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

DE-FE0025193

Principal Investigator:
Richard Axelbaum

Presented By:
Ben Kumfer

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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 - 08/31/2017

Project Participants
Washington University
Technology Background
SPOC Process Flow Diagram

LEGEND

- ASU: Air Separation Unit
- BFW: Boiler Feed Water
- GPU: Gas Processing Unit
- CT: Cooling Tower
- CW: Cooling Water
- DCC: Direct Contact Cooler
- Econ: Economizer
- SC: Steam Cycle
- FGR: Flue Gas Recirculation
Latent Heat Recovery – Direct Contact Cooler (DCC)

![Diagram showing the process of heat recovery](image)

- Cooling water (cw)
- Flue gas
- Wet flue gas
- DCC wash column
- Pressure:
  - 10 bar
  - 15 bar
  - 20 bar
  - 25 bar
  - 30 bar
  - 35 bar
- Exit Temp (C):
  - 16 bar: 167
  - 30 bar: 192
  - 36 bar: 199

**Legend:**
- Pressure (bar)
- Exit Temp (C)
SPOC Steam Cycle

- High Pressure Steam Turbine
- Intermediate Pressure Steam Turbine
- Low Pressure Steam Turbine
- Deaerator
- Direct Contact Cooler – Heat Exchanger
- Main Air Compressor Intercooler
- Booster Air Compressor Intercooler
SOx and NOx Removal Mechanism

\[ \text{NO} \rightarrow \text{NO}_2, \quad \text{N}_2\text{O}_4, \quad \text{N}_2\text{O}_3 \]

\[ \text{SO}_2 \]

\[ \text{HNO}_2 \rightarrow \text{HNO}_3 \]

\[ \text{HSO}_3 \rightarrow \text{H}_2\text{SO}_4 \]

>15 bar

Gas Phase

Liquid Phase
Project Objectives

• Develop a predictive model for reactor design & operation.
• Experimentally determine critical reactions and rates.
• Conduct parametric study to optimize process.
• Design, build, test prototype for 100 kW pressurized combustor.
• 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
  Gregory Yablonsky
  Oleg Temkin
  PhD student

Experiment
  Young-Shin Jun
  PhD student

Process Modeling
  Richard Axelbaum
  Zhiwei Yang

Prototype DCC
  Ben Kumfer
  PhD student
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 DCC operating & inlet conditions?
  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?
Technical Approach/Project Scope
Technical Approach

Experiment

Continuously stirred tank reactor - CSTR (bench-scale)

Modeling

Kinetic model & reduced mechanism development

Prototype DCC (100 kW)

Scale

DCC model w/ chemistry & transport

SPOC process & econ. model (550 MWe)
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<th>Task</th>
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<th>End Date</th>
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<td>Task 2.0: Assemble &amp; Test Bench-Scale System</td>
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<td>Task 4.0: Evaluate Prototype Performance</td>
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Knowledge Gaps and Challenges

1. **Mechanisms and kinetic parameters** of consumption/generation of different NO\textsubscript{x}- and SO\textsubscript{2}-species in **the gas phase** is well understood.
   - Mechanism for the NO- and SO- containing species in the **liquid phase** remains unclear, and some of the kinetic parameters are highly uncertain.

2. Literature regarding **influence of pH** on capture effectiveness is limited and sometimes contradictory. Because the pH changes as the reaction occurs, it is difficult to predict which mechanism is dominant.
   - To date, experimental systems have not controlled or directly measured the experimental pH values.

3. No systematic studies of the **effects of acid-base catalysts**, e.g., ion-exchange catalysis, on this gas-liquid process have been conducted.

4. **Difficult to experimentally measure** the concentrations of certain **key intermediate species**.
   - Lack of experimental data on the concentrations of critical species makes it challenging to obtain accurate kinetic data for key chemical reactions in such high pressure, high temperature systems.
Technical Approach:

Mechanism and Kinetics
Expected Outcomes of Model Development

• New kinetic data on the absorption and conversion reactions of NO, NO₂, and SO₂ under high temperature and pressure conditions with controlled pH.
  o This will be the first study to conduct experiments under well-characterized *in situ* pH conditions.
  o Catalyst performance will be evaluated.

• An experimentally-validated chemical mechanism

• A simplified but reliable kinetic model with experimentally-obtained kinetic parameters.

