reactions**

9. \(\text{HNO}_2 (aq) + \text{HSO}_3^- (aq) + \text{H}^+ (aq) \rightarrow \text{H}_2\text{SO}_4 (aq) + \frac{1}{2} \text{N}_2\text{O} (g) + \frac{1}{2} \text{H}_2\text{O} (aq)\)
10. \(2 \text{HNO}_2 (aq) + \text{HSO}_3^- (aq) + \text{H}^+ (aq) \rightarrow 2\text{NO} (g) + \text{H}_2\text{SO}_4 (aq) + \text{H}_2\text{O} (aq)\)
Technical Approach:

Bench-Scale Experiments
Objectives of bench scale experiments

• Determine contributions of different routes, and identify the key reactions and rates

• Justify or eliminate (add) steps from the hypothesized mechanisms

• Obtain estimates of optimal parameters (initial composition and pH, temperature) for the DCC operation
The reactor design is optimized for conducting experiments under high pressure and temperature and highly acidic conditions.

In situ pH measurements under high pressure/temperature conditions

**Tests:**
A) 900 ppm NO\textsubscript{x}; B) 450 ppm SO\textsubscript{2}; C) NO\textsubscript{x}/SO\textsubscript{x} ratio of 2
- 25 °C (this presentation); will increase to 150 °C in future
- **Pressure of 15 bar,** high enough for NO\textsubscript{x} and SO\textsubscript{x} removal and latent-heat recovery.
NO(g) and NO\(_2\) (g) dissolution in water

**Aqueous analysis:** 50 mL gas mixtures reacted with 250 mL water at 25\(^\circ\)C and 15 bar

- 900 ppm NO and 3% O\(_2\)
- 900 ppm NO\(_2\)

\[\text{NO}_2^-/\text{NO}_3^- \text{ close to } 1:1\]
Revisit NOx reactions

Gas Phase

1. $2\text{NO (g)} + \text{O}_2\text{(g)} \rightarrow 2\text{NO}_2\text{(g)}$ → NO quickly oxidized to NO$_2$
2. $2\text{NO}_2\text{(g)} \leftrightarrow \text{N}_2\text{O}_4\text{(g)}$
3. $\text{NO(g)} + \text{NO}_2\text{(g)} \rightarrow \text{N}_2\text{O}_3\text{(g)}$ → N$_2$O$_3$ is not significant

Gas + Liquid Phase

4. $2\text{ NO}_2\text{(g)} + \text{H}_2\text{O (g, aq)} \rightarrow \text{HNO}_2\text{(aq)} + \text{HNO}_3\text{(aq)}$ [Dominant]
5. $\text{N}_2\text{O}_4\text{(g)+ H}_2\text{O (g, aq)} \rightarrow \text{HNO}_2\text{(aq)} + \text{HNO}_3\text{(aq)}$
6. $\text{N}_2\text{O}_3\text{(g) + 2H}_2\text{O (g, aq)} \rightarrow 2\text{ HNO}_2\text{(aq)}$ → Not significant
7. $3\text{ HNO}_2\text{(aq)} \rightarrow \text{HNO}_3\text{(aq)+ 2 NO (g, aq)+ H}_2\text{O (g, aq)}$ → Not significant

- NO$_2^-$/NO$_3^-$ close to 1:1 is consistent with dissolution of NO$_2$ (N$_2$O$_4$)
  → Reaction 4 and 5 is dominant and reaction 6 is not significant

- In NO$_2$ experiment, after 1 hour reaction, we did not observed any change of HNO$_2$ (aq)/HNO$_3$(aq) ratio or NO (< 2ppm) in gas phase.
  → Reaction 7 is not important
Aqueous analysis: 50 mL of 450 ppm SO₂ reacted with 250 mL water at 25°C and 15 bar

Rapid dissolution
No significant amount of SO₄²⁻ (aq) (< 2.5 uM)

SOₓ Reactions
8. SO₂ (g) + H₂O (g, aq) → HSO₃⁻ (aq) + H⁺ (aq)
NO$_2$(g) + SO$_2$(g) dissolution in water

Aqueous analysis: 50 mL of 1066 ppm NO$_2$ + 659 ppm SO$_2$ reacted with 250 mL water at 25°C and 15 bar

In presence of NO$_x$, HSO$_3^-$ (aq) is oxidized to SO$_4^{2-}$ (aq)

No NO (g) (< 2 ppm) observed

SO$_x$ + NO$_x$ Reactions

9. HNO$_2$ (aq) + HSO$_3^-$ (aq) + H$^+$ (aq) $\rightarrow$ H$_2$SO$_4$ (aq) + $\frac{1}{2}$ N$_2$O (g) + $\frac{1}{2}$ H$_2$O (aq)

10. 2 HNO$_2$ (aq) + HSO$_3^-$ (aq) + H$^+$ (aq) $\rightarrow$ 2NO (g) + H$_2$SO$_4$ (aq) + H$_2$O (aq)
Proposed reduced mechanism  
(After experiment)

**NO\textsubscript{x} Reactions**

*Gas Phase*

1. \(2\text{NO (g)} + \text{O}_2(g) \rightarrow 2\text{NO}_2 (g)\)
2. \(2\text{NO}_2(g) \leftrightarrow \text{N}_2\text{O}_4(g)\)  
   Equilibrium
3. \(\text{NO(g)} + \text{NO}_2(g) \rightarrow \text{N}_2\text{O}_3(g)\)

