Oxidative degradation of triethylene glycol

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ABSTRACT

Triethylene glycol (TEG) is unstable in the presence of oxygen and at high temperatures, though the degradation mechanisms occurring are not properly understood. In attempting to close some of the knowledge gaps, laboratory-scale degradation experiments have been conducted to assess the effect of temperature and oxygen on the stability of TEG. Oxidative degradation experiments with TEG were conducted.

The oxidative degradation mechanism seems to change with temperature and oxygen concentration. Multiple oxidative degradation compounds of TEG were detected and quantified. These included MEG, diethylene glycol (DEG), formic acid, acetic acid, glycolic acid, formaldehyde, acetaldehyde, and water. Formic acid, MEG, and DEG are the dominant identified degradation products both at high temperatures and at high oxygen concentrations. In addition, the formation of CO_2 and larger polymeric glycols was confirmed. The carbon- and mass balance indicate unidentified degradation products in the liquid and gas phases.

1. Introduction

When extracting natural gas from reservoirs, it typically consists of a complex mixture of components, including water (Wang et al., 2013; Kong et al., 2018). The presence of water during processing and transportation can cause problems. The most severe one is the potential clogging of the pipelines caused by the formation of crystalline structures called hydrates (Englezos, 1993; Bai and Hydrates, 2019). These are cages of water surrounding smaller molecules, such as methane. Corrosion can also occur as water condenses on the equipment (Chebbi et al., 2019; Karimi and Abedinzadegan Abdi, 2009). Additionally, the presence of water in the natural gas increases the volume of the gas while decreasing the heating value (Mokhatab et al., 2015). To reach quality specifications for transportation and sale, water must therefore be removed from the natural gas.

The most used technique to remove water from natural gas is glycol dehydration (Chebbi et al., 2019; Stewart, 2014; Kohl and Nielsen, 1997). During this process, the glycol is brought into contact with the wet natural gas as it flows counter-currant through an absorber column. Water is here physically absorbed into the glycol solvent. The water-rich glycol is then passed through a flash tank to remove other soluble gasses from the glycol before being introduced into a stripper column. At near-atmospheric pressures, the absorbed water is boiled off the glycol by the application of heat, thus regenerating the glycol for reuse (John, 2004). Ethylene glycol (MEG), diethylene glycol (DEG), triethylene glycol (TEG) and tetraethylene glycol (TREG) are commonly available glycols for dehydration. For this application, they have high absorption efficiency, can be easily regenerated, are in themselves non-corrosive, have a minimal capacity to absorb hydrocarbons and have a low cost (Mokhatab et al., 2015). Throughout this process, the temperatures are kept below the cracking temperature of the glycol in use. Of the abovementioned glycols, TEG is the most common glycol used in the industry (Bahadori et al., 2008). This is because it gives lower solvent losses and has a higher thermal degradation temperature than the others, meaning that a higher purity of the lean glycol is possible to achieve. The cracking temperature of TEG has been reported to be 204 °C (Mokhatab et al., 2015).

When glycols are exposed to oxygen or high temperatures, it can lead to oxidative or thermal degradation of the glycol. The degradation products formed can cause operational issues, such as foaming, corrosion, and performance loss (Mokhatab et al., 2015; John, 2004). Glycol degradation is an acknowledged problem, but little has been published on the degradation reactions taking place or on the compounds formed. Of the glycols mentioned above, most literature is available on the

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degradation of MEG. Of the remaining, the published literature is scarce.

Oxidative degradation, often called thermal oxidative degradation, is the degradation mechanisms occurring when the glycol decomposes in the presence of an oxidizing agent, such as oxygen. In general, the literature on the oxidative degradation of TEG is lacking. There is, however, some literature available on the oxidative degradation of other glycols than TEG. This can be of relevance for the degradation of TEG, as the likeness in the structure of the glycols can make the chemical reactions occurring for other glycols transferable to the TEG system.

Mokhatab et al., (Mokhatab et al., 2015) describe that as TEG

oxidatively degrades, corrosive acids are formed. This is supported by Forster, (Forster, 1998) who further proposed that the oxidative degradation of TEG occurs through oxidation reactions of the ether groups to form peroxide radicals. These then degrade into smaller compounds, like smaller glycols (e.g., MEG), ethers, esters, organic acids, and aldehydes. These are presented as possible degradation products, but no data on their formation is provided. Their formation, however, is supported by literature on comparable reactions of ether and alcohol oxidation (Denisov, 1980).

In a study performed by Lloyd et al. (Lloyd et al., 1954), the oxidative

Table 1
Details on chemicals used in this study.

Chemical name	Abbreviation	Structure	CAS-number	% Purity
Triethylene glycol [a]	TEG	HO~~O~~O~~OH	112–27-6	> 99 %
Diethylene glycol [a]	DEG	HO~~O~~OH	111–46-6	> 99 %
Ethylene glycol [a]	MEG	HO~~OH	107–21-1	> 99 %
Acetic acid [a]		CH₃C(=O)OH	64–19-7	> 99.8 %
Formic acid [a]		HC(=O)OH	64–18-6	> 98 %
Glycolic acid [a]		HO-CH₂-C(=O)OH	79–14-1	99 %
Glyoxylic acid [a]		HC(=O)-C(=O)OH	298–12-4	50 wt% in water
Oxalic acid [a]		HO-C(=O)-C(=O)-OH	144–62-7	> 99 %
Glycolaldehyde dimer		HO-CH₂-CHO	141–46-8	–
Glyoxal		HC(=O)-CHO	131543–46-9	40 wt% in water
Formaldehyde		H₂C=O	50–00-0	- [b]
Acetaldehyde		CH₃CHO	75–07-0	- [b]
Sulphuric acid [a]	H₂SO₄		7664–93-9	95–98 %
Ethanolamine [a]	MEA	HO-CH₂CH₂-NH₂	141–43-5	99 %

[a] Purchased from Sigma-Aldrich Norway AS/Merck Life Sciences.
[b] Analysed by an external laboratory. Purity is not available.

degradation of DEG is studied. They report that formic acid, formaldehyde, diethylene glycol formate, water, MEG, and 1,3-dioxolane are formed during autoxidation of DEG. In addition to these, peroxides were suspected to have formed. No CO_2 was detected in the gas phase during these experiments.

The literature on MEG degradation mainly describes the formation of organic acids, formic acid, acetic acid, glycolic acid, oxalic acid, and glyoxylic acid (Rossiter et al., 1983; Brown et al., 1987; Madera et al., 2003; Psarrou et al., 2011). These are expected to form through the oxidation of the alcohol groups. There is a focus on these in the literature, as they have been found to be a simple but good indicator to determine the state of the glycol (AlHarooni et al., 2016). Brown et al. (Brown et al., 1986) reports the formation of CO_2 during the oxidative degradation of aqueous MEG solutions, and Psarrou et al., (Psarrou et al., 2011) propose the formation of water during the oxidation, but no data is provided for the latter.

Oxidative degradation of TREG has been reported to result in radical reactions forming hydroperoxides of the ethers in a study by Glastrup et al. (Glastrup and Padfield, 1993) and Glastrup (Glastrup, 1996). Hydroperoxides of the glycol ethers were reported to form through radical reactions. In addition, the oxidation of TREG was found to result in bond breakage and the formation of a shortened glycol molecule and formic acid. The formed formic acid was reported to react with TREG to form monoTREG formate followed by diTREG formate.

In this work, we endeavor to identify the degradation patterns of TEG. To do this, oxidation experiments have been conducted at lab-scale. In the oxidative degradation experiments, the effects of oxygen and temperature were studied by varying these parameters in solutions of pure TEG. The temperatures and oxygen concentrations included in this study were chosen to enhance the degradation rates of TEG to allow the investigation of trends and effects. In addition to studying the effect of oxygen and temperature on the stability of TEG, this study aimed at identifying and quantifying degradation products.

2. Materials and methods

2.1. Chemicals

All solutions were prepared gravimetrically. The chemicals used in the experiments and analyses are listed in Table 1. Oxygen (O_2, N5.0) was purchased from AGA. The deionized water was obtained from the local water purifying system at NTNU.

2.2. Experimental procedure

To study the oxidative degradation mechanisms of TEG, experiments were performed in a custom-made semi-open batch setup, as shown in Fig. 1. The glass reactors (1.5 L) were filled with 1.2 L of glycol and placed in electrical heating mantles from ITA with magnetic stirring. Condensers cooled to 5 °C by a water bath were connected to the reactors. The gas, a blend of nitrogen and oxygen, entered the system through mass flow controllers at 200 mL/min and was introduced into the solutions through glass spargers (grade 1). The gas was recycled with a pump. Using the pump allowed the large circulation of gas and enhanced contact between the solutions and oxygen, while the small addition of oxygen and nitrogen blends ensured relatively constant oxygen concentration in the circulating gas. A small fraction of the gas was bled out of the system through a 2,4-dinitrophenylhydrazine (2,4-DNPH, 800 mg) cartridge and an acid wash (1 M H_2SO_4). A similar approach to studying oxidative degradation has been employed previously in several works (Buvik et al., 2021).

