Study on the degradation mechanisms of new amines in the presence of CO$_2$ or O$_2$

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Outline

- Objective of the study
- Amines selection
- Experimental conditions
- Results
- Conclusion
Objective of the study

To be able to predict the chemical stability of a new solvent in CO₂ capture conditions

- Comparison ethanolamines with polyamines

- To have a better understanding of degradation mechanisms
  - Due to temperature
  - Due to CO₂ (in the absence of O₂)
  - Due to O₂ (in the absence of CO₂)

- To establish structure – properties relationships
Objective – Amines selection – Experimental conditions – Results – Conclusion

Amines selection

Cyclical Diamine

Reference case

Amine function nature
1: Primary 2: Secondary 3: Tertiary

Length between amine functions

Ethanolamines

Polyamines

Steric hindrance
### Experimental conditions

<table>
<thead>
<tr>
<th>Standard conditions for MEA pilot plant capture</th>
<th>Our experimental conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>15 - 30 wt %</td>
<td>4 mol.kg⁻¹</td>
</tr>
<tr>
<td>(= 2.5 - 4.9 mol.kg⁻¹)</td>
<td></td>
</tr>
<tr>
<td>50 - 120°C</td>
<td>140°C</td>
</tr>
<tr>
<td>open batch</td>
<td>stainless steel batch reactors</td>
</tr>
<tr>
<td>1 to 2 bars (75 % N₂, 15 % CO₂, 5 % H₂O, 5 % O₂)</td>
<td>P CO₂ = 20 bars</td>
</tr>
<tr>
<td></td>
<td>P air = 20 bars</td>
</tr>
<tr>
<td></td>
<td>(Pp O₂ = 4.2 bars)</td>
</tr>
</tbody>
</table>

**Strong degradation conditions**

- Significant degradation rates after 15 days
- Differences among amines are more pronounced
Experimental conditions

- Remaining amine and its degradation compounds quantification:
  
  => addition of an internal standard (TEG) in the degraded solution

- Gas Chromatography:
  
  - polar column: Carbowax-Amines
  - non polar column: CPSIL8-CB-Amines

  Good separation + identification of many compounds
Experimental conditions

- Degradation products identification:
  - **Mass spectrometry:**
    - GC-MS coupling:
      - Electronic Impact: molecule fragments
      - Chemical Ionization: molecular ion
    - FTICR-MS: high molecular weight compounds
  - **NMR:** $^1$H, $^{13}$C, DEPT

- Ionic compounds:
  - **Ionic Chromatography:** carboxylic acids (formic, acetic, glycolic, oxalic), nitrites and nitrates
Thermal degradation

4 mol.kg\(^{-1}\), 140°C, 15 days

- Effect of temperature (140°C) on amines degradation:
  - Negligible for 10 amines (\(\tau < 1.7\%\))
  - Not negligible for 7 amines:
    - Low degradation rates / degradation in the presence of \(\text{CO}_2\)
    - Radical mechanisms: same compounds as for oxidative degradation

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Objective – Amines selection – Experimental conditions – **Results: CO₂ degradation** – Conclusion

Degradation with CO₂

4 mol.kg⁻¹, 140°C, Pp CO₂ = 20 bars, 15 days

**ETHANOLAMINES**

- DMP
- PMDPTA
- TMEDA
- TMPDA
- N,N,N'-triMPDA
- N,N,N'-triMEDA
- DEA
- DMAE
- N,N-diMEDA
- TMEDA
- PMDPTAMDEA
- TMPDA

**POLYAMINES**

- MEA
- AMP
- DMP
- PMDPTA
- TMEDA
- TMPDA
- N,N,N'-triMPDA
- N,N,N'-triMEDA
- DEA
- DMAE
- N,N-diMEDA
- TMEDA
- PMDPTAMDEA
- TMPDA

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Degradation compounds from ethanolamines

<table>
<thead>
<tr>
<th>Amines II</th>
<th>Amines I</th>
<th>Hindered Amines I</th>
<th>Amines III</th>
</tr>
</thead>
<tbody>
<tr>
<td>R = $\text{CH}_2\text{-CH}_2\text{-OH}$</td>
<td>$\text{CH}_3$</td>
<td>$H$</td>
<td>$\text{CH}_3$</td>
</tr>
<tr>
<td>DEA</td>
<td>MMEA</td>
<td>MEA</td>
<td>AMP</td>
</tr>
<tr>
<td>DMMEA</td>
<td>MDEA</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Polyaddition cpds
- Cyclic cpds
  - Imidazolidinone
  - Oxazolidinone

