

Kinetics of oxidative and SO_x-induced degradation of monoethanolamine under accelerated laboratory conditions

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Outline

1. Introduction
2. Dissolved O₂ concentration
3. Mass transfer
4. Oxidative degradation : with and without presence of sulfur dioxide
5. Conclusion and perspectives

1. Introduction

Post-combustion capture with amine solvent is a mature technology,

But...

- *Large energy penalty*
 - *Potential amine degradation*
 - *Emission of degradation products*
 - *Corrosion*

Current solvent of choice: *monoethanolamine*

- *High capacity for CO₂ absorption*
- *Fast reaction kinetics*
- *High removal efficiencies*

1. Introduction

Accelerated laboratory conditions



pressure and
temperature more
severe than those of
the pilot plant

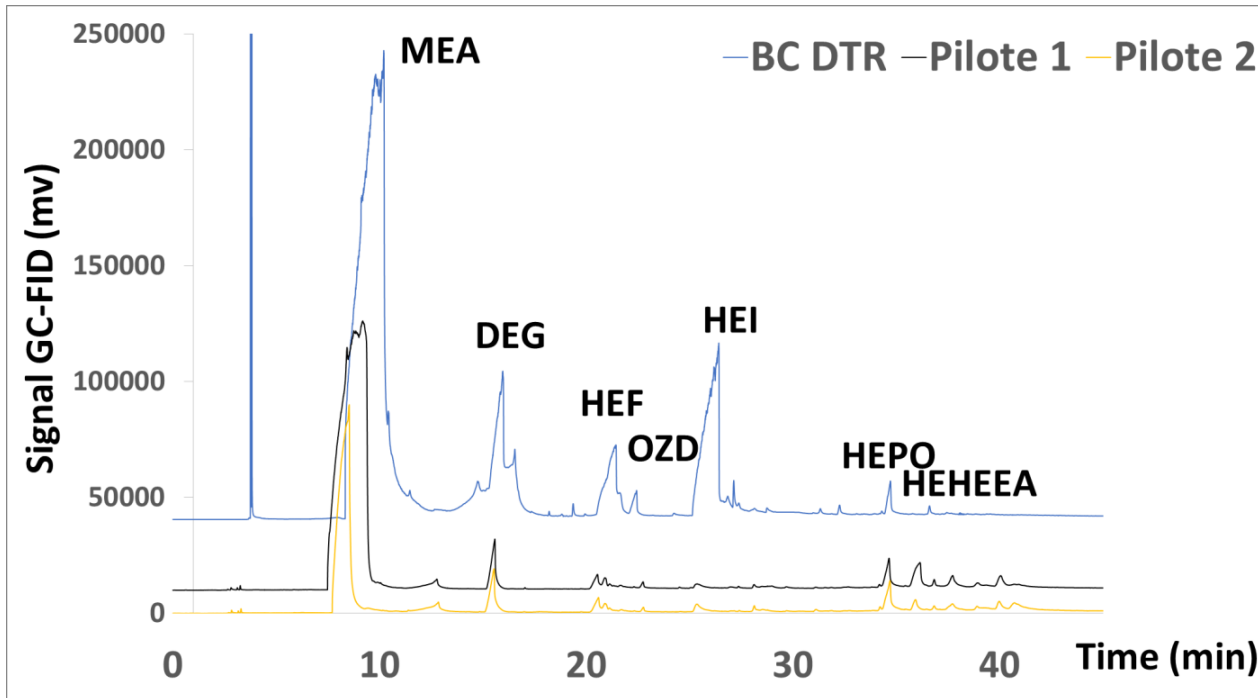


Mass transfer¹?
 $k_L a$?



1. Introduction

Degradation products obtained at lab scale vs. industrial scale



✓ Representativity
Ok

1. How does mass transfer affect oxidative degradation?
2. How sulfur dioxide affects amine degradation?

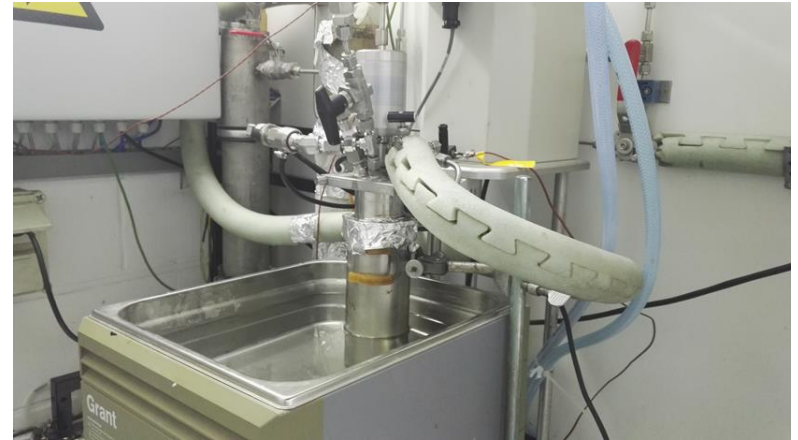
2. Dissolved O₂ concentration

Operating mode:

The gas flow is sparged into 400 gr of MEA 30 wt% until reaching a constant concentration in dissolved O₂

Experimental conditions:

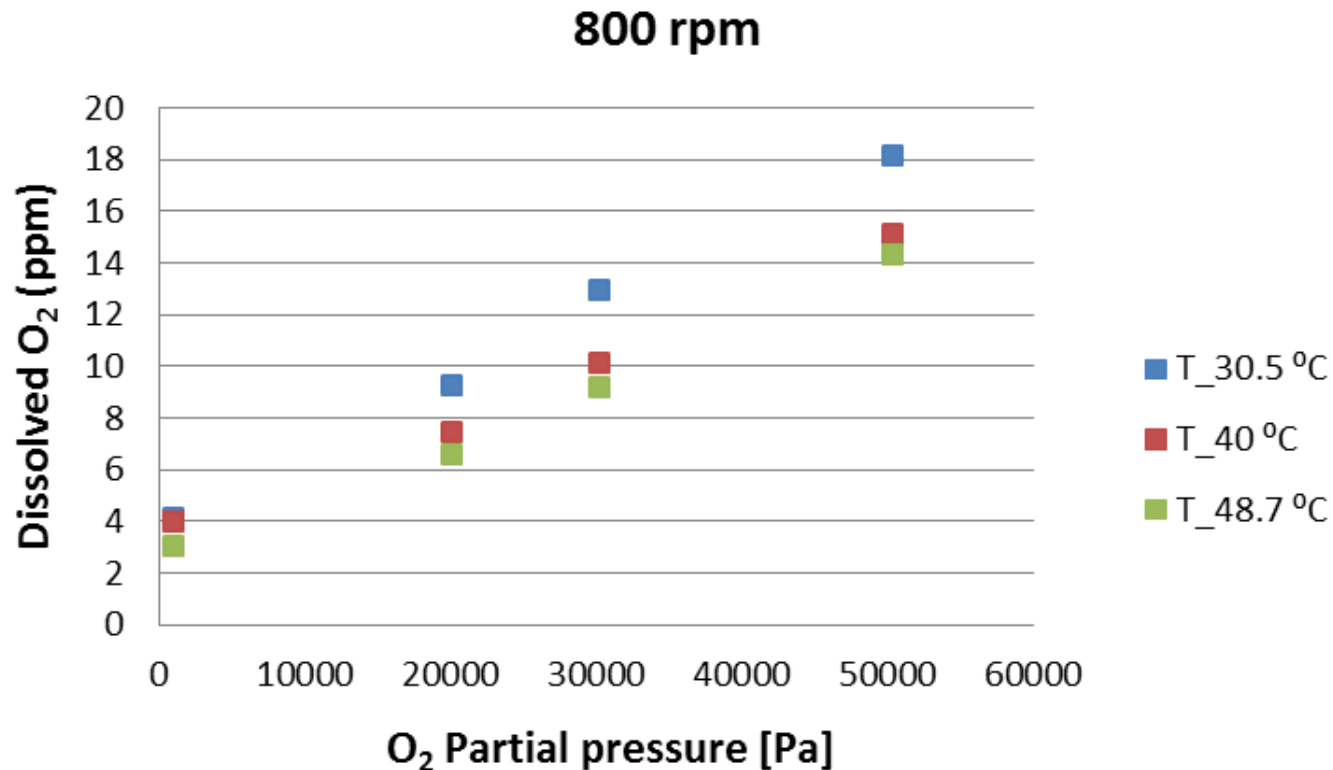
- $29,7^{\circ}\text{C} < T < 49,2^{\circ}\text{C}$
- 160 Nml/min gas flow
- Atmospheric pressure
- $1008,9 < P\text{O}_2 < 50445 \text{ Pa}$
- [800-1000] rpm



Galvanic probe (Accuracy +/- 1%)