• Recommendations on the optimal working regime, i.e., reactant concentrations, temperature and pH.
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
- cannot explain some experimental data in the literature
- kinetic expressions need verification

A reduced model has been constructed.
Proposed Mechanism

I. N (nitrogen) -block
1. \(2\text{NO (g)} + \text{O}_2(g) \leftrightarrow 2\text{NO}_2 (g)\)
2. \(2\text{NO}_2(g) \leftrightarrow \text{N}_2\text{O}_4(g)\)
3. \(\text{NO(g)} + \text{NO}_2(g) \leftrightarrow \text{N}_2\text{O}_3(g)\)
4. \(2 \text{NO}_2 (g \rightarrow \text{aq}) + \text{H}_2\text{O (aq)} \rightarrow \text{HNO}_2 (\text{aq}) + \text{HNO}_3 (\text{aq})\)
5. \(\text{N}_2\text{O}_4(g \rightarrow \text{aq})+ \text{H}_2\text{O (aq)} \rightarrow \text{HNO}_2 (\text{aq}) + \text{HNO}_3 (\text{aq})\)
6. \(\text{N}_2\text{O}_3(g \rightarrow \text{aq}) + 2\text{H}_2\text{O (aq)}\rightarrow 2 \text{HNO}_2 (\text{aq})\)
7. \(3 \text{HNO}_2 (\text{aq}) \rightarrow \text{HNO}_3 (\text{aq})+ 2 \text{NO (g, aq)}+ \text{H}_2\text{O (aq)}\)

II. S (sulfur) –block
8. \(\text{SO}_2 (\text{g}) + \text{H}_2\text{O (g, aq)} \leftrightarrow \text{HSO}_3^- (\text{aq}) + \text{H}^+ (\text{aq})\)

III. S&N -block
9. \(2\text{HNO}_2 (\text{aq}) + \text{H}^+ (\text{aq}) + \text{HSO}_3^- (\text{aq}) \rightarrow \text{H}_2\text{O (aq}) +2\text{NO (g)} + 2\text{H}^+ (\text{aq}) + \text{SO}_4^{2-} (\text{aq})\)
10. \(2\text{HNO}_2 (\text{aq}) + 2\text{H}^+ (\text{aq}) + 2\text{HSO}_3^- (\text{aq}) \rightarrow \text{H}_2\text{O (aq}) +\text{N}_2\text{O (g)} + 4\text{H}^+ (\text{aq}) + 2\text{SO}_4^{2-} (\text{aq})\)
Modeling to guide experiments

- NOx in gas phase
  - Literature: contradictory statements about whether $N_2O_4$ and $N_2O_3$ are important,
  - Modeling results: NO and NO$_2$ are the major species; $[NO_2] >> [N_2O_4] > [N_2O_3]$.
  - Gas-phase experimental data will be obtained.

- Mass transfer limited or kinetically limited
  - Literature: contradictory conclusions about which is limiting,
  - Modeling: better agreement with experimental data of Ting et al obtained when a higher mass transfer coefficient is used
  \[
  R_{\text{dissolution}} \approx R_{\text{liquid reaction}}.
  \]
  - We can change circulation rate, stirring, and residence time in our experiment, to determine which one is limiting.
Modeling to guide experiments

- Explain the difference between HNO$_3$ and HNO$_2$ concentration dependencies on pressure (Ting et al)

  • Modeling results: both concentrations increase with pressure.
  • Possible reason for the difference in acids concentrations: decomposition of HNO$_2$ (Reaction 7)
  • Decomposition of HNO$_2$ may need to be faster in model.
  • In future experiments, possible difference in acids concentrations has to be analyzed to obtain more accurate kinetic data.

Ting et al, 2013
Technical Approach:

CSTR Experiments
Experiment setup of preliminary tests

**In situ pH measurements and control** under high pressure/temperature conditions

1. Gas inlet and pressure gauge; 2. High pressure/temperature pH electrodes; 3. Liquid outlet; and 4. Mechanical stirrer

O₂, NO, and N₂

Gas Cylinder

Gas Mixer

High Pressure Pump

Batch Reactor

Temperature Controller

Ionic chromatography analysis for NO₂⁻ and NO₃⁻ concentrations

Gas analyzer for gas phase concentration analysis

- Washington University in St. Louis
Experimental variables used in preliminary tests

Testing NO\textsubscript{x} Reactions

<table>
<thead>
<tr>
<th>Variables</th>
<th>Conditions</th>
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<tbody>
<tr>
<td>Pressure (bar)</td>
<td>15</td>
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<tr>
<td>Temperature (°C)</td>
<td>25</td>
</tr>
<tr>
<td>NO concentration</td>
<td>0.9%</td>
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<tr>
<td>O\textsubscript{2} gas concentration</td>
<td>8%</td>
</tr>
<tr>
<td>Reaction time (min)</td>
<td>10 and 60</td>
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<tr>
<td>Stirring rate (rpm)</td>
<td>1200</td>
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</table>

**Gas Phase**

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

**Gas + Liquid Phase**

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

Aqueous NO\textsubscript{2} and NO\textsubscript{3} concentrations and pH measurement
In situ pH and ion chromatography-determined NO$_2^-$ and NO$_3^-$ concentration evolution during NOx gas dissolution

<table>
<thead>
<tr>
<th>Reaction time (min)</th>
<th>NO$_2^-$ (µM)</th>
<th>NO$_3^-$ (µM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>194.5</td>
<td>121.0</td>
</tr>
<tr>
<td>60</td>
<td>257.5</td>
<td>168.7</td>
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<tr>
<td>120</td>
<td>272.6</td>
<td>178.2</td>
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</table>
Unique reactor design optimized for conducting experiments up to:

- 325 °C
- 40 bar
- pH = 0

Coupled to in-situ FTIR measurements of aqueous species.

