Amine Degradation

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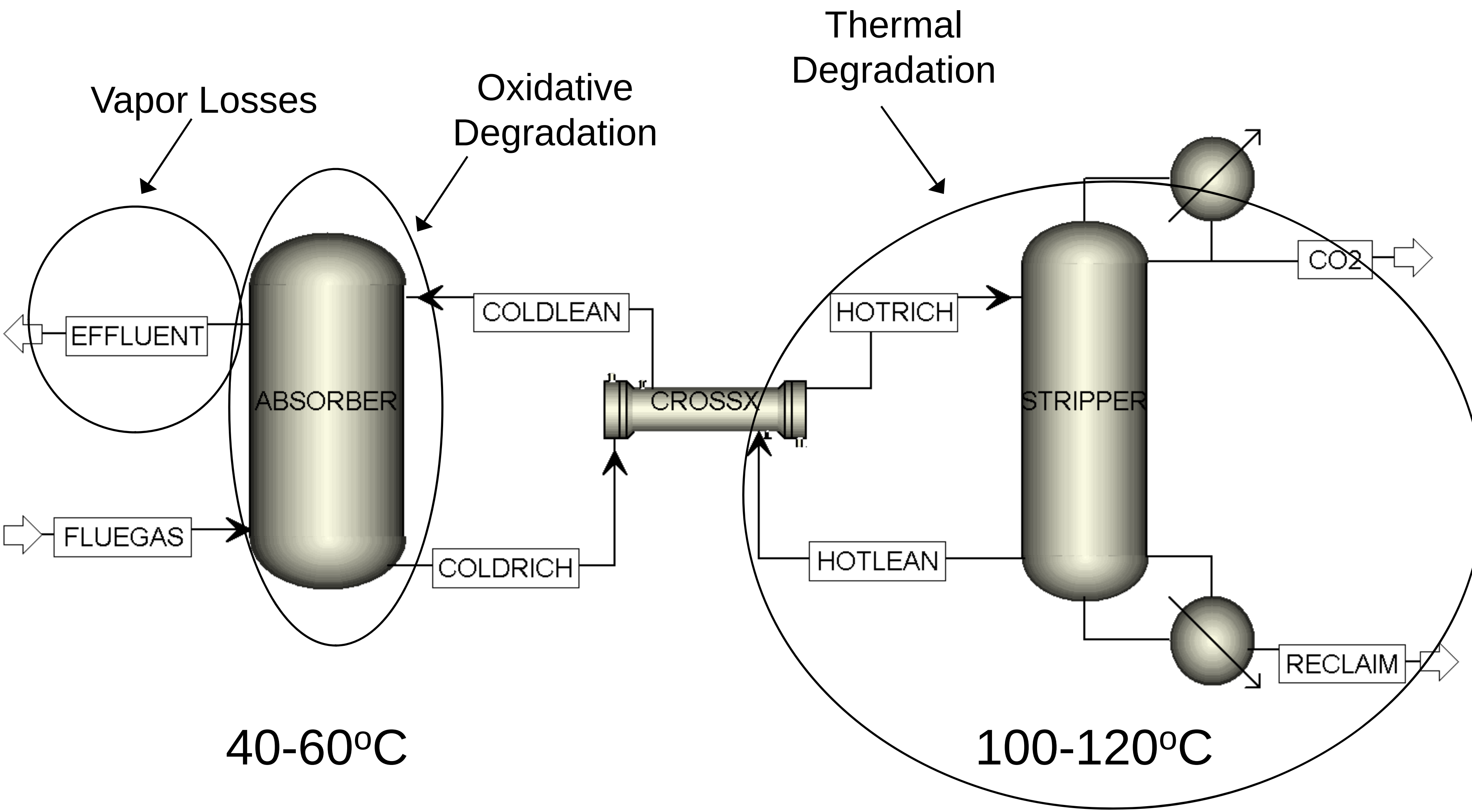
Amine Losses



Degradation Issues

- Solvent make-up costs can be a significant operating cost
- Trade off between energy/capital costs and solvent degradation
- Environmental implications of amine waste disposal
- System performance including corrosion and foaming

