Overview of degradation compounds from amines and factors influencing them

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Outline

• Introduction
• Experimental procedure
  – Degradation setups
  – Degradation compounds - analyses
• Results
  – Degradation compounds
  – Comparison
    • Esbjerg
    • SDR-rig
• Summary
Introduction

• Amine degradation causes problems
  – Solvent loss
  – Corrosion
  – Fouling
  – Foaming
  – Emission of degradation compounds

• Several analytical techniques necessary for identification of degradation compounds
  – GC-MS
  – LC-MS
  – IC
CO$_2$ absorption process

Oxidative degradation

Thermal degradation with CO$_2$

Experimental

- Oxidative degradation rigs
- Thermal degradation cylinders
Closed batch (CB) setup

a  Valve for loading solution into the system
b  Liquid pump
c  Valve for taking sample
d  Reactor
e  Packing area
f  Gas pump
g  Cooler before gas analysers
h  Flow meters for the CO₂ and O₂ analysers
i  Valve to empty the reactor
j  Water lock to avoid pressure build up

Open batch (OB) setup

a  Flow meters for O₂/air and CO₂
b  Gas pump
c  Saturation vessel
d  Reactor
e  Coolers
f  Gas bubble bottles
Thermal degradation

- Close batch cylinders – SS316
- Oxidative degraded solutions (from OB or CB)
- 135 °C for 5 weeks
- One cylinder taken out every week
- Leakages tested weighing cylinders before and after


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Experiment

• Oxidative degradation (50-55 and 75 °C):
  – OB: fresh 30 wt% MEA, $\alpha = 0.4$ mole CO$_2$ per mole amine
  – CB: fresh 30 wt% MEA, $\alpha = 0.4$

• Thermal degradation with CO$_2$ (135 °C):
  – fresh 30 wt% MEA, $\alpha = 0.4$ Oxidatively degraded end samples from both CB and OB setup (MEA)

• Main analyses: LC-MS and IC
Degradation cpds - quantified

Liquid phase

HEF

HEA

BHEOX

HEPO

OZD

HEI

HEGly

NO$_2^-$  NO$_3^-$

Oxalate  Formate

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Degradation cpds - quantified

Liquid phase

HEF
HEPO
OZD
HEA
HEI
BHEOX
HEGly

NO₂⁻
NO₃⁻
IC
Oxalate
Formate
Results
<table>
<thead>
<tr>
<th>Oxidative</th>
<th>Thermal</th>
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<tbody>
<tr>
<td>$O_2$ T Setup (OB toward CB2)</td>
<td>Used solvent &quot;Fresh&quot; solvent</td>
</tr>
</tbody>
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**Primary degradation compounds**

<p>| NO$_2^-$ | ↑ | ↑ | ↑ | --- | --- |
| NO$_3^-$ | ↑ | ↑ | ↓ | --- | --- |
| Formate  | ↑ | ↑ | → | ↑   | ↑   |
| Oxalate  | ↑ | ↑ | ↓ | --- | --- |</p>
<table>
<thead>
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<tr>
<td>HEA</td>
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</tr>
<tr>
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<td>↑️️</td>
</tr>
<tr>
<td>HEGly</td>
<td>→️️</td>
</tr>
<tr>
<td>HEPO</td>
<td>→️️</td>
</tr>
<tr>
<td>HEI</td>
<td>↑️️</td>
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Secondary degradation compounds

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<td>NO₂⁻</td>
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<tr>
<td>NO₃⁻</td>
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<tr>
<td>Oxalate</td>
<td>↑</td>
<td>↑</td>
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</tbody>
</table>
HEI

Absorber conditions

Stripper conditions

Blue: Closed batch setup

Green: Open batch setup

Grey: Only stripper conditions

Concentration (mmol/L)

Time (days)

50-55 °C

75 °C

55 °C
HEA

Absorber conditions

Stripper conditions

Blue: Closed batch setup

Green: Open batch setup

Grey: Only stripper conditions

Concentration (mmol/L)

75 °C

50-55 °C

55 °C

Time (days)
MEA
secondary degradation compounds

Concentration (µg/mL)

HeGly  HEPO  HEF  HEI

Rich MEA  Lean MEA  Lean MEA

Esbjerg campaign

CB_1  CB_1 Th  OB_1  OB_1 Th  Th

3 weeks  5 weeks  3 weeks  5 weeks  10 weeks

11 weeks  20 weeks

MEA secondary degradation compounds

- CB_1: 3 weeks
- CB_1 Th: 5 weeks
- OB_1: 3 weeks
- OB_1 Th: 5 weeks
- Th: 10 weeks

Esbjerg campaign

Rich MEA
Lean MEA

Concentration (µg/mL)

OZD  BHEOX  HEA

SDR / Ox-Thermal

- SDR (Einbu et al. 2013) and Ox/thermal ratio measured relative to Esbjerg (20 weeks)
- The relative trends are comparable for most of the degradation compounds
- Exceptions might be due to limiting amounts of intermediates for some of the degradation compounds in Ox/thermal

Summary

- Degradation compounds behaviour for thermal degradation on oxidative degraded solutions mimicks the behaviour of these compounds in fresh MEA solutions
- Lab experiments (separated and combined) seem to mimick formation of degradation compounds seen in pilot or cycled experiments (SDR)
Summary

- Degradation compounds:
  - OZD increases with oxygen content and higher temperature seems to favour further reaction of OZD to other compounds
  - BHEOX increases with oxygen content and seems to decompose at temperatures between 75 to 135 °C
  - HEA increases with oxygen content and temperature - intermediate formation favoured or the reaction is directly influenced by increasing temperature
  - HEGly seems to increase less with temperature than HEPO and a reduction was seen for ox-thermal. Increase over time for SDR. Limited by intermediates in the closed cylinder experiment?
  - HEPO shows a continuous increase with temperature – the reaction itself or formation of intermediate favoured by temperature
  - HEF: Increases over time SDR, not seen for thermal, limitated by intermediates?
  - HEI: HEI formation more favoured in separated degradation experiments (ox). Formation favoured by more closed setups, likely because of volatile intermediate present in solution
References


• Eide-Haugmo, I., 2011. Environmental impacts and aspects of absorbents used for CO₂ capture, Department of Chemical Engineering. Norwegian University of Science and Technology, Trondheim, p. 365.


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Thank you
More information

Chemical stability, nitrogen balance and degradation compounds

