



The Canadian Journal of
Chemical Engineering

**Relevance of accelerated conditions for the study of
monoethanolamine degradation in post-combustion CO₂
capture.**

Journal:	<i>The Canadian Journal of Chemical Engineering</i>
Manuscript ID:	CJCE-14-0273.R1
Wiley - Manuscript type:	Special Issue Article
Date Submitted by the Author:	n/a
Complete List of Authors:	Léonard, Grégoire; University of Liège, Dept. of Chemical Engineering Toye, Dominique; University of Liège, Dept. of Chemical Engineering Heyen, Georges; University of Liège, Dept. of Chemical Engineering
Keywords:	Clean coal technologies < Environment, Absorption < Separation methods, Energy, Reactor design and operation

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Manuscript's Most Relevant Contributions

- The degradation of monoethanolamine solvents (MEA) for application in post-combustion CO₂ capture was experimentally studied under accelerated conditions since the corresponding reaction mechanisms are very slow in industrial units.
- Analytical methods were developed to quantify MEA as well as liquid and gaseous degradation products. The nitrogen balance of the degradation experiments could be closed within the 10% range and the repeatability of the experiments was demonstrated.
- The relevance of accelerated conditions was established by comparing artificially degraded solvent samples with degraded solvent samples from industrial CO₂ capture pilot plants. A continuous gas feed was necessary to reproduce the same degradation mechanisms as observed in industrial conditions.
- The influence of the gas feed composition was studied. Oxidative degradation appears to be the main degradation pathway in industrial pilot plants. Thermal degradation with O₂ does not significantly take place at 120°C.
- Ammonia is the main product of MEA oxidative degradation and accounts for 45% of the MEA loss.
- Increasing the agitation rate in oxidative degradation experiments increases the MEA loss, evidencing that oxidative degradation is mass-transfer limited. However, higher agitation rates lead to alternative reaction pathways and products that are not representative of industrial CO₂ capture degradation anymore.
- This paper also evidences that accelerated conditions at laboratory-scale may provide relevant information for the study of slow phenomena taking place in large-scale industrial processes.

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3 Article Submission for publication in the Canadian Journal of Chemical Engineering.
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5 Invited article resulting from the SFGP 2013 Conference held in Lyon, France, 8-10 October
6 2013.
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10 **Title:**

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12 Relevance of accelerated conditions for the study of monoethanolamine degradation in post-
13 combustion CO₂ capture.
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Relevance of accelerated conditions for the study of monoethanolamine degradation in post-combustion CO₂ capture.

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Abstract

Solvent degradation represents one of the main operational drawbacks of the post-combustion CO₂ capture process. Degradation not only induces additional costs for solvent make-up, it also impacts the process efficiency and its environmental penalty due to the emission of various degradation products. There is still a gap of knowledge about the influence of process operating conditions on degradation, making it currently impossible to predict the solvent degradation rate in CO₂ capture plants. Moreover, the reaction mechanisms corresponding to solvent degradation are very slow, significantly complicating its study in industrial units. In the present work, appropriate experimental equipment and analytical methods are developed for accelerating the degradation of monoethanolamine solvents (MEA). The relevance of accelerated conditions is established by comparing artificially degraded solvent samples with degraded solvent samples from industrial CO₂ capture pilot plants. Two approaches are evaluated implying either discontinuous or continuous gas feed, this latest being the most representative of industrial degradation. The respective influences of the gas feed composition and the gas-liquid transfer are evidenced and quantified. Finally, the present study leads to a better understanding of solvent degradation in the CO₂ capture process with MEA. More generally, it also evidences that accelerated conditions at laboratory-scale may provide relevant information for the study of slow phenomena taking place in large-scale industrial processes. Further works include the development of a kinetic model for MEA solvent degradation and the extension of this methodology to other promising solvents in order to facilitate the operation and large-scale deployment of CO₂ capture.

Keywords: Post-combustion CO₂ capture, monoethanolamine solvent, accelerated degradation, industrial representativity.

1. Introduction

In response to the increasing environmental concerns and to the growing world energy demand, CO₂ capture and storage (CCS) technologies have been proposed to reduce the anthropogenic emissions of carbon dioxide. From 2011 to 2035, the energy demand is planned to increase by one third, with the share of fossil-fuels in the global energy mix still being estimated at 76% by 2035.^[1] In the perspective of limiting the climate change intensity, CCS technologies represent one of the main solutions to rapidly decrease the CO₂ emissions resulting from fossil fuel combustion while facing a growing world energy demand. Indeed, they have the potential of capturing CO₂ at a large-scale, especially in coal and gas power

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3 plants, cement plants, steel industries and other large CO₂ emitting facilities. According to the
4 International Energy Agency,^[2] CCS may represent up to 17% of the CO₂ emission reduction
5 in 2050.
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8 The CO₂ post-combustion capture with amine solvent is an almost mature technology that has
9 been applied for more than 20 years for the industrial production of CO₂. This end-of-pipe
10 technology treats the flue gas after the combustion so that already operating power plants can
11 be retrofitted to rapidly reduce their CO₂ emissions. The CO₂ is captured by absorption into
12 an amine solvent, the benchmark solvent for post-combustion capture being an aqueous
13 solution of 30 wt% monoethanolamine (MEA). After the absorption, the CO₂-loaded solvent
14 is regenerated at a higher temperature to release the captured CO₂ that can be re-used or
15 stored underground. Besides the high energy requirement of the process, the second main
16 operational drawback of post-combustion CO₂ capture is the degradation of the amine solvent
17 and the emission of degradation products to the environment.^[3] Indeed, in the conditions of
18 the CO₂ capture process, amine solvents degrade, forming a large range of degradation
19 products. The cost of solvent make-up alone may already account for up to 22% of the
20 process operating expenses (OPEX),^[4] so that quantifying solvent degradation is essential for
21 a proper process evaluation and design. Moreover, degradation products modify the solvent
22 properties, decreasing the process efficiency and implying additional costs. The emission of
23 amine solvents and volatile degradation products like ammonia also represents a significant
24 issue in CO₂ capture plants. Although emission reduction technologies exist (among others
25 the (acid) water washing of the flue gas at the column outlet), their efficiency has not been
26 demonstrated yet, so that the problem of volatile products emissions may still be significant.^[5]
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30 In the last few years, a few studies have already addressed the problem of amine solvent
31 degradation. In the case of aqueous MEA, Bedell^[6] has listed three main degradation
32 mechanisms: oxidative degradation, thermal decomposition and thermal degradation with
33 CO₂. While thermal decomposition occurs in the absence of O₂ and CO₂ by the cleavage of
34 the MEA molecule at temperatures higher than 200°C, thermal degradation with CO₂ implies
35 irreversible reactions between CO₂ and the amine solvent. Moreover, Epp et al.^[7] have also
36 reported about a fourth mechanism, i.e. solvent degradation with flue gas contaminants like
37 SO_x or NO_x. The influence of process parameters like temperature or oxygen concentration on
38 amine degradation has been studied in previous studies,^[8, 9] as well as the influence of
39 dissolved metals that may stem from vessel leaching and solvent impurities. Some
40 degradation inhibitors have been investigated by Goff^[10] and by Delfort et al.^[11] A kinetic
41 model of MEA degradation has been proposed by Supap et al.,^[9] but the degradation
42 experiments underlying this model took place with discontinuous gas feed, so that they may
43 not be representative of industrial conditions in which the gas phase continuously flows
44 through the mass transfer columns. Finally, conditions closer to industrial plants have been
45 adopted in a further study,^[12] although no kinetic model of solvent degradation was proposed.
46 As a consequence, previous studies have led to a better understanding of the solvent
47 degradation mechanisms, but there is currently no validated kinetic model of MEA
48 degradation that is able to predict industrial scale degradation. Thus, the objective of the
49 present work is to study solvent degradation in accelerated conditions at lab-scale and to
50 validate the degradation pathways observed in laboratory against industrially degraded
51 solvents.
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2. Materials and methods