The degradation experiment of TEG was conducted in the oxidative degradation set-up in two sets. In the first set, pure TEG was degraded at 75, 100, 125, and 150 °C, with 6 % oxygen in the gas flow. In the second set, pure TEG was degraded at 100 °C, with oxygen concentrations of 1 %, 6 %, 12 %, and 24 %. Lastly, an additional experiment with TEG was
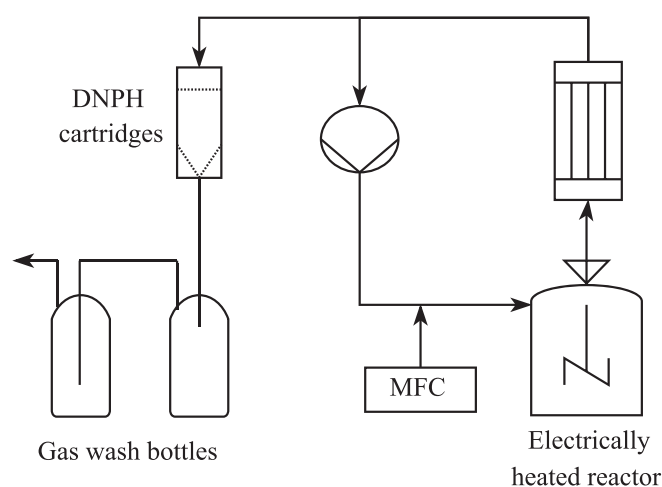

Fig. 1. Schematic of degradation set-up used for the oxidative degradation experiments. The two parallels were run simultaneously on two identical set-ups.

conducted at 100 °C, with 24 % oxygen. During this experiment, the 2,4-DNPH cartridge and the acid wash were removed and replaced by three base washes (30 wt% MEA, *aq.*), to capture and identify acidic components in the bleed gas. All experiments were conducted with two parallel runs, and all the results are presented as averages of two experiments.

2.3. Analytical methods

Quantification of MEG, DEG, and TEG was done using *Gas-Chromatography* coupled with a *Flame Ionization Detector* (GC-FID). This was done on an Agilent 7890A equipped with a DB-WAX Ultra Inert fused silica column (length 30 m, inner diameter 0.25 mm, film thickness 0.25 μm). The samples were diluted with methanol to contain < 1000 ppm glycol. The accuracy of the method was 3 %, and the precision was 1 %. The analytical method is described in detail elsewhere (Høisæter et al.,).

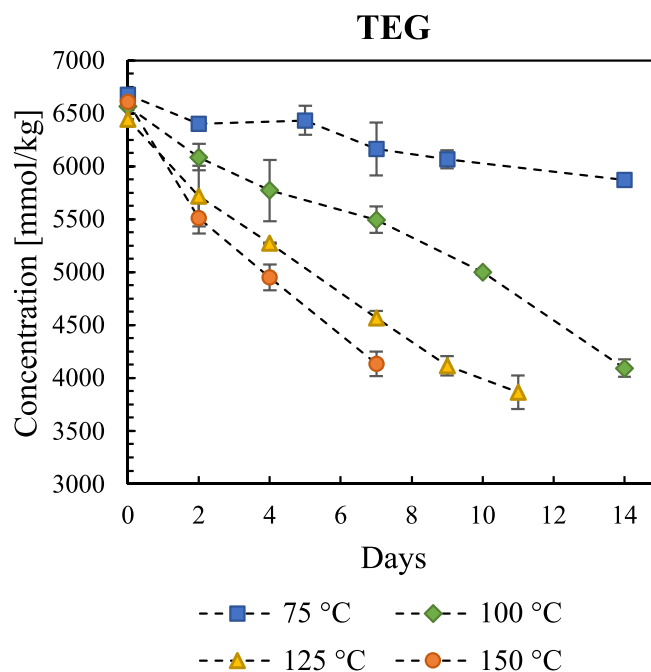Small organic acids were analyzed using *High-Performance Liquid*

Fig. 2. Effect of temperature on the oxidative degradation of TEG (6% O_2) at various temperatures.

Chromatography coupled with an *Ultraviolet* detector (HPLC-UV). The method was performed on a PL1170-6830 (Agilent HiPlex H) column. Real samples were diluted in MilliPore water to approximately 50000 ppm of the sample and filtered through 0.2 μm syringe filters before analysis. The accuracy for the quantification of formic acid and acetic acid was 2 %, glycolic acid was 4 %, glyoxylic acid was 8 %, and for oxalic acid it was 10 %. The precision for all acids was 2 %. The analytical method is described in detail elsewhere (Høisæter et al.,).

Aldehydes captured in the 2,4-DNPH cartridges and acid washes, as well as acids and nitrogen-containing components in the base washes, were analyzed by SINTEF Industries using *High Performance Liquid-Chromatography* (HPLC) coupled with a *Mass Spectrometer* (MS). All analyses were performed on an Agilent Technologies 1290 Infinity with an Agilent Technologies 6495 Triple Quad MS. For the analysis of formaldehyde and acetaldehyde, an Ascentis® Express C8, 2.7 μm HPLC column (53843-U) was used. The ionization technique was electrospray ionization (ESI). LOQ for both analytes were 10 ng/mL, and the uncertainty of the method was +/- 3 %. Before analysis, the 2,4-DNPH derivates were eluted from each of the cartridges with acetonitrile. Formic, glycolic, and acetic acid were analyzed using a Waters Acquity UPLC HSS T3 column (100 Å, 1.8 μm, 2.1 x 150 mm) and ESI. LOQ was 100 ng/mL, 10 ng/mL, and 50 ng/mL for formic, glycolic, and acetic acid, respectively. The uncertainty of the method was +/- 3 % for formic and acetic acid and +/- 5 % for glycolic acid. Sample preparation consisted of dilution and derivatization with 3–nitrophenylhydrazine. The concentration of MEA in the base washes was analyzed on an Ascentis® Express Phenyl-Hexyl, 2.7 μm HPLC column and ESI. LOQ was 1 ng/mL, and the uncertainty was +/- 3 %. Lastly, the various amine-containing species were analyzed on a Discovery® HS F5 HPLC column and with EI. Samples were diluted before analysis, and the uncertainties were +/- 5 %. Compounds and their LOQ are presented in Table A1 in Supporting Information.

Two analytical setups were used for the MS scans of the most degraded samples, on a GC–MS system and one on an ultra-performance liquid chromatography (UPLC)-MS system. The samples from the experiment were diluted 1:1400 with methanol. When running coelutions with standards, the solutions were diluted so the degraded samples had concentrations of 250 ppm and the standards had concentrations of
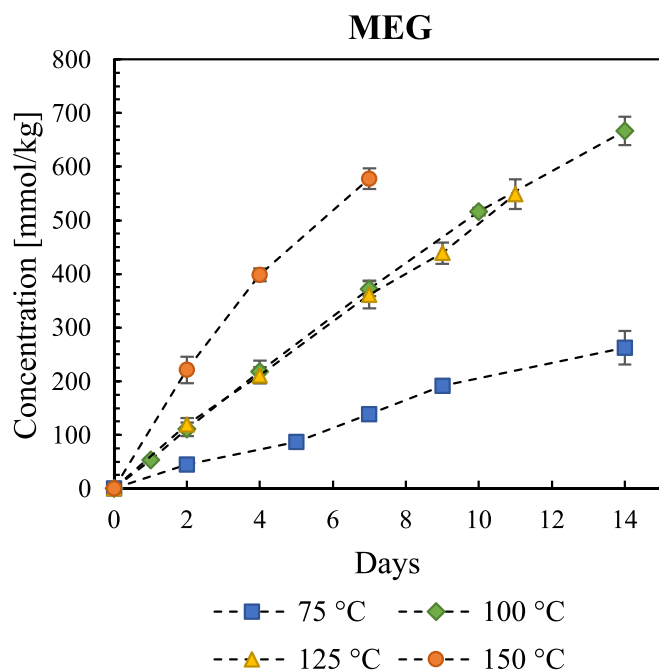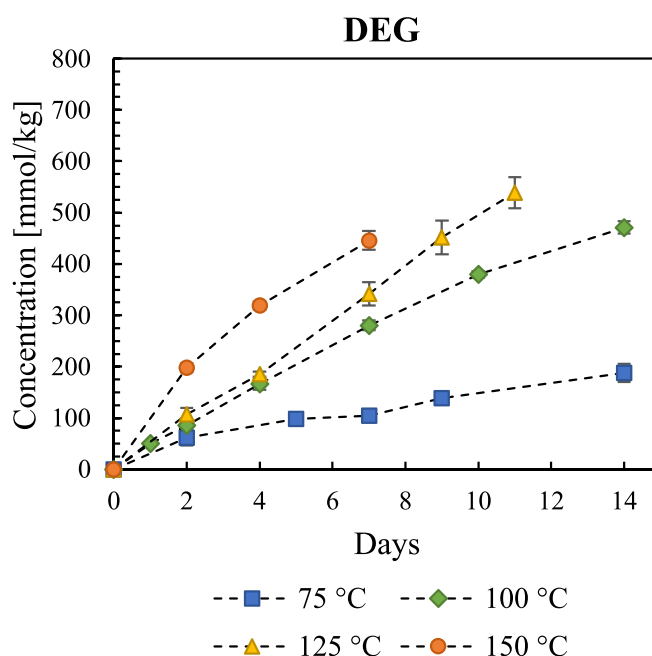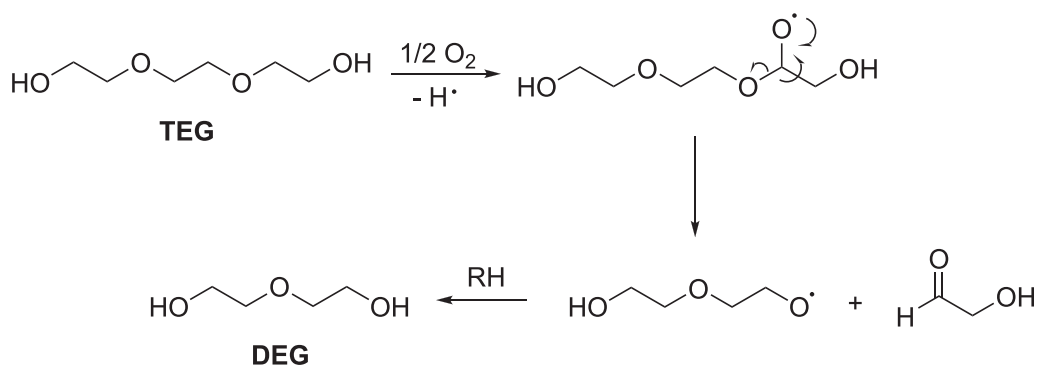

Fig. 4. Effect of temperature on the formation of DEG during oxidative degradation of TEG (6% O_2).