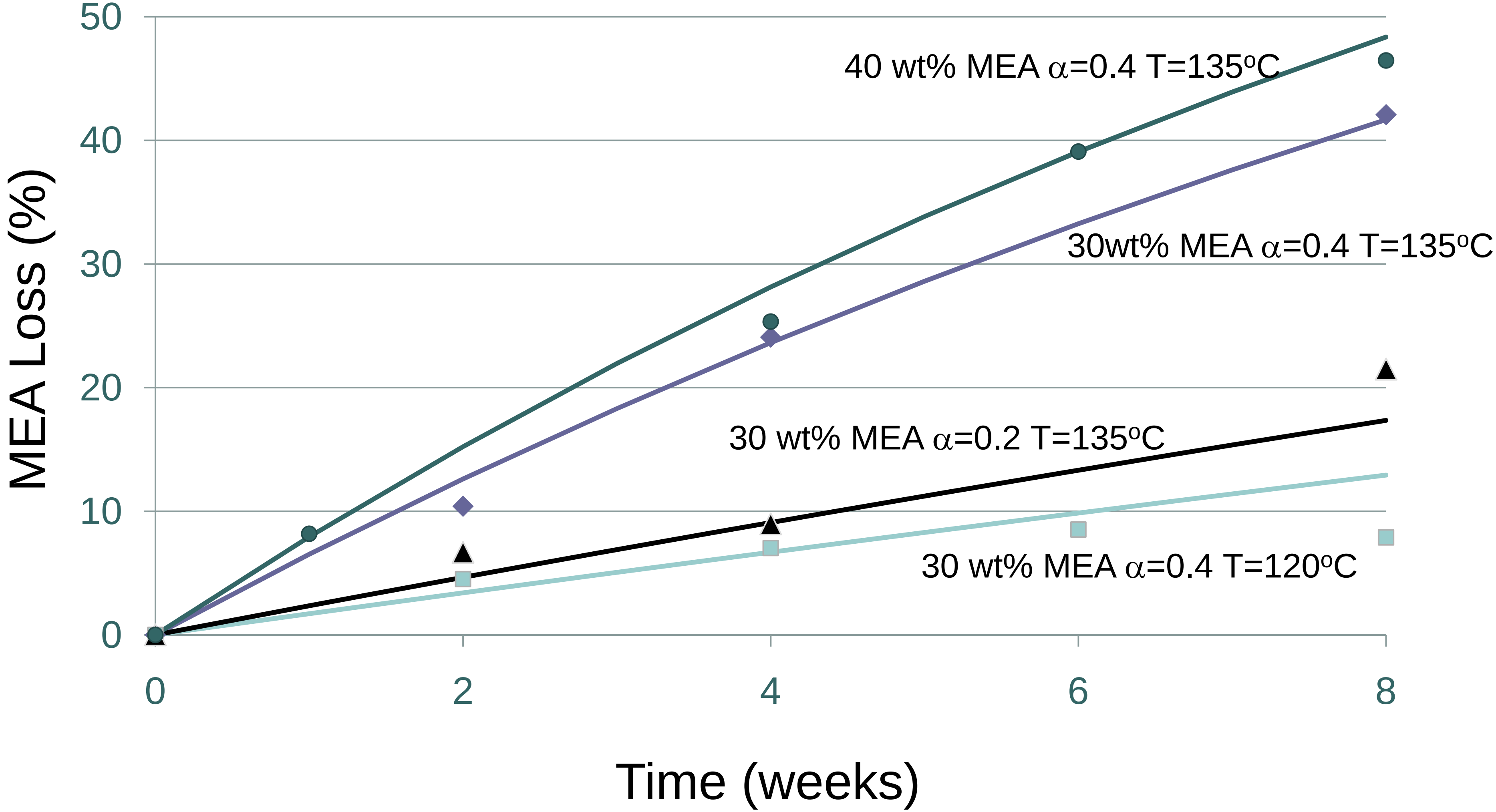
Thermal Degradation

- Experimental Set-up
- MEA Degradation
  - Varied amine concentration, loading and temperature
  - Regressed data
  - Identified unknowns
- Amine Screening
  - One set of conditions