2. Dissolved O₂ concentration

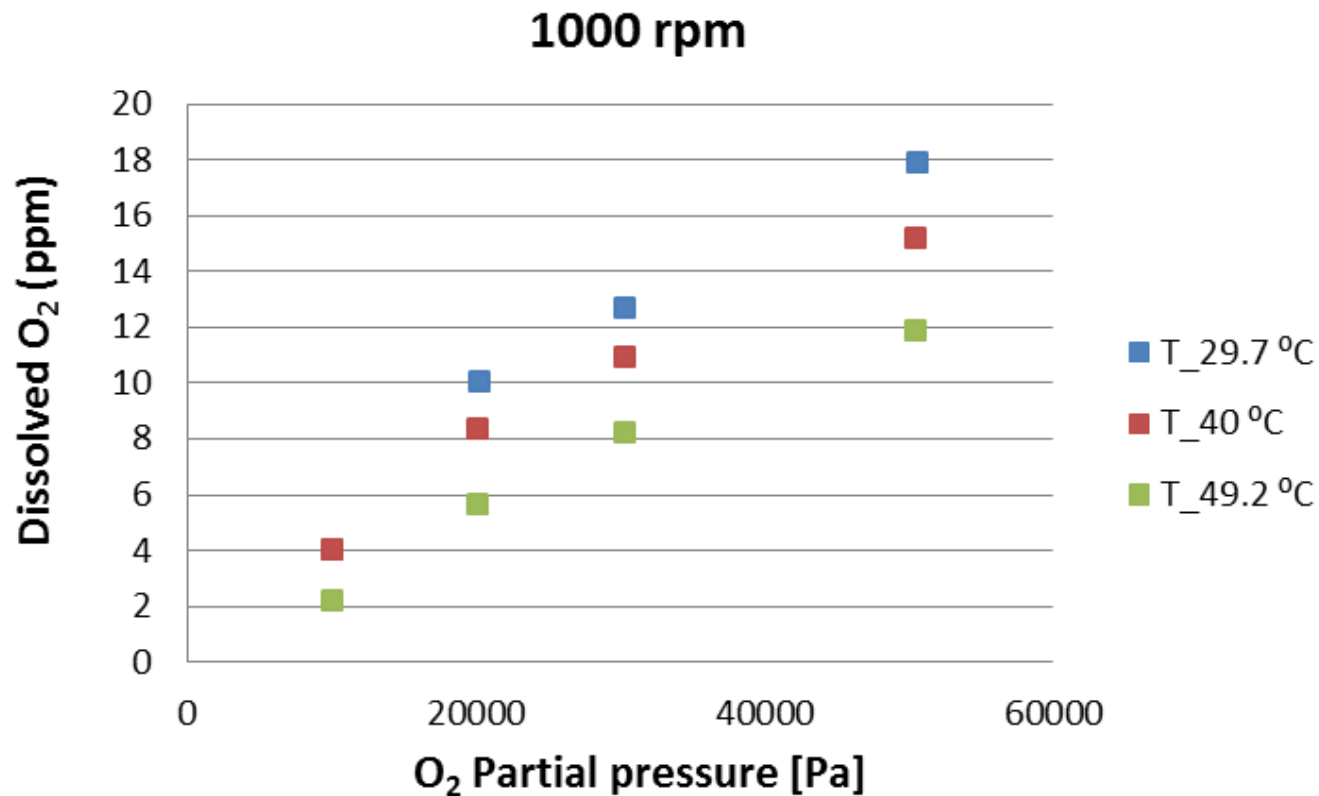
- Influence of the partial pressure on dissolved O₂ / 800 rpm



- ✓ **Henry's Law (T:cst, equilibrium):** the amount of dissolved gas is proportional to its partial pressure in the gas phase.

2. Dissolved O₂ concentration

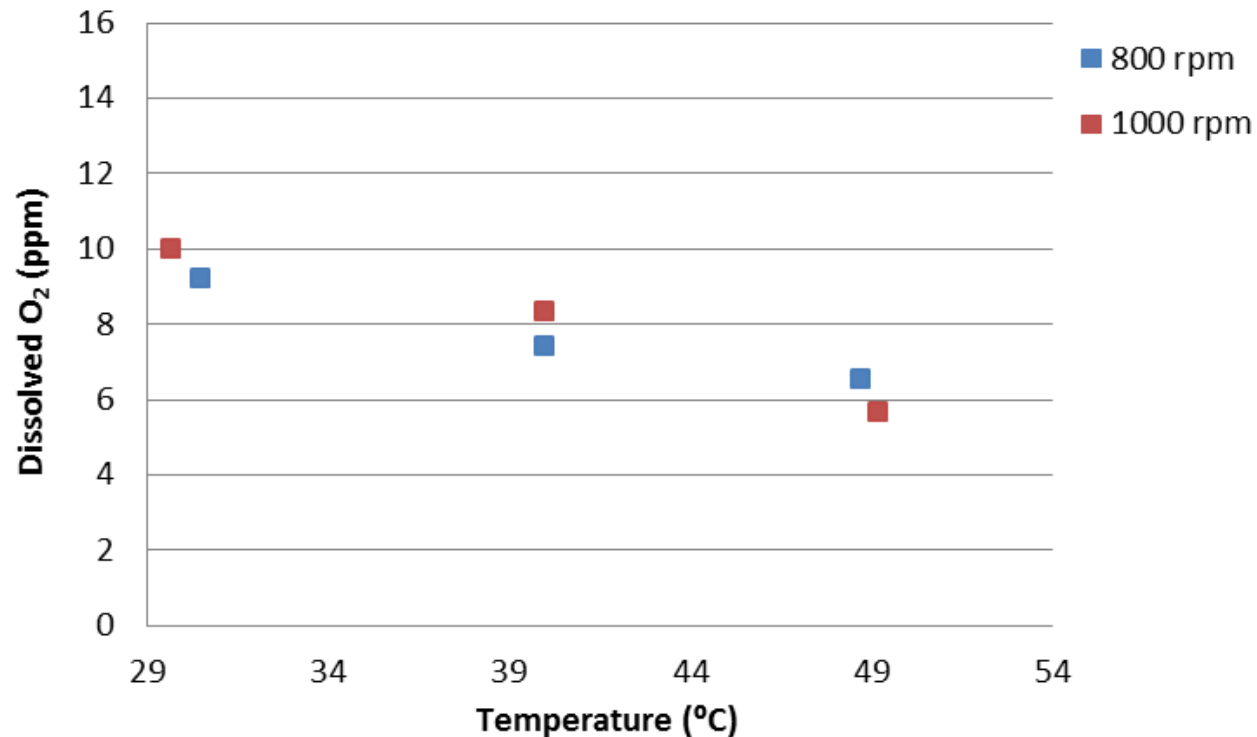
- Influence of the partial pressure on dissolved O₂ / 1000 rpm