70 ppm. The GC analysis of the samples was performed with an Agilent 7890A gas chromatograph with an injector ALS 7683B autosampler coupled to an Agilent 5975 single quadrupole mass spectrometer. Chromatographic separation was performed on a DB Wax-UI GC Column (30 m x 0.25 mm inner diameter x 0.25 μm film thickness), keeping the carrier gas flow (helium) at 1 mL/min, and the transfer line and the injection port temperatures at 250 °C. One short and one extended temperature method were performed. The short method's temperature program was as follows: starting at 100 °C for 1 min, followed by a temperature increase at a rate of 10 °C/min to 250 °C and held for 4 min. The overall analysis time for one sample with the selected temperature program was 20 min. The extended method's temperature program was as follows: starting at 100 °C for 1 min, followed by a temperature increase at a rate of 10 °C/min to 250 °C and held for 1 min, then temperature increase by 1 °C/min to 260 °C, and held for 5 min. The overall analysis time for one sample with the extended temperature program was 35 min. The injection volume was 1 μL in splitless mode and the solvent delay was set to 5 min. The mass detector was operated in full scan mode (from 30 *m/z* to 550 *m/z*) using electron impact ionization (EI) set at 70 eV. The source temperature was set to 230 °C and the quadrupole to 150 °C.

The LC analysis was performed using an ACQUITY UPLC I Class® system connected to a Synapt G2-S Mass spectrometry detector (Waters Corporation, Milford, USA) with positive electrospray ionization sources (ESI +). 200 ng/mL of leucine enkephalin was used as a Lockmass at a flow rate of 10 μL/min to allow correction of exact mass measurements. An Acquity UPLC HSS T3 (2.1 mm × 100 mm, 1.7 μm) chromatographic column was used for reverse-phase separation. Instrumental blanks were run before and after every sample to check for carryover or cross-contamination. A mix of water:methanol (95:5) with 2 mM ammonium acetate (A) and methanol with 2 mM ammonium acetate (B) was used as mobile phase. The injection volume was 1 μL and the flow rate was 0.3 mL/min. The chromatographic gradient used was: initial conditions 100 % A; 0.00–1.00 min, 100–80 % A; 1.00–6.00 min, 80–55 % A; 6.00–13 min, 55–20 % A; 13.00–14.00 min, 20–5 % A; 14.00–17.00 min, 5 % A; 17.00–18.00 min, 5–100 % A; 18.00–22.00 min, 100 % A. The column temperature was maintained at 35 °C. The capillary voltage was set at + 2.50 kV (ESI +), the desolvation flow was fixed at 800 L/h

Fig. 3. Effect of temperature on the formation of MEG during oxidative degradation of TEG (6% O_2).

Scheme 1. Proposed oxidation path for the formation of DEG from TEG.
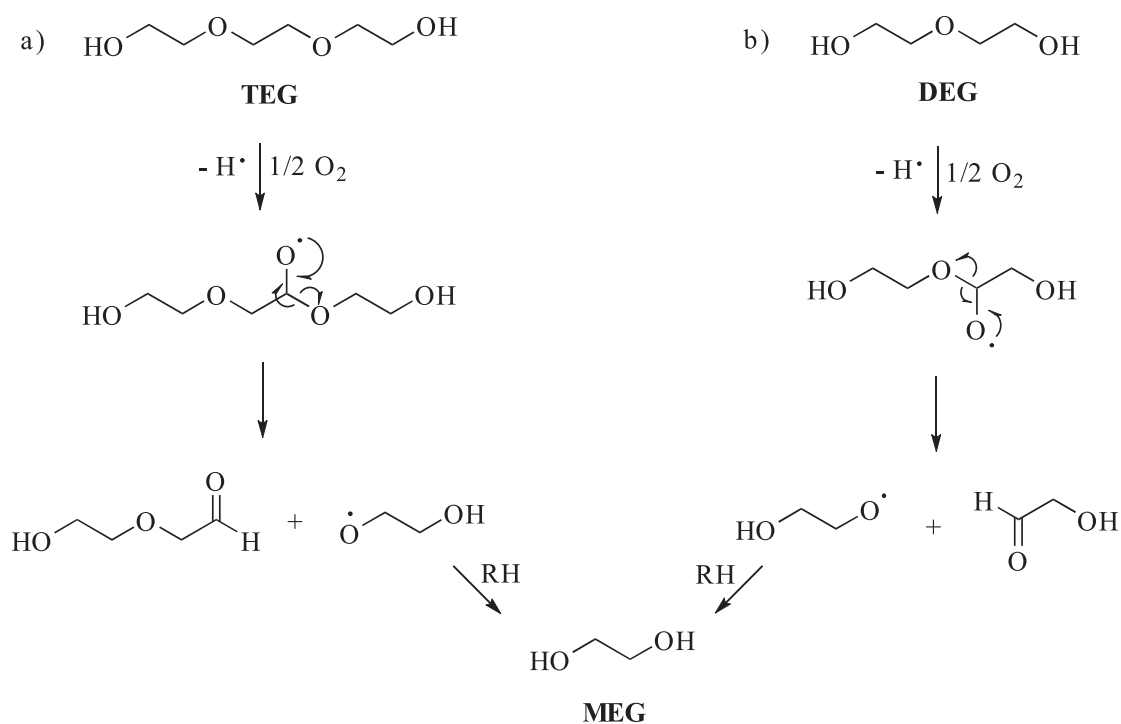
Scheme 2. Proposed oxidation path for the formation of MEG from TEG (a) or DEG (b).

with a desolvation temperature set at 350 °C and the cone voltage set at 20 V. Source Temperature was set to 120 °C. The full scan spectra were acquired within a range of 50 to 1500 m/z. The UPLC-QTOF-MS data was acquired using Masslynx V4.1 and processed with Progenesis QI V2.3 (Waters, Milford, USA).

The water concentration in the end samples was measured by *Karl Fischer titration*. SINTEF Industry performed this on a Mettler Toledo V20 with a volumetric titration method. The solvent used was Methanol dry (Hydranal®) and the titrant was Composite 5 (Hydranal®). Each sample was analyzed two times, and the presented value is the average of these results. The highest relative standard deviation for the degraded TEG samples was 4 %.

Amine titration with sulfuric acid (H_2SO_4, 0.2 N) as described by Ma'mun et al., (Ma'mun et al., 2006) was used to analyze the concentration of MEA in the base washes. This procedure has an uncertainty of $\leq$ 2 %.

Total Organic Carbon (TOC) analyses were performed on a Shimadzu TOC-L$_{CPH}$ analyzer equipped with an auto sample injector (ASI). The total amount of organic carbon in the end samples was determined by total carbon (TC) mode, subtracting the total inorganic carbon (TIC). The CO_2 content in the base washes was also determined by TIC analysis.

The instrument was calibrated with a TC calibration standard (1000 mg/ L) acquired from Sigma-Aldrich for the TOC analysis and sodium bicarbonate ($NaHCO_3$, CAS: 144–55-8) for the TIC analysis. Samples were diluted 1:100 with MilliPore water. The calibration range was 0–500 ppm. This was done over three calibration curves, 0–25 ppm, 25–150 ppm, and 150–500 ppm, which all had $R^2 > 0.9995$. The uncertainty was $\leq$ 2 %.

3. Results and discussion

This work aimed to identify degradation patterns in TEG and assess the effect of different parameters on degradation. This has been done through two sets of oxidative degradation experiments with pure TEG: one with varying temperatures of the liquid and one with varying oxygen concentration in the gas flow. The results from these will be presented in Sections 3.1 and 3.2, respectively. Following this, the mass balance will be evaluated in Section 3.3 and the identification of additional degradation products by mass spectrometry (MS) will be presented in Section 3.4. All degradation data given will be presented as figures. The error bars included in the plots represent the standard deviation between the two parallels. Data for these, and associated
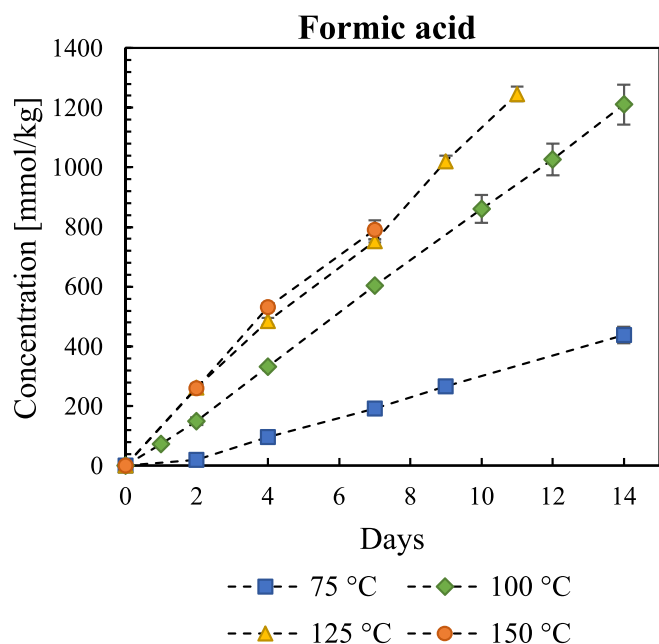
Formic acid