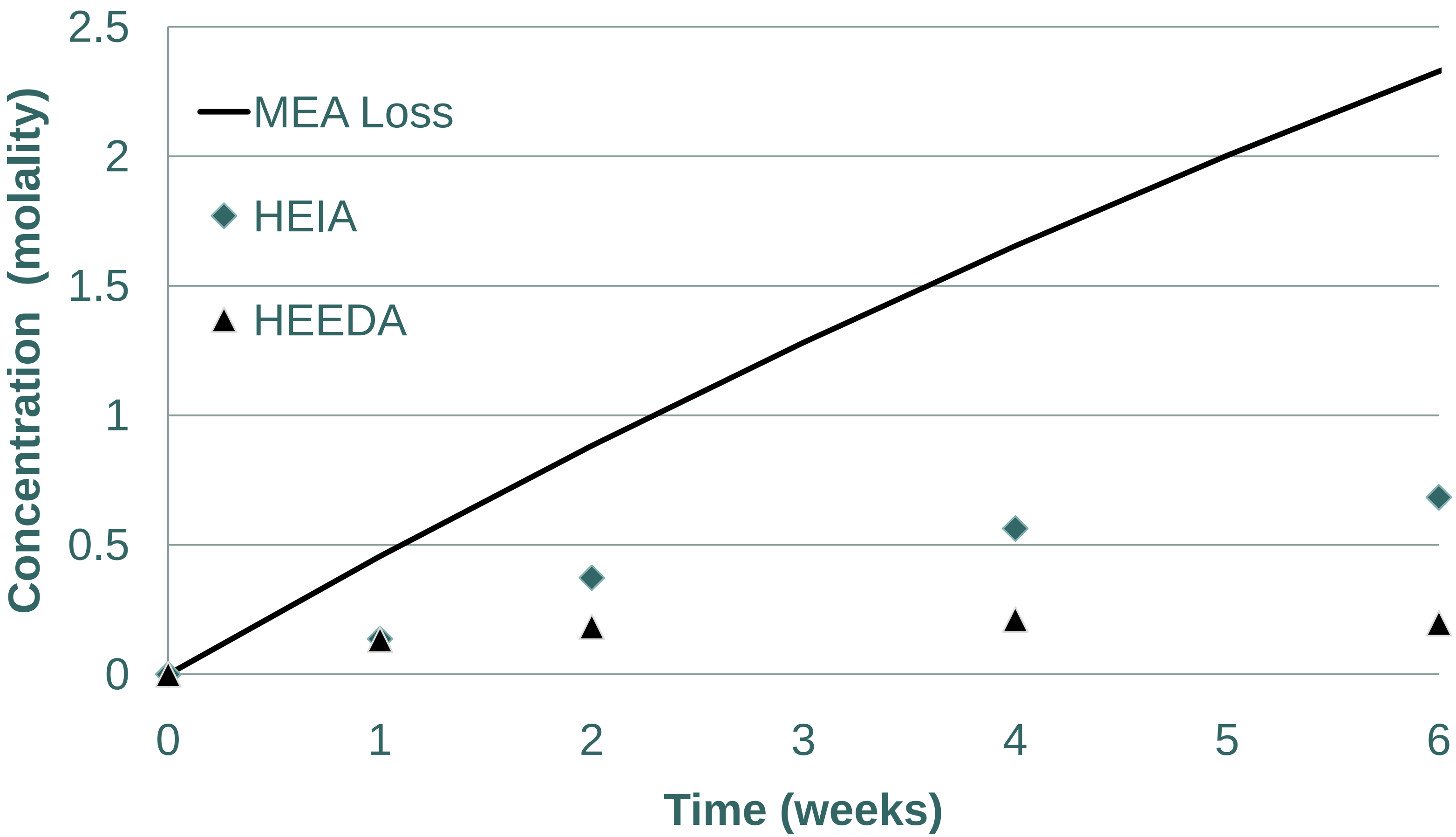
Thermal Degradation Experimental

- 10mL stainless steel sample containers filled with differing amine solutions
- Placed in forced convection ovens at set temperatures
- Analyzed for ionic products (amines) with IC and nonionic products with HPLC
- GC provided unreliable results with several solvent systems (overpredicted rates in all cases)

MEA Results


50
40
30
20
10
0
MEA Loss (%)
40 wt% MEA α=0.4 T=135oC
30wt% MEA α=0.4 T=135oC
30 wt% MEA α=0.2 T=135oC
30 wt% MEA α=0.4 T=120oC
0
2
4
6
8
Time (weeks)