*Gas + Liquid Phase*

4. \(2 \text{NO}_2 (g) + \text{H}_2\text{O (g, aq)} \rightarrow \text{HNO}_2 (aq) + \text{HNO}_3 (aq)\)
5. \(\text{N}_2\text{O}_4(g)+ \text{H}_2\text{O (g, aq)} \rightarrow \text{HNO}_2 (aq) + \text{HNO}_3 (aq)\)
6. \(\text{N}_2\text{O}_3(g) + 2\text{H}_2\text{O (g, aq)} \rightarrow 2 \text{HNO}_2 (aq)\)
7. \(3 \text{HNO}_2 (aq) \rightarrow \text{HNO}_3 (aq) + 2 \text{NO (g, aq)} + \text{H}_2\text{O (g, aq)}\)

**SO\textsubscript{x} Reactions**

8. \(\text{SO}_2 (g) + \text{H}_2\text{O (g, aq)} \leftrightarrow \text{HSO}_3^- (aq) + \text{H}^+ (aq)\)  
   Equilibrium

**SO\textsubscript{x} + NO\textsubscript{x} Reactions**

9. \(\text{HNO}_2 (aq) + \text{HSO}_3^- (aq) + \text{H}^+ (aq) \rightarrow \text{H}_2\text{SO}_4 (aq) + \frac{1}{2} \text{N}_2\text{O (g)} + \frac{1}{2} \text{H}_2\text{O (aq)}\)
10. \(2 \text{HNO}_2 (aq) + \text{HSO}_3^- (aq) + \text{H}^+ (aq) \rightarrow 2\text{NO (g)} + \text{H}_2\text{SO}_4 (aq) + \text{H}_2\text{O (aq)}\)
Future work

1. Examine the aqueous phase reactions between NO- and SO- containing species
   - Effects of NO$_2$/SO$_2$ and pH

2. Simulate the actual temperature in the DCC
   - Increase temperature from 25$^\circ$C to 150$^\circ$C

3. Investigate effects of different catalysts
   - e.g., Amberlyst, Amberlite, and activated carbon as catalysts
Technical Approach:

Prototype Direct Contact Cooler (DCC)
Prototype DCC

Technical Approach:
The DCC was designed for both synthetic flue gas and flue gas taken from a 100 kWth pressurized oxy-combustion pilot facility

Aims:

Synthetic Flue Gas
- To demonstrate simultaneous capture of pollutants and latent heat
- To parametrically investigate SO$_x$/NO$_x$ capture efficiency

Pressurized Oxy-Combustion Flue Gas
- To determine the pollutant removal efficiency
- To determine the potential energy recovery
Prototype DCC

Features:
- 316L column
- 30 bar vessel pressure rating
- Saddle ring packing
- Coupled to 100 kW pressurized combustion test facility
- Liquid recycle for pH control
- Reaction temperature control

Operational Conditions:
- pH: 3.5 – 6
- Liquid/Gas ratio: 3 – 80 (L/m³)
- Pressure: 1 – 15 bar
- \( \text{SO}_x, \text{NO}_x \) Concentration: 300 – 2200 ppm
- \( \text{NO}_x : \text{SO}_x \) Ratio: 0.5 – 2.0
- Liquid Temperature: 15 – 50 °C
- Gas Temperature: 15 – 300 °C
Progress to Date

• The DCC column has been designed, fabricated, and hydro-tested by Progressive Recovery Inc.

• An experimental procedure and matrix has been established based on modeling.

• Integration into the laboratory infrastructure complete. Commissioning September 2017.

• The automated control system designed: installation September 2017.
DCC Model Results:
Effect of NOx/SOx and residence time on removal

**Conditions:**
- Operation: Single pass
- Inlet Water Temp: 18°C
- Inlet Gas Temp: 300°C

**Flue gas inlet composition:**
- NO₂: 225 to 630 ppm
- NO: 225 to 630 ppm
- SO₂: 450 ppm
- SO₃: 450 ppm
- O₂: 1.6% (v)

**Graphs:**
- SOx removal vs. NOx/SOx ratio
  - Gas res. time = 17 sec
  - L/G ratio = 0.63
- NOx removal vs. NOx/SOx ratio
  - Gas res. time = 34 sec
  - L/G ratio = 1.26
## Milestone Log

<table>
<thead>
<tr>
<th>Status</th>
<th>Task No.</th>
<th>Milestone Description</th>
<th>Planned Completion</th>
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<tr>
<td>Complete</td>
<td>2.1</td>
<td>Purchase Bench-Scale Equip.</td>
<td>03/31/2016</td>
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<tr>
<td>Complete</td>
<td>3.1</td>
<td>Schematic Prototype Column Design</td>
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<td>Complete</td>
<td>2.2</td>
<td>Preliminary Bench-Scale Tests Complete</td>
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<td>Near Comp.</td>
<td>3.2</td>
<td>Construct Prototype</td>
<td>08/31/2017</td>
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<td>Beginning</td>
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<td>Performance Test w/ Simulated Flue Gas</td>
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<td>In progress</td>
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<td>Complete Improved Model</td>
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<td>Full-Scale Cost &amp; Performance Estimate</td>
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