Safeguarding Amines from Oxidation by Enabling Technologies (FE0031861)

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Point Source Capture — Lab, Bench, and Pilot-Scale Research
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Project Overview

• The project objective is to identify and test promising oxidation mitigation strategies for piperazine (PZ) and other solvents.

• Funding
  • Federal share $2,348,540
  • Cost share $587,058 (PI academic time + TxCMP funds)

• Overall Project Performance Dates
  • BP1: 3/1/2020 – 5/31/2021 (includes 3-month NCTE)
    • Bench-scale
  • BP2: 6/1/2021 – 2/28/2022
    • Bench-scale: HTOR, HGR, ASAP
    • SRP pilot (air/CO₂/0.2 MW)
  • BP3: 3/1/2022 – 2/28/2023
    • Bench-scale
    • NCCC pilot
Three important oxidation mechanisms

1. NO$_2$ oxidizes all amines at 0.2 to 5 ppm in the flue gas
2. Dissolved oxygen oxidizes amines at elevated T before the stripper
3. Fe$^{+3}$ oxidizes amines at stripper T and is regenerated from Fe$^{+2}$ in absorber

Amine selection is an important task of the developers. It will be important as some amines are more resistant to these mechanisms than others.
NO₂: Testing to quantify the effects of NO₂

• Does NO₂ have a catalytic effect on amine oxidation?

• Will incremental oxidation be 1-2 mol/mol NO₂ or 5-10 mol/mol NO₂?
  • More likely to see an effect in absence of other mechanisms, but it probably interacts with other mechanism.
  • More likely to be catalytic at lower NO₂

• Measure oxidation with and without 1-5 ppm NO₂
  • Bench-Scale High gas flow reactor [Baseline experiment completed]
    • absorber conditions missing other mechanisms
  • ASAP (Amine screening apparatus) [Commissioning almost complete]
    • Bench-scale absorber /120°C stripper
  • SRP pilot plant campaign, Fall 2021
  • NCCC pilot plant, summer 2022
**NO\textsubscript{2}**

High-gas flow reactor (HGF)

- **Pre-saturator**
  - 50 °C
  - 90-100 cc/min
  - 0.8% CO\textsubscript{2} in air

- **HGF**
  - 50 °C
  - 100 cc/min
  - 0-1 ppm NO\textsubscript{2}
  - 4 – 100 ppm NH\textsubscript{3}
  - Froth
  - 0.3 Loaded PZ
  - 500 ml

- **Hot gas FTIR**
  - 180 °C
  - 5 L/min
  - 5.1 L/min

- **50 ppm NO\textsubscript{2} in N\textsubscript{2}**
  - 0 - 10 cc/min
cumulative results 5m PZ from Alfa Aesar (0.3 loading), 50 °C, 0.8% CO₂ in air

Add 380 µmol/kg Fe³⁺

164 hours:

- NH₃ accumulation, formate and iron
  - NH₃
  - Total Formate

- 1.3 µmol/kg-hr
- 153 µmol/kg step change
- 2.1 µmol/kg-hr
- 0.9 µmol/kg-hr

0.7 µmol/kg-hr

Formate

Fe

Fe⁺

0 50 100 150 200 250 300 350

NH₃ accumulation, formate and iron (µmol/kg)

Time (Hours)
cumulative results

5m PZ from Alfa Aesar (0.3 loading), 50 °C, 0.8% CO₂ in air

\[
\text{Stoichiometric relation} \quad \frac{\text{Fe}}{\text{formate}} = \frac{380}{153} \approx 2.5
\]

\[
\text{NH}_3 \quad \frac{\text{formate}}{\text{formate}} = \frac{3.6}{2.1} \approx 1.7
\]

\[
PZ - \text{COH}_2 + 2\text{Fe}^{3+} \rightarrow PZ - \text{COH} + 2\text{Fe}^{2+} + 2\text{H}^+
\]

164 hours:
Add 380 µmol/kg Fe³⁺

153 µmol/kg step change

1.3 µmol/kg-hr

0.9 µmol/kg-hr

0.7 µmol/kg-hr

2.1 µmol/kg-hr
Dissolved Oxygen

• Vary residence time in high T rich line before stripper
  • SRP pilot plant will vary time from <1 s to 40 s [modifications completed]
  • Measure oxygen in product CO₂ at SRP (Fall 2021) and NCCC (Summer 2022)

