Overview of degradation compounds from amines and factors influencing them

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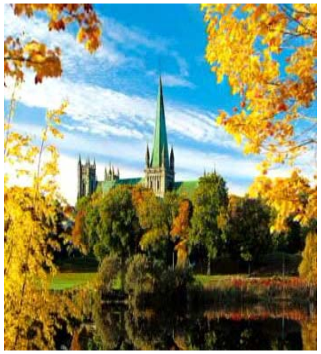


Outline

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

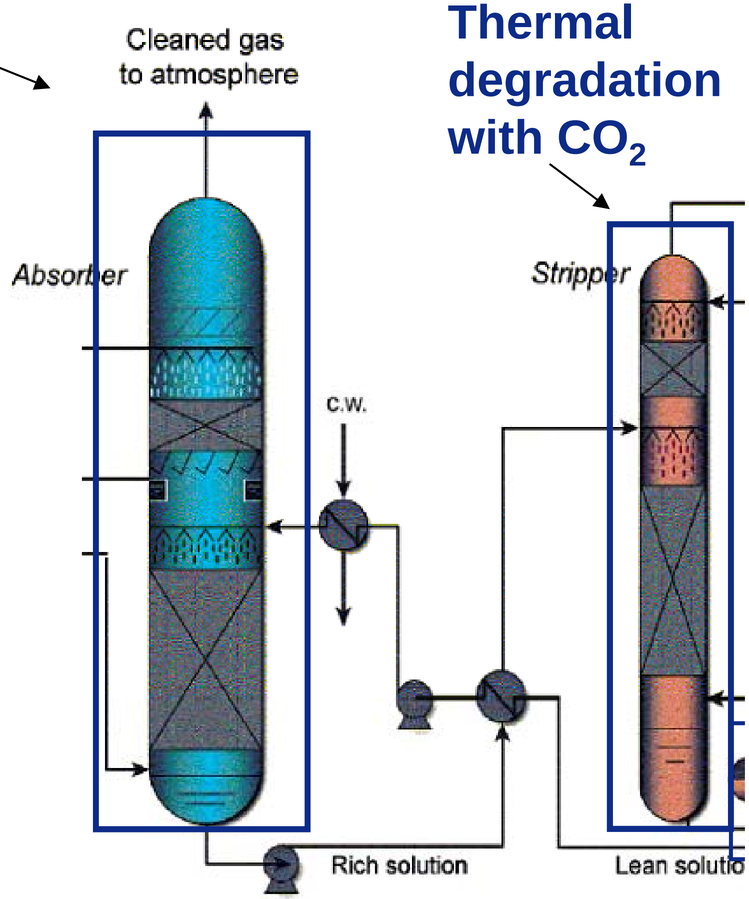
Introduction

- 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

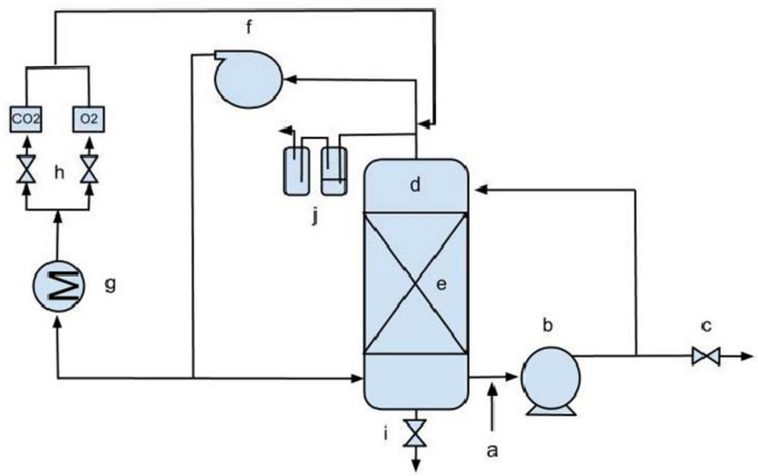


Tobiesen, F.A., Svendsen, H.F., 2006. Industrial & Engineering Chemistry Research 45, 2489-2496.