✓ Henry's Law

2. Dissolved O₂ concentration

- Influence of the temperature on dissolved O₂ PO₂ ~ 20178 Pa



- **At equilibrium:** dissolved O₂ concentration = f(temperature and pressure)

3. Mass transfer

$$\frac{dC_A}{dt} = K_L a (C_A^* - C_A)$$

$K_L a$ depends on several factors such as²:

- temperature, pressure,
- composition of the gas and liquid, viscosity
- liquid circulations and gas recirculations
- position of the probe in the reactor and assumptions on hydrodynamic conditions

3. Mass transfer

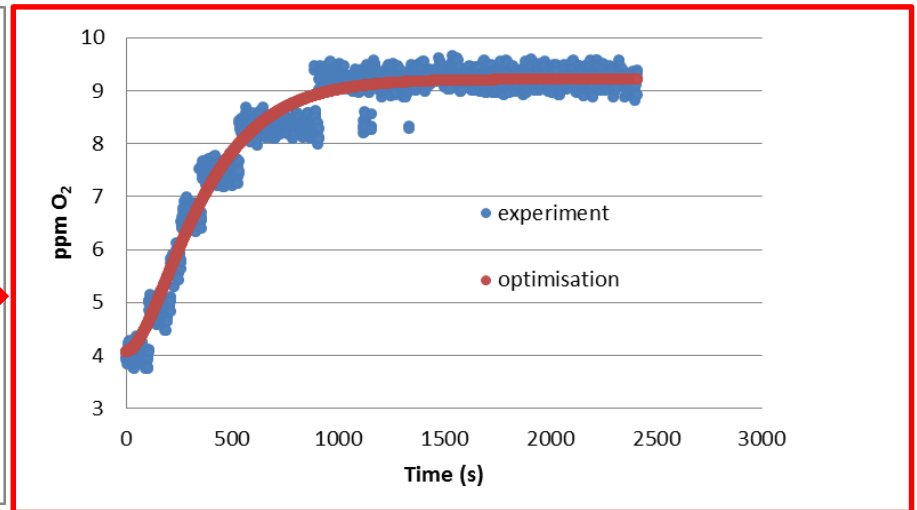
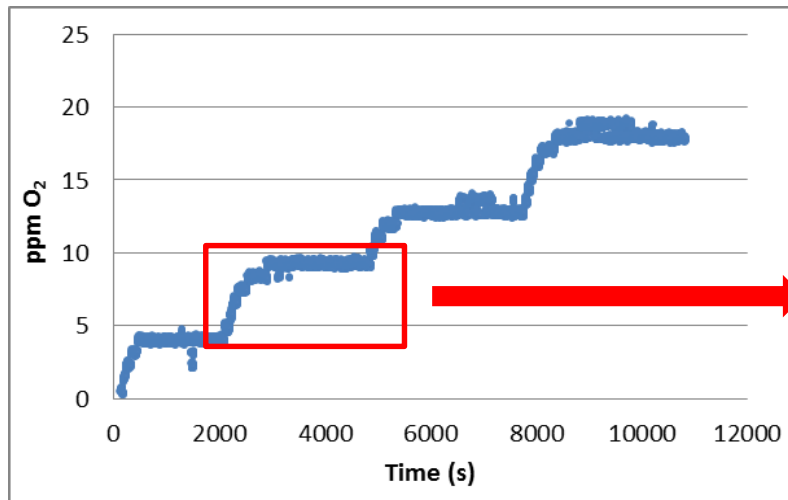
Determination of the $k_L a$ with consideration of the probe response time τ_p

$$\frac{C^* - C_P}{C^* - C_0} = \frac{1}{1 - \tau_P K_L a} \left(e^{-K_L a \cdot t} - \tau_P K_L a \cdot e^{\frac{-t}{\tau_P}} \right)$$