**Experiment setup to be used in future tests**

- CO₂, O₂, SO₂, NO, NO₂, and Inert gas (e.g., Ar or N₂)
- Gas analyzers
- High pressure charging pump for adjusting pH
- Temperature Controller
- Gas Cylinder
- Gas Mixer
- In situ aqueous species analysis by FTIR under high pressure and temperature
High temperature and pressure FTIR for in situ analysis

$\text{NO}_2^-$ peak around 1236 cm$^{-1}$

Detection limits and calibration have been performed for each species

$y = 0.0018x + 0.0023$
$R^2 = 0.9999$
Future plans for Bench scale experiments

• Obtain new kinetic data on the absorption and conversion reactions of NO, NO$_2$, and SO$_2$ under high temperature and pressure conditions with controlled pH.
  o This will be the first study to conduct experiments under well-characterized *in situ* pH conditions.
  o Catalyst performance will be evaluated.

• Experimentally obtain kinetic parameters for validating reaction mechanisms and models

• Provide recommendations on the optimal working regime, i.e., reactant concentrations, temperature and pH.
Accomplishments

- **Unique and new capabilities have been developed.**
  - *In situ* pH monitoring
  - *In situ* FTIR measurements of aqueous concentrations of nitrite or nitrate (> 2.5 mM) or sulfate (> 0.1 mM) or sulfite (0.025 mM)
  - *Ex situ* ion chromatography for lower concentrations of these species
    - *measure within a few minutes after sampling rather than long waiting time reported previous.*

- **All instruments have been purchased and set up.**

- **Safety protocols for experiments have been determined.**

- **Preliminary tests have been conducted.**
Technical Approach:

Prototype Direct Contact Cooler (DCC)
Prototype DCC

Aims:
• Demonstrate simultaneous capture of pollutants and latent heat in DCC
• Measure SOx/NOx capture efficiency vs. operating parameters

Features:
• Packed-bed column design
• Pressure up to 30 bar
• Coupled to 100 kW pressurized combustion test facility
• Both simulated and real flue gas will be used
• Liquid recycle for pH control
Progress to Date

• Vendors under contract:
  o Progressive Recovery Inc. - vessel and system design and fabrication
  o Process Engineering Associates, LLC – reactor modeling, sizing, process design

• Preliminary design completed:
  o Reactor sizing, packing type, ancillary equipment specifications
  o Process flow sheet & piping and instrument diagram
  o Reactor model (CHEMCAD) with our detailed chemistry and transport developed

• Detailed cost proposal under evaluation
• Construction to be completed Dec 2016
Reactor Design Specifications

- Vapor residence time: $\leq 120$ seconds
- pH range: $2.5 - 7$
- L/G ratio: $3 - 80$ (L/m$^3$)
- Number of stages of packing: 5
- Packing type: random saddle ring
- Material of construction: 316 stainless steel
Reactor Modeling for Preliminary Design

- SOx & NOx capture is sensitive to L/G
- Complete removal can be achieved

**Flue Gas:**
- 200 °C
- 180 kg/hr
- CO2 = 56%
- H2O = 39%
- N2 = 3%
- O2 = 2%
- NO = 876 ppm
- SO2 = 745 ppm
- SO3 = 143 ppm

**Clean Gas:**
- 27 °C
- 134 kg/hr
- CO2 = 92%
- H2O = 0.1%
- N2 = 3%
- O2 = 2%
- NO = < 1 ppm
- SO2 = < 1 ppm
- SO3 = < 1 ppm

**Liquid In:**
- 23 °C
- pH = 3
- 490 kg/hr

**Liquid Out:**
- 23 °C
- pH = 2.3
- 500 kg/hr
# Milestones

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<th>Task No.</th>
<th>Milestone Description</th>
<th>Planned Completion</th>
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<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>
<td>03/31/2016</td>
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<td>Complete</td>
<td>2.2</td>
<td>Preliminary Bench-Scale Tests Complete</td>
<td>06/30/2016</td>
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<td>3.2</td>
<td>Construct Prototype</td>
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<td>Performance Test w/ Simulated Flue Gas</td>
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<td>5.2</td>
<td>Complete Improved Model</td>
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<td>6</td>
<td>Full-Scale Cost &amp; Performance Estimate</td>
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