The influence of process operating conditions on the solvent degradation has been studied for the case of an aqueous solution of 30 wt% monoethanolamine (MEA), the benchmark solvent for post-combustion CO₂ capture. Since solvent degradation is a slow phenomenon taking place over months in industrial plants, experimental equipment and appropriate procedures have been developed to accelerate degradation reactions at the lab scale. The oxidative degradation and the thermal degradation of MEA with CO₂ have been considered, while the MEA thermal decomposition and the reactions with flue gas contaminants like SO_x or NO_x have been neglected in a first approach. Indeed, the highest temperatures usually observed in industrial CO₂ capture conditions are lower than 200°C so that thermal decomposition is not observed and the presence of SO_x and NO_x may be considerably reduced, assuming a high efficiency of the flue gas cleaning steps taking place before the CO₂ capture.

The experimental study of solvent degradation for CO₂ capture applications implied the development of experimental equipment and analytical methods that are presented in this section. First, the Degradation Test Rig that has been designed for the oxidative degradation of MEA is described. This reactor allows a continuous gas supply which is necessary to study the oxidative degradation mechanism. Then, the batch reactors used for the thermal degradation of MEA with CO₂ are presented. Batch reactors are best suited for thermal degradation because this degradation pathway requires higher temperatures but no continuous gas flow. In both cases, the base case conditions for a typical experimental run are reported. Finally, in-house analytical methods specifically developed to characterize degraded solvents are presented.

2.1 Degradation Test Rig experiments

The Degradation Test Rig (DTR) developed at the University of Liège is represented in Figure 1. Its main particularity is to allow a batch operating mode on the liquid side with a continuous gas feed flowing through the liquid under pressure. The test rig is composed of five main parts in order to enable flexible operating conditions: degradation reactor (1), gas supply (2), water balance control (gas saturator (3a) and condenser (3b)), gas outlet and analysis (4), and data acquisition and control panel (5).

The central part of the DTR is the degradation reactor (1). It consists in an agitated pressurized reactor model 4560 supplied by Parr Instrument Company. The reaction vessel is made of 316L stainless steel and has a capacity of 600 ml. The reaction temperature is controlled by a heating mantle and the pressure is regulated by a back-pressure regulator. The DTR has been proved and tested at pressures up to 2.6 MPa and temperatures up to 140°C and it allows agitation rates up to 1400 rpm. A gas entrainment impeller combined with a hollow shaft agitator enhances the gas-liquid contact by recirculating gas from the reactor head into the liquid. The continuous gas feed (2) is composed of a mixture of three different gases, usually O₂, CO₂ and N₂. The proportion of each gas can vary between 0 and 100% for a maximal total gas flow rate of 1590 Nml/min. Moreover, it is important to maintain the water balance because typical degradation experiments last for several days with continuous gas flow. Thus, before entering the degradation reactor, the gas is saturated with water (3a). Then, the gas exiting the reactor is cooled down in a condenser (3b) and the condensed water is recycled to the reactor. Without this equipment, the dry inlet gas would get loaded with water in the reactor and all the reactor water would be rapidly removed out of the system with the outlet gas. The exhaust gas is analyzed in an on-line FTIR analyzer (4) before being released

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3 to the atmosphere. To prevent gas condensation in the pipes, the line between the back-
4 pressure regulator and the FTIR analyzer is heated at 150°C. Finally, two control systems (5)
5 are combined to operate the DTR. A first controller provided with the reactor controls the
6 temperature and the agitation rate of the reactor. The other experimental parameters
7 (temperatures of other equipment, pressures, mass flows) are acquired and controlled using a
8 second controller based on a Labview application.
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10 The operating conditions of the DTR have been chosen to significantly increase the oxidative
11 degradation rate and to make it observable within reasonable time scales. In a typical
12 experiment, 300 g of 30 wt% MEA are weighted in the reaction vessel. Then the solvent
13 solution is loaded with CO₂ to reach a loading of about 0.40 mol CO₂/mol MEA (except for
14 experiments with no CO₂ in the gas feed composition, in which case there is no initial CO₂
15 loading). The temperature of the reactor is regulated at 120°C and the agitation rate is set at
16 600 rpm. The total pressure is controlled at 0.4 MPa (gauge) by a back-pressure regulator.
17 The gas flow rate equals 160 Nml/min with a gas supply composed of 5% O₂, 15% CO₂ and
18 80% N₂. Each experiment lasts for one week. In order to maintain the water balance of the
19 degradation reactor, the water temperature in the gas saturator is kept constant at 35°C while
20 the temperature of cooling water for the condenser is regulated at 16.5°C. This temperature
21 difference is related to the lower specific humidity of the gas at the reactor outlet due to the
22 reactor pressure drop. The analysis of the outlet gas occurs on-line in the FTIR analyzer after
23 dilution of the gas with 560 ml/min hot nitrogen. Liquid samples are taken at the experiment
24 start and after 3 and 7 days. They are immediately cooled down and kept refrigerated to avoid
25 further degradation.
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28 29 **2.2 Batch reactor experiments**