C^* [ppm]: is the dissolved oxygen concentration at saturation

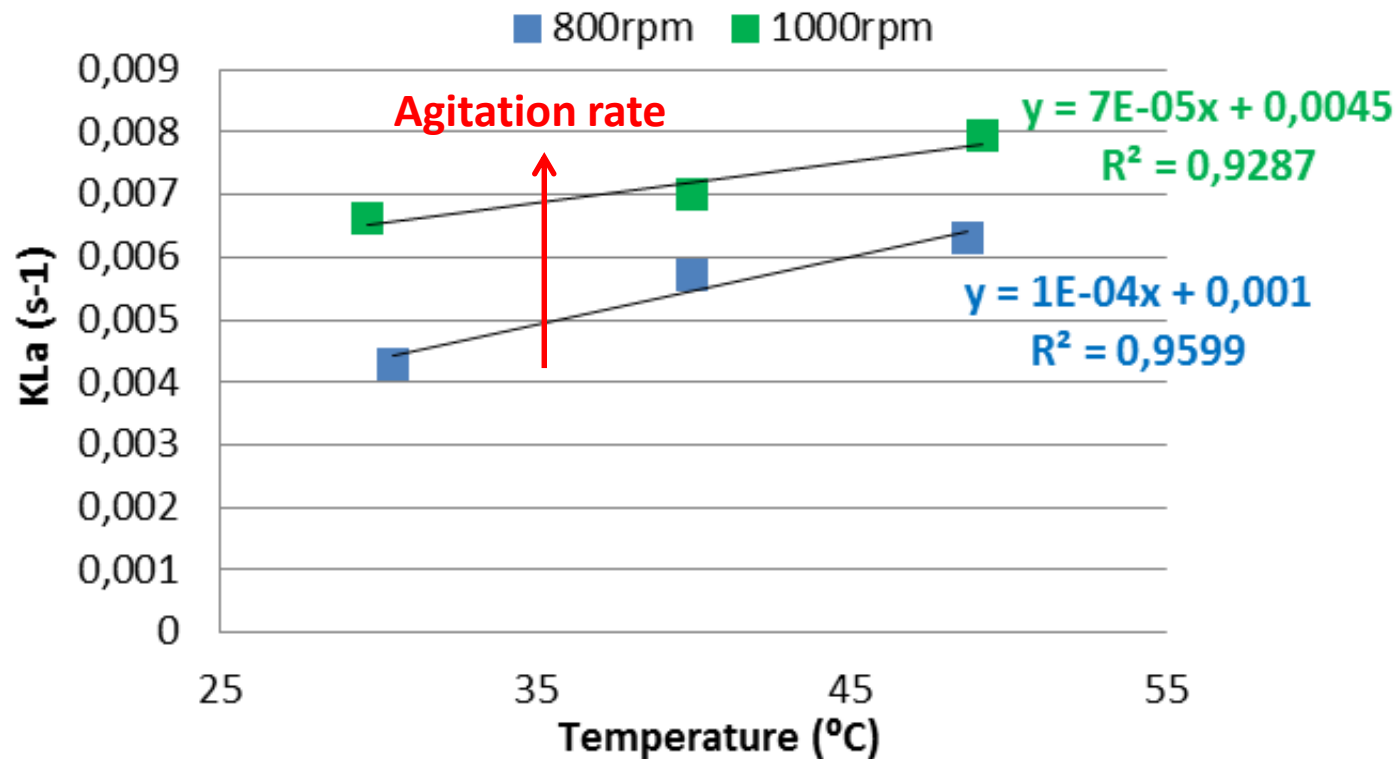
C_p [ppm]: is the concentration measured by the probe