Demethylated / dealkylated cpds

Objective – Amines selection
Experimental conditions – Results: CO$_2$ degradation – Conclusion
General pathway for ethanolamines degradation

Amines I or II → oxazolidinones

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General pathway for ethanolamines degradation

Amines I or II \[\rightarrow\] oxazolidinones \[\rightarrow\] addition compounds

very reactive
General pathway for ethanolamines degradation

Objective – Amines selection – Experimental conditions – Results: CO₂ degradation – Conclusion
General pathway for ethanolamines degradation

Objective – Amines selection – Experimental conditions – Results: CO\textsubscript{2} degradation – Conclusion

Amines II \xrightarrow{\text{addition}} \text{oxazolidinones} \xrightarrow{\text{polyaddition compounds}} \text{addition compounds} \xrightarrow{\text{cyclic compounds}}
General pathway for ethanolamines degradation

Objective – Amines selection
Experimental conditions
Results: CO₂ degradation
Conclusion

Amines I → oxazolidinones → addition compounds → cyclic compounds → polyaddition compounds

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General pathway for ethanolamines degradation

Objective – Amines selection  – Experimental conditions – Results: CO₂ degradation – Conclusion

very low reactivity of the corresponding oxazolidinone

Hindered amines I → oxazolidinones → addition compounds → polyaddition compounds

→ cyclic compounds

imidazolidinones

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General pathway for ethanolamines degradation

Amines I or II → oxazolidinones → addition compounds → cyclic compounds

polyaddition compounds

imidazolidinones

demethylation / dealkylation

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Degradation compounds from ethylenediamines

<table>
<thead>
<tr>
<th>Diamine II - II</th>
<th>Diamine III - II</th>
<th>Diamine III - I</th>
<th>Diamine III - III</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{N, N' diMEDA} )</td>
<td>( \text{N, N, N' triMEDA} )</td>
<td>( \text{N, N diMEDA} )</td>
<td>( \text{TMEDA} )</td>
</tr>
<tr>
<td>Imidazolidinone</td>
<td>Polyaddition cpds</td>
<td>Imidazolidinones</td>
<td>Demethylated / dealkylated cpds</td>
</tr>
<tr>
<td>( \text{Cyclic cpds} )</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>( \text{H}_3\text{C} - \text{N} - \text{CH}_3 )</th>
<th>( \text{H}_3\text{C} )</th>
<th>( \text{N} - \text{CH}_3 )</th>
<th>( \text{N} - \text{CH}_3 )</th>
</tr>
</thead>
</table>
General pathway for ethylenediamines degradation

Diamines III – II or I → addition compounds

leaving group

ammonium carbonate or carbamate

Objective – Amines selection – Experimental conditions – Results: CO₂ degradation – Conclusion

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General pathway for ethylenediamines degradation

Diamines III - II → addition compounds → cyclic compounds

polyaddition compounds

Objective – Amines selection – Experimental conditions – Results: CO₂ degradation – Conclusion

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General pathway for ethylenediamines degradation

Diamines III - I

addition compounds

polyaddition compounds

R_N[R_1N]_nN_R_2

R_3N

R_3N

imidazolidinone

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General pathway for ethylenediamines degradation

Diamines III - I

Diamines II - II

addition compounds

polyaddition compounds

cyclic compounds

imidazolidinone

Objective – Amines selection – Experimental conditions – Results: CO₂ degradation – Conclusion

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General pathway for ethylenediamines degradation

Diamines III - III

Demethylation / dealkylation

Diamines III - II or I

Addition compounds

Polyaddition compounds

Cyclic compounds

Imidazolidinones

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CO$_2$ degradation: structure $\leftrightarrow$ properties

- **Amine function nature:**
  Amine stability: III > I > II

- **Steric hindrance on $\alpha$ position:** Stability $\uparrow$
  - MEA: $\tau$ % 42%
  - AMP: $\tau$ % 22%

- **Cyclic structure:** Stability $\uparrow$
  - TMEDA: $\tau$ % 15%
  - DMP: $\tau$ % 4.5%
CO$_2$ degradation: structure ↔ properties

- **Alkyl chain length between the two amine functions**:

  - 2 atoms (TMEDA): favourable 3 member ring but very reactive
  - 3 atoms (TMPDA): unfavourable 4 member ring
  - 4 atoms (TMBDA): very favourable 5 or 6 member rings with $\tau = 15\%$ and $\tau = 45\%$
  - 5 atoms (PMDETA): $\tau = 74\%$
  - 7 atoms (PMDPTA): unfavourable 8 and more member rings