30 Besides the DTR, some thermal degradation experiments with CO₂ have been conducted in
31 batch conditions in smaller reactors. These batch reactors are 150 ml-cylinders made of
32 stainless steel 316L that may be set into an oven for testing the thermal degradation of MEA.
33 In a typical experimental run, the cylinders are filled up with 100 g of the solvent to be tested,
34 usually MEA 30 wt% that has been loaded with CO₂ to reach a loading of about
35 0.40 mol CO₂/mol MEA. The cylinders are then hermetically closed with caps and PTFE tape
36 to prevent any leakage and they are set into a laboratory oven (type Memmert HCP108) at
37 140°C for three weeks. Every week, the cylinders are cooled down to room temperature and
38 weighted to check for leakage. A sample is collected and the cylinder is returned back to the
39 oven. After three weeks, the cylinders are cooled down, weighted, and a final sample is
40 collected.
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43 **2.3 Analytical methods**

44 Different analytical techniques have been developed to characterize the degraded solvents in
45 both liquid and gas phase. First, the Fourier Transformed Infra-Red spectrometer (FTIR)
46 performs an on-line analysis of the gas phase emitted during the degradation experiment. The
47 FTIR device is a 6700 Nicolet FTIR supplied by Thermo Scientific with a 200 ml gas cell
48 (light pathway of 2 meters). The gas cell is heated at 150°C and the resolution of the analyzer
49 is set to 4 cm⁻¹. The analyzer interior is continuously purged with dry air and the detector is
50 cooled with liquid nitrogen. The only quantified component in the gas phase is ammonia and
51 the detector calibration has been performed by the dilution of a N₂ flow containing 9750 ppm
52 NH₃ supplied by Air Liquide. The relative standard deviation has been determined to 0.2% by
53 multiple measurements of a known sample.
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56 In the liquid phase, the amine content is quantified by High-Pressure Liquid Chromatography
57 (HPLC) using a new method specially developed for this application. The equipment consists
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3 in a Water 515 pump, a Water 717+ automatic injector, a Merck T-6300 Column thermostat
4 and a Water 410 refractive index detector. The HPLC column is a 150 mm long Kinetex
5 HILIC column (4.6 mm internal diameter and 2.6 μm particle size) supplied by Phenomenex
6 and using hydrophilic interactions as separation mode. The eluent is a mixture 90:10
7 acetonitrile-water containing 5 mM ammonium formate and set at a pH of 3.2 by adding
8 formic acid. The eluent flow rate is set at 1.0 ml/min and the column temperature is controlled
9 at 30°C. Samples are diluted 1:10 with a solution of acetonitrile-water 50:50 and the injection
10 volume equals 5 μL . The refractive index detector is calibrated before each measurement
11 campaign using six diluted samples of pure MEA. The relative error of this analytical method
12 was calculated to 0.76% by multiple measurements of a known sample. Furthermore, the
13 formation of liquid degradation products is evaluated by Gas Chromatography (GC). The GC
14 device is a GC 8000 Series (Fisons Instruments) coupled with a Flame Ionization Detector
15 (FID) of type EL980 (Fisons Instruments). Based on the work of Supap et al.,^[13] a 30 m long
16 capillary Optima-35MS column supplied by Macherey-Nagel has been chosen (0.25 mm
17 internal diameter and 0.25 μm film thickness). The carrier gas is helium and its pressure is
18 kept constant at 0.06 MPa (gauge). Samples are diluted 1:2 with deionized water containing
19 1 wt% of an internal standard (diethylene glycol, DEG). The 1 μL sample is injected at
20 280°C. The column temperature program starts at 35°C during 2 minutes and then increases
21 by 7°C/min for 15 minutes. From 140°C, the temperature increases by 5°C/min for 20
22 minutes and the temperature is finally maintained at 240°C during 8 minutes. The FID is fed
23 with a mixture of hydrogen and air. The pressure of the air flow is regulated at 0.11 MPa
24 (gauge), the pressure of H₂ at 0.07 MPa (gauge). The flame temperature is controlled at
25 300°C. Table 1 lists the main peaks identified and possibly quantified in the GC spectra of
26 degraded MEA samples (see also Figure 2). The spectrometer is calibrated for quantification
27 using standard components diluted in water and containing 1 wt% DEG. Depending on the
28 degradation product, the relative error (determined by multiple measurements of a known
29 sample) varies from 2.5% to 12% in the case of low concentrated products.

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34 The liquid samples were also analyzed to determine their total nitrogen (TN) content based on
35 the Dumas method using an ECS 4010 elemental analyzer supplied by Costech Instruments.
36 The calibration is performed by comparison with an acetanilide standard (containing 10.36
37 wt% of nitrogen) at different dilutions. A relative error of 2.5% was claimed. Finally, the
38 concentration of dissolved metals typically present in stainless steel (Fe, Cr, Ni and Mn) was
39 quantified in liquid solvent samples by Atomic Absorption Spectrometry (AAS). Analyses
40 were performed using a flame spectrometer novAA@300 supplied by Analytik Jena.
41 Calibration tests were performed with three solutions at 1.25, 2.5 and 6.5 mg/L for Fe, Cr, Ni
42 and Mn. Prior to the analysis, the amine sample was diluted with water and acidified with HCl
43 or HNO₃. According to the operator, the relative standard deviations are usually below 10%
44 for each metal but they may reach up to 45% in case of low metal concentrations.

45 46 47 48 **3. Experimental results**

49 In the CO₂ capture process, degradation reactions show slow kinetics. Lepaumier^[12] reported
50 that the amine concentration decreased by 4% in 45 days during pilot plant tests in the
51 framework of the European CASTOR project. The main objective of the present study is thus
52 to identify base case conditions that accelerate MEA degradation in a relevant way when
53 compared with industrial CO₂ capture degradation. A base case experiment for accelerated
54 MEA degradation is defined for both the Degradation Test Rig and the batch reactors and it is
55 compared to industrially degraded solvent samples. Then, the influence of process parameters
56 like the gas feed composition and the agitation rate is studied and quantified.