Fig. 5. Effect of temperature on the formation of formic acid during oxidative degradation of TEG (6% O_2).
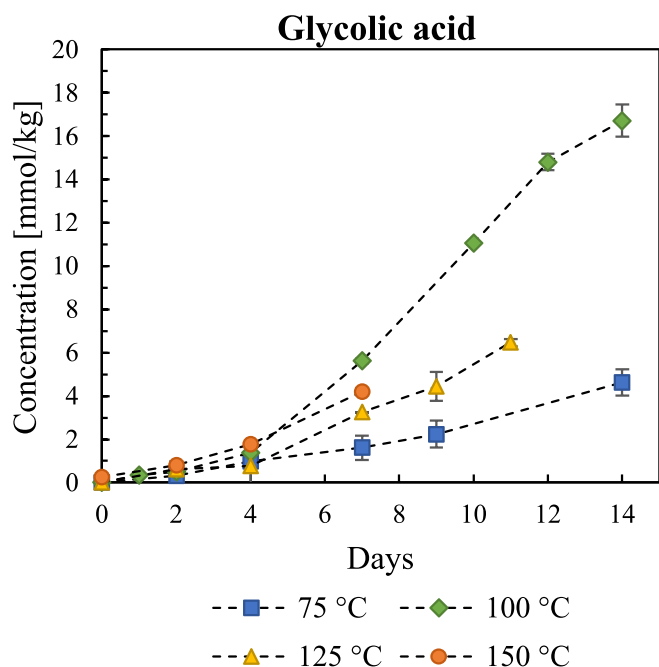
Glycolic acid

Fig. 6. Effect of temperature on the formation of glycolic during oxidative degradation of TEG (6% O_2).

analyses are given in Section B in Supporting Information.

3.1. Effect of temperature

In the first set of oxidative experiments, the focus was on studying the effect of temperature on the oxidative degradation mechanisms of TEG. This was done through the degradation of pure TEG at four different temperatures. The temperatures were: 75 °C, 100 °C, 125 °C, and 150 °C. In all four cases, the oxygen content in the gas was 6 %. Each experiment at 75 °C and 100 °C lasted for 14 days, while the experiments at 125 °C and 150 °C were ended at day 11 and 7, respectively, due to
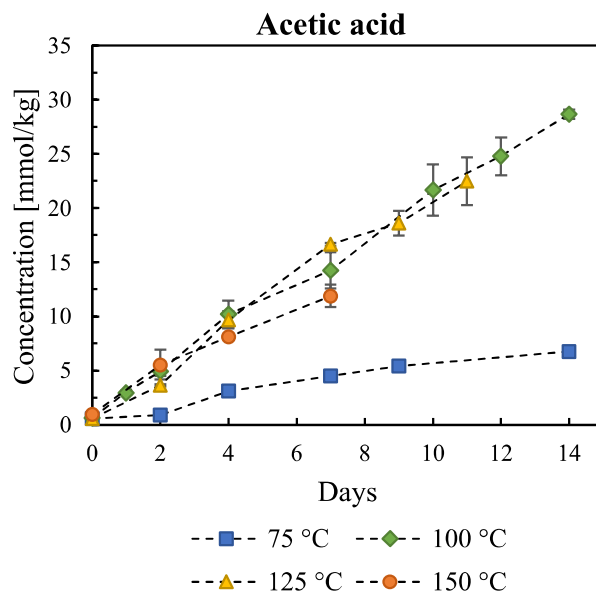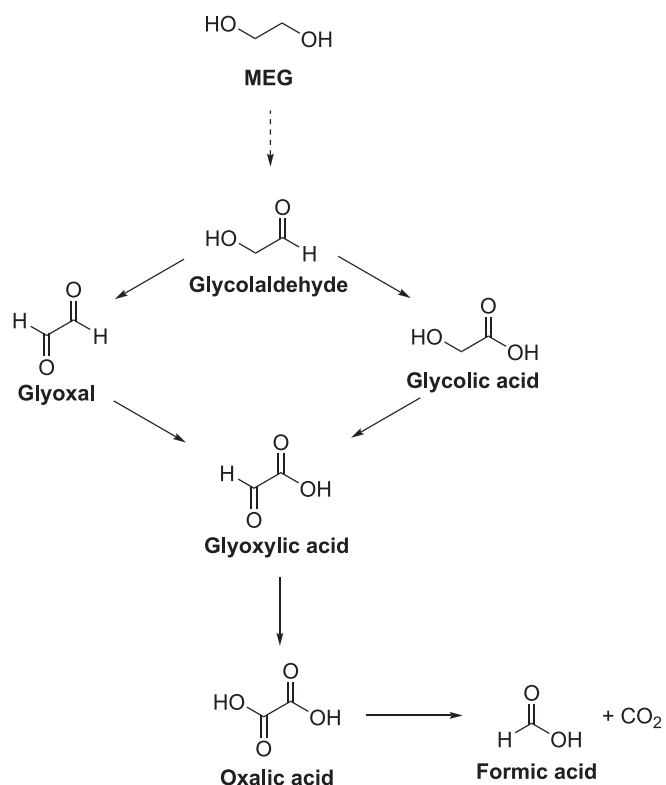
Acetic acid

Fig. 7. Effect of temperature on the formation of acetic during oxidative degradation of TEG (6% O_2).

Scheme 3. Proposed oxidation path from MEG to form the different organic acids.

problems with temperature control.

During the oxidative degradation experiments, the concentration of TEG was monitored with GC-FID. The results from the experiments at different temperatures are presented in Fig. 2. The oxidative degradation rate increases with increased temperature. This is in line with what has been suggested in the literature (Forster, 1998).

The formation of MEG and DEG was also monitored throughout the experiments with GC–FID. The results are presented in Fig. 3 and Fig. 4, respectively. Small amounts of DEG were found in the start solution of
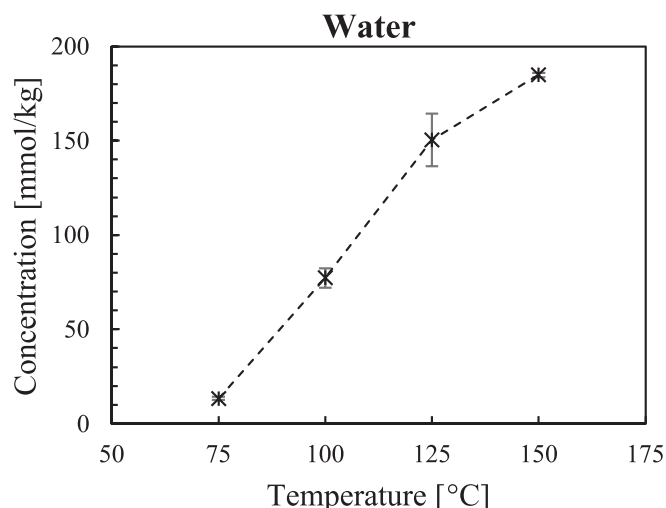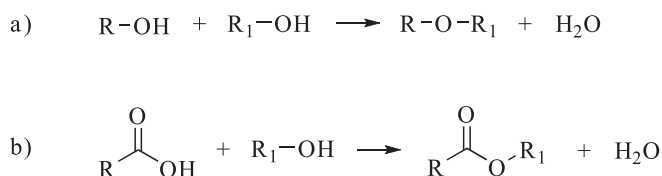
Water

Fig. 8. Formation of water per day during the oxidative degradation of TEG (6% O_2) at various temperatures.

a) $\quad R-OH \;+\; R_1-OH \;\longrightarrow\; R-O-R_1 \;+\; H_2O$

b)

Scheme 4. a) general etherification reaction resulting in the formation of water and b) general esterification reaction resulting in the formation of water.
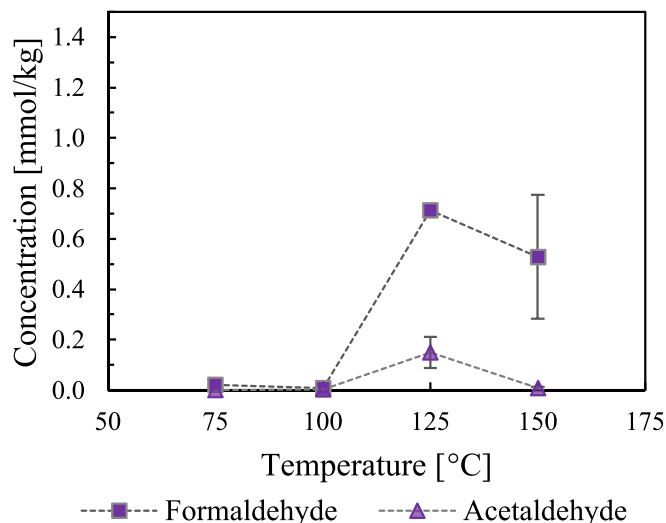

----■---- Formaldehyde   ----▲---- Acetaldehyde

Fig. 9. Total amount of captured formaldehyde and acetaldehyde in the 2,4-DNPH cartridge and acid wash (1 M H2SO4) per day during the oxidative degradation of TEG (6 % O2) at various temperatures. The values are corrected to correspond to per mass of the end solution in the reactor.