• Remove DO from rich solvent by N₂ sparging
  • Measure DO in cold rich solvent

• Previous testing in HTOR (High Temperature Oxidation Reactor)
• SRP pilot with N₂ sparging in sump (Fall 2021) [modifications completed]
• NCCC pilot with sparging in sump or new column (Summer 2022)
  • Design of sparging column – preliminary results
N₂ Sparging in HTOR Reduces NH₃ Production

- Start with moderately degraded 4 m PZ solvent
- Cycled from 40 to 150 °C
- Liquid depth of the sparger varied between 5 to 15 cm.
N\textsubscript{2} Sparging Model

- Mass Transfer in Liquid Phase
- \( Z = \text{NTU} \times \text{HTU} \)
- No Back-mixing
- Estimation of \( K_La \) were from experiments with batch liquid by Hikita

\[
\left( \frac{K_La \mu_G}{g} \right) = 14.9 \left( \frac{U_G \mu_L}{\sigma} \right)^{1.76} \left( \frac{\mu_L}{\rho_L \sigma^3} \right)^{-0.248} \left( \frac{\rho_G}{\rho_L} \right)^{0.243} \left( \frac{\mu_L}{\rho_L D_{G/L}} \right)^{-0.604}
\]

N₂ sparger design for NCCC

Liquid Rate: 1.89 kg/s (15000 lb/hr), 40 C, 90% DO Removal, CO₂ Capture Rate = 1.26 mol/s, D = 0.1 m so that liquid velocity is equal to bubble rise velocity

- 10.5 m tall
- N₂ rate = 30 mmol/s
  - = 20 mmol N₂/mol of CO₂ captured
  - = 16 mmol of N₂ / kg of solvent
Fe$^{+2}$/Fe$^{+3}$

• Measure Fe$^{+2}$ and Fe$^{+3}$ solubility as function of degradation [in progress]
• Measure Fe$^{+2}$ and Fe$^{+3}$ in solvent
• Adsorb dissolved Fe on activated C
  • NCCC 2018-19
  • Niederaussem 2021
  • HTOR 2021-22
  • Bench-scale experiments 2021
  • SRP pilot 2021
  • NCCC pilot 2022

• Measure corrosion with PZ solutions: a source of soluble Fe
Fe$^{+2}$/Fe$^{+3}$: Ferrous as an Oxidation Catalyst

- Fe increases the rate of oxidation of many amine solvents
- Work on MEA focused on oxidation in the absorber
- Ferrous can catalyze a free radical reaction between MEA and O$_2$
- Possible reaction pathway for PZ also
- In the absence of O$_2$, Fe still speeds up oxidation. How?
Fe$^{2+}$/Fe$^{3+}$: Iron as an Oxidation Carrier to Degrade PZ in the Stripper

- PZ oxidation occurs at high T in stripper
- Ferrous should oxidize readily in the presence of DO

\[
Fe^{3+} + PZ \rightarrow \text{Products} + Fe^{2+}
\]
Iron Becomes More Soluble as Degradation Products Accumulate

2012 CSIRO Tarong Campaign

- Fe
  - 125 °C
    - 0.11 μmol/kg/hr
  - 155 °C
    - 0.94 μmol/kg/hr
    - $E_a = 100$ kJ/mol

Nielson, 2018
Solubility of FeCl₃ in 5 m PZ at 55°C

Excess FeCl₃ added to PZ solvents
Total dissolved Fe determined by ICP

<table>
<thead>
<tr>
<th>Fe (mmol/kg)</th>
<th>Days</th>
</tr>
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<tbody>
<tr>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>0.04</td>
<td></td>
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<tr>
<td>0.08</td>
<td></td>
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<tr>
<td>0.16</td>
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<tr>
<td>0.32</td>
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<tr>
<td>0.64</td>
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<tr>
<td>1.28</td>
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<tr>
<td>2.56</td>
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Legend:
- HTOR Major Degradation
- NCCC Moderate Degradation
- Artificial Minor Degradation
- NCCC Minor Degradation
- Clean PZ
- HTOR Minor Degradation
Fe^{2+}/Fe^{3+}: C Treating Reduces NH_3 with PZAS at NCCC 2019

NGCC Gas Rate
\sim 8000 \text{ lb/hr}

24-hr NH_3 in water wash gas outlet (ppm)

Operating Hours (hr)

0.106 mmol/kg/hr
0.3 kg PZ/tonne CO_2

* NO concentration relatively stable at 50 ppm
Carbon Bed turned on at 5/14/2019 8:59 (3600 hrs)
Absorbance Change during the Campaign

Operating Hours (hr) vs. Absorbance (A) at 320 nm (UV) and 540 nm (Visible).