Experimental

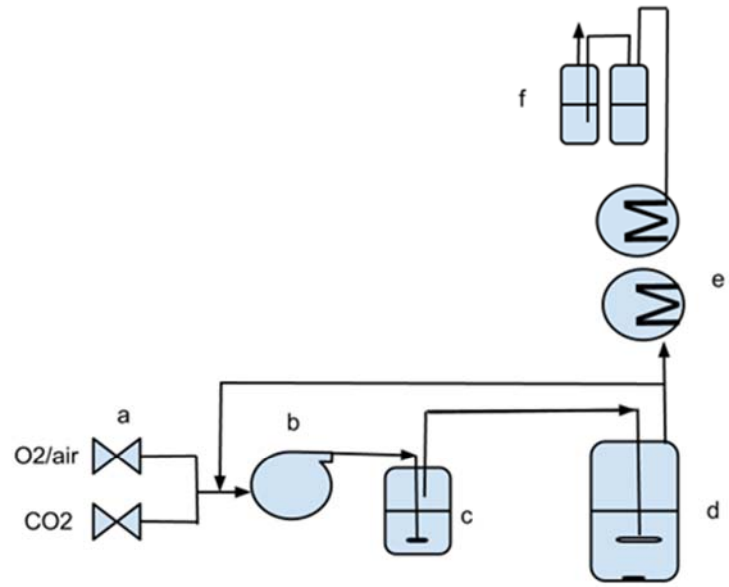
- Oxidative degradation rigs
- Thermal degradation sylinders

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 CO_2 and O_2 analysers
i Valve used to empty the reactor
j Water lock to avoid pressure build up

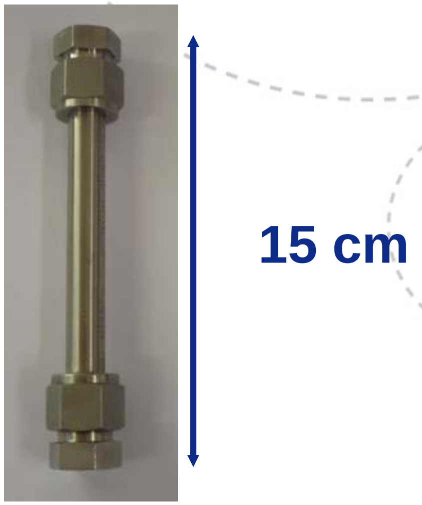
Open batch (OB) setup



a Flow meters for O_2/air and CO_2
b Gas pump
c Saturation vessel
d Reactor
e Coolers
f Gas bubble bottles

Thermal degradation

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



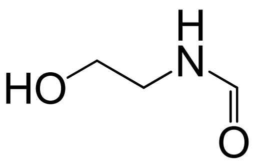
Eide-Haugmo, I., 2011. Department of Chemical Engineering. Norwegian University of Science and Technology, Trondheim, p. 365.

Experiment

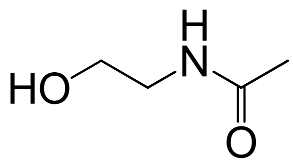
- Oxidative degradation (50-55 and 75 °C):
  - OB: fresh 30 wt% MEA, α =0.4 mole CO_2 per mole amine
  - CB: fresh 30 wt% MEA, α =0.4
- Thermal degradation with CO_2 (135 °C):
  - fresh 30 wt% MEA, α = 0.4 Oxidatively degraded end samples from both CB and OB setup (MEA)
- Main analyses: LC-MS and IC