C_0 [ppm]: is the concentration at t_0



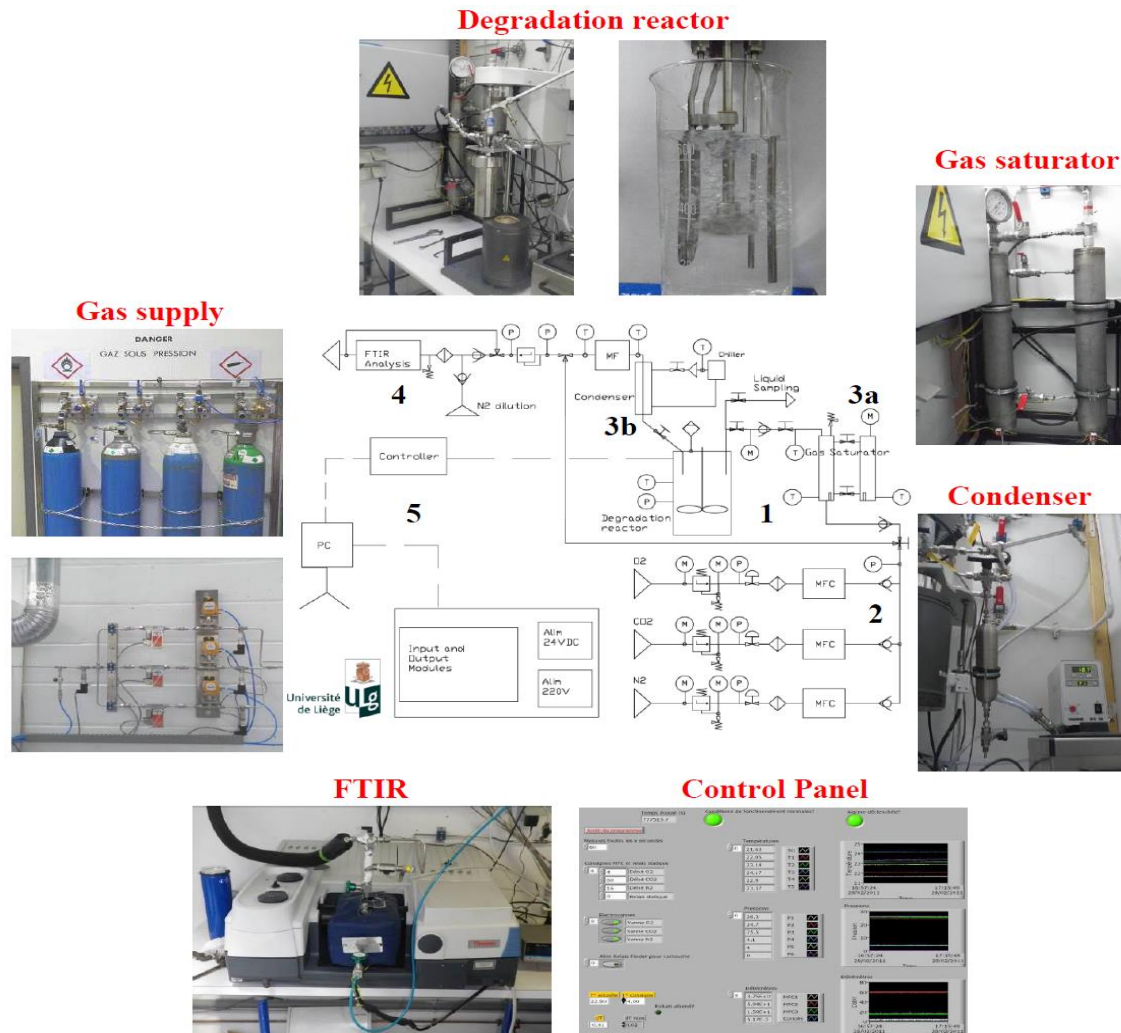
3. Mass transfer

- Influence of the temperature and the agitation rate



4. Oxidative degradation : with and without presence of sulfur dioxide

○ Without presence of sulfur dioxide

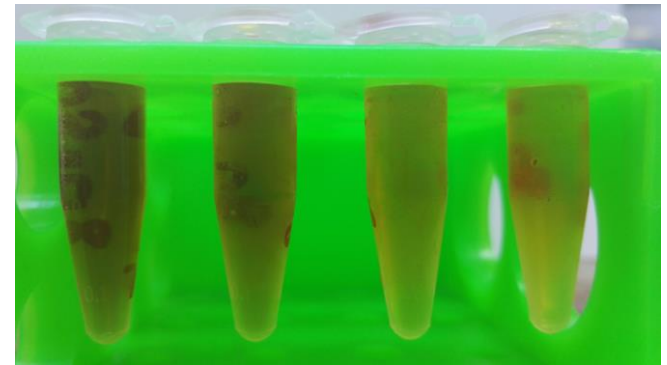


4. Oxidative degradation : with and without presence of sulfur dioxide

Lab conditions:

○ Without presence of sulfur dioxide

- 300 g of 30 wt% MEA
- 120°C, 4 barg, 800 rpm
- 2 days
- Enhanced gas-liquid contact
- Continuous gas flow: 160 Nml/min
- 5% O₂ / 95% N₂

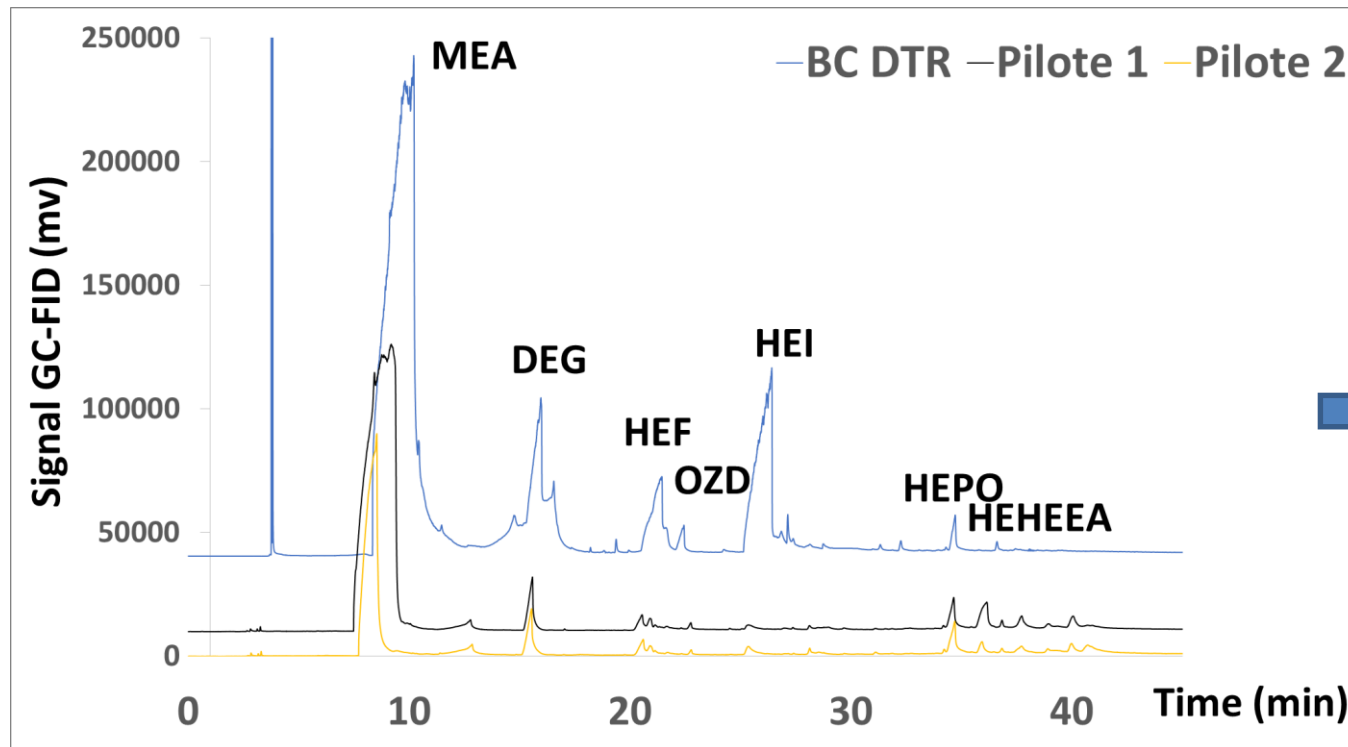


○ With presence of sulfur dioxide

- 100 ppm of aqueous H₂SO₃ was chosen and added directly to 30 wt% MEA solution

4. Oxidative degradation : with and without presence of sulfur dioxide

- Without presence of sulfur dioxide



Similar degradation products

Comparison of GC-FID spectra between samples degraded at lab scale (BC DTR) and at industrial scale