3.1 Comparison with industrial degradation

During the base case experiments with the conditions reported in sections 2.1 and 2.2 respectively, the total amount of MEA decreases by 24% in the DTR and by 37% in the batch reactor. Figure 2 compares the GC spectra of the solution degraded in batch and DTR base case conditions with the GC spectra of degraded MEA samples from two different European pilot plants. The peak numbers refer to Table 1.

Although some products could not be identified, most degradation products of MEA (peak 1) obtained in the DTR are similar to those obtained in industrial capture pilots: HEF (peak 4), OZD (peak 5), HEI (peak 6), HEPO (peak 8), HEHEAA (peak 9) and BHEOX (peak 10). On the contrary, the degraded samples obtained in batch reactors mainly contain HEEDA (peak 3) and HEIA (peak 7) which are not present in MEA samples originating from pilot plants. This indicates that the degradation reactions taking place in pilot plants are best represented by the accelerated degradation under base case conditions in the DTR, corresponding to oxidative degradation. On the contrary, most degradation products observed in batch reactors (corresponding to thermal degradation with CO₂) are different from products observed in industrial pilot plants for CO₂ capture. As a consequence, the present work further focuses on the oxidative degradation of MEA.

3.2 Oxidative degradation

In this section, MEA oxidative degradation is studied in the Degradation Test Rig. First, the total nitrogen balance of the base case experiment is presented and the distribution of liquid degradation products is detailed. Then, the gas feed composition and the agitation rate are successively varied and the results are compared to the base case experiment.

3.2.1 Nitrogen balance of degradation experiments

In order to check for leakages and to ensure that the analytical techniques are able to detect and quantify most degradation products, the nitrogen balance of the DTR base case experiment has been performed. The nitrogen balance includes MEA (measured by HPLC), liquid degradation products (measured by GC) and gaseous degradation products (measured by FTIR). Moreover, it may be noted that besides the NH₃ emission detected at the FTIR analyzer, some ammonia reacted in the condenser with CO₂ and condensing water, leading to the formation of crystal plugs that had to be removed regularly. An X-ray diffraction analysis clearly evidenced that the crystal was made of ammonium bicarbonate (NH₄HCO₃), so that its contribution to the emission of NH₃ was accounted for by weighting the crystal and considering that one mol ammonium carbonate contains one mol ammonia.

Figure 3 shows the nitrogen balance for the DTR base case experiment. This base case experiment has been performed twice in order to evaluate the repeatability of oxidative degradation experiments. The nitrogen content calculated from the HPLC, GC and FTIR analyses is represented in Figure 3 as well as the result of the total nitrogen analysis of the liquid phase. The dashed line at 1.47 mol represents the initial amount of nitrogen that is present in 300 g of 30 wt% MEA, i.e. at the beginning of the experiment. At the end of the base case experiment, residual MEA and identified degradation products contain 1.32 mol of nitrogen distributed as following: 1.16 mol MEA, 0.03 mol nitrogen in liquid degradation products and 0.14 mol of nitrogen emitted under the form of NH₃. As a result, the calculated error on the nitrogen balance is in the range of 10%. The repetition of the base case experiment gives similar results, with a relative difference on the total nitrogen content lower than 4% and a relative difference on the MEA degradation rate of 6%.

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3 Figure 3 also confirms that ammonia is by far the main degradation product of MEA under
4 base case conditions in the DTR. Indeed, the MEA loss equals 0.31 mol and the total
5 ammonia emission accounts for 0.14 mol, i.e. 45% of the MEA loss. This is in accordance
6 with Chi and Rochelle^[14] who have described ammonia as one of the main products of MEA
7 oxidative degradation. On the contrary, the total amount of nitrogen-containing degradation
8 products in the liquid phase only represents 0.03 mol, i.e. about 10% of the MEA loss. The
9 remaining MEA loss may be due to the precision of the analytical methods as well as to non-
10 quantified degradation products. When comparing the results of the total nitrogen analysis
11 with the amount of identified nitrogen in the liquid phase only (residual MEA + liquid
12 degradation products), it appears that the nitrogen mass balance in the liquid phase can be
13 closed within 5%. This difference may however represent up to 0.05 mol nitrogen, i.e. 16% of
14 the MEA loss.
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17 The distribution of identified degradation products in the liquid phase is represented in Figure
18 4 for the base case experiment (left) and its repetition (right). It appears that HEPO and HEI
19 are the two major nitrogen-containing products in liquid samples of degraded MEA. OZD and
20 BHEOX were also quantified while HEF and HEHEAA could be identified but not
21 quantified. This may be compared to the results of Lepaumier et al.^[15] that identified OZD,
22 HEF and HEI in oxidatively degraded MEA samples. They also reported the presence of
23 HEPO, HEHEAA and BHEOX in industrially-degraded solutions, although they could not
24 observe them in laboratory conditions. Moreover, the base case experiment and its repetition
25 lead again to very similar results, excepted that HEIA is formed instead of HEEDA. These
26 two products are formed in small quantities, both of them being typical products of MEA
27 thermal degradation with CO₂.^[16]
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30 3.2.2 Influence of the gas feed composition