- Carbon Bed: Absorbance at 320 nm increases significantly after 3500 hours of operation.
Equilibrium absorbance is linearly related to the carbon loading.

Equation:
\[ y = 0.003x + 0.095 \]

\[ R^2 = 0.916 \]
Fe removed from NCCC Used Carbon = 3.3 mmol/kg NCCC solvent

At NCCC: 14 canisters of carbon
41 lb carbon/canister
12000 lbs of solvent
→ 3.3 mmol Fe/kg solvent Removed

104.5 mmol Fe/kg carbon
from NCCC used carbon

36.3 mmol Fe/kg carbon
from clean carbon

Fe (mmol/kg)

Batch Number

0 2 4 6 8 10 12
High Temperature Oxidation Reactor (HTOR)

**Low Temp Reactor**
- Temperature: 50 °C
- Time constant: \( \tau = 1.75 \) min
- Flow rate: 7.5 L/min
- Stream: Sat’d air + 0.5% CO₂

**Cross Exchanger**
- Flow rate: 200 mL/min
- Pressure: 200 psig

**Trim Heater**
- Temperature: 150 °C
- Time constant: \( \tau = 1 \) min

**FTIR:** NH₃ and volatile amines

**Total inventory:** ~1.6 L

**8 min per cycle**

**Liquid samples:** amine loss, degradation products accumulation
(HPLC, Cation & Anion IC, ICP-OES, acid titration, UV-Vis)
NH$_3$ rate from FTIR

The graph shows the NH$_3$ rate (mmol/kg/hr) over operating hours (hr). The graph highlights periods where the carbon bed is on and off, with a notable event labeled "pump down."
Corrosion Method: Low-gas flow reactor

Inlet gas 100 cc/min

Mechanical agitation
L velocity around 0.5~1 m/s

25~75 °C

600 mL
C1010 corrosion & PZ concentration

1.5% CO₂ in air/N₂, 60 °C

Corrosion rate (μm/yr) vs. PZ (m)

- Tarong
- NCCC
- Fresh

CR = 2.4 Cₚᶻ⁻⁰.₆₈

- Corrosion - 1.5% CO₂/air
- Corrosion - 1.5% CO₂/N₂

5 m
<table>
<thead>
<tr>
<th>Modification</th>
<th>Purpose</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inject and measure NO₂ at 2 ppm</td>
<td>Create baseline oxidation similar to commercial</td>
</tr>
<tr>
<td>N₂ sparging in the absorber sump</td>
<td>Test efficacy of DO stripping</td>
</tr>
<tr>
<td>Increase τ on warm rich bypass from ~1 s to ~40 s</td>
<td>Confirm high-T degradation in rich amine</td>
</tr>
<tr>
<td>Bypass lean amine storage tank</td>
<td>Minimize amine inventory</td>
</tr>
<tr>
<td>Add carbon bed in rich amine line to remove iron</td>
<td>Test impact of removing oxidation catalysts</td>
</tr>
<tr>
<td>Adding O₂ analyzers on recovered CO₂ gas and rich amine</td>
<td>Monitor oxygen presence when perturbing system</td>
</tr>
<tr>
<td>Adding corrosion coupons</td>
<td>Monitor corrosion simultaneous with oxidation</td>
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Conclusions on $\text{Fe}^{+2}/\text{Fe}^{+3}$

1. $\text{Fe}^{+3}$ solubility in PZ varies solvent degradation from 0.02 to 2 mM
2. C treating reduced ammonia production at NCCC and in HTOR. C treating removed 3 mM of “soluble” iron from NCCC solvent system. All of the “soluble” Fe must be removed to reduce oxidation.
3. C treating removes PZ degradation products that adsorb at 320 & 540 nm
4. >0.01 m PZ protects carbon steel from corrosion at absorber T
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