TEG, though these were below LOQ. The increase in temperature results in an increase in the formation rate of both MEG and DEG. There is, however, little distinction between the amounts of MEG formed at 100 °C and 125 °C. The reason for this is unknown. In general, MEG was found in larger quantities than DEG, though throughout the experiment at 125 °C they are found at almost identical concentrations. Higher concentrations of MEG can either point to DEG having a shorter lifetime as an intermediate or that the mechanism forming MEG is favored.

The formation of MEG and DEG can be expected to stem from the oxidation of the ether groups of TEG (Denisov, 1980). Depending on which side of the ether groups the radical propagation occurs, either MEG or DEG can be formed. Scheme 1 shows a proposed oxidation pathway for the formation of DEG. In this case, the oxygen radical breaks the ether bond on the side closest to the alcohol group. After the termination of the radical by radical hydrogenation (RH), the result is DEG and glycolaldehyde (CAS: 141–46-8). If the oxygen radical breaks the ether bond on the other side following the same reaction path, MEG would be formed, see Scheme 2 a). The resulting aldehyde would in this case be 2–(2–hydroxyethoxy)acetaldehyde (CAS: 17976–70-4). Once DEG is formed, it is also possible that MEG forms from the oxidation of DEG. A proposed oxidation path for this is shown in Scheme 2 b). In this case, glycol aldehyde would be formed. Both aldehydes can potentially be further oxidized to form their corresponding carboxylic acids.

Formic, glycolic, acetic, and glyoxylic acids were analyzed with HPLC and found to have formed in all these experiments. Fig. 5 shows the formation of formic acid. The formic acid build-up increases with increasing temperature. At higher temperatures, however, the effect of this increase seems to lessen. A possible explanation can be the increased volatility of the acid at higher temperatures. To investigate this, the acid washes of the end solutions were analyzed, and formic acid was detected. It was, however, not found in significant amounts compared to the concentrations in the reactors. Ruling this out, a likely possibility can, therefore, be that the oxygen concentration becomes the limiting factor at a certain temperature above 100 °C. The concentrations of the organic acids found in the acid washes are presented in Table B5 in the Supporting Information.

Glycolic and acetic acid, presented in Fig. 6 and Fig. 7, were formed in lower concentrations than formic acid. In both cases, the formation does not seem to be temperature-dependent. Above 100 °C, the formation of glycolic acid goes down. This can be because it further oxidized more quickly at higher temperatures, thus becoming a less stable intermediate. It can also be that at temperatures above 100 °C, reactions between glycolic acid and other compounds in the solution become more favorable. These were not detected in the acid washes. Oxalic acid was only formed in a concentration above the LOQ at the end of the experiments, while glyoxylic acid was not detected at all.

The detected acids are known oxidative degradation products of MEG. It is, therefore, conceivable that they are formed as secondary degradation products of MEG in the degraded solutions. A proposed oxidation path of the acids starting from MEG is presented in Scheme 3. This pathway follows a general oxidation route where alcohols are oxidized to aldehydes, and aldehydes are oxidized to carboxylic acids (Denisov, 1980). Each step would consume 0.5 mol O_2 and could potentially produce one mole of water. The last step of this pathway is the decarboxylation of oxalic acid, forming formic acid and CO_2. Theoretical studies of the decarboxylation from oxalic acid to formic acid and CO_2 have been performed in other works (Kidd et al., 1976). Similar pathways have been proposed for oxidation reactions of MEG on palladium and platinum (Bambagioni et al., 2010; Wieland et al., 1996). If glycolaldehyde forms in the routes to MEG and DEG, as presented in Scheme 1 and Scheme 2, the oxidation of this will also contribute to the acid formation.

Two oxidative degradation experiments with MEG were conducted with 24 % O_2, one at 100 °C and one at 150 °C. Further details are presented in Section F in Supporting Information. In total, compared to TEG, MEG seems to be very stable under the same experimental conditions. Even with high temperatures and high oxygen concentration combined, the degradation rate of MEG stays low. Looking back to the acid formation during the TEG degradation, it was proposed that the formation could stem from the oxidation of MEG formed as a degradation product of TEG, see Scheme 3. As MEG seems to be stable under the given conditions, however, the possibility that the acids are formed through the oxidation of the aldehydes formed during the formation of MEG and DEG is strengthened, see Scheme 1 and Scheme 2. This is not
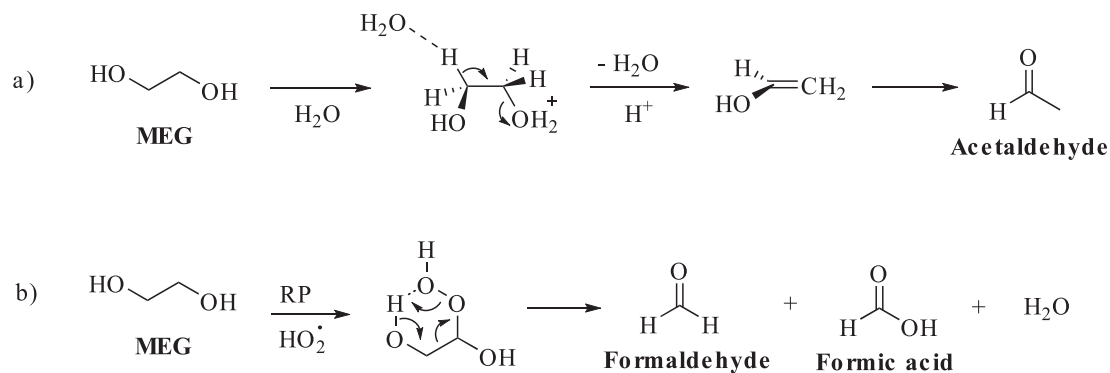
Scheme 5. a) Rearrangement mechanism from MEG to acetaldehyde (Smith, 2002) and b) proposed oxidation rearrangement from MEG to formaldehyde and formic acid.
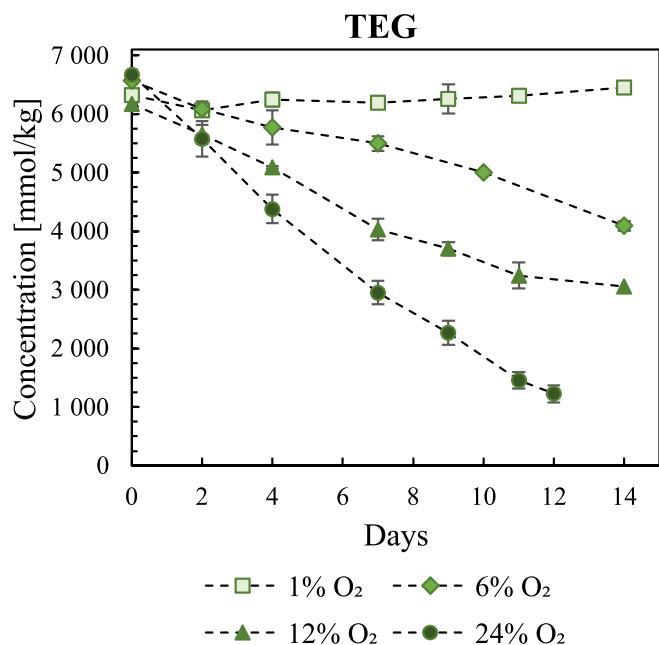

Fig. 10. Effect of oxygen on the loss of TEG (100 °C) with various oxygen concentrations.

Fig. 11. Formation of MEG during oxidative degradation of TEG (100 °C) with various oxygen concentrations in the gas flow.

conclusive, as it is still possible that factors within the degraded TEG system influence the stability of MEG.

The reaction path presented in Scheme 3 covers all the acids detected in the experiments except acetic acid. However, the formation of acetic acid can be accounted for as an expected oxidation product from the oxidation of acetaldehyde. The formation of acetaldehyde will be covered later in this section. The presence of glyoxal and glycolaldehyde was also tested with HPLC-UV and -RI, but these were not detected in any of the samples.

To investigate the possible formation of water during the oxidative degradation of TEG, the water concentration in the start and end solutions was measured by Karl-Fischer titration. Since the degradation rig is semi-closed and the gas is dry, the water that was found was expected to have formed through the degradation of compounds in the solution. Fig. 8 shows the amount of water formed in the different experiments. As the experiments had different durations, the values were normalized to show formation per day the experiment ran. It can be observed that with the increase in temperature, and thus the increase in TEG degradation, increasing amounts of water were formed.

In reactions including alcohols and carboxylic acids, water is typically formed through dehydration reactions like etherification and
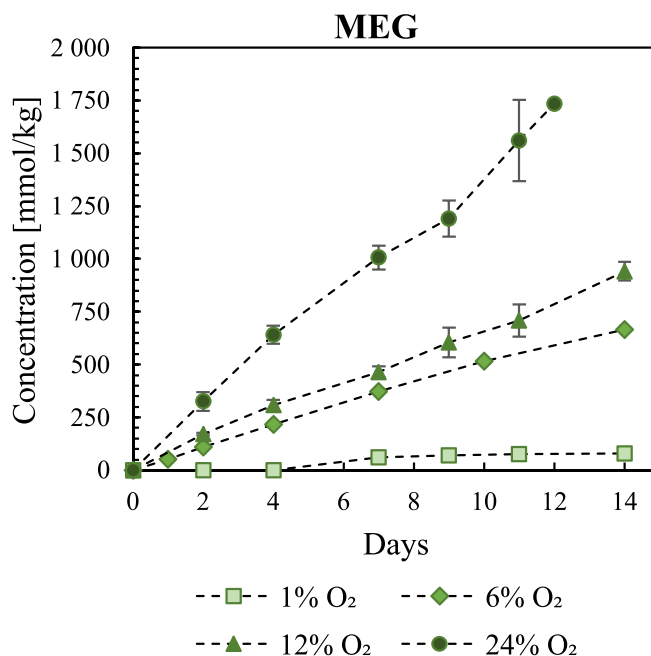
esterification. Etherification is a typically acid-catalyzed dehydration reaction between two alcohol groups, forming an ether. Scheme 4 a) shows a general etherification reaction. Depending on which glycols are reacting in this dehydration, bigger glycol compounds could be formed. Esterification is also typically acid-catalyzed and occurs as an alcohol attacks the carbon in a carboxyl group. A simplified reaction is shown in Scheme 4 b). Also, in this case, the resulting ester depends on which glycol and which acid is reacting. The water could potentially also stem from the radical propagation step involved in forming the initial radical components shown in Scheme 1 and Scheme 2 (Denisov, 1980). This would likely happen via formation of peroxides, as reported by Lloyd et al. (Lloyd et al., 1954) and Glastrup et al. (Glastrup and Padfield, 1993; Glastrup, 1996).