31 In industrial CO₂ capture conditions, the flue gas of a typical coal-fired power plant is
32 composed of 6% O₂, 14% CO₂, 12% H₂O and 68% N₂. Both O₂ and CO₂ play a significant
33 role in the degradation mechanisms of the amine solvent, so that their influence has been
34 studied in the DTR. Figure 5 (left) shows the influence of the gas feed composition on the
35 MEA loss and the NH₃ emission. It appears that almost no MEA loss is observed in the
36 absence of oxygen. As a consequence, the thermal degradation with CO₂ does not
37 significantly take place at 120°C in the DTR. On the contrary, in the presence of oxygen,
38 MEA degrades and NH₃ is emitted. These results clearly indicate that oxidative degradation is
39 the predominant degradation mechanism in the DTR. These experiments with varying gas
40 feed composition also confirm that NH₃ accounts for about half of the MEA loss when
41 oxygen is present in the system.
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44 Moreover, it also appears from this figure that the oxidative degradation rate and the NH₃
45 emission are about 40% lower with CO₂ present in the gas feed. Indeed, the MEA loss is
46 reduced from 0.55 mol in the O₂-N₂ system down to 0.31 mol in the O₂-CO₂-N₂ system
47 (initial MEA content: 1.47 mol). Similarly, the emission of ammonia is reduced from
48 0.23 mol to 0.14 mol in the presence of CO₂. According to Goff,^[10] the ionic strength of the
49 amine solution increases with the CO₂ loading, leading to a lower solubility and a lower
50 diffusion coefficient of O₂ so the rate of oxidative degradation is reduced. Another possible
51 explanation is that the MEA carbamate formed in CO₂-loaded solutions is less sensitive to
52 oxidative degradation than the free amine. It may also be noted that an initial CO₂ loading of
53 the amine solution is only performed for experiments with CO₂ in the gas feed.
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56 Figure 5 (right) shows the distribution of quantified degradation products in the liquid phase
57 of degraded MEA samples. Small amounts of HEPO are detected in the experiment with N₂
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only, maybe due to an oxygen contamination during the experiment. In the experiment with CO₂ only, 0.002 mol of OZD are formed. OZD may be due to both oxidative and thermal degradation with CO₂,^[12] but no further degradation product is detected. The formation of HEI is only observed in the O₂-N₂ and the O₂-CO₂-N₂ systems. HEI is a typical oxidative degradation product resulting from a reaction between two other oxidative degradation products.^[17] Like NH₃, its formation is reduced in the presence of CO₂. In the presence of both O₂ and CO₂, more HEPO is formed and further degradation products like BHEOX and HEIA appear. Finally, HEI and HEPO are the main liquid products of MEA oxidative degradation, confirming the results reported for the base case experiment.

3.2.3 Influence of the agitation rate

A further significant factor influencing MEA oxidative degradation is the gas-liquid transfer taking place in the absorption and desorption columns. This effect can be studied by varying the agitation rate in the DTR. Figure 6 (left) shows the influence of the agitation rate on the MEA degradation and the NH₃ emission in the O₂-N₂ and in the O₂-CO₂-N₂ systems. In the absence of CO₂, the MEA loss increases from 0.3 up to 1.26 mol when increasing the agitation rate from 400 to 1000 rpm. In the O₂-CO₂-N₂ system, a similar trend is observed and the inhibiting effect of CO₂ on MEA degradation appears once again. The emission of ammonia rises with the agitation speed, increasing by more than 250% from 0.19 at 400 rpm up to 0.67 mol at 1000 rpm in the O₂-N₂ system. This is also the case in the O₂-CO₂-N₂ system although the NH₃ emission was not measured during the experiment at 1380 rpm. As a consequence, there is a clear linear relationship between the agitation rate and the degradation extent for both O₂-N₂ and O₂-CO₂-N₂ systems. When increasing the agitation speed, the specific power given to the system is increased, as well as the overall mass transfer coefficient. Thus, more oxygen is transferred from the gas feed to the liquid solvent and the oxidative degradation is enhanced. These results confirm that the MEA oxidative degradation is limited by the oxygen mass transfer as suggested by Goff.^[10]

After 1-week degradation, HEI is the main degradation product in the liquid phase independently of the presence of CO₂ as presented in Figure 6 (right). At higher agitation rates, up to 0.11 mol HEI is formed. HEPO is also formed, but its formation seems less enhanced by the agitation rate. Moreover, Figure 7 compares the GC spectrum of a sample degraded at 1380 rpm in the DTR with the spectrum of an industrially degraded MEA solution (Pilot 2). The peak numbers refer to Table 1. It appears that high agitation rates clearly accelerate the oxidative degradation, but also lead to the formation of large amounts of alternative degradation products that are not representative of industrial CO₂ capture units. For instance, the formation of HEF (peak 4) is dramatically increased and neither HEPO (peak 8), nor HEHEAA (peak 9) or BHEOX (peak 10) are formed at high agitation rates although they are observed in industrially degraded samples. Thus, the mass-transfer limited degradation pathways observed at 600 rpm in the DTR lead to a distribution of degradation products that is more representative of industrially degraded solutions than the pathways observed at 1380 rpm.

Finally, the influence of metal ions on MEA oxidative degradation has been previously demonstrated by Blachly and Ravner,^[18] so that metal concentrations have been measured in all degradation experiments. While usual experiments at 400 and 600 rpm lead to metal ions concentrations in the range of 5 ppm, it appeared that experiments performed at 1000 rpm in the O₂-N₂ system and 1380 rpm in the O₂-CO₂-N₂ system give a final metal ion concentration of about 25 and 50 ppm respectively (total metal concentration based on the measurement of iron, chromium, nickel and manganese concentrations). This may be caused by two effects

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3 combining to produce a vicious circle. First, more metal ions leach from the vessel walls due
4 to the higher mechanical constraints, and then these dissolved metals catalyze the formation
5 of higher amounts of corrosive degradation products that further attack the vessel walls.
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8 **Conclusion**

9
10 The environmental impact related to solvent degradation and to the emission of degradation
11 products is one of the most important operational drawbacks of the CO₂ post-combustion
12 capture with amine solvents. In the present work, the degradation of the benchmark solvent
13 for this process (30 wt% MEA) is studied and the influences of the main operational
14 parameters are quantified. The two main degradation pathways of MEA are considered using
15 specially developed equipment: the oxidative degradation is evaluated in an experimental
16 Degradation Test Rig (DTR) with continuous gas flow and the thermal degradation with CO₂
17 is performed in batch cylinders. Moreover, appropriate analytical techniques are developed to
18 characterize solvent degradation by quantifying the amine content (HPLC) as well as the
19 formation of liquid (GC) and vapor (FTIR) degradation products.
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21

