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

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Outline

• Technology Background
• Project Objectives
• Technical Approach
• Project Management
Technology Background
Pressurized Oxy-Combustion

• The requirement of high pressure CO₂ for sequestration enables pressurized combustion as a tool to increase efficiency and reduce costs.

• Benefits of Pressurized Combustion
  – Recover latent heat in flue gas
  – Latent heat recovery can be combine with integrated pollution removal
  – Reduce gas volume
  – Avoid air-ingress
  – Fuel flexibility
  – Controlled radiation heat transfer
ASPEN Plus Results – Plant Efficiency


a. Cost and performance baseline for fossil energy plants volume 1: bituminous coal and natural gas to electricity. DOE/NETL-2010/1397, rev. 2

b. Advancing Oxycombustion Technology for Bituminous Coal Power Plants: An R&D Guide. DOE/NETL - 2010/1405
SPOC Process Flow Diagram

Std. ASU: $O_2 \ P = 1.1 \text{ bar}$
Latent Heat Recovery – DCC

Flue Gas Moisture Condensation (%)

Temperature (°C)

Pressure (bar)

Exit Temp (°C)

- 16: 167
- 30: 192
- 36: 199

DCC wash column

cooling water (cw)

flue gas

wet flue gas

cw + condensate
SOx and NOx Removal Mechanism

Gas Phase

NO → NO₂
N₂O₄
N₂O₃

SO₂ → HSO₃
H₂SO₄

Liquid Phase

HNO₂ → HNO₃

Washington University in St. Louis
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?

• Is one column sufficient?
Project Objectives

**Mission:** to develop an enabling technology for simultaneous recovery of latent heat and removal of SOx and NOx from flue gas during pressurized oxy-coal combustion, so as to eliminate conventional FGD and de-NOx processes and minimize the COE.

**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.
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

Scale

SPOC process & econ. model (550 MWe)
Technical Approach:
Mechanism and Kinetics
Knowledge Gaps and Challenges: Reaction Mechanism & Kinetic Model

1. The earlier understanding of the chemistry (the so-called lead chamber process) has been shown to be insufficient but this chemistry is still often used to describe the process.

2. New chemical mechanisms have been proposed but these have been based on existing kinetic data developed under conditions different from this system.

3. A “rational” kinetic model is needed where
   • the level of complexity of the model is just sufficient to characterize the chemistry, and
   • the kinetic parameters in the mechanism are obtain by experiment.
Building blocks of the Mechanism

1. *N (nitrogen) -block*
   - Gas-phase oxidation of NO into nitrogen oxides NO₂, N₂O₃ and N₂O₄
   - Liquid-phase dissolution of nitrogen oxides; production of nitrous and nitric acids (HNO₂, HNO₃)

2. *S (sulfur) -block*
   - Liquid-phase dissolution of SO₂

3. *S&N -block*
   - Liquid-phase interaction between S- and N-compounds.
   - Production of the sulfuric acid (H₂SO₄)
Development of the Mechanism

Mechanism reduction:


- A 10-step reduced mechanism has been constructed by Yablonsky and Temkin.
Rational 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. $2 \text{NO}_2 (g) + \text{H}_2\text{O} (g, \text{aq}) \rightarrow \text{HNO}_2 (\text{aq}) + \text{HNO}_3 (\text{aq})$
5. $\text{N}_2\text{O}_4 (g) + \text{H}_2\text{O} (g, \text{aq}) \rightarrow \text{HNO}_2 (\text{aq}) + \text{HNO}_3 (\text{aq})$
6. $\text{N}_2\text{O}_3 (g) + 2\text{H}_2\text{O} (g, \text{aq}) \rightarrow 2 \text{HNO}_2 (\text{aq})$
7. $3 \text{HNO}_2 (\text{aq}) \rightarrow \text{HNO}_3 (\text{aq}) + 2 \text{NO} (g, \text{aq}) + \text{H}_2\text{O} (g, \text{aq})$