MEA Degradation Products



7 molal MEA at 135^{o}C and a loading of 0.4

MEA Conclusions

- Thermal degradation quadruples every 15^{o}C
- CO_2 loading increase degradation more than 1st order
- Amine concentration increases degradation more than 1st order
  - Increasing the concentration from 15 to 40wt% would also increase the BP by 4^{o}C and degradation by 40%
- Analysis with ASPEN models showed
  - Highest degradation rates found at the bottom of the stripper where temperatures were highest
  - Lowering the stripper pressure/temperature is the surest way to decrease degradation
  - 30wt% MEA with average loading of 0.4 at atmospheric pressure yields <0.15kg MEA/ton CO_2

Thermal Screening (T=135^oC α=0.4 t=4wks)

Amine	Concentration (molality)	Remaining Amine Peak (%)
PZ	3.5	100
AMP	3	97
DGA	7	93
MEA / PZ	7 / 2	88 / 68
MEA	7	76
MDEA	50 wt%	71
EDA	3.5	64
DETA	2.3	9
HEEDA	3.5	3

Thermal Screening Conclusions

- Most amines degraded thermally under the specified conditions
- MEA mainly converted to nonionic products
- Piperazine degradation could not be detected under these conditions
- Industrially, MDEA does not significantly degrade but under these conditions it does shift to other amines
- In a blended system of MEA and PZ, both MEA and PZ did degrade in significant quantities

Oxidative Degradation (Andrew Sexton)

- Experimental setup
- Analytical
- High gas flow and low gas flow experiments
- Liquid and vapor phase products
- Relative rates of various amines

Experimental

- High gas flow apparatus
  - CO_2/O_2 mixture introduced by bubbling into bottom of reactor with agitation
  - Vapor phase analysis with FTIR
  - Liquid phase analysis with IC
- Low gas flow apparatus
  - CO_2/O_2 mixture introduced in headspace of reactor
  - Vortexing at high agitation rates used for vapor / liquid mixing
  - No vapor phase analysis

Analytical

- FTIR used to detect ammonia, amine volatility, NO_x, CO, acetaldehyde, formaldehyde
- Cationic IC for amine losses and anionic IC for heat stable salt products
  - Caustic addition used to measure for amide production
- HPLC with electrochemical detection for amino acids and UV detection for aldehydes

30 wt% MEA with 1mM Fe	High Gas Flow – Vapor (mM/hr)	High Gas Flow – Liquid (mM/hr)	Low Gas Flow (mM/hr)
Formate		0.181	0.289
Formamide		0.485	0.352
Acetate		0.018	0.002
Oxalate		0.003	0.020
Oxamide		0.092	0.090
Nitrite/Nitrate		0.0367	0.265
NH3	1.935		
NOx	0.154		
CO	0.027		
CH4 / C2H4	0.053		
Formaldehyde	0.010		
Acetaldehyde	0.011		
Methanol	0.025		
MEA	1.060		

Rate Comparisons

System	Iron (mM)	Inhibitor “A” (mM)	Carbon (mM/hr)	Nitrogen (mM/hr)
7m MEA	0.1	0	0.51	0.51
7m MEA	0.1	100	0.10	0.04
5m PZ	5	0	0.046	0.040
3m Amp	0.1	0	0.015	0.004
Glycine	1	0	0.026	0.001
EDA	1	0	0.065	0.042

Oxidative Conclusions

- MEA oxidative degradation is much faster than other amines tested when uninhibited
- AMP oxidative degradation is slower than other amine systems tested
- For MEA, amides of oxalate and formate are present in significant quantities
- Vapor phase FTIR shows NO_X and CO emissions present for uninhibited MEA systems

Conclusions

- MEA thermal degradation has been quantified over a wide range of conditions
- Most amines thermally degrade, but there is a wide variation in rates
- Thermally stable amines can degrade when used in a blended system
- MEA oxidative degradation was an order of magnitude faster than AMP and PZ under similar conditions
- Amides of common oxidative degradation products have been found at significant quantities
- NOx and CO emissions were found in the vapor phase analysis at absorber conditions

QUESTIONS?

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