22 Furthermore, the present work shows that similar degradation pathways and products are
23 obtained in the DTR compared with two European CO₂ capture pilot plants. This evidences
24 that the study of MEA degradation under accelerated conditions may reduce the experiment
25 duration while following the same degradation mechanisms that take place under industrial
26 conditions. On the contrary, the degradation products obtained in batch reactors are different
27 from those observed in pilot plants. This comparison evidences that the main degradation
28 pathway in CO₂ capture pilot plants is the oxidative degradation, in accordance with the
29 results presented by Lepaumier et al.^[15] As a consequence, the oxidative degradation of MEA
30 was the most studied degradation mechanism in the present study. The nitrogen balance and
31 the repetition experiments demonstrated that the experimental error of the DTR could be kept
32 lower or equal to 10%. In the base case conditions, ammonia accounts for 45% of the MEA
33 loss. On the liquid side, the main quantified degradation products of MEA are HEPO and
34 HEI.
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37 Then, the influence of the gas composition on MEA degradation also confirms oxidative
38 degradation as the predominant degradation mechanism in the DTR (and thus in industrial
39 capture plants) since almost no thermal degradation is observed in these conditions. An
40 inhibiting effect of CO₂ on MEA oxidative degradation is also reported. Moreover, it appears
41 that increasing the agitation rate dramatically increases the MEA loss and the formation of
42 ammonia and HEI. This highlights the role of the gas-liquid oxygen transfer as a limiting
43 factor of MEA degradation. It also appears that increasing the agitation rate leads to
44 alternative degradation pathways that are not representative of industrial CO₂ capture
45 conditions anymore, so that this option should not be selected for the accelerated study of
46 MEA solvent degradation.
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48

49 Finally, further work includes a systematic evaluation of the influence of some main operating
50 parameters of the post-combustion capture process on MEA oxidative and thermal
51 degradation. For instance, the influences of the temperature and the oxygen concentration in
52 the flue gas will be quantified. This will lead to the development of a kinetic model of solvent
53 degradation considering both oxidative and thermal degradation of MEA with CO₂.^[19] This
54 kinetic model of degradation will be included into a global model of the CO₂ capture process
55 previously described,^[20, 21] so that the results of the kinetic model can be validated against
56 pilot plant data. The objective is then to develop a practical tool that will be able to predict the
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environmental impact of an industrial CO₂ capture process regarding solvent degradation. This methodology developed for the case of monoethanolamine may also be extended to further promising solvents like piperazine.^[22] Such a model could and should be used for the design of CO₂ capture plants to contribute to their large-scale deployment.

Acknowledgements

The Belgian Fund for Scientific Research (F.N.R.S., bourse FRIA) and the company Laborelec, member of the GDF SUEZ group are gratefully acknowledged for their financial and technical support.

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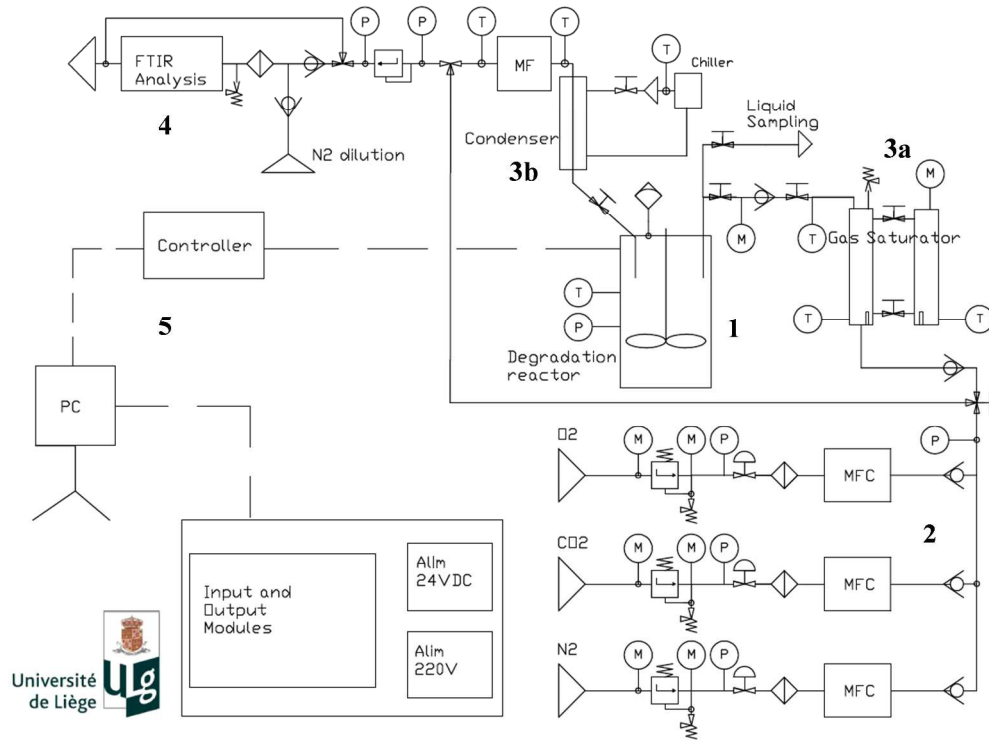
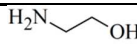
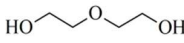

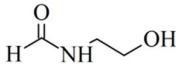

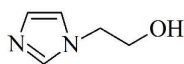
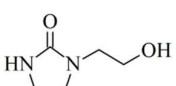
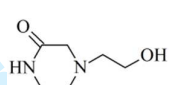
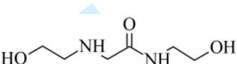
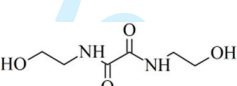


Figure 1. Flowsheet of the Degradation Test Rig (DTR).
408x301mm (300 x 300 DPI)

Table 1. Main peaks identified in GC spectra of degraded MEA samples

		Compound	Structure	Retention time (min)	Type
1	MEA	monoethanolamine		7.6	Start amine
2	DEG	diethylene glycol		15.0	Internal standard
3	HEEDA	<i>N</i> -(2-hydroxyethyl)ethylenediamine		17.0	Quantified
4	HEF	<i>N</i> -(2-hydroxyethyl)formamide		21.1	Identified
5	OZD	2-oxazolidinone		22.5	Quantified
6	HEI	<i>N</i> -(2-hydroxyethyl)imidazole		24.9	Quantified
7	HEIA	<i>N</i> -(2-hydroxyethyl)imidazolidinone		31.5	Quantified
8	HEPO	4-(2-hydroxyethyl)piperazine-2-one		34.3	Quantified
9	HEHEAA	<i>N</i> -(2-hydroxyethyl)-2-(2-hydroxyethylamino)acetamide		36.8	Identified
10	BHEOX	<i>N,N'</i> -bis(2-hydroxyethyl)oxamide		38.7	Quantified

