

Designing large-scale CO₂ capture units with assessment of solvent degradation

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Abstract

Solvent degradation is a major drawback for the large-scale implementation of post-combustion CO_2 capture due to amine consumption and emission of degradation products. In the present work, we refine a previous kinetic model for describing solvent oxidative and thermal degradation based on experimental results. The CO_2 capture process is then modeled in Aspen Plus with assessment of solvent degradation. As a result, this work provides a useful tool for the identification of optimal operating conditions that minimize both the

energy and environmental impacts of the process.

Solvent degradation and previous work

Solvent degradation reduces the process efficiency, increases corrosion, and implies additional costs for the removal of degradation products. It may represent up to 22% of the CO_2 capture $Opex^{[1]}!$

Acceleration of solvent degradation was necessary to study it within a reasonable timeframe. In a previous work, we achieved a 30-fold acceleration of the degradation rate of MEA in comparison to pilot plants while following similar degradation pathways. Both oxidative and thermal degradation were studied and a kinetic model was proposed^[2].







Kinetics of MEA degradation

The kinetic model of MEA oxidative degradation has been improved by studying the influence of operating parameters like temperature and O_2 content in the absence of CO_2 . A new relationship has been used to model oxygen solubility in MEA.

The resulting kinetic model of MEA degradation has been included into an Aspen Plus model of the CO_2 capture process:

MEA thermal degradation $C_2H_7NO + 0.5 \text{ CO}_2 \rightarrow 0.5 \text{ C}_5H_{10}N_2O_2 + H_2O$ $-r_{MEA, Thermal} = 8.00 \ 10^{11} \cdot e^{-144 \ 210/RT} \cdot [CO_2]$

MEA oxidative degradation $C_2H_7NO + 1.3 O_2$

 $\rightarrow 0.6 \text{ NH}_3 + 0.1 \text{ C}_5 \text{H}_8 \text{N}_2 \text{O} + 0.1 \text{ C}_6 \text{H}_{12} \text{N}_2 \text{O}_2 + 0.1 \text{ C} \text{H}_2 \text{O}_2 + 0.8 \text{ CO}_2 + 1.5 \text{ H}_2 \text{O}_2$

 $-r_{MEA, Oxidative} = 1.360 \ 10^6 \ . \ e^{-55 \ 111/RT} . [O_2]^{1.03}$

Global process modeling

The simulation calculates a total MEA loss of 80 g MEA/ton CO₂, which is by far due to oxidative degradation in the absorber. This is however about 3 times lower than values reported in pilot plants^[4], so the model must be further refined. Nevertheless, this global model predicts MEA losses much more accurately than any previous model!

Finally, this work provides a useful tool for the design of CO_2 capture plants to consider not only the process energy penalty, but also its environmental penalty.

References

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Parameter	Unit	Absorber	Stripper	Total
MEA degradation	kg/ton CO ₂	7.94 10 ⁻²	9.64 10-5	7.95 10 ⁻²
NH ₃ formation	kg/ton CO ₂	1.33 10-2	1.53 10-5	1.33 10-2
HEIA formation	kg/ton CO ₂	6.56 10 ⁻⁹	5.92 10-6	5.93 10-6
MEA emission before washing	kg/ton CO ₂	2.29 10 ⁰	1.17 100	3.46 10 ⁰
NH ₃ emission before washing	kg/ton CO ₂	1.13 10 ⁻²	3.16 10-3	1.44 10 ⁻²
HCOOH emission before washing	kg/ton CO ₂	1.15 10-3	4.09 10 ⁻⁴	1.55 10-3
MEA emission after washing	kg/ton CO ₂	1.10 10-3	9.02 10-9	1.10 10-3
NH ₃ emission after washing	kg/ton CO ₂	1.02 10 ⁻²	2.91 10-3	1.31 10 ⁻²
HCOOH emission after washing	kg/ton CO ₂	1.44 10-4	1.73 10-5	1.62 10 ⁻⁴
MEA consumption (degradation + emission after washing)	kg/ton CO ₂	8.05 10-2	9.64 10-5	8.06 10 ⁻²
Top stage liquid temperature	°C	57.5	96.7	
Bottom stage liquid temperature	°C	51.1	115.6	-
Top stage O ₂ content (vapor phase)	mol%	6.3	9.5 10-3	-
Bottom stage O ₂ content (vapor phase)	mol%	6.1	1.7 10 ⁻¹³	-

MEA loss determined from the global model with assessment of degradation

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