A 2,4-DNPH cartridge and an acid wash were added to the bleed gas outlet of the oxidation rig. With these connected, volatile, organic compounds such as small aldehydes could be captured and detected if these formed during the degradation experiments. The compounds that were analyzed are formaldehyde and acetaldehyde. The total amount of each compound captured in the 2,4-DNPH cartridge and acid wash in each experiment, normalized per day, is shown in Fig. 9. At the two lower temperatures, the concentrations of formaldehyde are quite low,
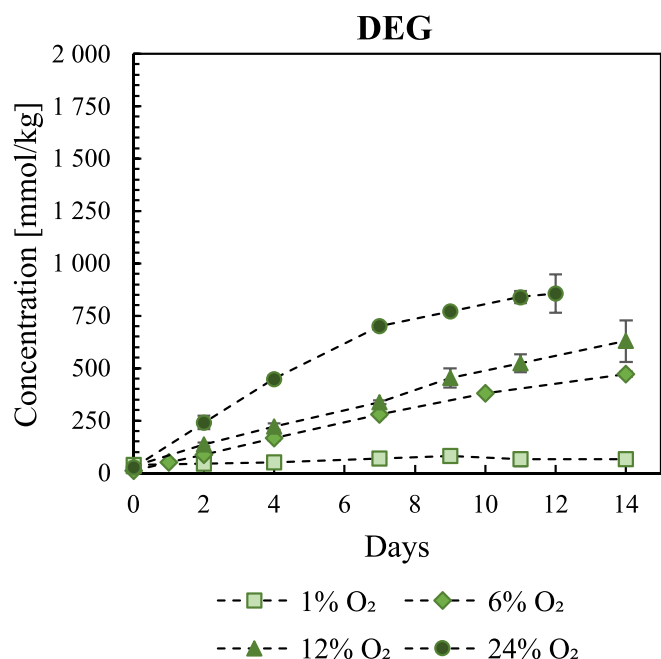
Fig. 12. Formation of DEG during oxidative degradation of TEG (100 °C) with various oxygen concentrations in the gas flow.
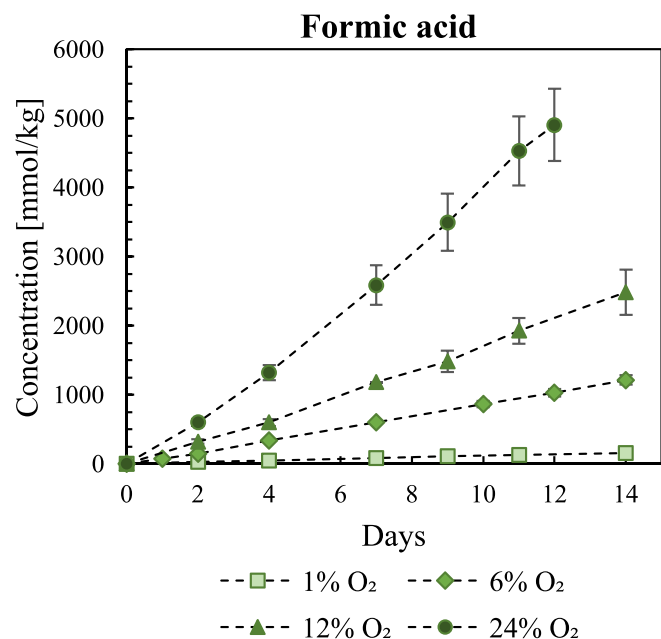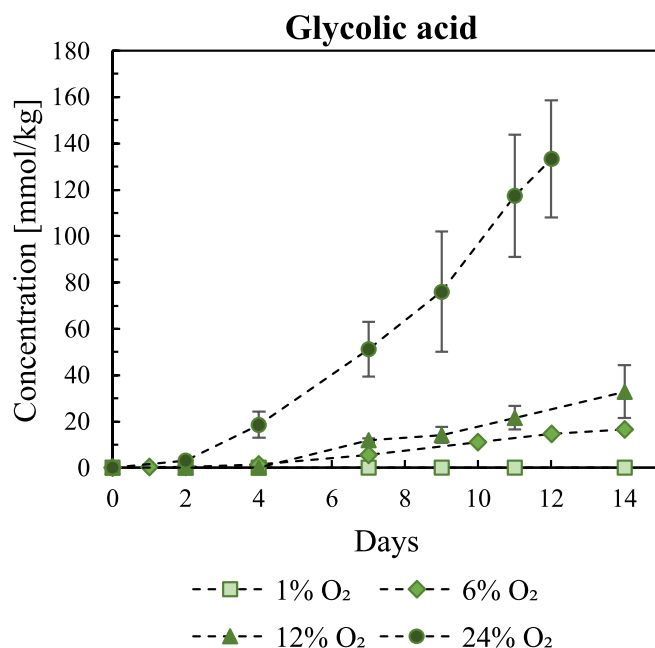

Fig. 14. Fig. 11: Formation of glycolic acid during oxidative degradation of TEG (100 °C) with various oxygen concentrations in the gas flow.

Fig. 13. Formation of formic acid during oxidative degradation of TEG (100 °C) with various oxygen concentrations in the gas flow.
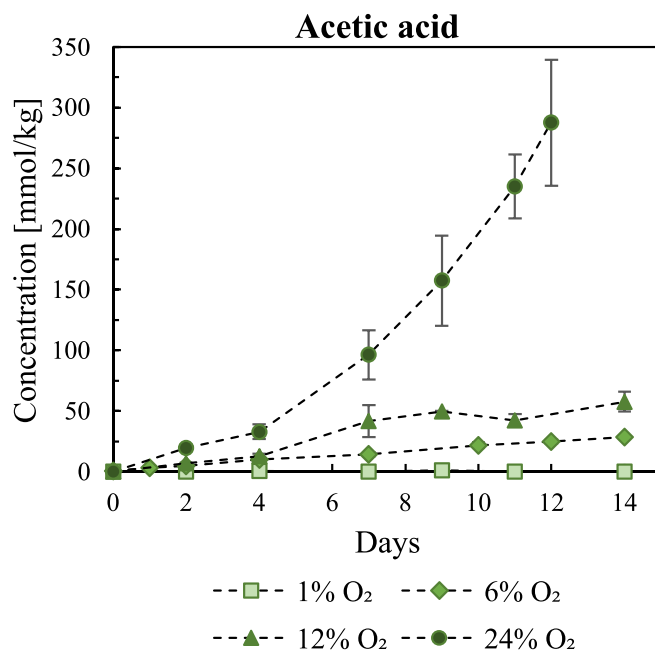

Fig. 15. Formation of glycolic acid during oxidative degradation of TEG (100 °C) with various oxygen concentrations in the gas flow.

while in the higher temperature ranges, more is being captured. This can be because more of the compounds are formed and/or because the volatility is higher at higher temperatures. The formation of acetaldehyde seems to increase with the increasing temperature but falls again at 150 °C. The cause of this is unknown. If it is an intermediate, it might be that the relative rate of formation and disappearance reaction changes with the temperature. It should be noted that it is uncertain whether all the volatile compounds formed were captured, so the actual amount formed might be higher than what is presented in the graph.

The formation of the aldehydes can occur along the formation of MEG and DEG, as described in Scheme 1 and Scheme 2. The formation of

acetaldehyde could also be taking place through a rearrangement reaction from MEG. This rearrangement involves a hydrogen migration and is acid catalyzed. The mechanism for this rearrangement reported to be the most favorable by Smith (Smith, 2002) is presented in Scheme 5 a). The formation of formaldehyde could potentially happen through a rearrangement of the oxidized MEG, following a radical propagation (RP) and an addition of a hydroperoxyl radical. In addition to formaldehyde, formic acid would be formed through this reaction. This proposed oxidation rearrangement is presented in Scheme 5 b). Forster (Forster, 1998) reported the formation of ethanol and methanol during the degradation of TEG. This work does not analyse these due to a lack of
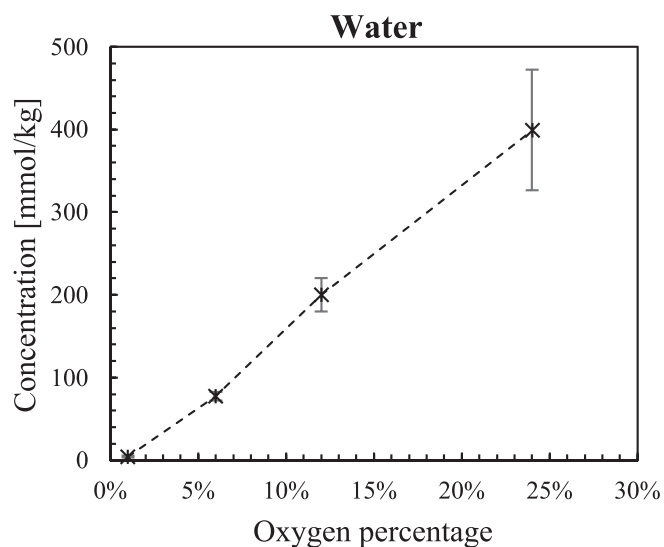
Water