Degradation cpds - quantified

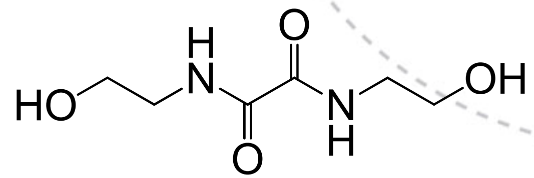
Liquid phase



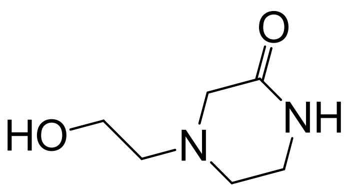
HEF



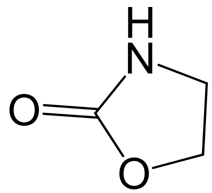
HEA



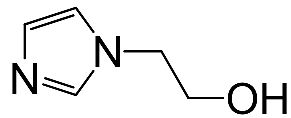
BHEOX



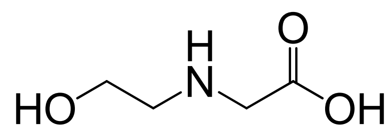
HEPO



OZD



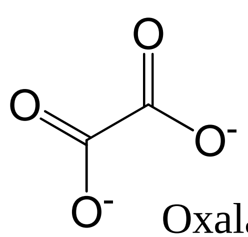
HEI



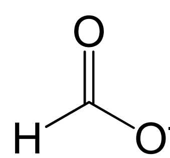
HEGly

NO_2^-

NO_3^-



Oxalate

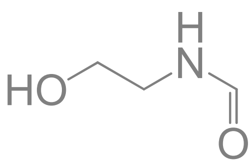


Formate

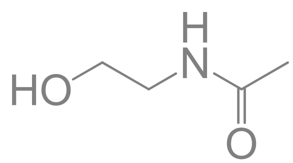
Degradation cpds - quantified

Liquid phase

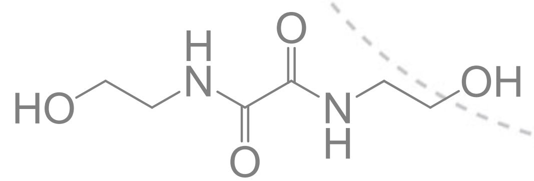
LC-MS



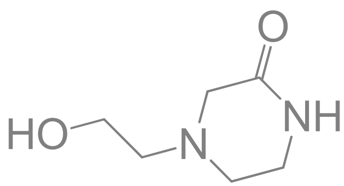
HEF



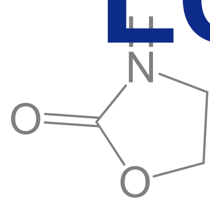
HEA



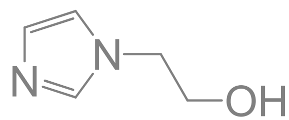
BHEOX



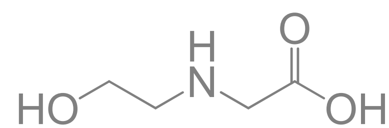
HEPO



OZD



HEI

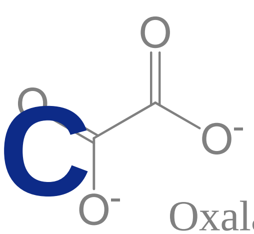