**SO\textsubscript{x} Reactions**
8. $\text{SO}_2 (g) + \text{H}_2\text{O} (g, \text{aq}) = \text{HSO}_3^- (\text{aq}) + \text{H}^+ (\text{aq})$

**SO\textsubscript{x} + NO\textsubscript{x} Reactions**
9. $\text{HNO}_2 (\text{aq}) + \text{HSO}_3^- (\text{aq}) + \text{H}^+ (\text{aq}) \rightarrow \text{H}_2\text{SO}_4 (\text{aq}) + \frac{1}{2} \text{N}_2\text{O} (g) + \frac{1}{2} \text{H}_2\text{O} (\text{aq})$
10. $2 \text{HNO}_2 (\text{aq}) + \text{HSO}_3^- (\text{aq}) + \text{H}^+ (\text{aq}) \rightarrow 2\text{NO} (g) + \text{H}_2\text{SO}_4 (\text{aq}) + \text{H}_2\text{O} (\text{aq})$
Kinetic Modeling: Goals

1. Justify or eliminate (add) steps in the mechanism based on gas- and liquid-phase experimental data conducted in the domain of the anticipated operational conditions.

2. Estimate contributions of the different routes and accurately determine reaction parameters for the key reactions.

3. Obtain estimates of optimal parameters (initial composition and pH, temperature and residence times).
Technical Approach:

CSTR Experiments
1. Mechanisms and kinetic parameters of consumption/generation of different NOx- and SO$_2$-species \textit{in the gas phase} and their dissolution in water are well understood.

   - Kinetic mechanism for the NO- and SO- containing species \textit{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. 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.
Novel bench-scale experiment setup to obtain kinetic data

The reactor design is optimized for conducting experiments under high pressure and temperature and highly acidic conditions.

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

1. Gas inlet/liquid outlet with filter; 2. High pressure/temperature pH electrodes; 3. Gas outlet and pressure gauge; and 4. Mechanical stirrer
## Experimental variables to be used in bench scale studies

<table>
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<tr>
<th>Variables</th>
<th>Conditions</th>
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<tbody>
<tr>
<td>Pressure (bar)</td>
<td>5, 10, 15, 30</td>
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<tr>
<td>pH</td>
<td>0.5, 1, 2, 3, 4, 5</td>
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<tr>
<td>Temperature (°C)</td>
<td>25, 75, 125, 175, 225, 275, 325</td>
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<tr>
<td>NO$_x$/SO$_2$ ratio</td>
<td>0, 0.1, 0.2, 0.4, 0.8, ∞</td>
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<tr>
<td>SO$_2$ concentration</td>
<td>0.09 – 0.9%</td>
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<tr>
<td>O$_2$ gas concentration</td>
<td>0 – 3%</td>
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</table>
Expected Outcomes of Model Development

• New kinetic data on the absorption and conversion reactions of NO, NO\textsubscript{2}, and SO\textsubscript{2} under high temperature and pressure conditions with controlled pH.
  - This will be the first study to conduct experiments under well-characterized \textit{in situ} pH conditions.

• 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.
Prototype DCC Design & Testing

- Packed-bed column design
- Pressure up to 15 bar
- Coupled to 100kW pressurized combustion facility
- Test with both simulated and real flue gas
- Model using software, e.g. ASPEN and KG Tower

Figure adapted from: M. J. Jafari, et al., Iranian J. Environ. Health. 9(1) (2012) 20.
## Milestones

<table>
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<tr>
<th>ID</th>
<th>Budget Period</th>
<th>Task No.</th>
<th>Milestone Description</th>
<th>Planned Completion</th>
<th>Verification Method</th>
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<td>Purchase Bench-Scale Equip.</td>
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<td>Preliminary Bench-Scale Tests Complete</td>
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<td>Construct Prototype</td>
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<td>Performance Test w/ Simulated Flue Gas</td>
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<td>Full-Scale Cost &amp; Performance Estimate</td>
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<td>Final Report</td>
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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
- Postdoc

**Prototype DCC**
- Ben Kumfer
- PhD student
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