4. Oxidative degradation : with and without presence of sulfur dioxide

- Without presence of sulfur dioxide
- kinetic model of solvent degradation

Arrhenius kinetics (mol/l.s):

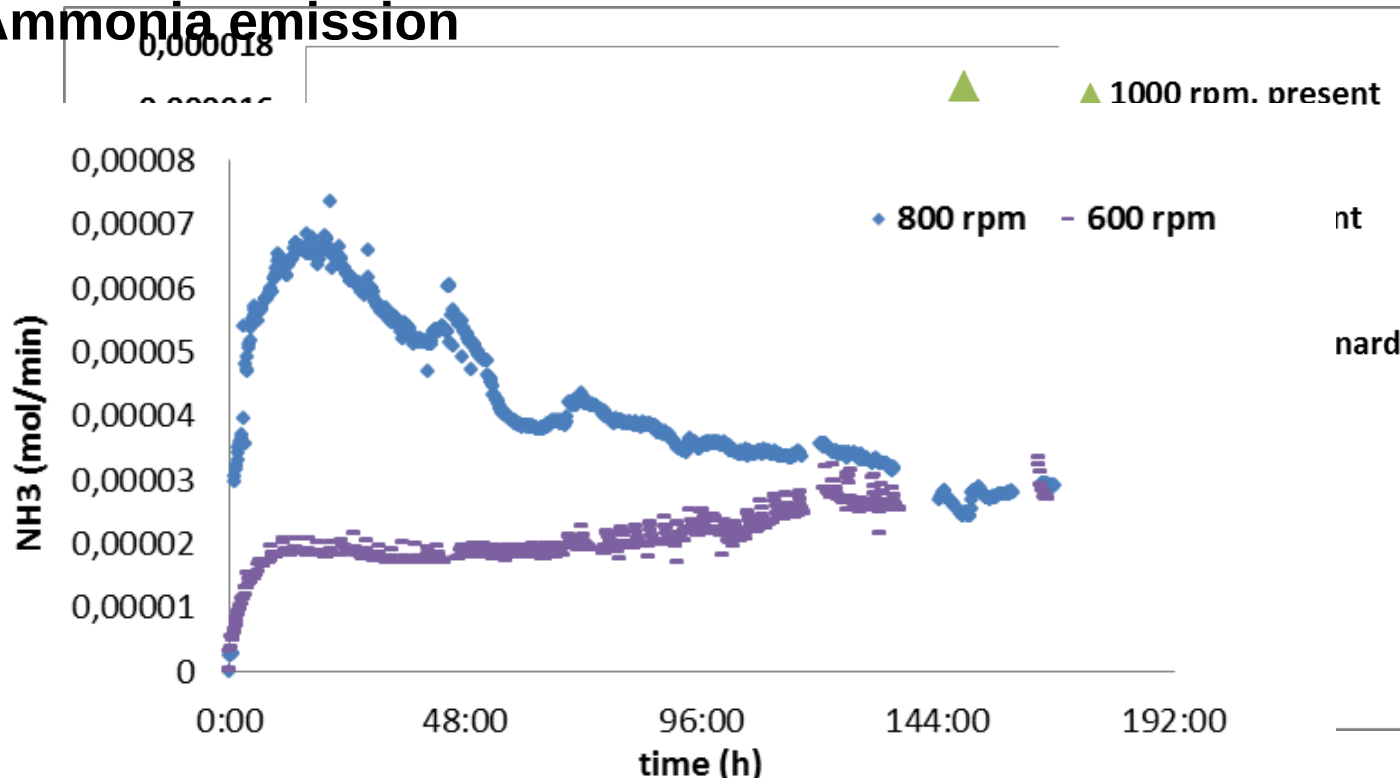
Parameters are identified by minimizing the difference between calculated and observed degradation rates.