Fig. 16. Formation of water per day during oxidative degradation of TEG (100 °C) with various oxygen concentrations in the gas flow.
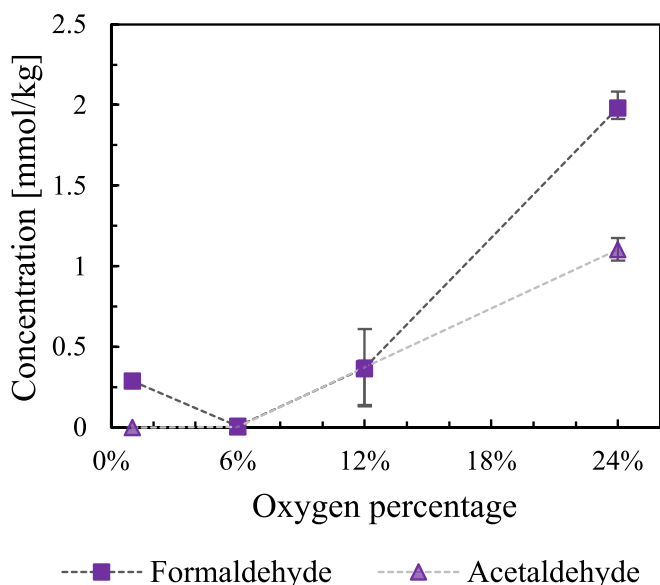

Fig. 17. Total amount of captured formaldehyde and acetaldehyde in the 2,4-DNPH cartridge and acid wash (1 M H2SO4) per day during the oxidative degradation of TEG (100 °C) with various oxygen concentrations in the gas flow. The values are corrected to correspond to per mass of the end solution in the reactor.

suitable analytical methods. However, if these are formed, acetaldehyde and formaldehyde can also form through the oxidation of these.

3.2. Effect of oxygen concentration

In the second set of experiments, the effect of varying the oxygen concentration on the oxidative degradation of TEG was investigated. This was done through four oxidative degradation experiments of pure TEG at 100 °C, with 1 %, 6 %, 12 %, and 24 % oxygen in the gas flow. As in the previous set, the TEG degradation was monitored using GC-FID. The resulting loss of TEG in these experiments is shown in Fig. 10. The degradation rate increases substantially with oxygen concentration.

The results from the analysis of MEG and DEG are shown in Fig. 11 and Fig. 12, respectively. The formation rates increase with the increase

in oxygen available in the system, and in all experiments, MEG was formed in larger quantities than DEG. At the three lower oxygen concentrations, the formation of MEG and DEG follows a similar trend. At 24 % oxygen, however, the formation of DEG seems to somewhat stagnate, while the MEG formation still has a steep increase. This can indicate that DEG is an intermediate that reaches an equilibrium at a certain stage.

The concentration of formic, glycolic, and acetic acid formed in these experiments are presented in Fig. 13, Fig. 14, and Fig. 15, respectively. The formation of all three acids increases with the increase in oxygen concentration. For the experiment with 1 % O_2, only formic acid is found above LOQ. The formation of formic acid with 24 % in the gas flow is quite substantial, as it even surpasses the concentration of TEG in the system. Temperature and oxygen concentration do not seem to influence any favoritism of the acids. Although almost all acids were in higher concentration in this set of experiments, the formation of the acids is in the same order in the experiments with varying temperatures. In both cases, formic acid is the predominant acidic compound formed, followed by acetic acid and then glycolic acid. Glyoxylic and oxalic acid were only detected at the end of the experiment with 24 % oxygen.

The formation of water was also measured for the solutions with increasing oxygen concentration. The resulting water concentrations are presented in Fig. 16. The values are normalized to show formation per day the experiment ran. With an increase in oxygen concentration in the gas flow, the water formation increases linearly. The water formation in the experiment at 150 °C and 6 % oxygen was 0.51 mol water formed per mol TEG degraded, while it was 0.88 in the experiment at 100 °C and 24 % oxygen. Hence, increasing either oxygen concentration or temperature increased the degradation rate, but this difference in water formation indicates that the degradation mechanisms are not the same.

Volatile, organic compounds were also captured in the experiments with higher oxygen concentrations. Fig. 17 presents the total amount captured in the 2,4-DNPH cartridge and the acid wash (1 M H_2SO_4) normalized per day. With an increase in oxygen concentration, an increase in the formation of both compounds can be seen. The formaldehyde found at 1 % oxygen is unexpected. At this oxygen concentration, there was very little degradation of TEG. It is unclear what is the reason for this, but the formaldehyde was found in both parallel experiments.

3.3. Mass and carbon balance

An estimate of the unidentified degradation compounds in the solution can be made by summarizing the masses of the quantified degradation products and comparing this to the total mass of the end solutions. An overview of the composition of the end solution of the two experiments with the highest degradation in the two sets of experiments is presented in Fig. 18. "High temperature" is the solution from day 7 of the experiment at 150 °C and 6 % oxygen, while "High O_2 concentration" is the solution from day 12 of the experiment at 100 °C and 24 % oxygen. The term marked "Unknown" accounts for the mass in each end-solution not covered by the quantified degradation products. It is important to note that as oxygen is added to the solutions, some of the detected mass might stem from oxygen that was not in the solution originally. Likewise, volatile degradation compounds have left the system, reducing the mass. Nevertheless, the quantified degradation compounds do not account for 20 % and 27 % of the mass in the end-solutions.

An interesting side note when comparing the composition of these two degraded solutions is their color. After the experiment with the highest oxygen concentration, the solution was still transparent and colorless like pure TEG. However, the solution got a yellow tinge during the experiment at the highest temperature. This indicates that the component or components giving color to the solution have probably not been identified and are predominantly formed at high temperatures.

To further investigate the possibility of volatile degradation compounds no longer in the system, the total amount of carbon at the
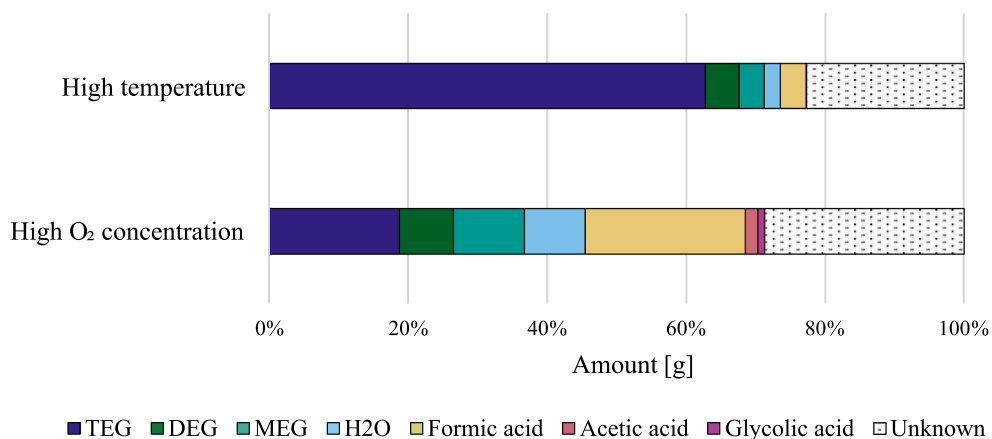
Fig. 18. Overview of the different components' contribution to the total mass of the end solutions in high temperature (150 °C, 6 % O_2, day 7) and high O_2 concentration (100 °C, 24 % O_2, day 12) experiments.
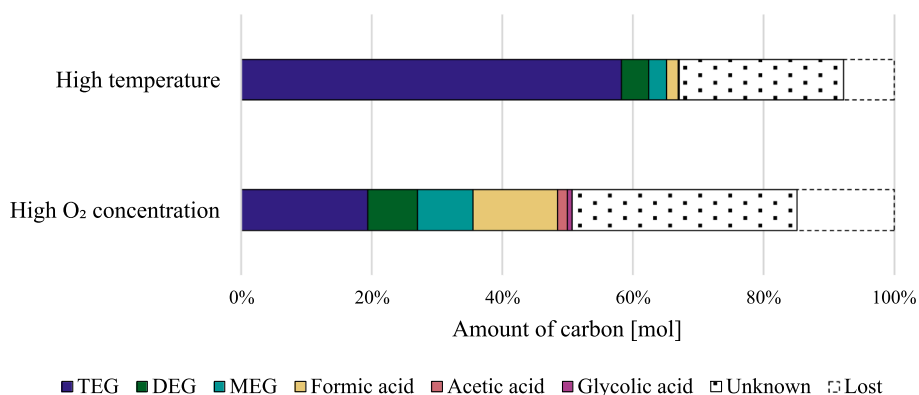

Fig. 19. Overview of the different components' contribution to the carbon balance in high temperature (150 °C, 6 % O_2, day 7) and high O_2 concentration (100 °C, 24 % O_2, day 12) experiments.

beginning of the experiments was compared to the amount of carbon detected in the solutions with TOC analysis. Fig. 19 shows the overview of the carbon in the solutions with the highest loss of TEG in the two sets. The part named "Unknown" is the total sum of organic carbon detected in the solutions with the carbon accounted for by the quantified degradation compounds subtracted. The remaining part, named "Lost", corresponds to the difference in carbon found in the end sample compared to the start sample of pure TEG. Glyoxylic acid, formaldehyde, and acetaldehyde are not included, as they do not contribute significantly to the end sum.