HEGly

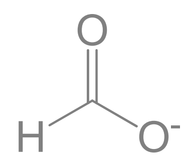
IC

NO_2^-

NO_3^-



Oxalate



Formate

Results

Primary degradation compounds

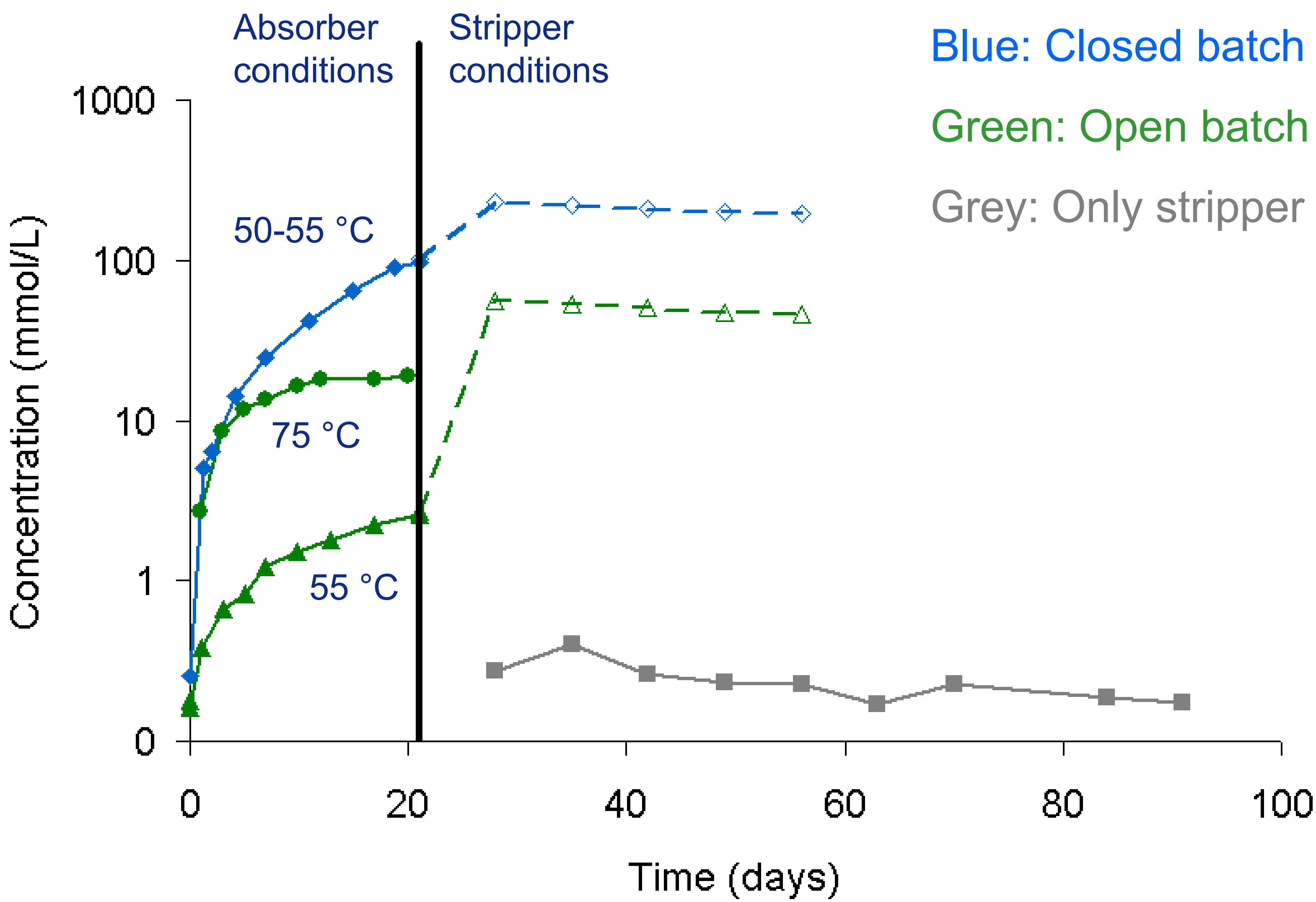
	Oxidative			Thermal	
	O_2	T	Setup (OB toward CB2)	Used solvent	”Fresh” solvent
NO_2^-	↑→	↑→	↑	---	---
NO_3^-	↑	↑	↓	---	---
Formate	↑	↑	→	↑→	↑
Oxalate	↑	↑	↓	---	---

	Oxidative			Thermal	
	O_2	T	Setup (OB toward CB2)	Used solvent	”Fresh” solvent
OZD	↑	↑	→	↓	↓
HEF	↱	↱	→	↑↘	↑
HEA	↑	↑	→	↱	→
BHEOX	↑	↑↘	→	---	---
HEGly	→	↑↘	↓	↑↘	↑↘
HEPO	→	↱	↓	↱	↘
HEI	↑	↱	↑	↱	→

Secondary degradation compounds

	Oxidative			Thermal	
	O_2	T	Setup (OB toward CB2)	Used solvent	”Fresh” solvent
OZD	↑	↑	→	↓	↓
HEF	↑→	↑→	→	↑↘	↑
HEA	↑	↑	→	↑→	→
BHEOX	↑	↑↘	→	---	---
HEGly	→	↑↘	↓	↑↘	↑↘
HEPO	→	↑→	↓	↑→	↘
HEI	↑	↑→	↑	↑→	→
NO_2^-	↑→	↑→	↑	---	---
NO_3^-	↑	↑	↓	---	---
Formate	↑	↑	→	↑→	↑
Oxalate	↑	↑	↓	---	---