$$\text{800 rpm} \quad -r_{MEA} = 3.9 \times 10^5 e^{-48.116/RT} [O_2]^1$$

$$\text{1000 rpm} \quad -r_{MEA} = 5.3 \times 10^5 e^{-48.116/RT} [O_2]^1$$

4. Oxidative degradation : with and without presence of sulfur dioxide

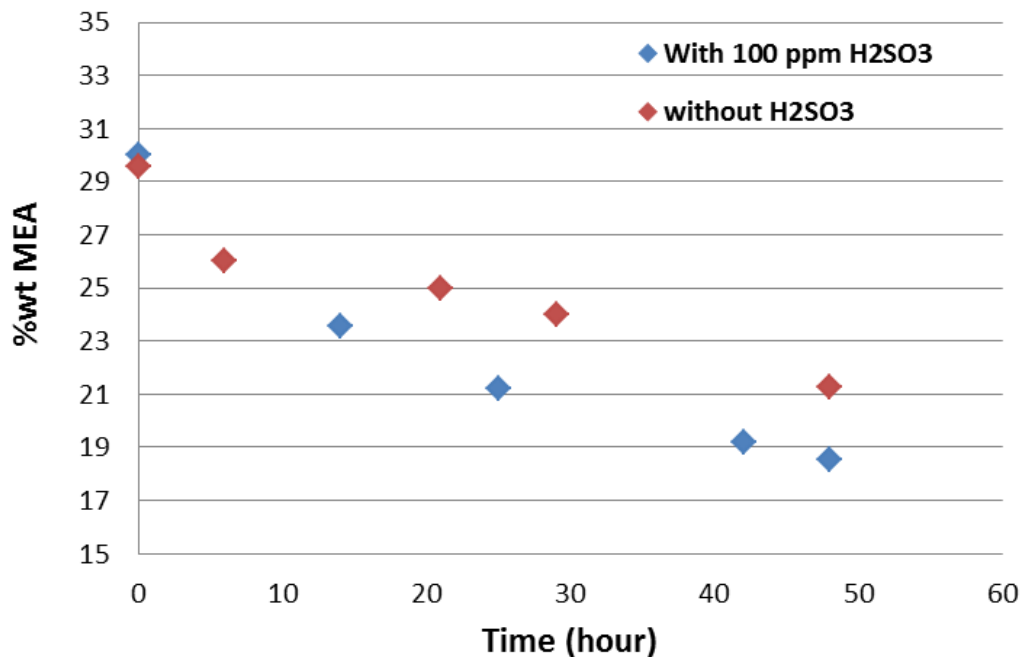
- Without presence of sulfur dioxide
 - Kinetic model of solvent degradation
 - Ammonia emission



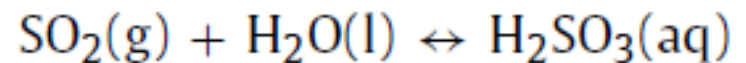
- Larger agitation rate → higher overall mass transfer coefficient.
- As a consequence, more oxygen is transferred to the gas/liquid interface → acceleration of the degradation

4. Oxidative degradation : with and without presence of sulfur dioxide

○ With presence of sulfur dioxide



48h	Without H ₂ SO ₃	With H ₂ SO ₃
%wt MEA	21,27	18,54



- SO₂(g) was reported to accelerate MEA degradation with O₂ present^{3,4}
- MEA oxidative degradation is significantly reduced with SO₂⁵

5. Conclusion and perspectives

- Measurements of dissolved O_2 concentrations in 30 wt% MEA
- The $K_L a$ of the experimental Degradation Test Rig is determined at 800 and 1000 rpm, 0,0057 and 0,007 s^{-1} respectively
- It appears to be smaller than typical $k_L a$ for structured packing used in industrial conditions ($0.01 < K_L a < 0.04^5$)
- The acceleration of the oxidative degradation rate was mainly due to the higher temperature and PO_2 , but we also notice that the coefficient of mass transfer has an impact on oxidative degradation rate.
- Solvent degradation is experimentally studied and a kinetic model is proposed
- The effect of the presence of sulfur dioxide is studied experimentally

5. Conclusion and perspectives

- Kinetic model that considers both the chemical and the physical kinetics separately instead of usual apparent kinetics will be proposed

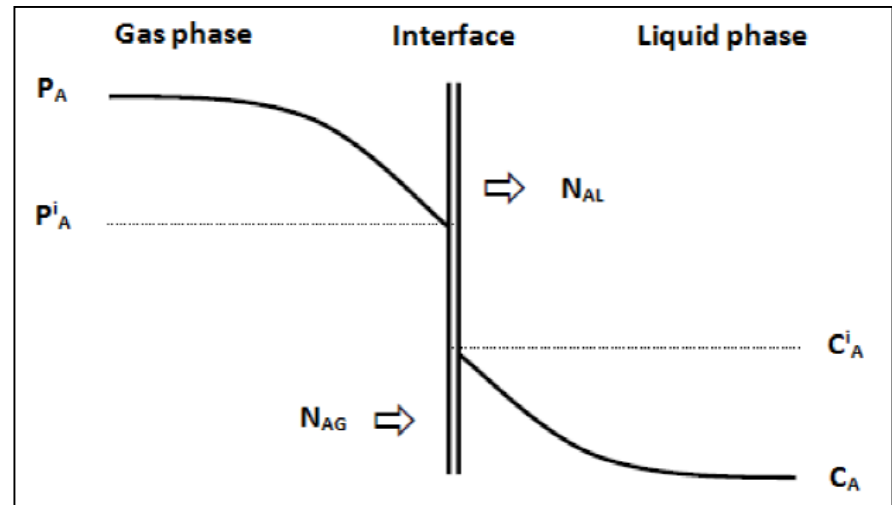
$$\frac{dC_A}{dt} = \underline{\underline{\nu_A r_A}} + \underline{\underline{a N_{AL}}}$$

$$\underline{\underline{r}} = A \cdot e^{-\frac{E_a}{8.314 T}} \cdot [O_2]^n$$

$$\underline{\underline{a N_{AL}}} = K_L a (C_A^* - C_A)$$



**F(Temperature
and agitation rate)**



- kinetic model of the oxidative degradation in presence of sulfur dioxide will be proposed

Thank you for your attention!