**Objective** – Amines selection

**Experimental conditions** – Results: CO$_2$ degradation – Conclusion

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Objective – Amines selection

Experimental conditions

Results: oxidative degradation

Conclusion

Oxidative degradation

4 mol.kg\(^{-1}\), 140°C, Pp Air = 20 bars (Pp O\(_2\) = 4.2 bars), 15 days

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Degradation reactions ⇒ Radical mechanisms

- Main degradation reactions quantified
  - Demethylation / dealkylation + methylation
  - Ethanolamines
    - alcohol oxidation
  - Ethylenediamines
    - piperazinones formation
  - Propylenediamines
    - Allylic compounds formation
  - ionic compds: formic, acetic, oxalic, glycolic, nitrite, nitrate...

- Other reactions (non quantified):
  - volatile compds formation: NH₃, NR₃, NOx, HCOH, CH₃COH...
  - amino acids, amides...

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O₂ degradation: structure ↔ properties

- **No effect of OH function replacement by amine function**

\[
\begin{array}{ccc}
\text{HO} & \text{N} & \text{N} \\
\text{H} & \text{N} & \text{N} \\
\text{H} & \text{N} & \text{N}
\end{array}
\]

\[\tau\% \quad 17\% \quad 17\% \quad 18\%\]

- **Low effect of the amine function nature**

  amine stability III ≥ I ≥ II

- **Cyclic structure: low improvement**

\[
\begin{array}{c}
\text{TMEDA} \\
\text{N} \quad \text{N} \\
\text{16}\%
\end{array}
\quad \begin{array}{c}
\text{DMP} \\
\text{N} \quad \text{N} \\
\text{13}\%
\end{array}
\]
O$_2$ degradation: structure ↔ properties

- Steric hindrance on $\alpha$ position: stability $\uparrow$
  - Prevents volatile compounds formation

<table>
<thead>
<tr>
<th></th>
<th>MEA</th>
<th>AMP</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tau$ %</td>
<td>21</td>
<td>8.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
O₂ degradation: structure ↔ properties

- **Alkyl chain length between the two amino groups**

4 or 5 atoms between amine functions

5 or 6 member ring formation

Stability ↓
Conclusion

Mechanistic study of ethanolamines and polyamines degradation

- identification and quantification of the main degradation compounds
- Proposition of mechanisms
- structure - property relationships
  - Nature of degradation compounds
  - Amines chemical stability

PREDICTION TOOLS

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Thank you!
**colonne A : apolaire**

**colonne B : polaire**
Ethanolamines degradation

Degradation rate $\tau \%$

Objective – Amines selection – Experimental conditions – Results: CO$_2$ degradation – Conclusion

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Objective – Amines selection – Experimental conditions – Results: CO₂ degradation – Conclusion

Ethylenediamines degradation

Degradation rate τ %

- other reactions
- cyclic compds
- addition compds
- imidazolidinones
- methylation
- demethylation / dealkylation

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Polyamines degradation

Degradation rate $\tau$ %

- TMEDA $x = 2$
- TMPDA $x = 3$
- TMBDA $x = 4$
- PMDETA $x = 5$
- PMDPTA $x = 7$

- Other reactions
- Cyclic compound
- Addition
- Imidazolidinone
- Methylation
- Demethylation / dealkylation
- Specific reactions

Objective – Amines selection – Experimental conditions – Results: CO$_2$ degradation – Conclusion

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Effet de l’encombrement stérique sur le C en α de N

Encombrement stérique

pas H en α

H⁺

H₂N

OH

cation radical aminium

H₂N

OH

NH₃

H⁺

autres :
- légers
- acides aminés
- produits non identifiés

pipérazinones

dimère

N-méthylation

Introduction – Présentation du sujet – Dégradation sous CO₂ – Dégradation sous O₂ – Dégradation sous CO₂ + O₂ – Conclusions – Perspectives
Example: MAE solution degraded with CO$_2$

FW = 189 g/mol
Example: MAE solution degraded with CO₂

Objective – Amines selection – Experimental conditions – Results – Conclusion

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Example: TMBDA solution degraded with CO₂
Objective – Amines selection – Experimental conditions – Results: oxidative degradation – Conclusion

Carboxylic acids

No obvious relationships between the structure and the amount of carboxylic acids!
Material balance

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