HEI

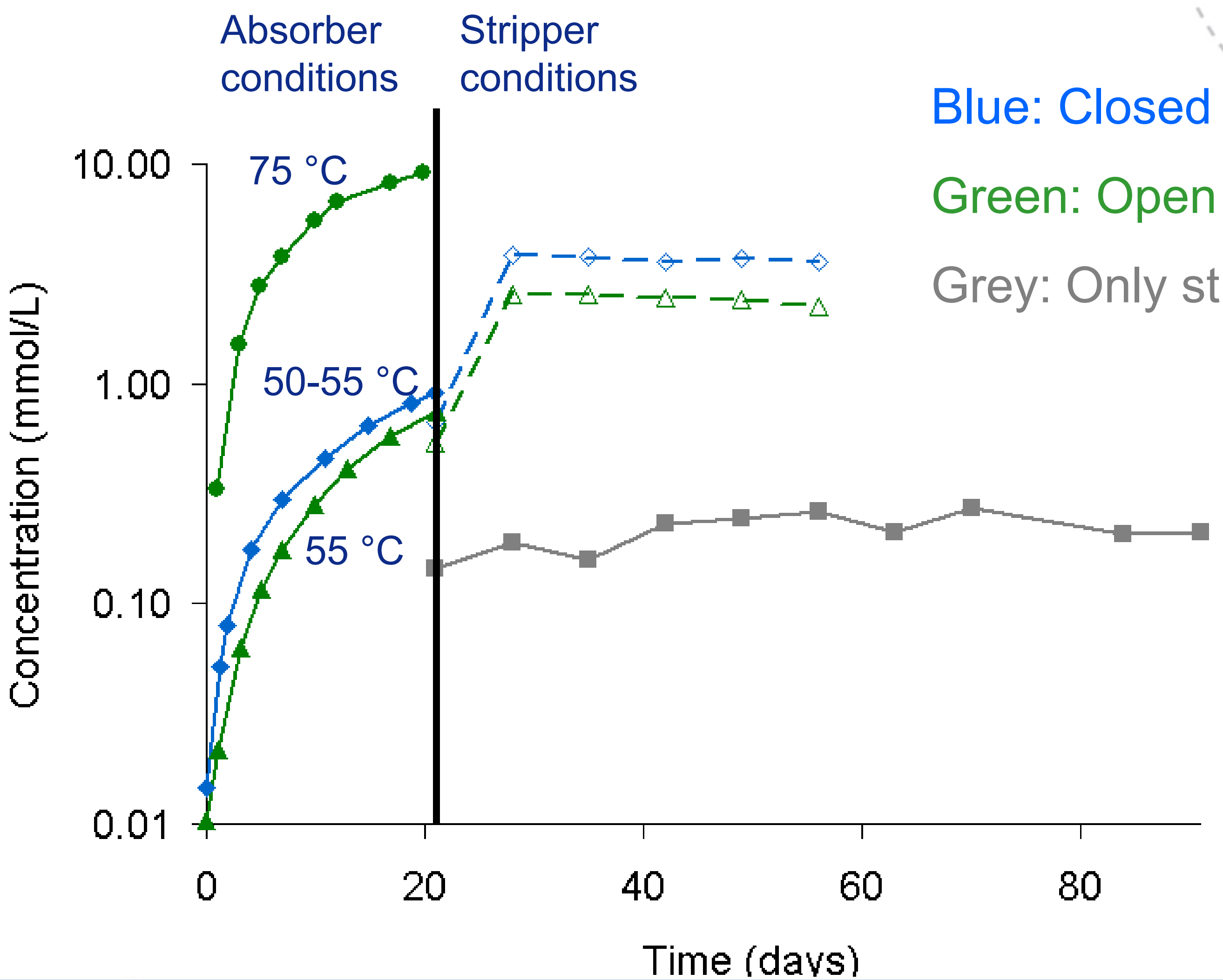


Blue: Closed batch setup

Green: Open batch setup

Grey: Only stripper conditions

HEA

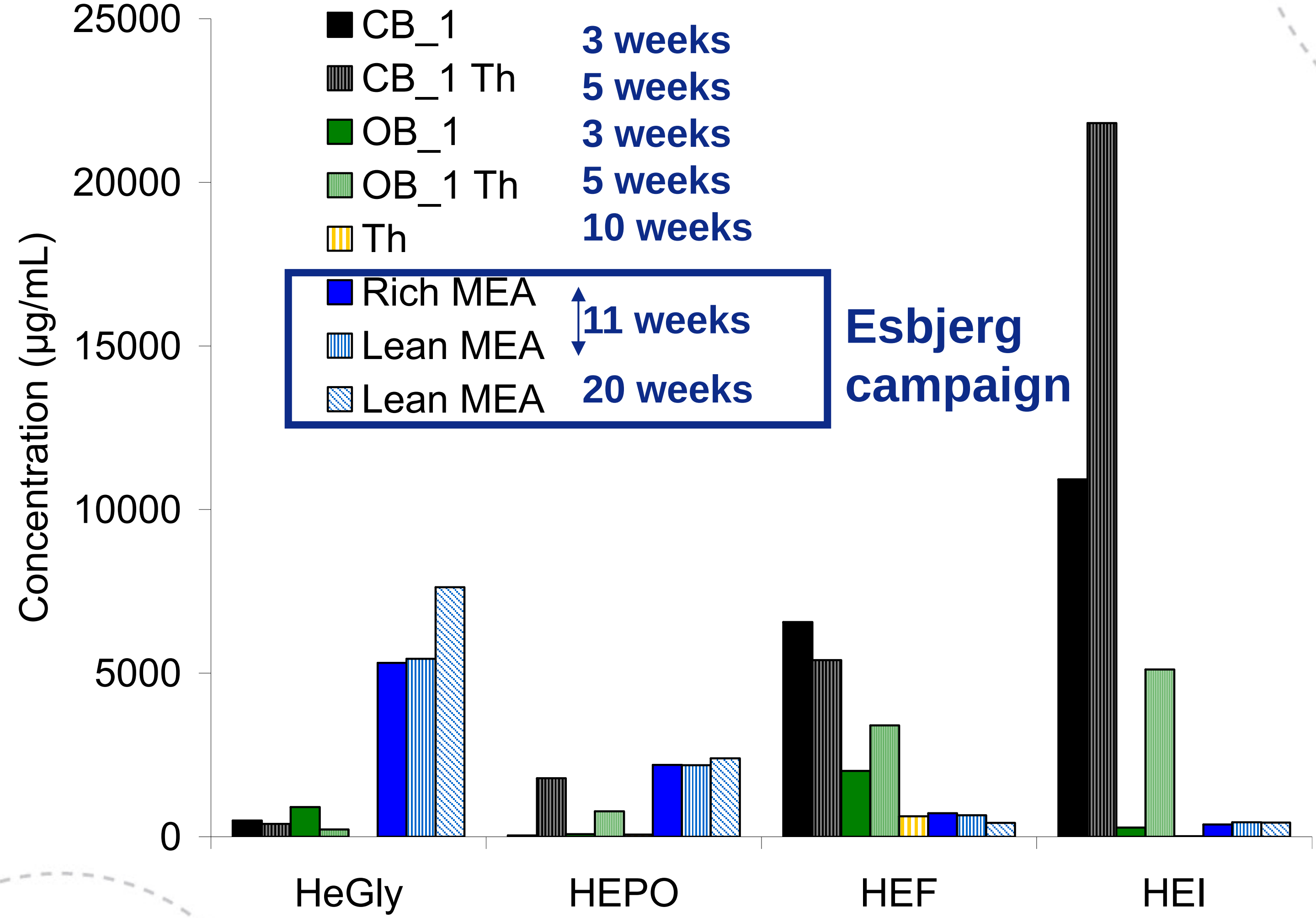


Blue: Closed batch setup

Green: Open batch setup

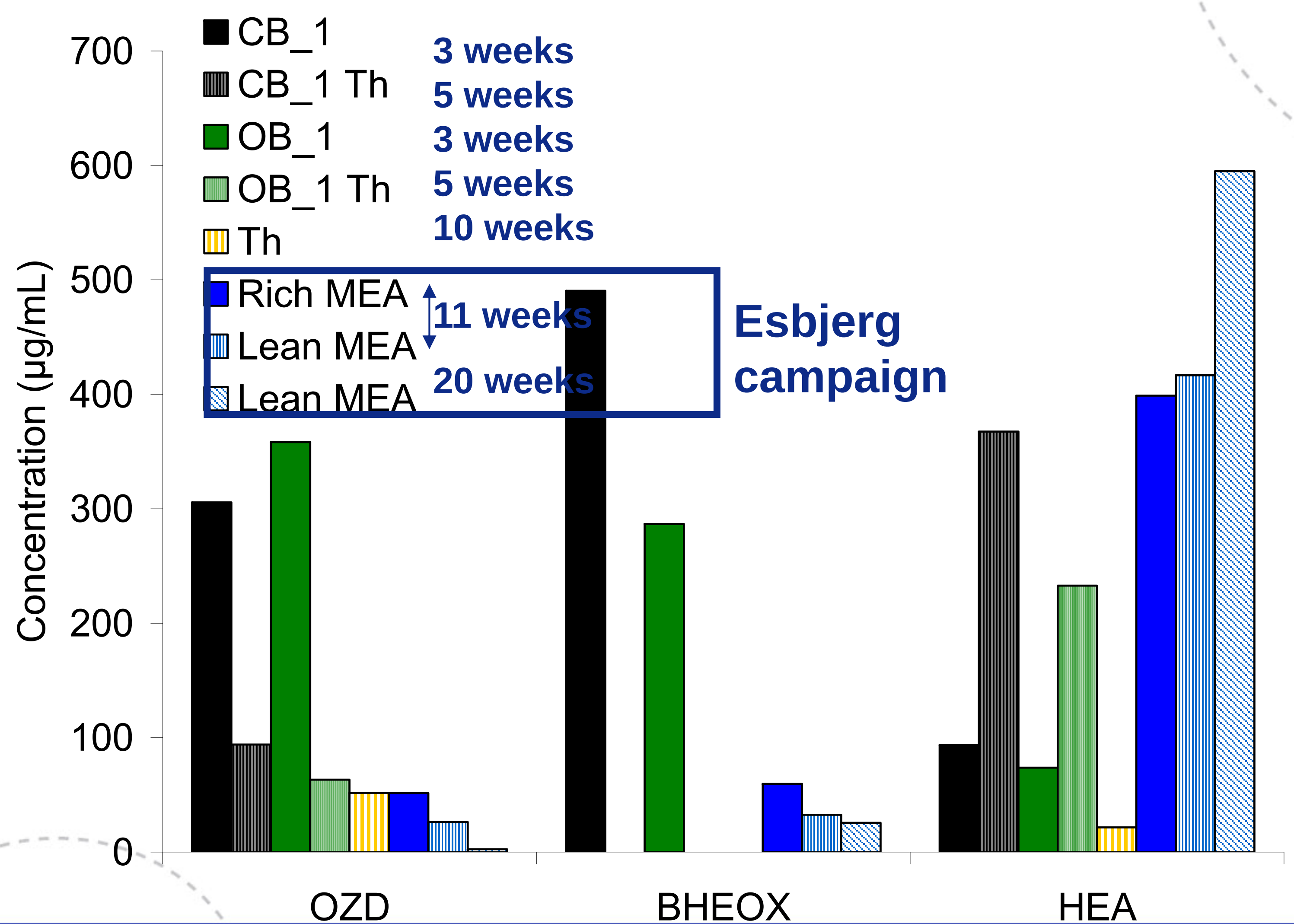
Grey: Only stripper conditions

MEA
secondary degradation compounds



da Silva, E.F., Lepaumier, H., Grimstvedt, A., Vevelstad, S.J., Einbu, A., Vernstad, K., Svendsen, H.F., Zahlsen, K., 2012. Industrial & Engineering Chemistry Research 51, 13329-13338.

MEA
secondary degradation compounds



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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 limitating amounts of intermediates for some of the degradation compounds in Ox/thermal