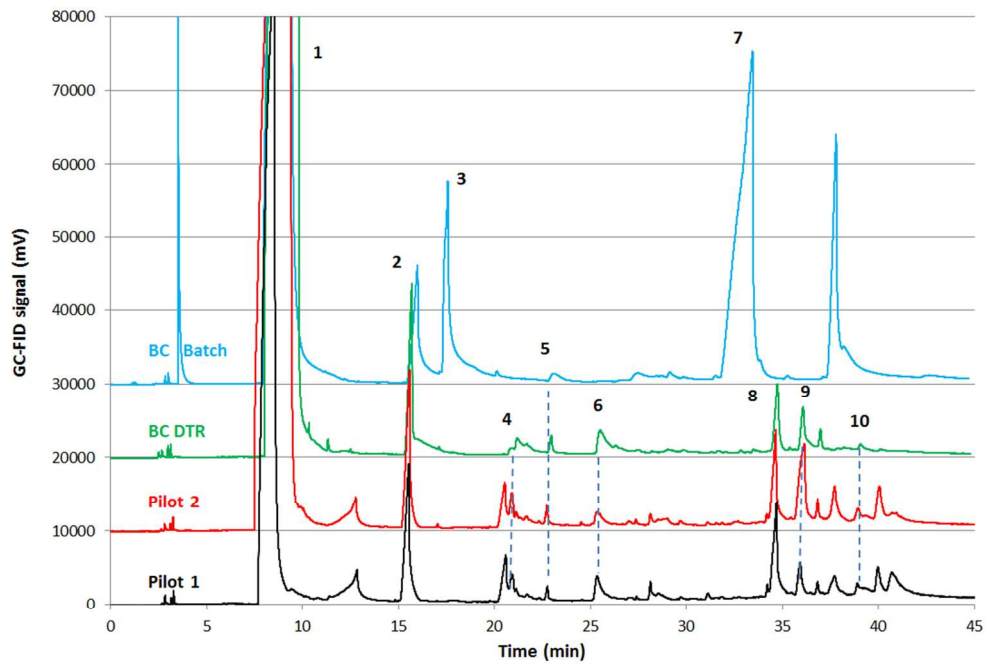


Figure 2. GC comparison of base case (BC) degradation in batch reactors, in the DTR and in two European pilot plants for CO₂ capture.
93x68mm (300 x 300 DPI)

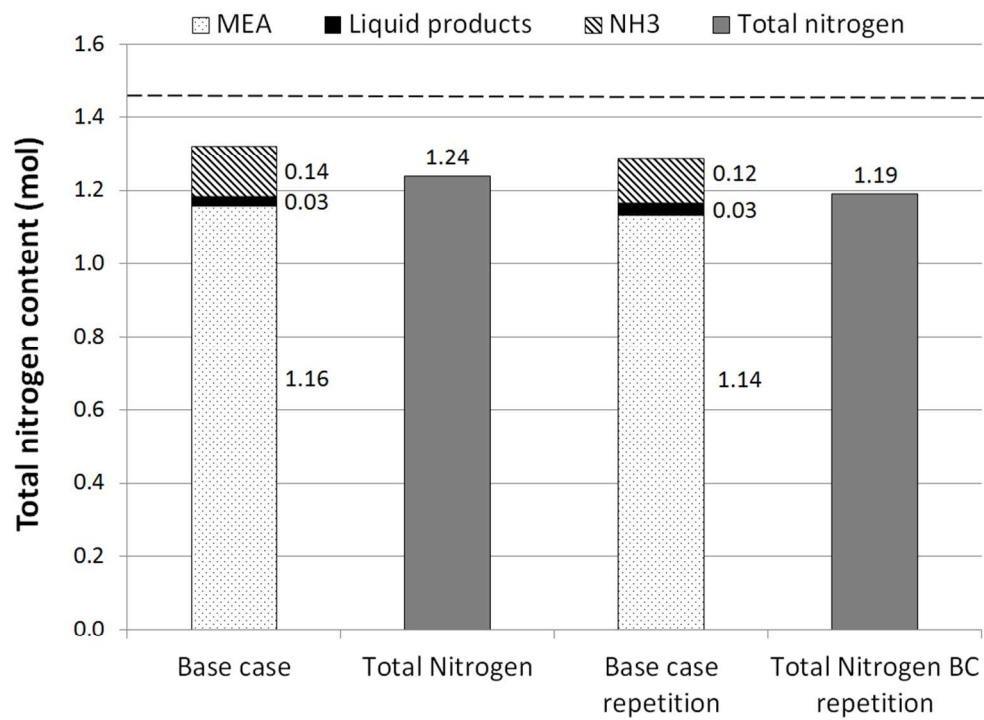


Figure 3. Nitrogen balance of the base case experiments (300 g, 30 wt% CO₂ loaded MEA, 600 rpm, 120°C, 0.4 MPa (gauge), 160 Nml/min gas feed, 5% O₂/15% CO₂/80% N₂, 1 week).
92x71mm (300 x 300 DPI)