As becomes clear from this overview, some carbon-containing compounds have left the system and have not been trapped or analyzed in the cartridges or the acid washes. A probable candidate as a volatile, carbon-containing degradation product is CO_2. As shown in the oxidation path in Scheme 3, CO_2 can potentially form through the decarboxylation of oxalic acid. It might also be formed through the decarboxylation of bigger compounds containing carboxylic acids. The mechanism of a general decarboxylation reaction is shown in Scheme 6 (Denisov, 1980). To investigate the possible formation of CO_2 during the degradation of TEG, a new experiment with pure TEG was conducted with the purpose of capturing CO_2. Instead of the 2,4-DNPH cartridge and acid wash, three base washes (30 wt% MEA, *aq.*) were added to the outlet of each reactor. MEA is a well-known solvent commonly used for capturing CO_2 industrially. The reaction occurs between two moles of MEA with one mol of CO_2 resulting in the formation of MEA-carbamate and protonated MEA (Gouedard et al., 2012; Feron, 2016). The reaction is presented in Scheme C1 in Supporting Information.

The CO_2 captured in the base washes was analyzed with TIC and the total alkalinity with titration. These results can be found in Section C in the Supporting Information. The end solutions of the base washes were then analyzed with LC-MS for quantification of the organic acids and possible compounds formed through the reaction of MEA and the different acids (Lepaumier et al., 2011). In the latter category, the main compounds detected were (2-hydroxyethyl)-formamide (HEF, CAS: 693–06-1) and *N*-(2-hydroxyethyl)-acetamide (HEA, CAS: 142–26-7) shown in Figure C1 in the Supporting Information. These compounds are expected to stem from the reaction between MEA and formic acid and acetic acid, respectively. The resulting carbon balance for the last experiment is presented in Fig. 20. In the carbon sum, each HEF molecule detected was assumed to stem from formic acid leaving the degradation setup. Oxidative degradation of MEA itself has been shown to form both HEF and HEA, but this is not expected to contribute significantly here due to the low temperature in the base washes (Vevelstad et al., 2016). The base washes were also analyzed with GC-FID to determine whether any glycol had left the system. None were detected. With regards to the CO_2, though it was captured and quantified, it is plausible that some have escaped due to mass transfer limitations.

3.4. Identification of new degradation compounds

In attempting to identify some of the unknown compounds in the liquid phase of the degraded TEG, a GC–MS analysis and a UPLC-MS analysis were conducted. Scans of the solution from day 12 of the experiment at 100 °C and 24 % oxygen were conducted. The signal identification was confirmed by using standards and the full scan EI
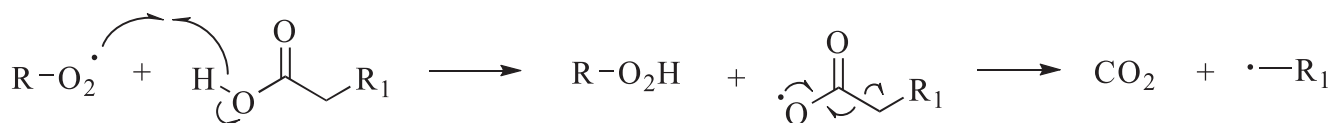
Scheme 6. General decarboxylation mechanism (Denisov, 1980).
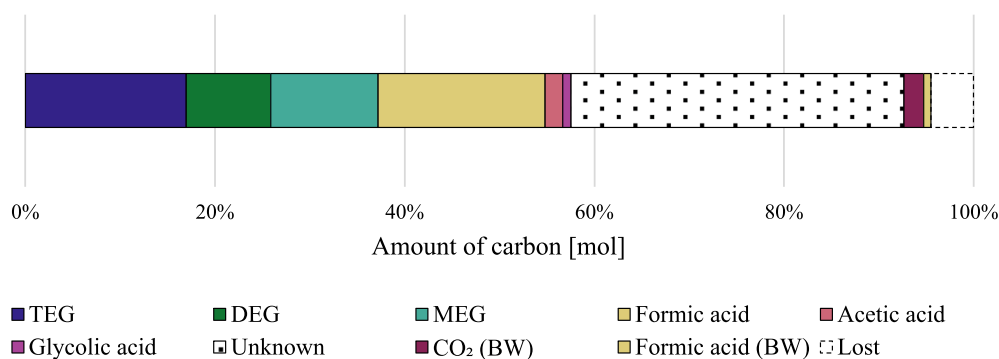
Fig. 20. Overview of the different components' contribution to the carbon balance in the oxidative degradation experiment of TEG (100 °C, 24 % O_2, day 14). BW indicates components detected in the base washes.

mass spectra of the identified compounds were in agreement with available MS Library spectra (NIST MS library). Additionally, some standards were acquired based on theoretically possible degradation compounds. All compounds positively identified with GC–MS are presented in Table 2, and all compounds tested with standards are presented in Section E in Supporting Information. All identified compounds were identified by retention time (RT) matching with known standards. However, a potential positive identification of 12-Crown-4 was debunked. This was because, even though the retention times and mass matched with a compound in the degraded solution, their fragmentation patterns did not match.

Processing the UPLC-MS data, Progenesis DFS studio software was used to create a library with mol files of possible molecules of interest. The peaks that were tested were based on this library, as well as the online Chemspider library. In addition, the tentative identifications were limited to those with ppm error below 5 ppm, and with the highest isotopic similarity and fragmentation score. From the results, one peak was tentatively identified, presented in Table 2. A standard was not available for the confirmation of this compound. Additional data for the UPLC-MS analysis can be found in Table E3 in Supporting Information.

The route for the formation of tetraethylene glycol and pentaethylene glycol is likely through etherifications of various glycols. TEG,

DEG, and MEG are known to be present in the reaction mixture. From these, tetraethylene glycol can either form through the etherification of a TEG and a MEG or from two DEG molecules. Likewise, pentaethylene glycol can form either through the etherification of tetraethylene glycol and MEG or from TEG and DEG. These reactions result in the formation of a water molecule, as presented in Scheme 4 a). The formation of the bigger glycols opens the possibility for bigger polymerization compounds being formed over longer timespans. Diethylene glycol monoethyl ether is likely formed through the dehydration reaction of TEG. This reaction is acid-catalyzed and like the etherification reaction it results in the formation of a water molecule. The formation of diethylene glycol monoethyl ether presents an additional possibility for the formation of acetaldehyde. Starting with diethylene glycol monoethyl ether and following an oxidation path as presented in Scheme 1, acetaldehyde and DEG would be formed.

The formation of triethylene glycol formate could be the result of a dehydration reaction with TEG and formic acid. Some tests were conducted to strengthen this possibility. By mixing the TEG and formic acid at room temperature and analyzing with NMR, triethylene glycol formate was found to have formed. Details of this test can be found in Section F in the Supporting Information. The possible formation of triethylene glycol formate also opens to the formation of other mono- or

Table 2
Compounds positively and tentatively identified with MS scans.

Name	CAS	Structure
Positively identified compounds on GC–MS		
Diethylene glycol monoethyl ether	111–90-0	
Tetraethylene glycol	112–60-7	
Pentaethylene glycol	4792–15-8	
Tentatively identified compounds on LC-MS		
Triethylene glycol formate	1240369–67–8	

even dialdehydes of the glycols. Various ethers could potentially form following a similar reaction path with other acids. These possibilities should be further investigated, as there are still prominent peaks in the spectrums that are unidentified. Further work should include the identification of these. In addition, quantification of all new degradation compounds should be attempted to close the mass and carbon balance.

4. Conclusions

The oxidative degradation of triethylene glycol (TEG) increases with temperature (above 70 °C) and with oxygen concentrations. However, the reaction mechanisms favored with each variable seem to be different. The degradation products of TEG detected and quantified were mono- and diethylene glycols (MEG and DEG), formic, acetic, and glycolic acid, formaldehyde and acetaldehyde, water, and CO_2. In the experiment with increasing oxygen concentration, the formation of all degradation products increased with the increase in oxygen. The formation of MEG, DEG, water, formaldehyde, and acetaldehyde increased with the increase in temperature. The concentration of acids increased when the temperature was raised from 75 to 100 °C, but the rise diminished with a further increase in temperature. On the other hand, the formation of acids increased with an increase in oxygen concentration at 100 °C.

A separate oxidative degradation experiment with base washes was conducted to capture formed CO_2. In addition to formic and acetic acid, CO_2 was captured and quantified. A mass and carbon balance for the solutions were studied, and it was found that a considerable part is not accounted for by the degradation products quantified so far. Also, some carbon-containing compounds are leaving the system with the gas flow and are not accounted for by compounds identified in the base washes.

An MS scan of the solutions allowed for the positive identification of the tetraetyhylene glycol, pentaethylene glycol, and diethylene glycol monoethyl ether. Furthermore, there are indications from the carbon- and mass balance of here to unidentified degradation compounds. The identified longer chained glycols open the possibility of polymerization of glycols. Further work is needed to identify the unknown compounds in the degraded TEG solution. One should also investigate what effect the degradation products, especially the longer chained glycols, have on the dehydration efficiency of TEG.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Experimental data generated in this work is available in Appendix A. Supplementary data.

Acknowledgement

Appendix A. Supplementary data

Supporting information: Additional experimental details, extensive experimental results, and NMR spectra of selected components (PDF). Supplementary data to this article can be found online at https://doi.org/10.1016/j.ces.2024.119706.

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