Einbu, A., da Silva, E. F, Haugen, G., Grimstvedt, A., Lauritsen, K.G., Zahlsen, K., Vassbotn, T., 2013. Energy Procedia 37, 717-726.

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 sylinder 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

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- Einbu, A., DaSilva, E., Haugen, G., Grimstvedt, A., Lauritsen, K.G., Zahlsen, K., Vassbotn, T., 2013. A new test rig for studies of degradation of CO2 absorption solvents at process conditions; comparison of test rig results and pilot data of degradation of MEA. Energy Procedia 37, 717-
- Voice, A.K., Closmann, F., Rochelle, G.T., 2013. Oxidative I Amines With High-Temperature Cycling. Energy Procedia 3

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Thank you

More information

Chemical stability, nitrogen balance and degradation compounds

- OB: See Vevelstad, S.J., Grimstvedt, A., Elnan, J., da Silva, E.F., Svendsen, H.F., 2013b. Oxidative degradation of 2-ethanolamine: The effect of oxygen concentration and temperature on product formation. International Journal of Greenhouse Gas Control 18, 88-100.
- CB: See Vevelstad, S.J., Grimstvedt, A., Einbu, A., Knuutila, H., da Silva, E.F., Svendsen, H.F., 2013. Oxidative degradation of amines using a closed batch system. International Journal of Greenhouse Gas Control 18, 1-14.
- Thermal degradation: See Vevelstad, S.J., Grimstvedt, A., Knuutila, H., Svendsen, H.F., 2013. Thermal Degradation on Already Oxidatively Degraded Solutions. Energy Procedia 37, 2109-2117.