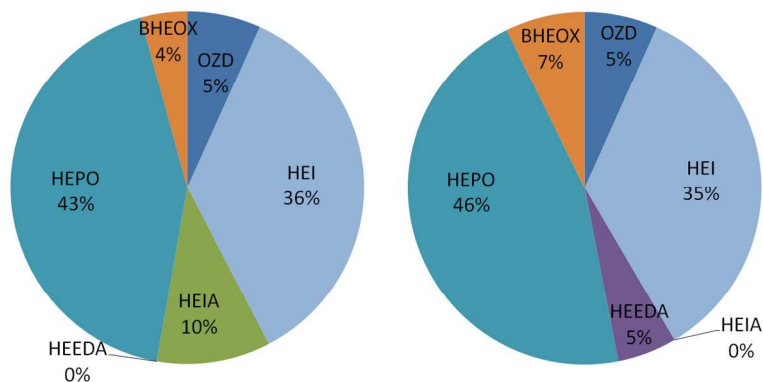


Figure 4. Distribution of identified nitrogen-containing liquid degradation products in the base case experiment (left) and its repetition (right) (300 g, 30 wt% CO₂ loaded MEA, 600 rpm, 120°C, 0.4 MPa (gauge), 160 Nml/min gas feed, 5% O₂/15% CO₂/80% N₂, 1 week).
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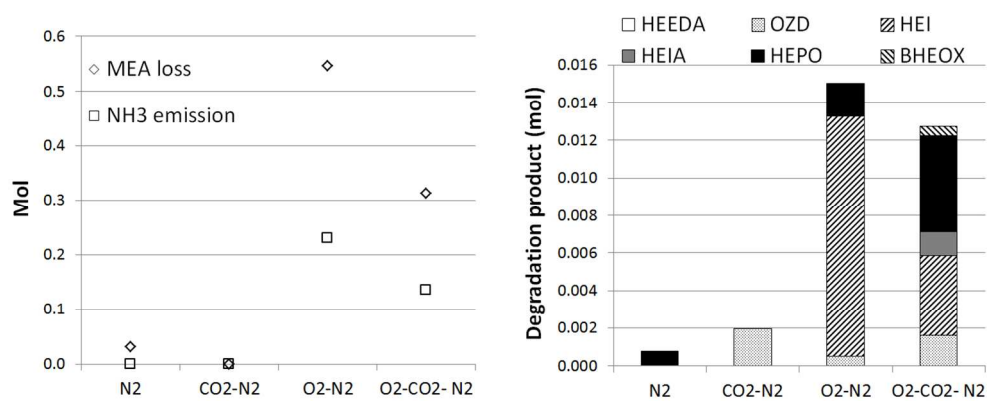


Figure 5. Influence of the gas feed composition on MEA degradation and NH₃ emission (left) and on liquid degradation products (right) (300 g, 30 wt% CO₂ loaded MEA, 120°C, 0.4 MPa (gauge), 600 rpm, 160 Nml/min gas feed, 1 week). There is no initial CO₂ loading in experiments with no CO₂ in the gas feed and the experiment with N₂ only was conducted at 2.0 MPa (gauge), 400 rpm, 200 Nml/min N₂.
117x48mm (300 x 300 DPI)

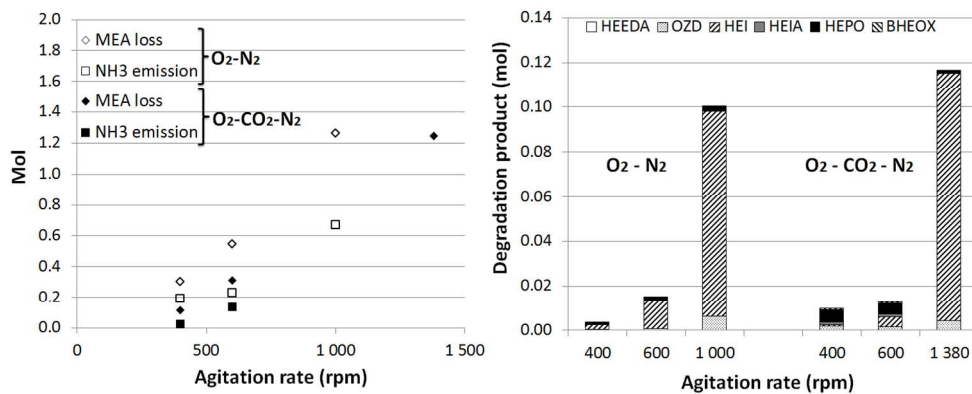


Figure 6. Influence of the agitation rate on MEA degradation and NH₃ emission (left) and on liquid degradation products (right) (300 g, 30 wt% CO₂ loaded MEA, 120°C, 0.4 MPa (gauge), 5% O₂, 160 Nml/min gas feed, 1 week). There is no initial CO₂ loading in experiments with no CO₂ in the gas feed. 128x54mm (300 x 300 DPI)

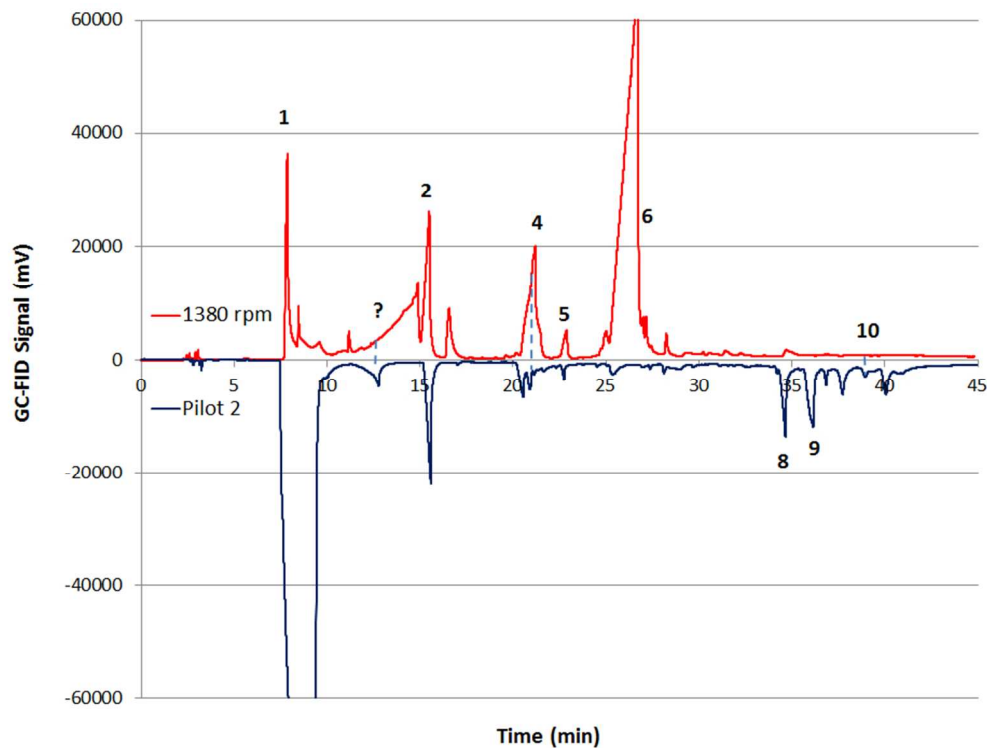


Figure 7. GC comparison of pilot plant degradation (Pilot 2) with degradation in the DTR at high agitation rate (300 g, 30 wt% CO₂ loaded MEA, 120°C, 0.4 MPa (gauge), 1380 rpm, 160 Nml/min gas feed, 5% O₂/15% CO₂/80% N₂, 1 week).
78x59mm (300 x 300 DPI)